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The Origins of Solid-State Physics in Italy: 1945-1960

edited by G. Giuliani
Pavia, 21-24 September 1987

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FOREWORD

As written in the leaflet announcing the meeting, its "principal aim" was "*to gather, through the recollections of the physicists who have contributed significantly to the development of the discipline in Italy, data and elements of analysis which may be precious for future historical reconstructions. The contributions of foreign physicists and historians will help to view the Italian case in a wider context*".

A meeting of this kind, focused on lectures given by the men who did the physics under study, represents by no means a novelty. The one held in London in 1979 and organized by Sir Nevill Mott is a good example (to remain in the field of solid state). However, the meeting held in Pavia was perhaps the first focused on the birth of an important branch of twentieth century physics in a single country.

It is by now a common attitude among historians to look at scientists' reminiscences with circumspection when not with suspicion. A particularly cautious stand seems to be justified, because of the direct involvement in the events recollected. However, it should not be forgotten that any witness has been more or less personally involved in the facts he is trying to reconstruct. Therefore a scientist's reminiscence should be looked as a testimony whose reliability must be, as any other, evaluated with respect to all the available knowledge. Finally, one must take into account the role played by scientists' reminiscences in suggesting to the historian paths of research or in giving him hints for otherwise painstaking discoveries.

I am sure that the historians who will study the development of physics in Italy after the second world war will find in this book, thanks to the physicists' contributions, many tracks worth following.

The picture that emerges from the first-person accounts, presents, in fact, many interesting features. Here are some of them:

a) the relevance of the links of Italian physicists with research groups of scientifically leading countries. Their impact on the development of solid state physics in Italy can hardly be overestimated. These links had an important feature, at least in the early stages of development of the discipline: they had been established by individuals or (less commonly) by groups who did not have relevant scientific exchanges among them. Therefore, the international links had been established mainly on the basis of individual scientific interests and views of the on-coming developments of the discipline; they were also, of course, partly determined by personal acquaintances. This resulted in a somewhat casual character of the links, as, on the other hand, it seems to be typical of the early stages of a discipline in a scientifically peripheral country. This feature is well reflected in what we may call the "polycentric" process of growth of solid state physics in Italy.

b) the absence of any government concern for the new discipline. The stand of the Consiglio Nazionale delle Ricerche (CNR) and of the physics community, does not come out clearly and deserves a careful investigation. However, perhaps, we will not grossly miss the point, by saying that the CNR had to be won over to support solid state physics and the community of physicists (as a whole, and apart from individual exceptions) had to be convinced of the importance of the new discipline. In this context, it is worth stressing that some lines of research had been prompted or supported by the Consiglio Nazionale per le Ricerche Nucleari (CNRN) inasmuch as they were connected with the development of nuclear reactors (as it was the case of radiation damage of materials) or to particle physics (as in the case of the low temperature physics laboratory in Frascati).

c) the hard work needed to set up the experimental instrumentation and/or to master new techniques. We know that this has been true for many countries just after the war; but in Italy this pioneering period lasted too much, going deeply into the sixties.

d) in the "polycentric" map of the pioneering Italian solid state physics there has been a centre whose history deserves particular attention: the university of Pavia. This peculiarity is evidenced by the fact that in the late fifties six of the Italian (physicists) lecturers of this meeting were in Pavia (to them, we must add the late Professor Giulotto). That was not by chance. In fact, the arrival of Fumi in Pavia in 1958 was part of a project, favoured by Caldirola, of establishing a group of solid state physicists including both experimentalists and theoreticians. The group of theoreticians began to develop in the years before in an interesting way: alumni of the Collegio Ghislieri (Bassani, Fieschi, Tosi) who addressed Caldirola for a thesis were turned over to Fumi (then in Milano), and thus to theoretical solid state physics. I believe that the role played by the Collegio Ghislieri in providing brilliant students selected over the entire region of Lombardia (and, to a lesser extent, also outside) was not a secondary one in the building up of what could have become the most important Italian solid state group of those times. The same was true also for the experimental side (Camagni, Chiarotti), under Giulotto's guide. But the ambitious project conceived by Caldirola, Fumi and Giulotto failed. A future history of Italian solid state physics will have to deal with this missed chance.

e) the development of solid state physics in France offers stimulating elements of comparison with the Italian case. Some of them are worth mentioning. It appears that, just before the second world war, the institutional background was similar in France and in Italy. Also the role played by the international links in the starting up of solid state physics was fundamental in both countries. Notwithstanding, the French case appears to be characterized by a more dynamic trend owing to the intervention of several public and private institutions. However, also in France the CNRS, though apparently better arranged and more efficient than the Italian CNR, was, at the beginning, left over by other agencies in the support of solid state physics. Anyway, only a careful investigation can substantiate the relevance of the above similarities and differences* between the Italian and French case. By the way, I would like to stress that the study of the growth of new disciplines in countries located at the scientific periphery but with a reasonable institutional background (like France and Italy in those times), seems particularly suitable for pointing out the influence of cultural, institutional, economic, social and political factors on the development of science. As a matter of fact, in these cases, the smallness of the groups involved and the almost self-evident relevance of the institutional aspects make it easier an attempt at a comprehensive historical reconstruction. Furthermore, the possibility of studying more similar processes but with different relevance of some important factor or variable, may give stronger reliability to the entire historical reconstruction.

The period covered by this conference leaves the Italian solid state physics still in its pioneering phase. The formal recognition by CNR (accompanied by certain financial support) came only in 1966 with the foundation of the Gruppo Nazionale di Struttura della Materia (GNSM). From then on the development has been great and many significant changes have occurred in the landscape of Italian physics in a context of wider changes on the international scale.

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* And of course of other factors like, for instance, the different tradition in research on solid state topics and the common weakness of theoretical research before the second world war.

The reader may wonder why this book include also lectures not directly connected with solid state. One reason is related with the fact that all the groups included in the conference have been involved, at least after 1960, in solid state research. But the more important one is connected with the fact that all these groups played an active role in the foundation of GNSM. So, the historians could also look at these proceedings as a source for the history of a scientific organization that has played a fundamental role in the development of condensed matter physics in Italy.

I can not conclude without some acknowledgments. The list should be long. However, this task may be greatly simplified by referring to the acknowledgments made by Tagliaferri in his conclusive remarks. With only two additions: thanks to Professors Fumi and Tagliaferri for their friendly and wise contribution in dealing with the many problems that the organization of a conference of this kind ever implies; and thanks to Professor Belvedere, rector of Collegio Ghislieri, for his warm hospitality.

Giuseppe Giuliani

Pavia, January 1988.

INTRODUCTION

Fausto Fumi

Dipartimento di Fisica dell'Università, Genova

Ladies and Gentlemen,

It is a pleasure to welcome you all to Pavia and to the Conference on "The Origins of Solid State Physics in Italy: 1945- 1960" on behalf of the Organizing Institutions and of the Organizing Committee.

I believe it was a very good idea of Giuseppe Giuliani and the Group for History of Physics at Pavia to propose this conference to try and relive the years of the postwar period in which a number of small Italian groups started research in the physics of condensed matter, in general quite independently in different institutions. These groups operated on an essentially artisan basis but produced already work at a good international level. People active in this phase have been invited to present the research with which they had been connected*.

These papers are integrated by a study by Galdabini and Giuliani on early lines of research in the same general area in Italy between 1900 and 1940.

The reports by André Guinier, Sir Nevill Mott and Frederick Seitz on the development of solid state physics in France, in England and Germany and in the U.S.A., and the reports by three European Historians of Physics on specific areas of solid state physics complete the agenda of the conference.

I am sure we will all find the conference stimulating and on behalf of the Organizing Committee I wish you a pleasant stay in Pavia.

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* Perhaps I might be permitted to interject here a personal element recalling my great indebtedness to Carlo Perrier, the discoverer of technetium with Emilio Segrè, Professor of Mineralogy at the University of Genoa during the 1940's, who first introduced me to solid state science.

EARLY LINES OF RESEARCH IN ITALY:1900-1940

Silvana Galdabini[b] and Giuseppe Giuliani[a,b]

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Solid state physics, as a definite field of research, developed in Italy only after the second world war. However, if we look back at earlier times, we find a great deal of works on the physics of solid matter: many of them belong to rather well defined lines of research; others appear instead as more or less isolated contributions. They can be divided into seven groups:

a) elastic properties

b) thermal properties

c) electrical properties

d) magnetic properties

e) galvanomagnetic and thermomagnetic effects

f) Volta and photoelectric effects

g) optical properties of ions in solid solutions or crystals

In this communication it is impossible to report on all these topics or even to fairly substantiate the conclusions we have arrived at. Therefore, we prefer to commit ourselves to an exposition primarily based on our conclusions (that we will try to support in coming publications) and present some exemplars taken from the above topics as sketchy illustrations of the conclusions.

In a paper to be published (1) we have studied the institutional development of physics in Italy between 1871 and 1940 with particular emphasis on the first four decades of our century. Quoting from the conclusions of that paper: "*In the period taken into consideration (1900-1940) the Italian physics community appears as a small group of scientists facing formidable challenges with inadequate means (both cultural and material). The smallness of the group limited the possibility of a collective and prompt assimilation of the new developments within the discipline. Its slow rate of increase made this task even more difficult.*

The more general cultural, economic, social and political context was not a fertile field for the growth of scientific disciplines. The distribution of academic power and of students between the various faculties, the scarce funds devoted to research, the technological underdevelopment of the industry, are at the same time causes and effects of a looped process typical of a country in which the overall demand for science is far behind in the list of priorities.

Therefore, the necessary conditions were lacking for either bringing Italian research up to competitive levels or favouring the diffuse rooting of new fields of research. Isolated and temporarily limited cases such that of Fermi's group are interesting not for their exceptionality but for how they can be fitted into the general frame we have described."

We can implement this picture on the basis of our investigation of the physics of solid matter. Therefore, the description given below relies on the assumption that the features of Italian physics which depended primarily on the institutional context and/or on the general traits of the Italian physics community, were reflected fairly well in the subfield of the physics of solids. This does not seem a strong assumption, because of the quantitative relevance of the research on the properties of solids (2) and of the fact that this type of research has not been, during the entire period considered, a specialized field of activity.

In the period considered, the main part of physical research in Italy has lived on the borders, when not far apart, of the main streams of advancement of physics. As partially argued in our paper on the institutional context (1), exceptions like that of Fermi's group should be viewed as hints of a possible new trend which however never acquired enough strength to modify the general situation, not only because of the outbreak of the war.

We can speak of an apartness of the Italian physics community with respect to the international one. This apartness had many features of the centre-periphery interaction. The hard core of this apartness endured through the four decades we have studied. Some traits instead changed over the years. The international community followed and used results of Italian research, at least when they were published in foreign reviews. Of course Italian physicists too used results obtained abroad; however they were allowed to ignore foreign contributions even on fundamental issues. The term ignore had three applications: not being able to follow and/or master recent theoretical developments; neglecting theoretical approaches diffused abroad and different from their own; not quoting foreign contributions to which their papers were more or less tightly connected. Of these three applications only the first one may be attributed to the entire period considered. The other two can be found in the habits of the important Italian group which worked on galvanomagnetic effects in the tens; they were no more in use in the thirties and it is to be verified if widespread before. Today's reader may rightly wonder how that was possible. The only reasonable answer one can find is that the evaluation of scientific achievements was based on an average background and/or specialized knowledge mainly derived from Italian publications. This restraint was obviously related to what we have called in the above self-quotation "the limited capacity of a collective and prompt assimilation of the new developments within the discipline". But there was more. There was the difficulty of grasping, not as illuminated individuals but as a group, the mains directions that the developments of the discipline would have taken.

This apartness had also some consequences on publication habits. Italian physicists published firstly and mainly on Italian magazines (3): "Il Nuovo Cimento", "I Rendiconti dell'Accademia dei Lincei" and, starting 1930, "La Ricerca Scientifica". Often, papers published in "I rendiconti" were republished unchanged in "Il Nuovo Cimento".

The same was true, to a lesser extent, for "La Ricerca Scientifica". Only a few papers were translated and published, with the same content, in foreign magazines, mainly german. Fermi too, particularly in his first years, followed this habit. However, he was among the few who published some papers only on foreign reviews. These publication habits were at the same time a manifestation of the apartness and a reinforcement of it. Papers published only in Italian magazines, in spite of their possible relevance, were often ignored, poorly or not at all quoted, and easily forgotten.

The ravaging effects of the war upset also the little world of Italian physics. Not only the research activity has been greatly slowed down during the war, but, at the end, the world appeared dramatically changed not only in its general political, economical and social traits but also from the viewpoint of the scientific community. For western countries the centre, not only from the scientific point of view, has been displaced on the other part of the Ocean. European countries suffered losses of eminent scientists, because of racial persecutions. Periphery started reconstruction as more peripheral than before. Therefore, no wonder if Italian solid state physics moved its first steps after the war with all the features and difficulties typical of a peripheral location. That situation was shared by all Italian scientific disciplines. However, as far as physics is concerned, not all the various subfields restarted on the same line. Nuclear and cosmic-rays physics had attracting and renowned reference points behind them; solid state physics, apart from the long lasting tradition in experimental research on ferromagnetic properties that the "Galileo Ferraris" National Institute helped survive through the war, had lost any reminiscence of the past and had to start from scratch in a situation in which, very rapidly, the funds began to be concentrated anew on nuclear physics.

To illustrate this general picture, we shall discuss three cases, chosen because of being particularly illustrative of our conclusions and of the fact that they cover three of the four decades studied.

I) Galvanomagnetic and thermomagnetic effects

Already in 1850 we find a work of G.A. Maggi (4) in which he reported to have observed an effect of the magnetic field on the thermal conductivity of iron. Later, the study of the influence of the magnetic field on the transport properties of solids was carried on by several Italian physicists. Among them we can not avoid mentioning Augusto Righi who in 1887, independently and about contemporaneously of Leduc, discovered what was later called the Righi-Leduc effect (5). Righi studied also the Hall effect: his first paper on the argument is dated 1883.

In the first decades of our century the Italian contributions have been primarily, but not exclusively, focused on the galvanomagnetic effects. The leading figure was Orso Mario Corbino, then in Roma. In fact not only he gave contributions whose importance was immediately recognized abroad, but, as we shall see, his theoretical approach characterized the Italian contributions in spite of the fact that it was not shared by all Italian physicists working in the field.

Corbino's first paper on the argument was published in 1911 (6) and deals with what was later called the "Corbino effect". The most relevant aspect of this work is given by the use, instead of the usual rectangular plate, of a disc with a circular hole at its centre: the electrodes carrying the current are placed on the internal and external circumference and the magnetic field is perpendicular to the disc. In these conditions the primary current is radial and the effect of the magnetic field is that of producing a circular current: this is the "Corbino effect". Corbino did not say how he had conceived or borrowed the idea of using a disc instead of a rectangular plate. The fact is that 25 years before, i.e. in 1886, Boltzmann (7) had published a theoretical paper in which the Hall effect is studied not only in the usual conditions but also in a circular plate, that is in a configuration identical with Corbino's. Did Corbino know of the Boltzmann's paper? We do not know the answer. We only know that, Trabacchi, a Corbino's assistant and coworker, cited Boltzmann's papers in a work published in 1918 (8). We also know that none of the foreign physicists who worked on and discussed about Corbino effect, recalled that the essential features of the theoretical treatment of the disc had been already given by Boltzmann. Nor did it L.L. Campbell in his beautiful review book on the galvanomagnetic and thermomagnetic effects published in 1923 (9). Anyway, Boltzmann's papers were not the only possible source of inspiration for Corbino. During the nineteen century circular plates had been widely used for the study of electromagnetic effects; we may recall Faraday's disc and Barlow's wheel. Maggi himself used a circular plate for searching a magnetic field effect on the thermal conductivity of iron.

From an historical point of view, the major interest in the first of Corbino's papers is perhaps given by the fact that he used a theory of electrical conduction based upon the existence of two types of carriers which Corbino called the positive and negative ions or, in later papers, electrons. Now the point is that, in those times, the dominant theory of electrical conduction was based on the existence of only one type of charge carriers, namely the electron. No surprise then if the first paper published abroad on Corbino effect (10) is simply an interpretation of Corbino's experimental results in terms of the monistic theory of conduction.

The choice of Corbino in favour of the dualistic theory may be defined as "strong" in the sense that Corbino committed himself to the existence of two types of charge carriers, to the temperature dependence of their concentrations, and to its general validity. However, Corbino did not say a word to justify his choice and kept silent on this fundamental issue till 1920.

We can not follow here even the main lines of development of the study of galvanomagnetic effects in Italy after the basic Corbino's work of 1911. We will restrict ourselves to some highlights and comments. 1915 may be considered as the year in which the Italian studies on galvanomagnetic effects assumed the contour of a line of research. The IX volume of "Il Nuovo Cimento" opens with an article by Hall on "A possible explanation of the Hall and Ettingshausen phenomena", followed by a paper by Corbino and a lengthy article by Volterra, both on galvanomagnetic effects. But that is not all. In addition to these three papers, that volume contains five more papers on galvanomagnetic effects. Other papers will be published in the three following years and this highly productive period culminated in 1918 with the paper by Corbino on magnetoresistance.

Viewed as a whole, this Italian work is characterized by three features. The first is the committment to the dualistic theory of conduction. The second, is the kind of theoretical approach, which may be defined as typical of mathematical physics. It was clear from the beginning: Corbino's aim was more oriented to the determination of currents and potentials distribution than to understand how the magnetic field influences the transport properties. Of course in Corbino's equations we find the carriers' mobilities, but their role is auxiliary and unproblematic. The third feature is given by the apartness of the Italian group with respect to the international community. Apart from the choice of the dualistic theory in a context of widespread diffusion of the monistic one, it must be stressed that, in spite of the attention given by foreign physicists to Corbino effect in terms of extended and more accurate measurements and of alternative theoretical interpretations, the Italian group ignored foreign contributions and rarely quoted them. If one reads only Italian papers on the subject, he gets the clear impression that the study of galvanomagnetic effects was carried on mainly in Italy with scarce and minor contributions by foreign countries. Eventually, Corbino will be forced to assume a more critical approach by the intervention of another Italian physicist, Michele La Rosa. So, while Corbino (and the other Italians) ignored for years the signals coming from abroad, he answered with impressive engagement to La Rosa's remarks. It is perhaps impossible to find a better example of what we have called the apartness of Italian physics community.

However, before discussing the La Rosa-Corbino debate, we must say some words on what must be considered the crowning achievement of the Italian group: the paper by Corbino on magnetoresistance published in 1918 (11). In an article published two years before, Elena Freda (12) showed the possibility of explaining the magnetoresistance effect on the basis of the dualistic theory. As Corbino explicitly acknowledged in his paper, he was firmly convinced that dualistic theory could not explain magnetoresistance effects. Anyway, when eventually Corbino dealt with them, he exploited all the potentialities of the dualistic approach. He showed that magnetoresistance effects in a rectangular plate can occur only in the presence of two types of carriers; that the effect is larger in circular plates; and, finally, that the Hall coefficient depends on the applied magnetic field only if two types of carriers are present. Furthermore, combining the relations obtained for the resistance and the Hall coefficient as functions of the magnetic field, it would have been possible, through appropriate measurements, to obtain the concentrations and mobilities of the two types of carriers. We now know that the relations obtained by Corbino, though qualitatively correct, were quantitatively wrong. But, of course, Corbino's contemporaries did not know or could prove that. Therefore, Corbino's results should have been cheered as at least interesting achievements, also because the subsequent experimental work of Trabacchi (8) seemed to support the relations found by Corbino. But that did not happen (we are here referring to the international community): the large majority of physicists simply distrusted dualistic theories and Corbino's calculations were probably considered no more than a formal exercise.

Now to Corbino-La Rosa debate. In a note of a paper published in 1918 in "Il Nuovo Cimento" (13) La Rosa writes:

> *"Drude's hypothesis about the existence of a double current of electrons of opposite sign may explain the positive Hall effect, but, as it is known, this hypothesis had shown untenable for various theoretical and experimental reasons during the following development of the entire electronic theory".*

And one year later, again in a note:

> "*.....Prof. Corbino has published a work on this argument* [La Rosa is referring to the article of 1918 we have just discussed] *in which the presence of two kind of electrons is supposed. As it is known, this hypothesis is not supported by experimental facts, and leads to very great difficulties in the development of other branches of the electrons' theory.....so that every effort towards an explanation of the facts in the framework of the generally accepted theory (which admits of negative electrons only) maintains all its value*" (14).

The answer of Corbino to La Rosa remarks was uneasy. In a period of thirteen months (June 1920-July 1921) he presented to the Accademia dei Lincei five memoirs in which he strove to parry the blow. He acknowledged that

> "*A further formulation* [of the theory] *must ideally lead.....to the dismissal of those hypothesis which do not fit well into the general frame of the physical phenomenology. In this sense, we must consider as a true progress every ef-*

fort to explain on the basis of the presence of only one kind of electrons, the negative ones, those facts which seem to call for the presence, postulated by Drude, of two kind of carriers: the positive and the negative" (15).

This statement though important as the first critical reflection on his own theoretical approach, may be misleading. In fact, one might expect that Corbino would have adopted a more critical approach towards dualistic theory or/and would have contributed to achieve a "true progress" by trying the monistic one. His choice was completely different. In the memoirs cited and in two others published in 1926, Corbino strove to show that the application of Lorentz's theory and of its modifications to galvano and thermomagnetic effects leads to "categorical contradictions" and to predictions that are at odds with experiments.

With the two memoirs of 1926, Corbino ended his contribution to the studies of galvanomagnetic effects. Italian physicists, not belonging to what we may call Corbino's group, kept on studying these effects till late thirties. But the isolation of the Italian contribution became more pronounced. The advent of quantum mechanics and of the band theory of solids was simply ignored by Italian researchers who kept on studying galvanomagnetic effects.

II) A paper on paramagnetism

Miss Rita Brunetti was appointed to a chair in Ferrara in 1926, but owing to the poor state of the physics institute, she worked for the next two years, before leaving for Cagliari, at the physics institute of Bologna. The paper that we shall discuss was presented on the seventh of April 1929 to the Accademia dei Lincei and was never published elsewhere (16). The title was "Theory of paramagnetism for ions in strong molecular fields". However, to follow the path of discovery, we must go back a little. In Bologna Miss Brunetti began to study the optical properties of rare earth ions in liquid and solid solutions and in crystals. We will report on these works elsewhere. What interests us here, is that Miss Brunetti, in dealing with these problems, became familiar with the possible influence of molecular or crystalline fields on the optical properties of rare earth ions when in solutions or in crystals. Her next step was the study of the possible contribution of the highest of the two allowed multiplet states to the paramagnetic behaviour of the Ce^{3+} ion (17). To explain her experimental results, Miss Brunetti supposed that the molecular field in some way increases the effective charge of the nucleus of the cerium ion so that the separation between the two multiplet levels should be lower than that expected. As we shall see, the effect of molecular fields on multiplet levels will become for Miss Brunetti the clue for finding the way to the solution of the puzzle presented by the paramagnetic behaviour of the ions of the iron group.

When Miss Brunetti looked at this problem, the state of art was as illustrated in fig. 1, taken from the paper of E. C. Stoner (18). Curve 2 is the theoretical number p of Bohr magnetons calculated using Hund's formula (1925) (19), according to which

$$p = g\,[(J(J+1)]^{1/2}$$

This formula (20) should apply when the separation between the multiplets (corresponding to different J values) is large when compared with KT. With two exceptions (Eu^{3+} and Sm^{3+}), this formula describes the paramagnetism of rare earth ions (21).

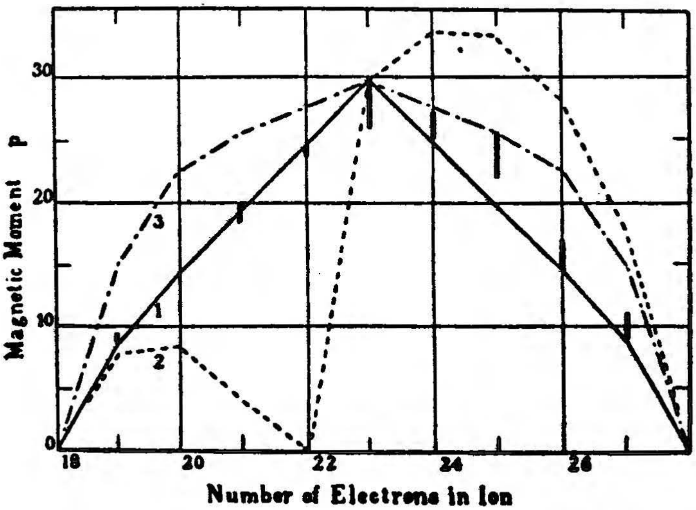

Fig. 1 Observed and calculated numbers of Bohr magnetons for the ions of the iron group. (From ref. 18)

The vertical lines represent the experimental data for the ions of the iron group. No question that they can not be fitted by Hund's formula. Curve 1 represents the formula suggested in 1927 by Bose (22)

$$p = [4S(S+1)]^{1/2}$$

and obtained supposing that only the spins contribute to the magnetic moments. It fits well the experimental data for the first ions of the iron group, but the magnetic moment of the ions containing more electrons are definitely greater than those calculated. Furthermore, Bose gave no theoretical justification of the hypothesis he used. Finally in 1928, Van Vleck (23) showed that, while Hund's formula works well, as already known, when the multiplets' separation is high with respect to KT, the formula that must be used in the opposite case - small multiplets' separation with respect to KT - is

$$p = [4S(S+1)+L(L+1)]^{1/2}$$

This formula is reported as curve 3 in the figure.

Stoner (18) and Brunetti showed, contemporaneously and independently, the way to the solution. We present the two approaches side by side in table I in order to emphasize similarities and differences.

TABLE I

BRUNETTI	STONER
The multiplet separation in the ions of the iron group is much smaller than that of rare earth ions. An estimate indicates that there is a factor of about ten. The molecular field may then break up the L-S coupling, destroying the multiplet levels in the case of the iron group but not in the other.	In the iron group, the electrons responsible for the paramagnetism are the outer ones. In the rare earth case they belong to an inner shell and do not take part in the molecular bond. Therefore, in the case of the iron group there will be a strong "l" interaction not only inside the ions but also with neighboring ions.
The molecular field, supposed having a randomly oriented simmetry axis, aligns the angular momentum along its axis.	The "l" interaction between neighboring ions tend to orient the angular momentum along a definite direction.
Calculates the energy levels in a magnetic field supposing that spin magnetic moments orient freely in the external field.	Treats the "l" interaction between neighboring ions as an effect of a virtual magnetic field H_i. Supposes that the virtual field is parallel or antiparallel to the external field. Spin magnetic moments orient freely in the external field.

As we can see, the conceptual approach is different: while Stoner links the possible effect of the molecular field to the fact that the paramagnetic electrons are in outer or inner shells, in Brunetti's view the reference term is the multiplet energy separation. The two points of view are not equivalent, but, since their role was mainly that of sound arguments in favour of the breaking of the L-S coupling by the molecular field, they did their job. No wonder then if the two models, in spite of their different conceptual foundation and structure, led to substantially the same results. The reduced contribution to the paramagnetism of the orbital moments arises from the fact that they are pre-oriented by the molecular field. The formulas obtained are:

$$p = [4S(S+1) + (1/3)L(L+1)]^{1/2} \qquad \text{(Brunetti)}$$

$$p = [4S(S+1) + f(KT/\mu H_i)L(L+1)]^{1/2} \qquad \text{(Stoner)}$$

where in Stoner's formula μ is the orbital magnetic moment and f is a function which can take on the values between 0 and 1.

Stoner's formula, more flexible than Brunetti's, has the advantage of covering continuously the gap between the two extreme cases discussed above and reported in fig 1. Brunetti, on the other hand, comments:

> "*We do not exclude that, for a particular distribution of the ions in the molecule, one could get an orbital contribution greater or smaller than (1/3)L(L+1)*" (24).

The way was traced. The treatment of Brunetti and Stoner was characterized by models in which the reduced contribution of the orbital moments comes out as a purely classical effect. The quantum mechanical treatment of the quenching of the angular momentum would have been given soon afterwards. In the book by Van Vleck on electric and magnetic susceptibilities (25), published in 1932, the problem was presented as settled for good. Van Vleck referred to Stoner's paper but did not mention Brunetti's contribution. Both contributions instead, had been quoted by Sommerfeld at the Solvay Conference on Magnetism held in Brussels in 1930 (26). But Sommerfeld went on by following Stoner's paper. This is not surprising. Apart from Stoner's international reputation and long lasting activity on magnetic properties, Stoner's paper was clear, well presented and based on the essential distinction between inner and outer shells for the paramagnetic electrons. Brunetti's paper on the other hand, was less brilliant. Brunetti's paper has been rapidly forgotten. Also this audience is probably familiar with Stoner's contribution but unaware of Brunetti's work. The publication of the paper in "I Rendiconti" certainly limited its diffusion abroad. However, what about Italy? Apart from the memorial paper written by Zaira Ollano after Brunetti's death in 1942 (27), as far as we know, there are no Italian quotations of Brunetti's work. Polvani too, in his paper dedicated to a century of Italian Physics (1839-1939) (28), quoted Brunetti's work on Ce^{3+} ions we referred to above, but did not say a word on her more important contribution on the quenching of angular momentum. If we would to describe this case in a few words, we should have to speak of isolation into the apartness.

III) Electrical properties of metallic films

In a paper published in the Physical Review in 1898, Miss Stone (29) reported that electrical resistivity of thin silver films is larger than that of metal samples of normal dimensions and that resistivity becomes very large if the film is thin enough. Stone's work received great attention by physicists, mainly experimental; in a few decades the literature on the argument amounted to hundreds of papers.

In 1901, J.J. Thomson put forward the hypothesis that the increased resistivity was to be connected with the reduction of the electron mean free path due to surface reflections (30). However, it was soon found that the thickness dependence of the mean free path predicted by Thomson well known formula for diffusive reflections was too weak for very thin films.

In 1910 L. Houllevigue (31) suggested that very thin films are made up of grains and that electrical conduction between two grains takes place only when they come into contact. In 1917, R.W. King (32) tried to put the granular hypothesis on a quantitative basis, assuming random grain distribution during the film deposition and introducing some simplifying assumptions.

We will not go on discussing the various modifications of the granular hypothesis. Only one comment. The striking feature of thin films' story before the second world war is that the two hypothesis, mean free path reduction and granular constitution, had been largely viewed as mutually exclusive. It is not easy to understand why. Maybe that the almost despairing discrepancies between experimental data obtained by different authors had induced a diffuse mutual distrust among experimentalists. Then, it was perhaps easier than normally it is, to discard others' data than to put under discussion our own hypothesis. Only in the thirties, the awareness of the many deceitful pitfalls waiting for the unsuspicious thin film researcher began to diffuse and first reproducible data obtained in high vacuum began to appear. So, all the data accumulated before (and many of those obtained in the thirties too), are characterized by not sufficiently controlled experimental conditions and therefore appear to us as worthless of any explanation effort.

Italian contribution in this field is mainly related to the name of Eligio Perucca, then in Torino. Perucca began to work on thin films along with but independently of Pierucci (33) during the late twenties and ended about ten years later. With respect to the best experimental conditions and facilities available abroad, Italian researchers in this field suffered heavy drawbacks. Pierucci, experimented with the deposition of a tungsten filament of a worned out bulb. Perucca, in his review paper (34) presented at the bicentenary celebration of Galvani's birth held in 1937 in Bologna, acknowledged with a tenous vein of sadness the impossibility for his laboratory of keeping the pace of the necessary technological innovations. Therefore, you will be no surprised in hearing that the results obtained by Italian researchers in this field have not been so good as those obtained abroad, in spite of the experimental skill of Perucca. Our main interest lies, in this case too, in a particular hypothesis assumed for explaining the experimental data. Perucca believed, during about all the period of his work in the field, that the increased resistivity of films could not be explained either by mean free path or granular constitution theories. Therefore, already in his first paper published in 1930 (35), Perucca suggested that

> "*...metallic films a few atomic diameter thick are not conductive, that is they do not contain conduction electrons; a metal has normally a superficial layer which is metallic but not conductive. Metallic films are insulators till they become twice thicker than the insulating superficial layer..... The hypothesis is certainly audacious and forces us to consider from a new viewpoint an entire set of fundamental phenomena*".

Perucca did not worry about the plausibility of his hypothesis with respect to the available theoretical background nor did he make any effort to give it an independent theoretical foundation. He maintained his hypothesis without substantial modifications almost till the end of his work on metallic films. Only in 1937, in the review paper already cited, Perucca began to assume a more cautious stand with respect to his "audacious" proposal. In his last paper on the subject, published in 1938, Perucca, spurred by his new experimental results, revised his position towards the granular hypothesis (which he had considered untenable), and wrote in the abstract:

> "*.....The consequent strengthening of granular hypothesis suggests to consider premature every other attempt of pure theoretical interpretations of the anomalies (electron free path reduction; deficiency of conduction elec-*

> *trons) till experiments on metallic films of well defined crystalline structure, possibly monocrystalline, could be carried out"* (36).

Was it a suspended judgment or an elegant way to give up? Perhaps a mixture of both.

Perucca's case reminds in some way that of Corbino. But the differences are many. We will touch upon only two. The relations between Italian and international physics community, though the same from the basic viewpoint of centre-periphery interaction, have changed at least in one relevant aspect. The Italian physicists who, like Perucca, were working on up to date topics, had, from Corbino's times, changed the audience which now was primarily the international one. This change is clearly reflected in the references network of Italian papers and was already noticeable in Brunetti's articles we talked about before. Another hint is given by the fact that in Perucca's case the criticism to his hypothesis came, as far as we know, only from abroad and was promptly answered by Perucca. We have not so deep a knowledge of the Italian physics community for saying with certainty when this important change took place. However, we believe that the period can be reasonably placed in the late twenties (37).

There is another important difference between Corbino's and Perucca's case. Corbino did know and master Lorentz's theory of metallic conduction: simply he decided, and, as we have seen, he was allowed to do so, to ignore it. Perucca instead had probably some problem in dealing with the new born band theory of solids and in evaluating his hypothesis with respect to it. However, both cases are but different manifestations of what we have called the apartness of Italian physics community.

This reminds us of the fate of solid state physics in Italy during the thirties. In the first four decades of our century, the fraction of papers published in "Il Nuovo Cimento" and devoted to the physics of condensed matter (including liquids, but by far, mainly solids) is about eighteen per cent (1). However, to this production does not correspond a constant quality level. In the thirties, particularly the late ones, the quality crisis is evident. Two may have been the main reasons. The first was related to the already recalled difficulty of the Italian physics community of promptly assimilating the new developments within the discipline, in this case, mainly quantum mechanics and its application to crystals. The second may have been the attraction of nuclear physics so brilliantly advertised by the successes of Fermi's group.

By the way, those were the years in which the physics of solids as a definite subfield began to emerge in Germany, England and United States on the wave of the unifying theoretical approach provided by quantum mechanics. Now it should be clear to us why Italy missed the appointment.

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2 See below.

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12 E. Freda, Il Nuovo Cim., 12, 177 (1916).

13 "*L'ipotesi del Drude dell'esistenza di una doppia corrente di elettroni di segno opposto può giustificare l'effetto Hall positivo, ma come si sa, essa per varie ragioni di ordine teorico e sperimentale si è dimostrata insostenibile, nel successivo sviluppo di tutta la teoria elettronica.*" M. La Rosa, Nuovo Cim. 15, 89 (1918).

14 "*.....il Prof. Corbino ha pubblicato un lavoro su questo argomento, nel quale si ammette la presenza di due specie di elettroni. Come si sa, questa ipotesi non è suffragata da fatti sperimentali, e conduce a gravissime difficoltà nello sviluppo delle altre branche della teoria degli elettroni,.....cosicchè ogni tentativo diretto a ricondurre la spiegazione dei fatti nel quadro della teoria generalmente ammessa (che suppone l'esistenza dei soli elettroni negativi) conserva tutto il suo valore.*" M. La Rosa, Nuovo Cim. 18, 39 (1919).

15 "*Una elaborazione ulteriore deve idealmente condurre .....alla eliminazione di quelle ipotesi che non si assestano bene nel quadro generale della fenomenologia fisica. E in tal senso è da considerare come un vero progresso ogni tentativo di spiegare con la presenza di elettroni di una sola specie, i negativi, quei fatti che sembrano richiedere l'esistenza postulata dal Drude, di due specie di centri mobili: i positivi e i negativi.*" O.M. Corbino, Rend. Acc. Lincei, 29, 282 (1920).

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20 Hund proposed his formula before the introduction of the electron spin. Therefore, the quantum number J was then the total angular momentum defined as the sum of the orbital angular momemtum of the outer electron and the angular momentum of the

"rest of the atom". After the discovery of the electron spin, Hund's formula was read as we use today.

21 The paramagnetic behaviour of these ions must be described by a non-approximate formula because of the fact that their multiplet separation is comparable with KT.

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24 *"Non escludiamo che per particolare distribuzione degli ioni nella molecola si possa avere un contributo più grande o più piccolo di (1/3)L(L+1) da parte delle orbite elettroniche".*

25 J.H. Van Vleck, "Electric and magnetic susceptibilities", Oxford, 1932.

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31 L. Houllevigue, Compt. Rend. 150, 1237, (1910).

32 R.W. King, Phys. Rev. 10, 291 (1917).

33 Probably the two began to work on metallic films more or less in the same period. However, the first published report is that of Pierucci, Rend. Acc. Lincei, 7, 400 (1928).

34 E. Perucca, Nuovo Cim. 11, 531 (1937).

35 "*.....pellicole metalliche dello spessore di pochi diametri atomici non sono conduttrici, cioè non contengono elettroni di conduzione; un metallo è normalmente fornito di una pellicola superficiale metallica non conduttrice. Le pellicole metalliche sono isolanti finchè non raggiungono uno spessore doppio di quello che compete allo strato superficiale isolante.....L'ipotesi è certamente ardita, ed essa obbliga a considerare sotto un punto di vista nuovo tutta una categoria di fenomeni fondamentali.*" E. Perucca, Nuovo Cim. 7, 50 (1930).

36 ".....Il conseguente consolidarsi della teoria granulare induce a ritenere prematuro ogni altro tentativo di interpretazione teorica pura delle anomalie (riduzione del cammino libero degli elettroni; deficiente numero di elettroni di conduzione) finchè non si sperimenti su pellicole metalliche a struttura cristallina ben definita, possibilmente a struttura monocristallina." E. Perucca, Nuovo Cim. 17, 365 (1938).

37 The relationship between Italian physics community and the international one was clearly more complex than it may appear from our report. To be more precise, at least on one point. Also for Corbino, from the scientific point of view, the audience was primarily the international one. It was in fact the international community the one which used, dis-

cussed, improved, extended and explained in the framework of the monistic theory Corbino's effect. However, the evaluation of Corbino's work and achievements made by the Italian community was largely independent from the international context but essentially based on the national one. To some degree this was also true in Perucca's time. But while Corbino's papers were clearly written for the Italian audience, Perucca wrote with the international community as a reference point.

FERROMAGNETIC MATERIALS AND THE ISTITUTO ELETTROTECNICO NAZIONALE "GALILEO FERRARIS"

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1 - Organization

The Istituto Elettrotecnico Nazionale Galileo Ferraris was founded by Giancarlo Vallauri, professor of Electrical Engineering at the Politecnico of Torino.

It was constituted of several sections having specific interests, as, for instance Electrical Engineering, Radio technology, Electrical machines, high voltage technology, magnetic and dielectric materials etc.

The purpose of the Institute was that of forming high level researchers and technicians both for the executive staff of the electrical industry and for teaching at the University.

The Magnetic Material Department was set under the direction of the professors Carlo Chiodi and Valentino Zerbini, and the research works developed in this section were followed personally by prof. Vallauri, who had a strong interest on Ferromagnetics and had already published since the year 1910 papers on ferromagnetism based on the theory of Weiss.

In 1947 the Consiglio Nazionale delle Ricerche (CNR) set up, within the Institute,a Centro Studi per l'Elettrofisica, having prof. Romolo Deaglio as a director. This was a great help for the possibilities of the Magnetic Material Department, whose research work was developed along two different lines. One line was on the fundamental aspects of Ferromagnetism, while the other one had the aim of improving the magnetic material technology through a collaboration with industry. Only after the year 1960, when was founded the Gruppo Nazionale Struttura della Materia of the CNR, which had the purpose of coordinating the research on the structure of matter on a national basis, the Centro Studi per l'Elettrofisica was substituted by a section of this new Institution which is still operating within the IENGF.

2 - Studies and developments of set-ups for magnetic measurements.

It must be stressed that the first years of activity were spent in developing apparatuses for the measurement of magnetic characteristics.

Fig. 1 - Annealed electrolytic Fe Bitter pattern due to typical pine tree structure of magnetic domains for an orientation close to (110) (x180).

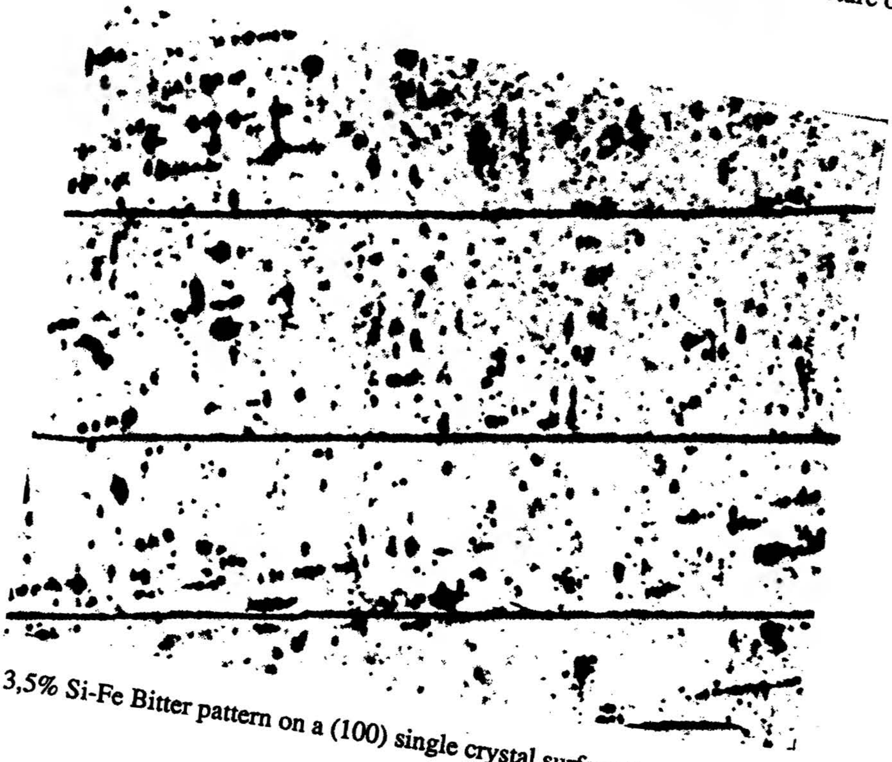

Fig. 2 - 3,5% Si-Fe Bitter pattern on a (100) single crystal surface (x180).

In that period some papers were published on the use of ballistic galvanometers for the measurement of the magnetic induction(1), and on the use of magnetic hysteresigraphs for the recording of hysteresis loops(2). Another paper(3) was done on the use of a wave form harmonics analyzer for the measurement of the characteristics of the hysteresis loop within the Rayleigh zone.

It was also developed, with very good results, an instrument for the measurement of small d.c. magnetic fields based on the fact that a second harmonic component is generated in the voltage induced in a coil linked to a small probe of high permeability material (permalloy) when a d.c. magnetic field is present, together with a perfectly sinusoidal driving field generated by a suitable primary winding. The instrument worked at a frequency of 5 KHz and could measure static field within the range between 0.1 and 800 A/m.

Particular care was used to develop an apparatus for the measurement of magnetic losses in a.c. on Epstein square or on toroids. At that time, it was rather difficult to obtain good sinusoidal waveform of the magnetic induction and to have accurate measurements of the peak values of this quantity making use of average value a.c. instruments. An electronic hysteresigraph having a very low drift and a feedback circuit capable of maintaining the derivative of the magnetic induction constant during the loop tracing was developed only toward the 1960. This instrument is still working and is unique in its possibility of tracing a loop in a period as long as 1200 s, thus allowing magnetic measurements on high permeability massive specimens without the errors due to the presence of slow decaying eddy currents. In the development of all these instruments particularly useful has been the help of A. Gobetto. In more recent years several seminars on the use of this instrumentation have been given to people working in industry by A. Gobetto and collaborators at IENGF with a large participation (more than 100 people attending).

3 - Development of high permeability alloys.

After the development of the instrumentation suitable for the measurement of the magnetic characteristics of ferro magnetic materials, the activity of the laboratory staff was aimed to the development of a suitable equipment for the production and characterization of high permeability alloys.

Particular interest was devoted to Fe-Ni alloys melted under vacuum as ingots of a few kilograms with the possibility of a subsequent annealing in a controlled atmosphere (as for instance in high purity hydrogen) within programmable furnaces capable of reaching temperatures up to 1600 ^{o}C.

It was possible in some Fe-Ni alloys to reach coercive fields of about 1.2 A/m, against values of 2.8 A/m of the commercial alloys.

Monocrystals of Ni and Fe, having dimensions of the order of a few cm^3 in the case of Ni, were obtained by means of different techniques.

In the case of Fe, crystals of a few cm^2 were grown on laminations by means of plastic deformation and subsequent annealing.

On 1955 prof. F. Venturello, of the faculty of Chemistry at the University of Torino, was a guest, together with his collaborators, of the IENGF. He remained at the Institute for a few years giving a strong contribution to the preparation of alloys and high purity metals.

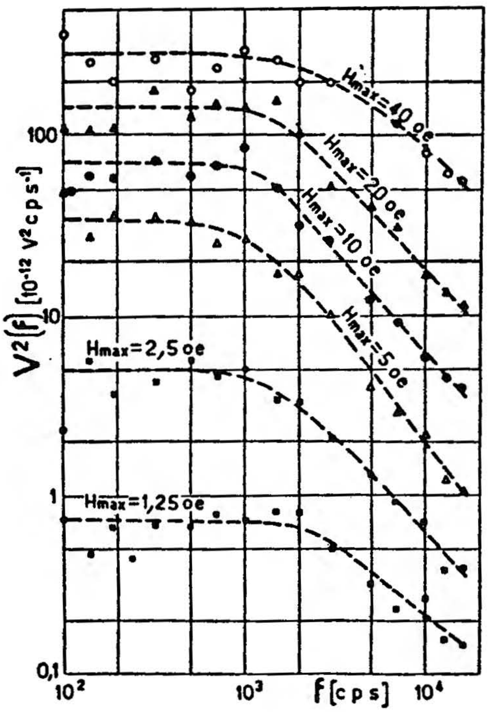

Fig. 3 - Spectral density of Barkhausen noise in iron. The frequency of the magnetizing field is 4 cps.

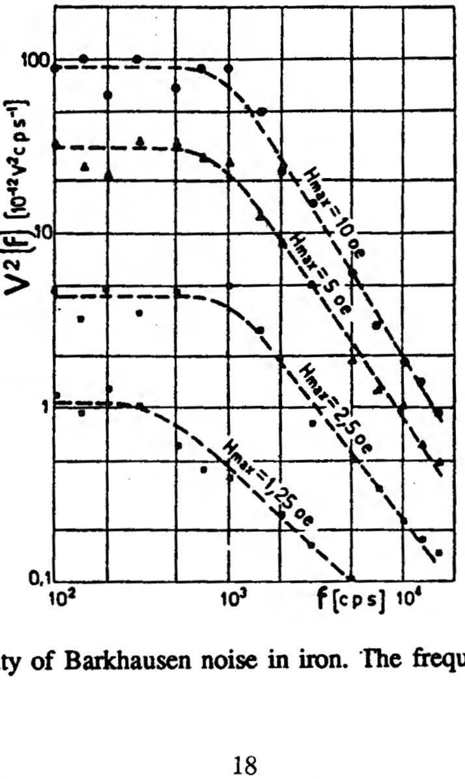

Fig. 4 - Spectral density of Barkhausen noise in iron. The frequency of the magnetizing field is 2 cps.

It is worth mentioning a particularly interesting paper(5), worked out at that time, on the possibility of finding the orientation of the microcrystals on a lamination from the observation of the magnetic domains by means of the Bitter technique.

A few years before, in 1950, at the IENGF was installed the first electronic microscope of the whole Piedmont region. It was used, jointly with the Institute of Chemistry of the University of Torino, for research in the field of metallurgy.

In the following years it was instituted a Department of Electronic Microscopy under the direction of Prof. G. Bonfiglioli, and the electronic microscope was used for the study of dislocation in germanium and silicon. Other research topics were the study of the electrical conductivity of thin metallic films and of the thermoluminescence in alkali halides.

4 - Barkhausen Effect.

In 1919 Barkhausen discovered the existence of a noise superimposed to the e.m.f. generated in a small coil linked to an iron wire placed within an alternating magnetic field. This was the first experimental proof of the existence of the Weiss magnetic domains: the magnetization was changing in a discontinuous way.

It was shown by Montalenti(7) that this noise is very low in the initial part of the magnetization curve (about 2 orders of magnitude lower than in the steepest part of the magnetization curve), and this should be considered a good verification of the theory of Néel on the Rayleigh law.

Subsequently, Biorci and Pescetti(8) of the same group, performed the first measurements of the power spectrum of the Barkhausen noise by means of an home-made spectrum analyzer and found out that the spectral density in the low frequency range was very little affected by the frequency of the magnetizing field, and remained almost constant if this frequency was doubled (from 2 Hz to 4 Hz, see figs. 3 and 4). If the assumption of the statistical independence of the elementary Barkhausen jumps is made, then from the Campbell's theorem it is expected that the power spectrum of the pulse sequence is proportional to the number of pulses per unit time. Thus the discrepancy of this assumption with the experiments show that the Barkhausen pulses are not distributed according to the Poisson statistics. This was at the origin of a series of papers on the Barkhausen noise, which is still going on on the amorphous ferromagnets.

5 - Magnetic hysteresis

Torn Kamei(9) in 1951 evidenced that a Barkhausen noise could be induced in a ferromagnet by a mechanical tension. This was the proof that a mechanical tension could produce an irreversible motion of the Bloch walls.

It was thus decided to extend this investigation(10) by developing a strain gauge with a sensitivity of 10^{-7}. Measurements on specimens of nickel evidenced an elongation of 1.5 . 10^{-6}after applying and removing a mechanical tension.

This elongation disappeared when the specimen was demagnetized. A similar effect was observed on the electric resistivity. Some typical results are shown in fig. 5. These results show the equivalence, for what concerns the ir reversible motion of the Bloch walls, between a mechanical tension and a magnetic field.

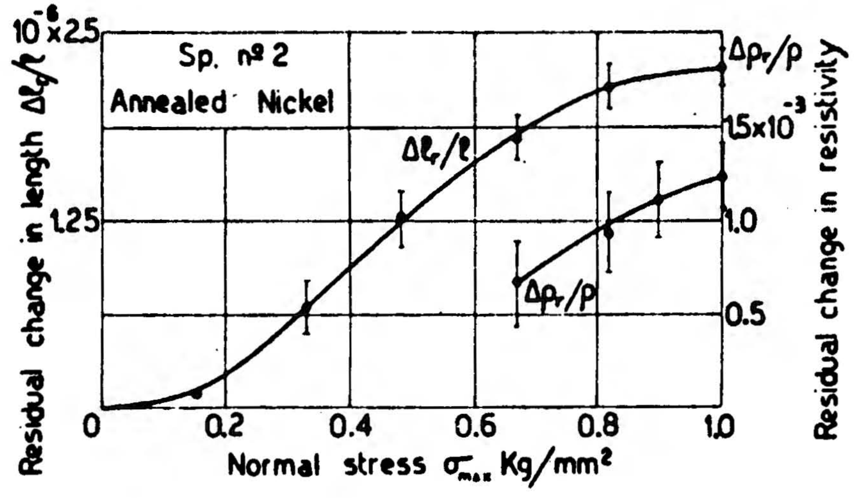

Fig. 5 - Curves of remaining strain versus maximum stress and of remaining resistivity variation versus maximum stress for annealed cast nickel. The uncertainty in the ordinate scale of $\Delta l_r/l$ is about +- 40 percent.

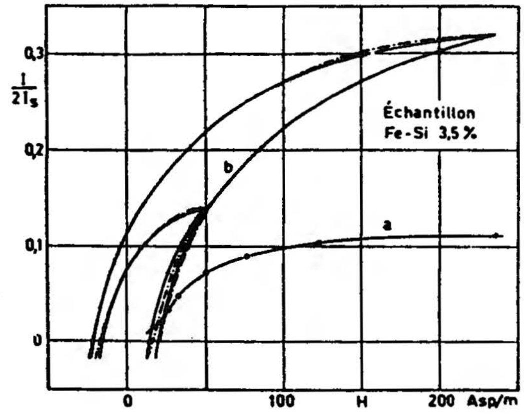

Fig. 6

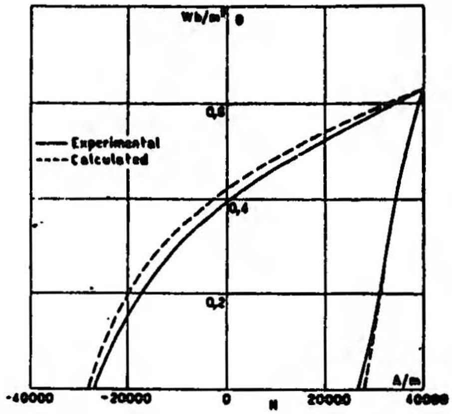

Fig. 7

Fig. 6 - 3,5% Si-Fe sample. Solid lines: experimental hysteresis loops. Dashed lines: calculated loops. The predicted behavior of residual induction of symmetrical loops as a function of peak field is given by curve a). The points represent the experimental data.

Fig. 7 - A symmetrical loop of the Alnico specimen. Solid line: experimental; broken line: calculated.

Preisach(11) in 1935 worked out a model where a ferro magnetic material was assumed to be constituted of several regions having a rectangular hysteresis loop with saturation magnetization J_S and transition fields between - J_S and J_S, characterized by two quantities a and b distributed over the different regions according to a function $\phi(a,b)$. This function was assumed to be independent of the actual value of the macroscopic magnetization and of the magnetic field applied to the specimen.

Biorci and Pescetti in 1953 evidenced that the distribution function $\phi(a,b)$ can be calculated for every material if the first magnetization curve and the hysteresis loop are known. Once $\phi(a,b)$ is known, the theory allows to calculate any other hysteresis loop within arbitrary magnetization limits smaller than the saturation magnetization. The theory has been verified on specimens of Fe-Si 3.5% and Alnico. The results are reported in figs. 6 and 7.

6 - Radiation damage

The study concerns the defects introduced within a metal by neutron irradiation with doses between 10^{17} and 10^{19} n/cm^2 and energy above 1 mev. All the authors agree that, under these conditions, no variations on the X-rays diffraction spectra are observed, as for instance shifts of the Debye lines or changes in the Laue diagrams.

On the contrary, the irradiation induces large variations in the electrical resistivity and an increment of the elastic limit as well as of the fragility.

For what concerns the variation of the magnetic characteristics of irradiated ferromagnetic materials, an extensive review has been made by Gordon and Sery(12). This paper, which has eminently a practical character, shows that in some high permeability alloys, like Permalloy, there is a strong reduction of the magnetic permeability, while, for instance, in a silicon iron lamination the magnetic characteristics are only slightly changed. Materials like pure iron have not been investigated.

Among the papers having an interpretative character are of particular interest the papers of Friedel(13) Seitz and Koehler(14). These authors assume that, in addition to point defects, like vacancies and interstitials or clusters of them, neutron irradiation can produce dislocations and thermal spikes.

The last defect could be produced by the fact that the energy of the incident particle would be sufficient to melt a small volume of the material for a very short time (10^{-11} s), giving rise to a small highly disordered region.

Experimentally it is observed that point defects and clusters of point defects are certainly generated. Because it is well known that the Bloch walls are hindered in their motion by defects having dimensions comparable with the wall thickness, it was considered very interesting to investigate how the magnetic properties of pure iron are changed after neutron irradiation with doses of 10^{18} n/cm^2 and particle energy larger than 1 Mev.

In a first series of experiments the materials irradiated with $1.14.10^{17}$ n/cm^2 were pure commercial iron, Armco iron and Ferrital. In these materials no changes in the X rays spectra were observed, while the mechanical properties changed according to literature data. The maximum permeability was reduced of about 20%.

Owing to the fact that these materials contain impurities of carbon and nitrogen and remain for about 4 weeks within the reactor at 60 ^{o}C, there was the possibility that the permeability reduction were due to aging effects.

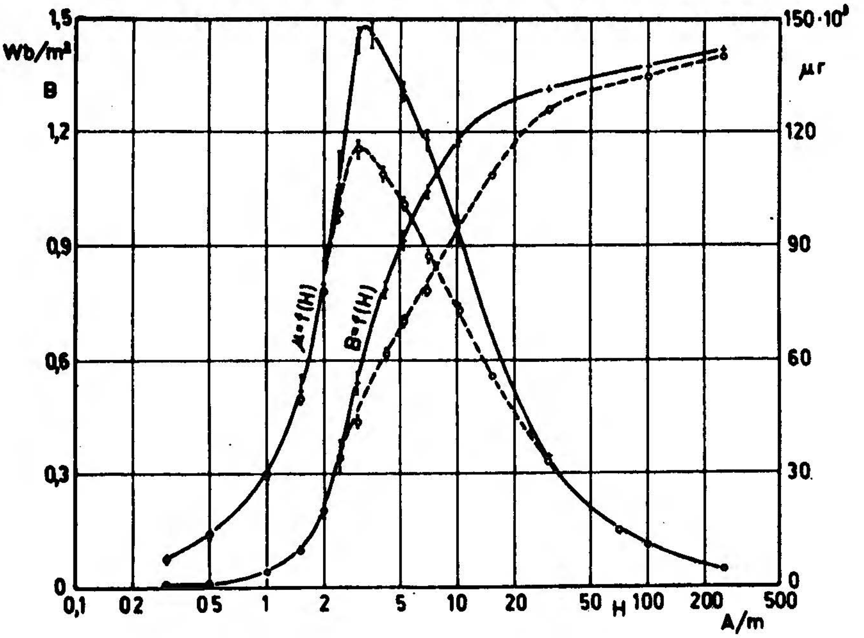

Fig. 8 - Magnetization and permeability curves. Specimen of Fe annealed in H_2 at 1480 ^{o}C for 18 hours. Irradiation with fast neutrons (1 Mev). Dose: 1,2 x 10^{18} fast and 1,24 x 10^{19} total n/cm^2 (MELUSINE, Grenoble). Solid lines: before irradiation; dotted lines: after irradiation.

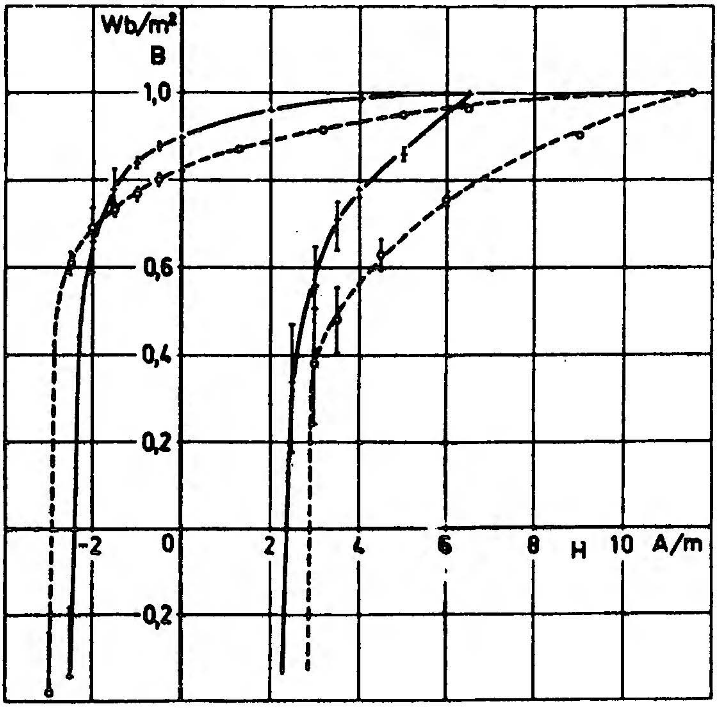

Fig. 9 - Hysteresis loops at a maximum induction of 1 Wb/m^2. Same as Fig. 8.

Thus a new series of experiments was planned on nickel and iron purified in H_2 for 18 hours at 1480 ^oC, which were free of impurities of carbon and nitrogen and had a relative permeability of 5000 and 150.000 respectively.

After neutron irradiation with an integrated flux of 10^{19} n/cm^2 a decrease of the permeability of the iron of 30% and an increase of the coercive field from 2.5 A/m to 3 A/m were observed, while nickel did not show any change in its magnetic characteristics.

These results prove that in metals neutron irradiation produces defects which can interact with a Bloch wall. The fact that recovery takes place between 100 and 200 ^oC suggests that such defects are very nearly point like (see Figs. 8, 9, 10).

In another paper it was shown that recovery of the defects which influence the mechanical properties takes place at on higher temperature (400-500 ^oC), a fact that shows that changes of the mechanical properties are due to defects different from those giving rise to changes of the magnetic properties.

7 - *Diffusion magnetic aftereffect.*

In 1925 Wild and Perrier(17) evidenced that the initial permeability of Fe-Si 3% is up to 100% higher if measured immediately after demagnetization, obtained either by cycling the material with hysteresis loops of gradually decreasing amplitude or by means of a mechanical shock. The permeability did relax to its normal value after a time interval which, at room temperature, was a few hours. A similar effect was observed also in pure iron, but in this case the temperature had to be lower, i.e, about -20 ^oC. Many other investigations on this field were done by other authors(18) (see fig. 11).

An important contribution to the understanding of this phenomenon was given by Snoek(19).

This author, by means of experiments on very pure iron annealed at 1480 ^oC in H_2, proved that the observed effect was due to interstitial atoms of carbon and nitrogen.

A very plausible assumption was given by Néel(20), who assumed that there is an interaction between the position of the interstitial atom in the crystalline matrix and the magnetization vector.

After demagnetization the Bloch walls are in random positions and the distribution of the interstitial atoms is uniform along the three crystallographic axes, but at a suitable temperature a directional ordering by diffusion occurs that has a stabilization effect on the walls.

In the theory a new quantity, the viscosity field H_t (see fig. 12), is introduced. It is defined as the intercept between the first magnetization curves obtained immediately after demagnetization and after a time sufficiently long to allow diffusion effects to take place completely.

The quantity Ht is particularly useful because it is directly related to the interaction energy, while the permeability relation depends also on other quantities, like the coercive field and the domain structure of the material.

The Néel theory was improved by Biorci, Ferro and Montalenti(21), who, by an instability effect, evidenced that, ,the Bloch walls at 180^o and 90^o have a very similar be-

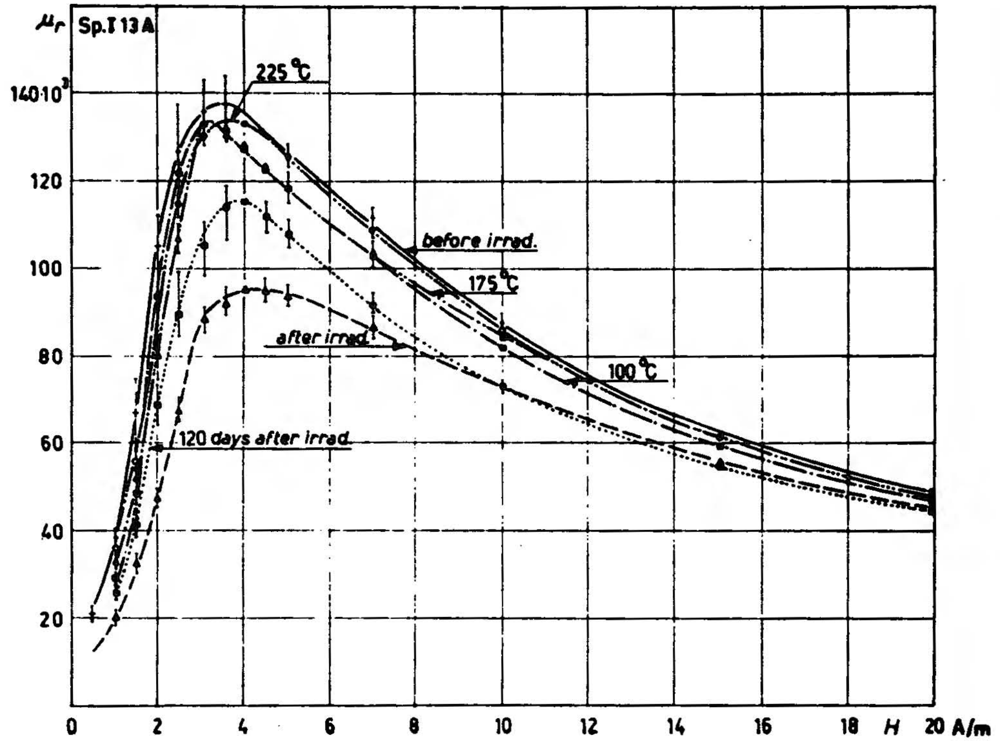

Fig. 10 - Specimen T13A. Permeability curves before irradiation (full line), after irradiation (dotted line) and after the different recovery stage).

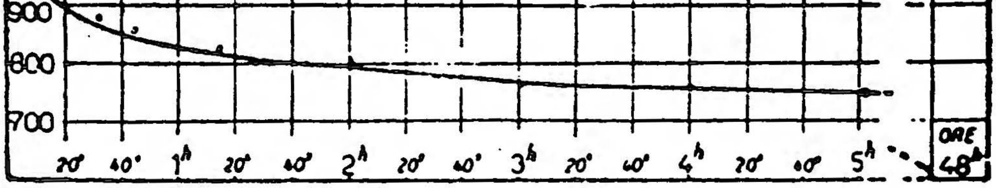

Fig. 11 - Absolute variation of 4% Si-Fe permeability following demagnetization as a function of time. H = 1 A/m; T = 20 oC; f=1000 Hz.

haviour, while the original theory predicted a completely different one. This fact was also experimentally proved by making experiments on specimens under a mechanical tension, which changes the ratio between walls at 180° and at 90°. The viscosity field H_t did not change by effect of the tension.

Fahlenbrack(22) on 1948 reported that a magnetic aftereffect was present in a Fe-Si alloy at a temperature of 450 °C. This effect could not be explained by a diffusion of impurity interstitial atoms and thus it was assumed that a rotation of the Si-Si pairs, randomly present in the disordered alloy, could play a role similar to that of the diffusion of the interstitial atoms.

To prove this assumption several alloys of different composition (Fe-Co, Fe-V, Fe-Si, Fe-Ni, Fe-Al, Fe-Mo) were prepared in our laboratory. Measurements of the viscosity field were done at 450 °C.

. From the viscosity field, the interaction energy between atom pairs and magnetization was calculated and a value of 1–2 x 10^{-16} erg/atom pair, against a value of 6 x 10^{-16} erg/atom in the case of the interstitial carbon, was obtain ed. These results show that in the iron solid solutions many properties depend only on the concentration of solute atoms and not on their nature(23).

Another effect is the induction of a magnetic anisotropy by means of annealing under a magnetic field (24). The hysteresis loop becomes more rectangular. If the specific heat anomaly is measured, a value (5 x 10^{-9} cal/mole) much lower than for the order-disorder transitions is obtained. This explain what was called the Bozorth's enigma on the annealing under magnetic field of the ferromagnetic alloys.

A complete theory of this effect has been given, together with additional experimental results by Biorci et al.(26).

It can be concluded that the magnetic aftereffect is the origin of wasp-waist shaped loops in the Rayleigh region and of the rectangularization of the loops after annealing in a magnetic field.

These effects are actually aspects of the same phenomena, i.e. the diffusional rotation of atom pairs in the disordered substitutional alloys or the diffusion of interstitial atoms within crystalline ferromagnetic structures.

As known, mechanical aftereffects can also be caused by dislocations or grain boundaries. In a paper of Biorci, Ferro and Montalenti(27,28) it is shown that this effect is also the origin of a small magnetic aftereffect(29).

In connection with this discovery, a study of the magnetic aftereffect due to carbon atoms anchored to dislocations was initiated. The dislocations were introduced by means of plastic deformation. In this way it was possible to evidence aftereffect phenomena having an activation heat of 32000 cal/g-atom for nitrogen and 36.000 cal/g-atom for carbon, in perfect agreement with the values found by K(30) and Ksten(31) by means of mechanical aftereffect measurements.

8 - Miscellaneous papers

It is opportune to quote here a paper of Ferro(32) on the calculation of the activation heat which characterize the diffusion of the interstitial atoms. Starting from a rigid spheres model, the energy of elastic distortion needed to allow the diffusion of an atom

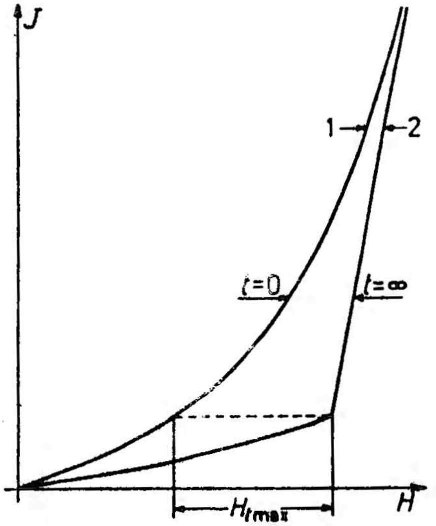

Fig. 12 - Magnetization curves: 1) immediately after demagnetization; 2) at infinite time after demagnetization. The horizontal difference is the viscosity field.

TABLE I

Metal	Symmetry	$\lambda \cdot \Lambda$ $\times 10^6$
Cs	c.c.c.	1810
Rb	-	1850
K	-	1810
Na	-	1890
Li	-	2150
Pb	c.f.c.	1380
Al	-	1530
Ag	-	1320
Au	-	1300
Cu	-	1350
Ni	-	1254
Pd	-	-
Pt	-	1105
Cd	Hex.	838
Zn	-	940
Mg	-	910
Bi	Trig.	630
Sb	-	698

λ= linear thermal dilation coefficient at 20°C.

Λ= formation heart per atom-gram.

from on interstice to another one is calculated. The atomic diameters are obtained from the data given by Pauling. In this way it is calculated the diffusion heat for hydrogen, carbon, nitrogen, boron within iron and some iron alloys with tantalum and molybdenum.

The results coincide, within +- 15% with those experimentally observed.

In another paper(33) some important quantities related to the crystalline structures are measured. In table I some results concerning the product of the formation heat and the thermal elongation coefficient are reported.

Even the product of the compressibility coefficient and the formation heat divided by the cube of the atomic diameter has a peculiar behaviour which has not been explained until now.

Finally the item "Magnetism" for the Enciclopedia Italiana Treccani was prepared.

These are the most significant results obtained at the IENGF of Torino within the period 1945-1960.

Many research works cited here were done with the help of the United States Air Force and with contracts with other organizations.

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DISLOCATION RELAXATION AND OTHER ASPECTS OF ELASTICITY AND ANELASTICITY AT THE ISTITUTO DI ACUSTICA "O.M. CORBINO"

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Summary. The elastic and anelastic behaviour of solids at low temperatures (300 - 4.5 K) has been investigated in Italy since 1947 at the Istituto Nazionale di Elettroacustica (now Istituto di Acustica) "O.M. Corbino". The experiments made in 1948-49, in collaboration with the M.I.T. (Boston, USA), under the auspices and with the support of the italian C.N.R., showed the existence, in some FCC metals (Pb, Cu, Al, Ag) of a new relaxation effect due to an intrinsic type of motion of the dislocations introduced by plastic deformation. Later investigations have shown that the effect exists in other plastically deformed FCC metals, as well as in HCP and BCC ones. In addition to a direct proof of the existence of dislocations, the above relaxation effect has given rise to a satisfactory atomic model of their motion, which is still applied not only to the intrinsic effect, but also to the case of dislocations interacting with interstitial impurities. This model is based on a new type of structural imperfections, the *kink-pairs* or *2nd order dislocations*, whose introduction has improved our picture of solid structure.

Riassunto. Ricerche sul comportamento elastico ed anelastico dei solidi a bassa temperatura (300 - 4.5 K) sono state eseguite in Italia, a partire dal 1947, presso l'Istituto Nazionale di Elettroacustica (ora Istituto di Acustica) "O.M. Corbino". Gli esperimenti effettuati nel 1948-49 in collaborazione con lo M.I.T. (Boston, USA), sotto gli auspici e con il contributo del C.N.R. italiano, mostrarono l'esistenza in alcuni metalli FCC (Pb, Cu, Al, Ag) di un nuovo effetto di rilassamento, dovuto al moto intrinseco delle dislocazioni introdotte da una deformazione plastica. Successive ricerche hanno mostrato che l'effetto esiste anche in altri metalli deformati plasticamente, non soltanto CFC, ma anche EC e CCC. Oltre ad una prova diretta dell'esistenza delle dislocazioni, il precedente effetto di rilassamento ha dato luogo ad un soddisfacente modello atomico del loro moto, che viene tuttora applicato non soltanto agli effetti intrinseci, ma anche quando le dislocazioni interagiscono con impurezze interstiziali. Questo modello é basato su di un nuovo tipo di imperfezioni strutturali, le *coppie di kink*, o *dislocazioni di seconda specie*, la cui introduzione ha perfezionato la rappresentazione della struttura dei solidi.

1 - Introduction

The relation between the *linear anelastic* (1) behaviour of crystalline solids and their *structural imperfections* is the object of a particular branch of Solid State Physics; in Italy investigations in this branch were started towards 1947 at the Istituto Nazionale di Elettroacustica "O.M. Corbino" and are still performed at the same Institute, which will be indicated in the following by its present name of Istituto di Acustica "O.M. Corbino" (I.D.A.C.). The choice of this Institute, which may appear somewhat surprising, is justified by the following reasons: i) the basic aspects of linear anelasticity are characterized by the values of frequency f and of internal energy dissipation coefficient Q^{-1} corresponding to the different vibration modes of each solid; ii) the most convenient techniques for measuring f and Q^{-1} are based on the direct or inverse transformation of mechanical vibrations into electrical oscillations; iii) in 1947 the I.D.A.C. had already acquired a decided specialization in the measurements of f and Q^{-1} by means of an "electrostatic" technique (2) which had several advantages on other techniques employed earlier for the same purpose (3).

The total activity of the I.D.A.C. in Solid State Physics, between 1945 and 1960, can be evaluated from the publications listed in the Bibliography. In the following Sections the attention will be focused on *the relaxation effect due to the intrinsic motion of dislocations*, because the investigations on this effect are those which have given the more significant and permanent contributions to the knowledge of structural imperfections.

2 - Investigations at low temperatures: collaboration between I.D.A.C. and M.I.T.

In 1948 it was "thought worth while to make a systematic investigation of the elastic and anelastic behaviour of solids at very low temperatures, since a new experimental technique i.e. the electrostatic one made it possible to measure very small dampings in a wide temperature range, and the large facilities provided by the low-temperature laboratory of Massachusetts Institute of Technology in which a new Colling cryostat had just been installed gave an almost unique chance of making a large number of measurements at liquid helium temperature" (X). It may be added that, at those times, the elastic and anelastic behaviour of solids between room temperature and 4.5 K was almost unexplored. A collaboration was therefore started between I.D.A.C. and M.I.T., under the auspices and with the financial support of the Consiglio Nazionale delle Ricerche.

The apparatus available for this investigation was so sensitive that it could measure vibrations which were smaller than the reticular constants of metals (fig. 1), and which had therefore only a statistical meaning (I)(III). The essential part of this apparatus, the *vibrometer*, was built at I.D.A.C. and sent to M.I.T. to be assembled with the conventional oscillator, amplifier etc. required by the electrostatic technique (fig. 2). The joint investigation made by I.D.A.C. and M.I.T. gave therefore not only one of the first examples of international collaboration after 1945, but also a rather uncommon instance of experiments performed in an american laboratory by means of an apparatus whose essential part was made in Italy.

Figure 3 shows one of the electrostatic apparatus which are actually in operation at I.D.A.C., and which differ from the older one of figure 2 only because tubes have been replaced by transistors, and because the investigator is now helped in some subsidiary operations, by the computer which is seen at the right of the figure.

The collaboration between I.D.A.C. and M.I.T. met, at its very beginning, with an unforeseen obstacle because, towards the middle of July 1948, the rails of the main lines joining Rome to northern Italy were cut, in the literal sense of the word, owing to some

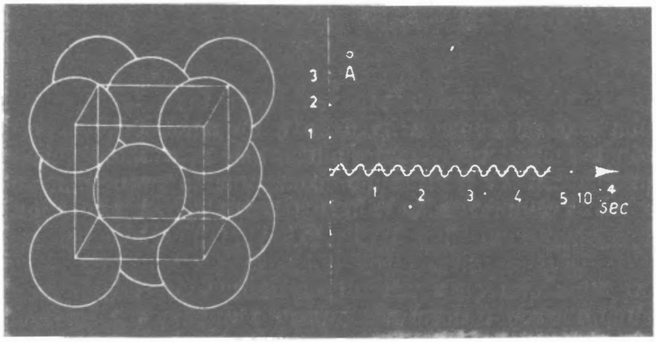

Fig. 1 Comparison between the aluminum lattice and the smallest vibrations which could be measured with the electrostatic technique in 1948 from (3), fig. 2 .

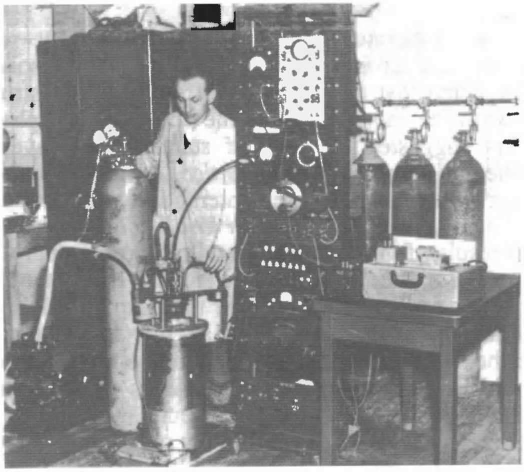

Fig. 2 Electrostatic apparatus for the excitation and measurement of vibrations at low temperatures employed at M.I.T. in 1948.

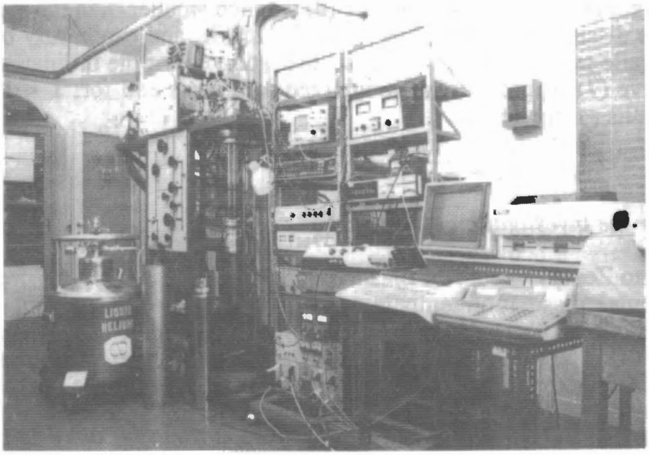

Fig. 3 Electrostatic apparatus actually in operation at I.D.A.C.

political troubles. This made somewhat arduous to reach the port of Amsterdam, from which would sail the ship on which the passage to the USA had been booked. It may be added that, at those times, transatlantic flights were still in their infancy. However these travel difficulties were overcome, and the planned investigations were not retarded; this episode would therefore not have been mentioned if it were not possible to derive a little lesson from it. The political troubles which originated the unprecedented, and luckily unrepeated, phenomenon of rail- cutting, appeared then of an almost cosmic importance, but are now entirely forgotten. On the contrary the results obtained in the low temperature investigations are still so present to the mind of the physicists interested in the structure of solids, that they have acquired an almost obvious character.

3 - Choice of the FCC metals: dissipation peak in lead

The fact that, at low temperature, elasticity and anelasticity were still substantially unexplored in 1948, left a great arbitrariness in the choice of the solids to be investigated. It could however be expected that the difficulty offered by the structural explanation of results would increase with the complexity of the chemical and physical structure of the solids considered. This suggested the idea of starting the investigations from some *elements*, having a *simple and common type of lattice*. A particular attention was also given to *geometrical imperfections* (vacancies, self-interstitials, dislocations, grain boundaries) because each of them has a *character common to all solids having the same lattice*. "In order to get significant results, four chemically and/or commercially pure metals of cubic face-centered crystal structure (Pb, Cu, Al, Ag) were chosen for the measurements; a large copper single crystal was also employed, beside the normal polycrystalline samples, to find out if grain boundaries were important even at low temperatures" (10). Moreover it was controlled that, on the basis of results obtained above room temperature by Zener and Ting Tsui Kê(4) it could be expected that, in the fields of temperature and frequency investigated (5), the dissipation due to the grain boundaries and to the heath exchanges between grains, would be very small, and would vary monotonically with temperature.

The first "runs" of low-temperature measurements showed that: "From room temperature down to 200 K, vibration damping in lead undergoes a strong decrease fig. 4 as it was qualitatively known from the lead bell in liquid air experiment ... From 200 K to 50 K only a small decrease in absorption is observed, but at still lower temperatures a slight rise is found and the curve has a flat maximum about 35 K".(10). This maximum, or, in the actual language, this *dissipation peak* (6) is much smaller than the "dramatic change undergone by the dissipatiion in the interval 300 - 200 K, and can hardly be seen in figure 4, but becomes quite evident when a larger scale is adopted for the ordinates, as in figure 5, whose lower curve (7) reproduces, with enlarged ordinates and for: T < 150 K, the same experimental results as figure 4.

4 - Procedure for the investigation of dissipation peaks

According to Zener's theory of Elasticity and Anelasticity (1), the presence of a peak in the experimental dissipation-temperature curve is a *necessary*, but in general not sufficient condition, for the existence, in the solid considered, of a thermally activated relaxation effect (8). The same theory also shows that such an effect is generally due to the motion of *lattice imperfections* (geometrical or material) under the combined action of thermal agitation and vibrational stresses. It follows that: *every time a dissipation peak like that of figures 4 and 5 is observed in an experimental curve, there is a possibility, or rather a reasonable chance, of investigating the distribution and the microscopic motion of some type of lattice imperfections by measurements of macroscopic variables, such*

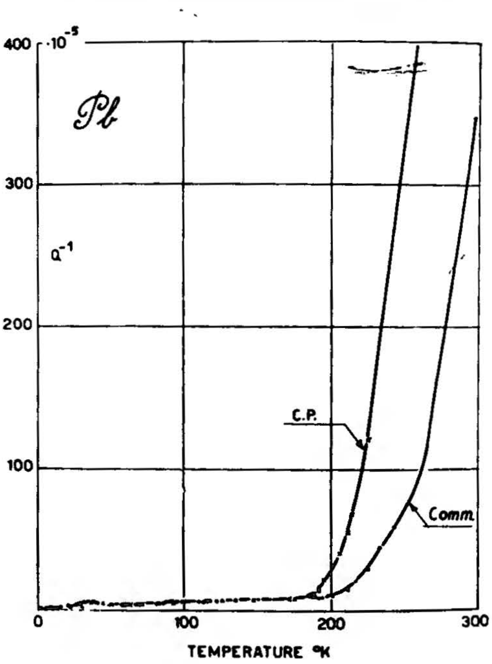

Fig. 4 First measurements of dissipation as a function of temperature in chemically and commercially pure lead: small peak at $\simeq$ 35 K from (10), fig. 5 .

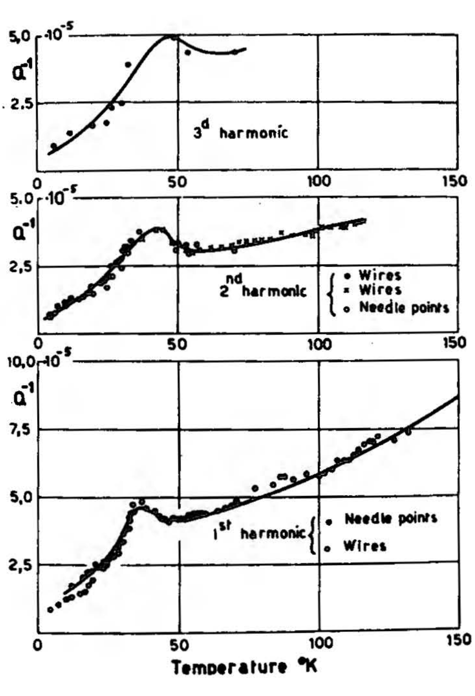

Fig. 5 Increase of the peak's temperature with frequency in chemically pure lead: proof of the existence of a thermally activated relaxation effect from (10), fig. 8.

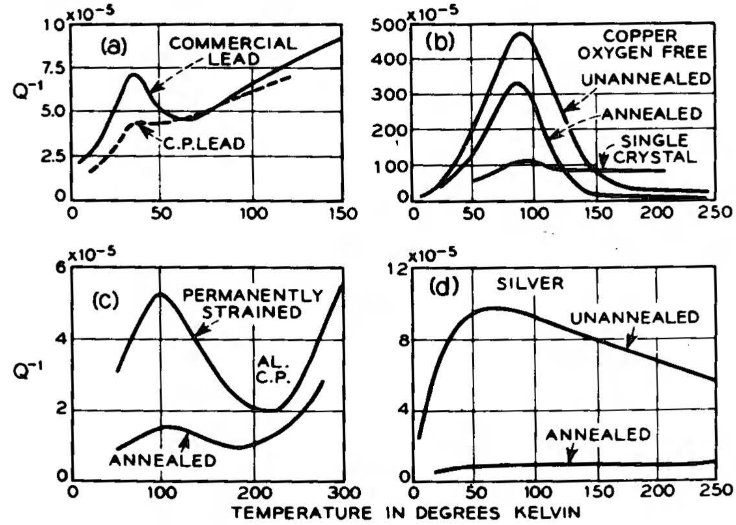

Fig. 6 Relaxation peaks in Pb, Cu, Al, Ag; influence of plastic strain and annealing from Mason, note (6), p. 266.

CONSIGLIO NAZIONALE DELLE RICERCHE

ISTITUTO DI ACUSTICA
«O.M. CORBINO»

50° ANNIVERSARIO

Fig. 7 Dislocation relaxation peak in polycrystalline copper unannealed or annealed and in a single crystal from the publications for the 50th I.D.A.C. anniversary.

as the resonant requencies and the dissipation coefficients of vibration modes.

This explains the interest roused by this kind of measurements, and the considerable development they have taken during the last decades.

in order to take advantage of the above chance, when a dissipation peak is observed, it is necessary:

1) *to control if it is due to a relaxation effect;*

2) *to identify - in the affirmative case - the particular imperfections responsible for it.*

This control and this identification were made, for the peak of figures 4 and 5, by means of an investigation procedure which is also valid for any other dissipation peak, and which has therefore been applied to all the peaks observed in experimental curves since 1948, and is still adopted for the same purpose. In conformity with its wide field of application and with its actual interest, this procedure will be outlined in its most general form, while its particular application to the peak observed in lead will be illustrated and discussed in the next Section.

Each of the points 1) and 2) corresponds ordinately to a separate phase of the investigation procedure. The first of these phases is directly based on Zener's theory (1) which shows that the presence of a dissipation peak becomes *sufficient* for the existence of a thermally activated relaxation effect if the peak satisfies to the following conditions: a) does not change when the measurements are iterated, after the solid has been kept at the highest temperature of the interval investigated (in the 1948 measurements at room temperature), for a time comparable to that required by the complete investigation of the same interval (usually a few hours); b) its temperature T_M increases with the vibration frequency f in such a way that lnf is a linear function of $1/T_M$. When both these conditions are satisfied, and only then, the dissipation peak is due to a thermally activated relaxation effect, and can be correctly called *a relaxation peak* (9).

On the basis of the above theoretical results, the first phase of the investigations consist of several runs of measurements, all covering the whole temperature interval investigated; during these runs the only changes of the chemical and physical structure of the solid must be those that are produced by the time and temperature variations required by the measurements, and which cannot therefore be avoided. Some of these runs must correspond to the same vibration frequency, and must be separated by time intervals of the order indicated in a), during which the solid is kept at the highest temperature considered. If the results of these measurements satisfy the condition a), other runs are made, at different frequencies, to control if also b) is satisfied. When this is the case, the proof that the peak is due to a relaxation effect is reached; moreover the height Q^{-1}_M of the peak, its activation enthalpy W and its limiting time τ = lim τ (for: T —) are directly given by the measurements or easily computed from them; finally, according to the theory of the effects with a relaxation spectrum(10), the strength S of the effect can be approximately determined from the value of Q^{-1}_M and from the halfheight width Δ of the peak plotted against the "universal" variable $(T^{-1}_M - T^{-1})$ W/k. However the values of these five parameters give little or no information on the structural origin of the relaxation effect, and a second phase of investigations is required in order to identify the imperfections responsible for it. To this purpose it is necessary to determine, as separately as possible, the influence exerted on the five parameters Q^{-1}_M, W, τ , Δ, S by: j) the chemical nature of the atoms located at the corners of the lattice considered; jj) the density of each type of geometrical imperfection; jjj) the concentration of each kind of impurity.

A *quantitative* determination of this influence is generally hindered by the difficulty of evaluating accurately enough the quantities jj) and jjj), or of varying them by small and controlled amounts. However, even a *semiquantitative* determination of the same influence is sufficient, in many cases of interest, to identify the imperfections whose motion gives rise to the peak. To this purpose, the quantities jj) and jjj) must be submitted to successive variations of a *known type* (increases or decreases), *quantitatively undetermined*, and the corresponding changes of the peak's parameters must be measured. By relating the *qualitative* variations of jj) and jjj) to the *quantitative* changes measured in the parameters, it is generally possible to identify the imperfections whose presence is necessary and sufficient for the existence of the effect.

To confirm the above identification, and to give it a final character, it is necessary to prove, on theoretical grounds, that the imperfections individuated move, under the combined action of thermal agitation and vibrational stresses, in such a way that they give rise to a strain of anelastic type(1), with a characteristic time (or times) related to the temperature by an *Arrhenius equation.* In particular a reasonable agreement must be obtained between the values of W and τ predicted by theory and those given by experiment, while the agreement that can be expected between the theoretical and experimental values of the other parameters is generally poorer.

5 - Intrinsic dislocation relaxation in FCC metals

When the first phase of the general investigation procedure outlined in the previous Section was applied to the peak of figures 4 and 5, for which it had been planned, it was immediately found that both the conditions a) and b) were satisfied. In particular, for the second of these conditions, the increase of the peak's temperature with the vibration frequency is clearly shown by the three curves of figure 5, which is taken from one of the original papers (10). It was thus proved that *the peak was due to a relaxation effect*, and the second phase of the investigation procedure could be started, to identify its structural causes.

The influence exerted on the parameters of the peak by the chemical nature j) of the atoms located at the corners of the lattice was determined by measuring the dissipation of the other FCC metals indicated in Section 3 (Cu, Al, Ag), in the whole temperature interval (300 - 4.5 K), and for similar fundamental frequencies (10 - 40 kHz); each of these metals was machined in the shape of a rod, and was kept - like lead - for some days at room temperature before the measurements. After these treatments, an evident peak was observed in each of the dissipation- temperature curves, and a summary control of conditions a) and b) showed that *all these peaks had a relaxation character.* For comparison purposes, the peaks found in the four FCC metals investigated are shown together in figure 6, taken from a review published in 1958 by Mason(11), who introduced the habit, successively generalized,of indicating this relaxation peak with the name of its first observer.

As it appears from the last figure, in copper the height of the peak is about two orders of magnitude above that of the other three metals. Owing to its particular evidence, the peak observed in copper has successively been the object of a great number of investigations, and, in the recent celebration (april 1987) of the first fifty years of activity of I.D.A.C., the same peak as been taken as a symbol of the results obtained, as it is shown by figure 7.

The influence exerted on the peak's parameters by the geometrical and material imperfections was determined in a *semiquantitative* way, for the reason indicated in the previous Section. In particular the density jj) of all the geometrical imperfections contained in the rods of copper, aluminum and silver was reduced by keeping the same rods, for a few hours, at a temperature intermediate between the room value and that corresponding to recrystallization(12).

For every metal it was found that: *the height of the peak decreased together with the density of geometrical imperfections*, without any significant change of its temperature. Conversely it was found that: *the peak rose when the density of geometrical imperfections was increased by means of a plastic deformation of* $\simeq$*1 - 2%*, while the peak's temperature remained substantially unvaried.

In its turn the influence of impurity concentration jjj) was determined in a very simple way by measuring, for each metal, the dissipation in several samples, which had undergone the same mechanical and thermal treatments, but differed in their impurity content,being either *chemically* or *commercially pure*. It was found that: *the impurity content did not affect the temperature of the peak, but only its height, in a manner which differs from one metal to another*. For instance, in lead, the highest peak corresponds to the commercially pure metal, while in copper to the chemically pure material.

On the basis of these experimental results it was concluded that: *the presence of the geometrical imperfections introduced by plastic deformation is necessary and sufficient for the existence of the relaxation effect observed in the FCC metals*. However, for a given density of geometrical imperfections, the presence of impurities may alter appreciably the height that the peak would assume in an ideal solid, entirely devoid of material imperfections.

It remained to decide which of the different types of geometrical imperfections is in particular responsible for the effect; *the grain boundaries could immediately be excluded*, because the effect had been found even in a *single copper crystal*, as it appears from figures 6 and 7. Moreover, according to the results of Ting Tsui Kê(4), the relaxation peak due to grain boundaries is observed, for the frequencies considered, at temperatures much higher than those corresponding to the peaks of figures 6 and 7.

The vacancies and selfinterstitials could also be excluded, owing to the *persistence* of the effect after the material had been treated at temperatures near to those at which the recrystallization takes place. Moreover, after a plastic deformation of $\simeq$ 1 - 2%, vacancies and self-interstitials are widely separated from each other, and would eventually give rise to a peak with a single relaxation time, much narrower than those of figures 6 and 7.

Owing to these exclusions, the only geometrical imperfections that could be identified with the structural causes of the effect were *the dislocations introduced by plastic deformation*, which generally lay along minimum energy regions (XI). This identification appeared very reasonable because it explained the experimental facts observed, *i.e.* the presence of the peak in a single crystal, its persistence when the solid is treated at temperatures near that of recrystallization, and finally the large width of the peaks of figures 6 and 7, in comparison with that of a singletime peak.

A final sanction of this identification was obtained by following the last indications of the procedure of Section 4, and submitting the motion of dislocations, in the neighbourhood of their equilibrium positions of minimum energy, to a theoretical investigation, in which the methods of Statistical Mechanics were employed: "Il movimento che le dislocazioni preesistenti nei solidi subiscono sotto l'azione di una piccola sollecitazione esterna é stato studiato con i metodi della meccanica statistica" (VIII). It was found that, under the combined action of thermal agitation and vibrational stresses, dislocations move in such a way that they give rise to a strain of anelastic type, whose characteristic time is of the order of 10^{-9} at room temperature, and increases of maybe orders of magnitude when the temperature is lowered to 4.5 K: "Esiste quindi una temperatura intermedia ...

per la quale ... in base alla teoria formale dell'anelasticità già citata ... si ha ... un massimo nella dissipazione e nel decremento. ... L'ampiezza del massimo dipende dal numero delle dislocazioni preesistenti nel cristallo: essa deve quindi diminuire se il materiale é preventivamente sottoposto a rinvenimento, mentre deve aumentare se nuove dislocazioni sono introdotte con una deformazione permantente" (8). On the basis of this theoretical sanction of the experimental identification, the paper quoted above, which was published in 1949, formally stated that:

"E' stato possibile identificare con sicurezza la causa della dissipazione nel moto delle dislocazioni". (8)

This result gave an experimental proof of the existence of dislocations in FCC metals some years before that the same dislocations were visualized by Hedges and Mitchell (13) in transparent crystals of silver halides. It must be added that visualization provides no direct information on dislocation dynamics; on the contrary the thermally activated character of the relaxation effect shows that dislocations - or rather dislocation segments - move, in their glide plane over *energy barriers*. Such barriers are provided by Peierls potential for those segments - and only for them - whose extremes are *anchored in the same valley*. The relaxation effect is therefore due to the motion of these particular dislocation segments in the neighbourhood of their equilibrium positions.

6 - Further investigations on dislocation relaxation in FCC metals

As De Batist(14) said in 1972: "Since the original publication by Bordoni (1949) of his observation of an internal friction peak in plastically deformed face-centered cubic metals ...an ever increasing number of investigations, experimental as well as theoretical, has been devoted to this effect, which is generally known now as the Bordoni peak." The results obtained till 1960 either by the I.D.A.C. group (XV), or by investigators of other countries (16) have been reviewed in 1958 by Mason (6), and in 1960 by Niblett and Wilks (2), which gave a list of about 130 papers. Later contributions have been reviewed in 1966 by Niblett (17), in 1972 by Nowick and Berry (1), and in the same year by De Batist (14); finally in 1979 Fantozzi, Benoit, Esnouf and Perez (17) published a paper in which about 280 contributions to the study of this effect are listed.

As it is natural, the following exposition will consider essentially the *results obtained by the I.D.A.C. group till 1960* (and published not later than 1961); however for a correct evaluation of these results it will be also necessary to give some information on the contributions due to other investigators whose work has a particularly close relation with that of I.D.A.C.; for the same reason, some of the results obtained before 1960 will be correlated with later investigations. Two experimental results are worth of a special attention; they concern respectively the existence of:

y) the intrinsic dislocation relaxation effect in some other FCC metals (Au, Pd, Pt);

yy) "a smaller internal friction peak occurring in cold-worked copper ... which appears to be associated to the main Bordoni peak". (II)

The first result was obtained in 1959 by the I.D.A.C. group, which observed, for the first time, the existence of dissipation peaks in plastically deformed gold, palladium and platinum (XIV), (XVI), as it appears in figure 8. By applying the procedure of Section 4, the same investigators proved that these peaks had a *relaxation character*; in particular the increase of peak's temperature with vibration frequency is clearly shown by figures 9 and 10 for gold and platinum. They also concluded that the same peaks were due - like those

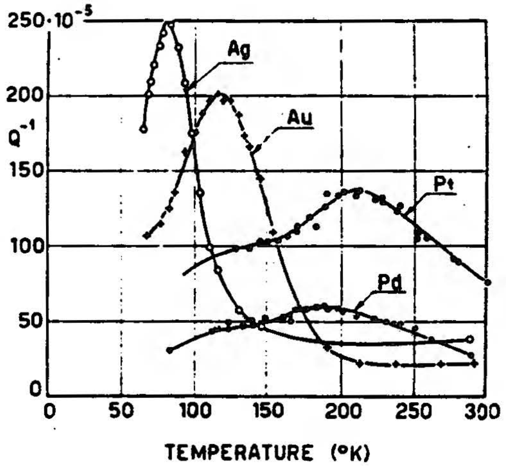

Fig. 8 Dislocation relaxation in silver (≃50.6 kHz), gold (≃ 16.0 kHz), palladium (≃88.4 kHz) and platinum (≃112 kHz) from (14), fig. 1 .

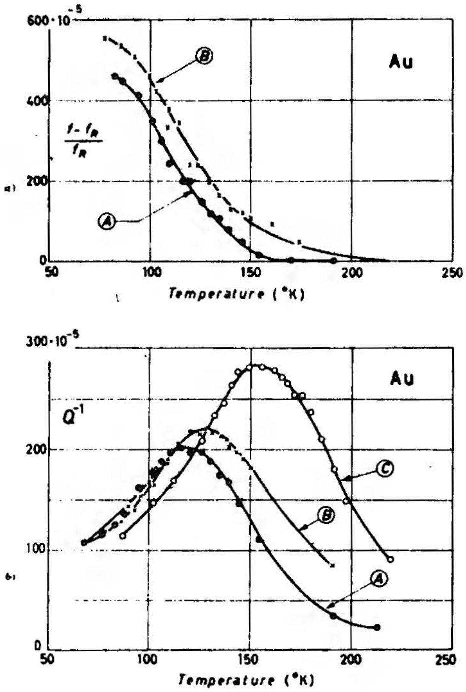

Fig. 9

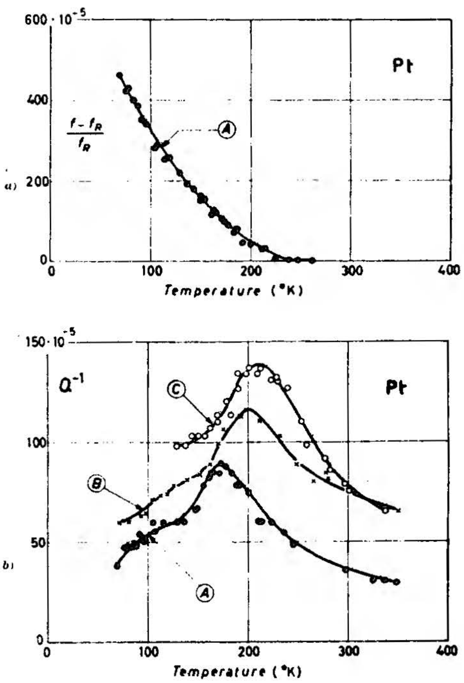

Fig. 10

Fig. 9 Dislocation relaxation in gold: increase of the peak's temperature with vibration frequency: A, ≃ 16.0 kHz: B, ≃ 55.6 kHz; C, ≃561 kHz from (16), fig. 4 .

Fig. 10 Dislocation relaxation in platinum: increase of the peak's temperature with vibration frequency: A, ≃ 9.60 kHz; B, ≃ 42.4 kHz; C, ≃112 kHz from (16), fig. 4 .

considered in Section 5 - to an *intrinsic dislocation motion*, which did not require the presence of other imperfections.

Some years later, another member of I.D.A.C. (XVIII), by introducing electrolytically hydrogen in palladium, found a new relaxation effect, due to *hydrogen-dislocation interaction*, whose peak, for the same frequency, fell very near to that of figure 8. It could then be suspected that, in palladium, the peak of figure 8 was also due to an interaction between the dislocations and the *residual hydrogen* which is generally contained in this metal, and which is not easily removed even by the high temperature treatment in vacuum to which palladium was submitted before plastic deformation (XIV), (XVI). A recent investigation (19) has confirmed that the peak of figure 8 is due to an intrinsic dislocation motion, and possesses some properties essentially different from those of the interaction peak: the two types of peaks can therefore be clearly distinguished.

From what has been said it appears that, before 1960, *the intrinsic dislocation relaxation effect had already been found in seven of the more common FCC metals (Pb, Cu, Al, Ag, Au, Pd, Pt); for each of these metals, the first observation had been made by I.D.A.C. group, and had been confirmed by several investigators of other countries* (16). Later investigations (14) (17) have shown that, in nickel, the situation in less clear, owing to the successive appearance of two relaxation peaks, corresponding to different amounts of plastic deformation. However it is generally agreed that the peak observed for the lower values of deformation is due to an intrinsic dislocation motion (17). It may therefore be concluded that: *the intrinsic dislocation relaxation effect has been found in all the FCC elements whose anelastic behaviour can reasonably be investigated* (20).

The second experimental result worth of a special attention concerns, as it has been indicated in yy), "A second internal friction peak, at a lower temperature than the main Bordoni peak, which was first observed in cold-worked copper by Niblett and Wilks (1955)" (17), and which is "often referred to as the Niblett-Wilks peak". (1) "Most subsequent measurements on copper have also shown this peak ... but in some cases it appears only as a small bump on the low temperature side of the main peak" (17) as it happens, for instance, in the 1959 measurements on copper of the I.D.A.C. group (XI), (XII), and as it can be seen in figure 11.

A careful inspection of the curves published in 1953 and 1954 (10), shows that the bump could have already been observed in these curves, not only in the case of copper, but also of lead, aluminum and perhaps silver. However, in the first experiments on the relaxation effect, it was natural to pay more attention to the existence of the main peak than to the details of its low temperature branch.

In gold, palladium and platinum, the second peak was observed for the first time, like the main peak, by the I.D.A.C. group in 1959, as it may be seen in figure 8.

According to Niblett and Wilks: "...the general similarity in behaviour of the Bordoni peak and the subsidiary peak suggests that the two arise from similar mechanisms" (2). It may therefore be concluded that: *the intrinsic motions of two different types of dislocations* (both lying along minimum energy regions) *give respectively rise to the main peak and to the subsidiary one.* In 1959 Thompson and Holmes, and successively Lauzier and Minier (19) (21) have ascribed the main peak to dislocations lying along <110> directions (screw or mixed, forming an angle of 60° with their Burgers vectors), and the subsidiary peak to <121> dislocations (edge or mixed, with and angle of 30°). Seeger (22) has suggested a partially different explanation of the main and subsidiary peak, ascribing them respectively to screw and non- screw dislocations.

Other significant results have been obtained by determining the values of the peak's parameters (Section 4), for all the metals considered above. These values vary somewhat with the chemical nature j) of the metal, but are *substantially independent of the density jj) of geometrical imperfections, and of the concentration jjj) of material imperfections*; moreover, in the linear range, they are also *independent of vibration amplitude.* Typical values for the enthalpy and the limiting time are:

$$W \simeq 0.15\ \text{eV} \qquad \tau \simeq 10^{-12}\ \text{s},$$

while the width of the peaks is always three or four times larger than for a single relaxation time. The most accurate values of the peak's parameters are those obtained in 1959 for copper by the I.D.A.C. group (11), (12), whose measurements cover the *widest frequency range* investigated, till today, *in the same vibrating solid* (fig. 12).

7 - Dislocation relaxation in HCP and BCC metals

Fantozzi et al. (17), resuming the results obtained in the study of dislocation relaxation, observed that "La relaxation de Bordoni a d'abord été abondamment étudiée dans le cas des métaux cubiques a faces centrées, puis cette etude a été étendue a d'autres métaux". A reason for this extension was indicated by Nowick and Berry (1) which stated that "the Bordoni relaxation has been interpreted in terms of the fundamental properties of isolated dislocation lines: it follows that the same relaxation phenomenon should exist for materials other than FCC metals". In particular, according to the same authors "For HCP metals one would expect a closer similarity to the FCC in comparison with other lattices because of the similar closepacked structure, as well as the absence of the unusually strong impurity-dislocation interaction present in BCC metals".

The above considerations explain why, toward 1960, the I.D.A.C. group extended its investigations to solids with lattices different from the FCC, starting with the HCP and considering successively the BCC. "En 1960 Bordoni et al. ont montré clairement que le zinc pouvait présenter, après déformation plastique, un comportement comparable a celui des métaux C.F.C." (17), as it is shown by figure 13. Similar results have been obtained later by other investigators in several HCP metals (Mg, Zr, Ti, Rh) and it may be concluded that: *intrinsic dislocation relaxation takes place also in HCP lattice.* However, in every case the peaks observed in the HCP lattice are considerably wider than those found in the FCC metals.

For BCC metals, the measurements made by the I.D.A.C. group towards 1960, proved that in plastically deformed niobium (XXI), tantalum and molibdenum (184), (185) (23), the dissipation peak observed at a single frequency by other experimenters (24) was due to a relaxation effect, as in FCC metals (fig. 14). This result was successively confirmed by other investigators, and extended to tungsten (25). Later experimental evidence collected by Mazzolai and Nuovo (210), Verdini and Vienneau (213), Cannelli and Mazzolai (221), Verdini and Bacci (26) has shown that the peaks observed in the investigations on BCC metals quoted above were due to the *interaction* between the *dislocations* introduced by plastic deformation, and the *residual hydrogen,* left by an incomplete outgassing of the material. If the hydrogen content undergoes a further drastic reduction, an *intrinsic dislocation* peak is observed in plastically deformed BCC metals, at a temperature much lower than that of the interaction effect.

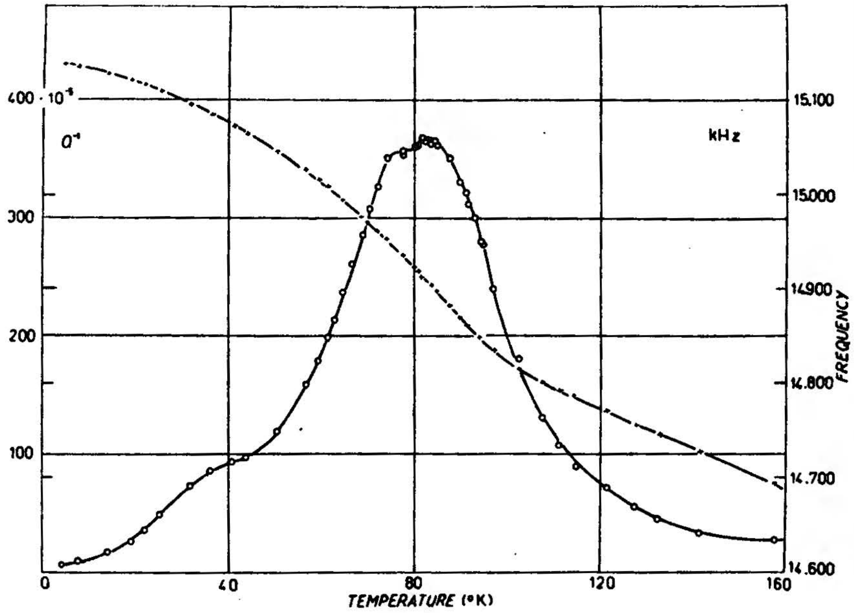

Fig. 11 Dislocation relaxation in copper: dissipation-temperature and frequency-temperature curves: main peak (~ 80 K) and subsidiary Niblett-Wilks peak (~ 37 K) from (11), fig. 8.

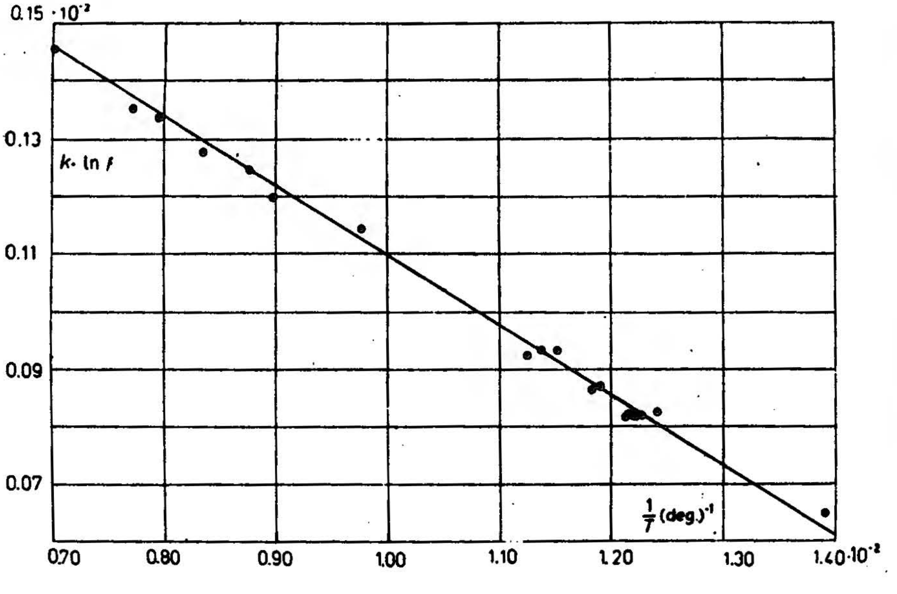

Fig. 12 Dislocation relaxation in copper: linear dependence of the logarithm of vibration frequency on the inverse of temperature from (11), fig. 17 .

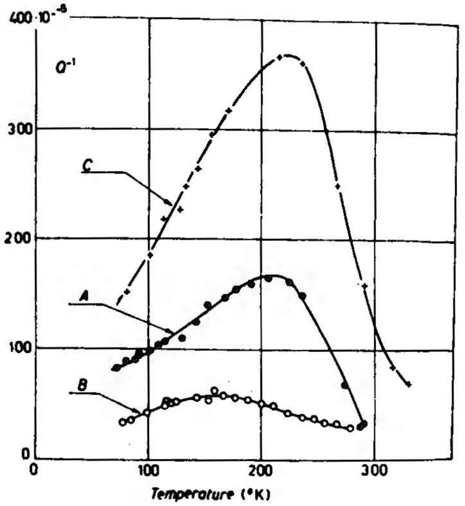

Fig. 13

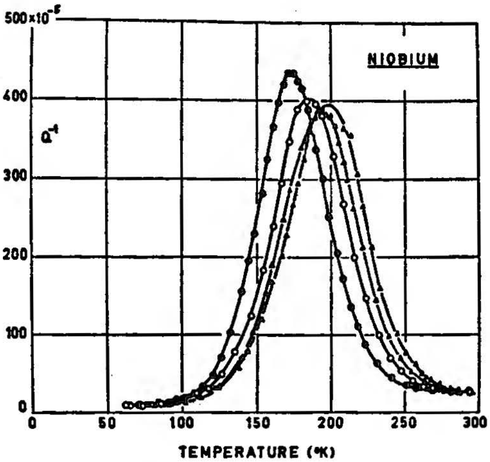

Fig. 14

Fig. 13 Zinc single crystal: influence of geometrical imperfections on the relaxation peak: A, after the chemical cut of the specimen; B, after 30' at 300 °C; C, after a plastic compressional deformation from (20), fig. 2.

Fig. 14 Niobium, plastically deformed: increase of the peak's temperature with vibration frequency; full circles ≃ 18.6 kHz; open circles ≃ 67.7 kHz; full triangles ≃ 118 kHz; open triangles ≃ 174 kHz from (21), fig. 1 .

8 - Model of dislocation motion derived from their intrinsic relaxation effect: conclusions.

The results obtained in Italy on the intrinsic dislocation relaxation, from its first observation in 1948 till 1960, have proved that:

I) under the influence of thermal agitation, the dislocation segments whose extremes are anchored by other imperfections in the same Peierls valley, move - as a whole or in portions - in their glide planes, over the energy barriers provided by the Peierls potential (Sect. 5);

II) the activation enthalpy of intrinsic dislocation relaxation is substantially independent of the content of other imperfections (Sect. 6); moreover Weertman (27) observed that this enthalpy is proportional to the length of the *moving portion* of a segment, which must therefore be independent of the total length of the segment.

On the basis of I) and II), Seeger and his school (27) have developed, towards 1956, a model of dislocation motion which, in the following investigations, has proved substantially correct, and is still applied, not only to the intrinsic motions, but also to those in which dislocations interact with interstitial impurities, according to a suggestion due to Schoek (27), and to the later work of Seeger (27).

In this model, a segment, whose extremes are anchored in the same valley, bulges, owing to thermal agitation, into a next and parallel valley, and then extends the bulge in the direction of the valley, under the action of applied stress. The motion of the segment is therefore *gradual*, as that of a crystal plane which glides over another, not rigidly, but increasing progressively the region in which glide has already occurred. It is well known that this region is encircled by a dislocation; in a similar way, the central part of a bulge is bounded by a pair of opposite S-shaped kinks; it follows that *kink-pairs* have, in regard to the motion of dislocation segments, the same function that dislocations have for the glide of a crystal plane over another. Kink-pairs are therefore a new type of imperfection, not of the lattice, but of the dislocations themselves, *i.e.* they are *dislocations of dislocations*, or *2nd order dislocations*.

It may be concluded that the experimental proof of the existence of dislocation, the model which can be applied to their motions (of intrinsic type or in interaction with interstitial impurities) and the introduction of 2nd order dislocations, on which the above model is based, are the more significant and permanent contributions to the knowledge of structural imperfections which have been obtained from I.D.A.C. investigations on intrinsic dislocation relaxation.

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(2) "Bordoni (1947) used a single electrode placed adjacent to one end of the specimen, both to excite the specimen into longitudinal vibrations and to detect them (using frequency modulation)" D.H. NIBLETT, J. WILKS: *Phil. Mag. Suppl.*, 9, 1, (1960). This technique, whose gradual development was the major achievement of I.D.A.C. during the first ten years of activity (1937-1947), was introduced by G. Sacerdote and M. Nuovo, and successively improved ad adapted to solid state investigations by the writer (I), ..., (VII).

(3) As in the well-known case of a pudding, whose best proof is in the eating of it, the best proof of the advantages presented by the electrostatic technique is given by the large number of applications that it has received, and still receives, not only at I.D.A.C., but also at several Universitary Institutes, in Italy and abroad (Milano; Bologna; Pisa; Perugia; M.I.T., Cambridge, USA; N.R.C., Ottawa, Canada; Dept. Phys. Univ. Alberta, Edmonton, Canada; Lab. Phys. des Vibrations, Limoges, France).

(4) See the two first books quoted in note (1).

(5) All the measurements were made in the low ultrasonic range.

(6) As it is indicated by its name, a dissipation peak corresponds to *any type* of function $Q^{-1}(T)$ having a relative isolated maximum at the temperature of the peak. Dissipation peaks must not be confused with relaxation peaks, which will be defined later, and correspond to a *particular type* of functions $Q^{-1}(T)$. The distinction between the two peaks was introduced by W.P. MASON: *Physical Acoustic and the Properties of Solids*, Van Nostrand Ed., New York (1958), 267.

(7) The two upper curves of figure 5 will be discussed in Section 5.

(8) This condition is valid not only for the effects associated with a *single relaxation time* - which were the only ones known in 1948 - but also for the effects with a *bell-shaped spectrum* of relaxation times.

(9) Owing to its definition, a relaxation peak is a *particular type* of dissipation peak, which corresponds, according to Zener's theory, to a dependence of dissipation upon temperature expressed by a *hyperbolic secant*, or by a linear combination of such functions; see also note (5).

(10) See the last book quoted in note (1).

(11) See the book quoted in note (6).

(12) Such a treatment was not required in the case of lead which recrystallizes near room temperature.

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(16) In particular: NIBLETT and WILKS, CASWELL, PARE', THOMPSON and HOLMES, BIRNBAUM and LEVY, SHIBATA, HUTCHISON and FILMER, HUTTON, EINSPRUCH and TRUELL, BOEMMEL, MASON, WELBER and QUIMBY, SEEGER, DONTH and PFAFF, BRIGGS, LAX and FILSON, BRUNER.

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MAGNETIC RESONANCE SPECTROSCOPY IN PAVIA UNDER LUIGI GIULOTTO: 1945-1960

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I - *Introductory Remarks*

The authors of the present paper did not have the real opportunity to be a large part of the research activity in Pavia during the years 1945-60. The paper is based on a survey of the works published during those years, on conversations that later on the authors had with L. Giulotto and on an interview, with a tape recording, that G. Giuliani and S.Galdabini made with him in 1983. Furthermore, the text of the celebration lecture that Giulotto gave in May 1981, at the end of his last official course, has also been used.

NMR was really the major topic of research in Pavia during the years 1945-60, particularly the long-lasting one. However, at least two other subjects had a certain relevance in Pavia at that time, in the field of the optical and Raman spectroscopies. Thus we are going to recall, in the next section of the paper, the conclusive results of the Giulotto's studies on the relativistic structure of Hα line and on Raman spectroscopy in calcite and isomorphous crystals. Section III of the paper is devoted to the studies in nuclear magnetic resonance (NMR), with a mention of an experiment of electron paramagnetic resonance. The Section could be separated into three main parts: detection of the phenomenon of magnetic resonance in bulk matter, its description and the clarification of its major features; development of methods for the measurements of relaxation times; application of NMR and relaxation measurements in solid state physics. In Section IV summarizing remarks on the cultural background underlaying the scientific activity in those years and few conclusive comments are presented.

II - *Fine structure of Hα and Raman spectroscopy in calcite*

From a discussion with Piero Caldirola, at that time assistant professor in Pavia, Giulotto got the suggestion to carry out an experiment of high resolution spectroscopy in hydrogen in order to investigate the relativistic effects, in the light of the Dirac theory. Since 1942-43 Giulotto improved the performances, particularly resolution and thermal stability, of a spectroscopic device of Littrow type (nicknamed "the crocodile"). Five years later, in 1947, including the interruption due to the Second World War events, the research could be completed.

As is known, the problem of the detailed structure of the eigenvalues in the hydrogen atom had a fundamental role in atomic physics and in quantum electrodynamics.

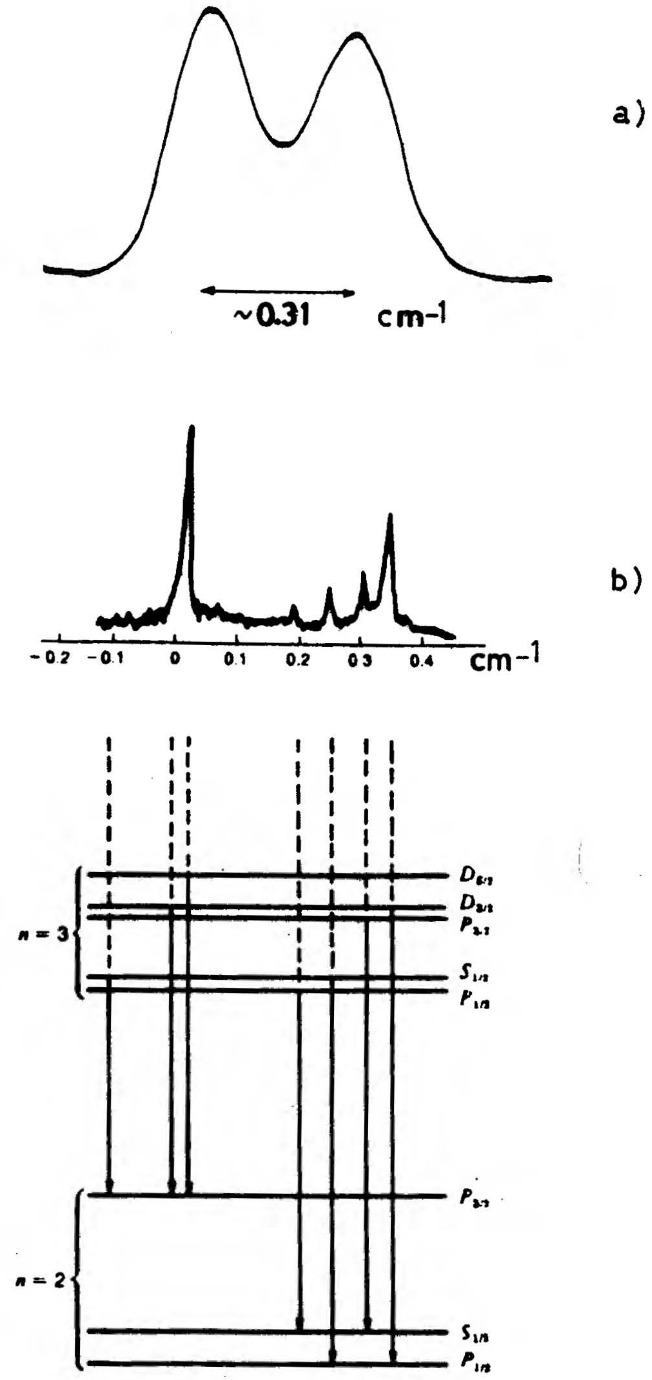


Fig. 1 - Energy levels for the hydrogen atom, as they can be deduced from the detailed structure of the Hα line as obtained with the use of lasers (part b - Figure adapted from A.P. French and E.F. Taylor "An Introduction to Quantum Physics", Van Nostrand, 1986, p. 544) - Part a) of the Figure shows the asymmetric doublet as it appeared in 1947, Ref. 2).

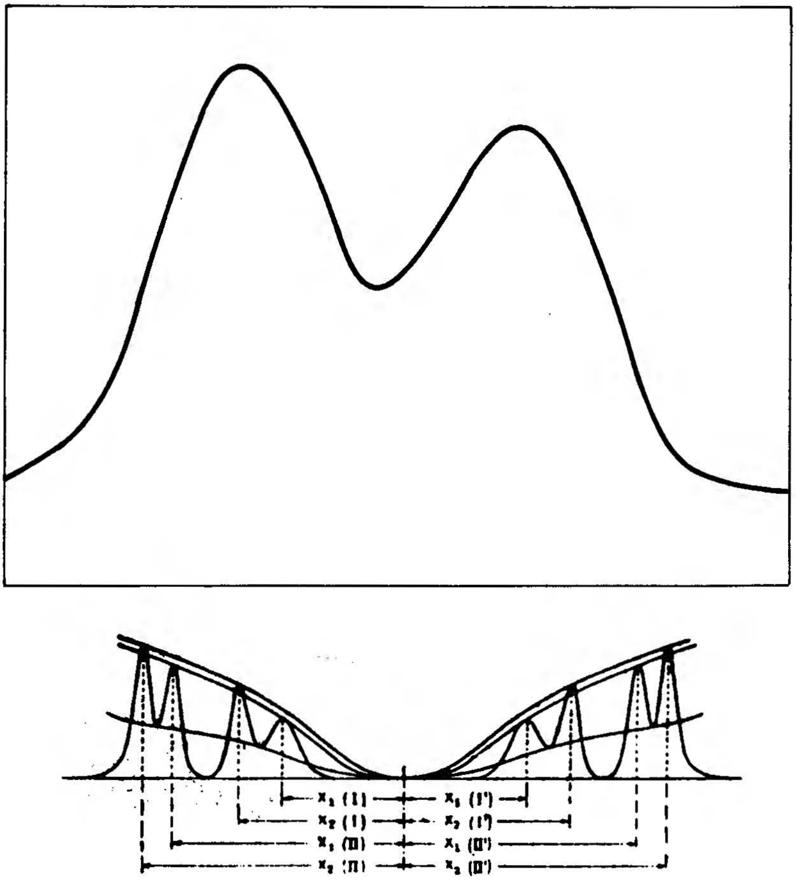


Fig. 2 - The microphotometric plot of the Hα line in hydrogen observed by L. Giulotto and details of the fitting procedure from which the shift of the n = 2 l = 0 level was deduced. (Figure adapted from Ref. 3).

According to the relativistic Dirac theory the eigenvalues at quantum numbers n = 2 and l = 0 or l = 1, with the same value of j = 1/2, should have the same energy (see Fig. 1). From "painstaking spectroscopic measurements" (the definition is from Van Vleck, in the Encyclopaedia Britannica (1) and a careful fitting of the asymmetric doublet which covered the real detailed structure even in the best measurements possible through conventional spectroscopy, (see Fig. 2), Giulotto (2) (3) could argue that the level at l = 0 was shifted from the one at l = 1. Giulotto's paper (2) came to the following conclusion "However, it is not certain that the formalism of quantum mechanics maintains its validity for problems involving distances of the order of the nuclear radius. Therefore, we may hope that, when a suitable formalism is found, the small observed deviation may be justified". The new key was found later on by W.E. Lamb: by using the new techniques of microwave spectroscopy he gave the exhaustive confirmation of the shift of the l = 0 level, elaborating also the theory for the new quantization of the electromagnetic field (4).

It might be interesting to mention that, according to Caldirola, Giulotto's results were disregarded as experimental errors by a distinguished physicist, Wolfgang Pauli. This, needless to say, is not a comment against Pauli, but just a piece of support for the belief that in science a particular biasing occurs: for some time, the experimental results are good only if they show that a theory is right (only later on, as evidence in favor of the theory accumulates, one might have an inversion).

Giulotto began his studies based on Raman spectroscopy from the years 1938-39, devoting his attention mostly to the fine structure of the low-frequency Raman lines in liquids, in part in collaboration with P. Caldirola. Later on, during the years 1948-1951, Giulotto and Olivelli applied the Raman spectroscopy to the study of the coupling between lattice modes and internal modes in the calcite ($CaCO_3$) and isomorphous crystals. The problem of the various lines observed in these crystals was a rather general one and other authors, including Raman himself and Kastler, had already worked on it (5). From the analysis of the Raman spectra (see Fig. 3) Giulotto and Olivelli were able to conclude that two low-frequency lines had to be related to the fact that the angular oscillations of the CO_3 ions cannot be decoupled with the oscillations of the two Ca and CO_3 lattices. Thus, the only possible motions consist in translational motions perpendicular to the optic axis accompanied by periodical oscillations in the orientation of the CO_3 ions, yielding the two eigenfrequencies characteristic of coupled oscillators. On the basis of this picture, Giulotto and Loinger evaluated all the lattice constants and the specific heat (6). The interpretation provided by Giulotto and Olivelli was inspiring to Kastler (7), who extended the picture also to the far-infrared spectrum, being able to explain the occurrence of three frequencies for the ordinary ray and two frequencies for the extraordinary one.

III - *NMR and Relaxation Studies*

The magnetic resonance experiments performed by Rabi and coworkers on atomic and molecular beams since 1937 had shown that the nuclear magnetic moments in a static magnetic field could exchange energy with a weak magnetic field oscillating perpendicularly with proper frequency. Thus, an analogous phenomenon was somewhat expected also in bulk matter. The first attempts were made by Gorter and coworkers, from 1936 to about 1942, who tried to detect nuclear magnetic resonance by absorption, through the detection of thermal effects in the crystal. Their failure was essentially due to an unfortunate choice of a material with a long time required for the exchange of energy from the nuclear spins to the crystal lattice.

The success in producing NMR in bulk matter came in 1945 by two groups, working independently: the Bloch group at Stanford and the Purcell group at Harvard. The

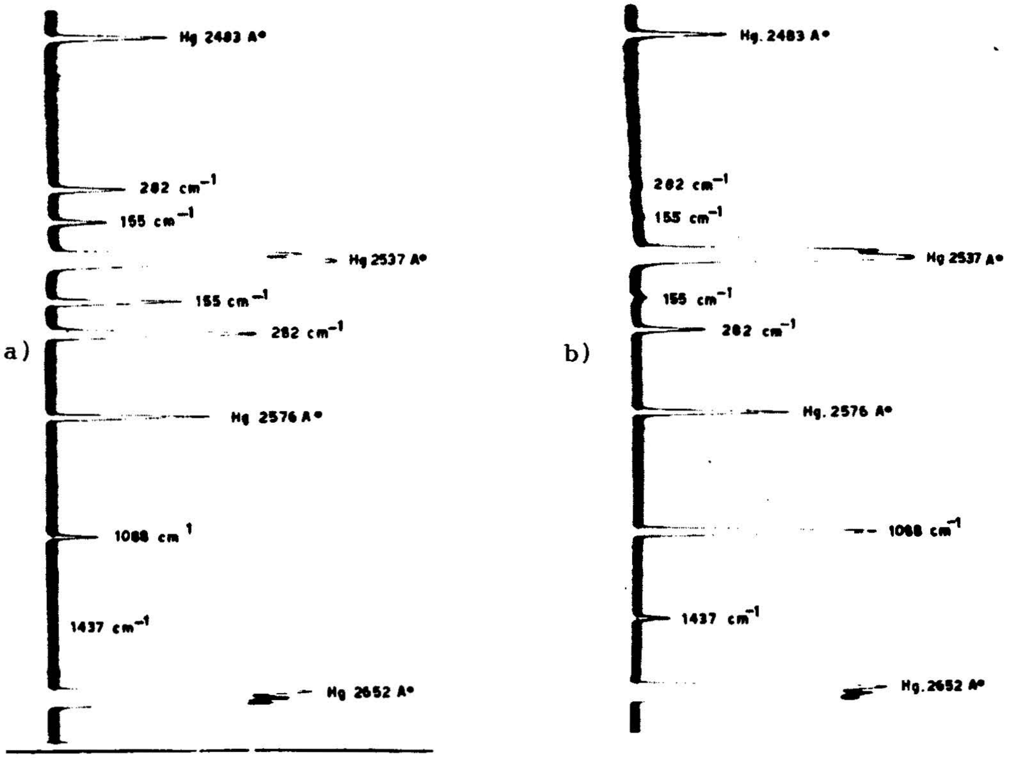
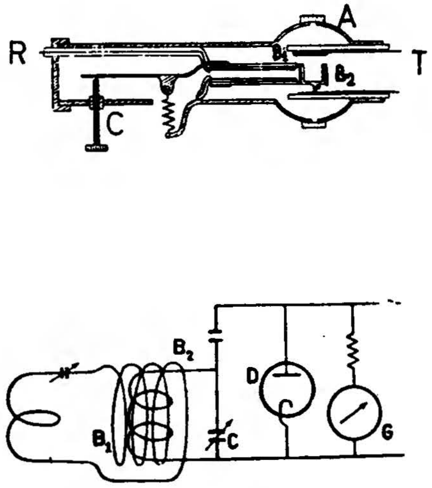


Fig. 3 - Raman spectra observed by L. Giulotto and G. Olivelli in calcite.



A) metallic screen

B_1) transmitter coil

B_2) receiving coil

C) device to move the receiving coil

T to the RF generator

R receiver (a rectifying diode with a voltmeter and a low-frequency amplifier)

Fig. 4 - The radio-frequency head of the first NMR equipment in Pavia.

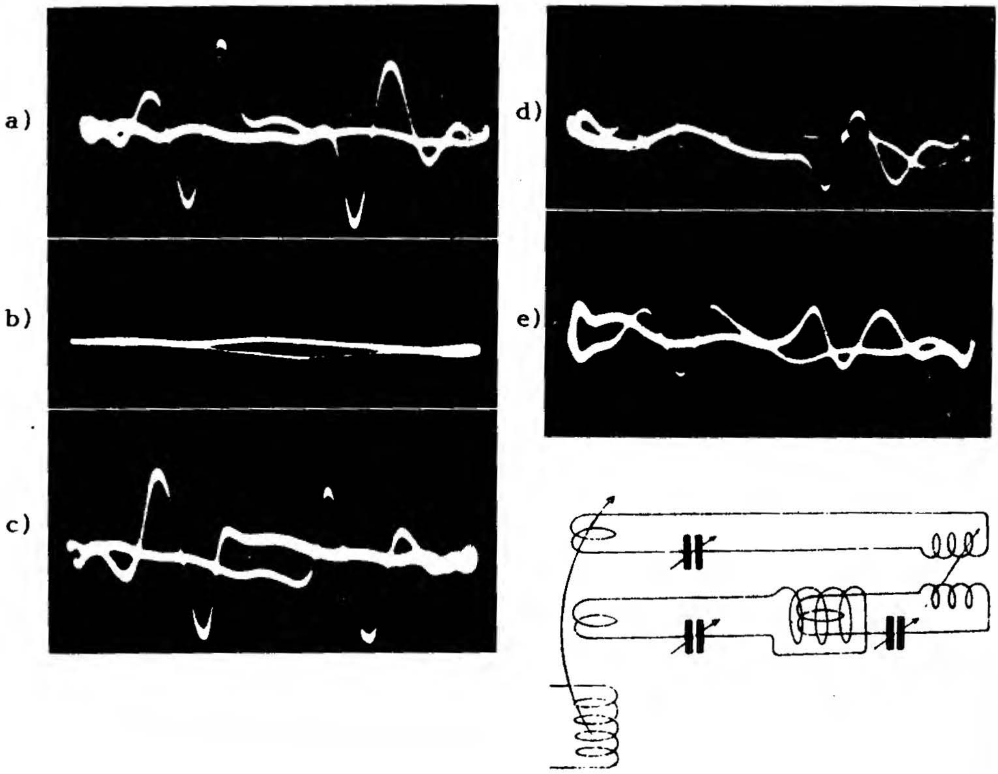
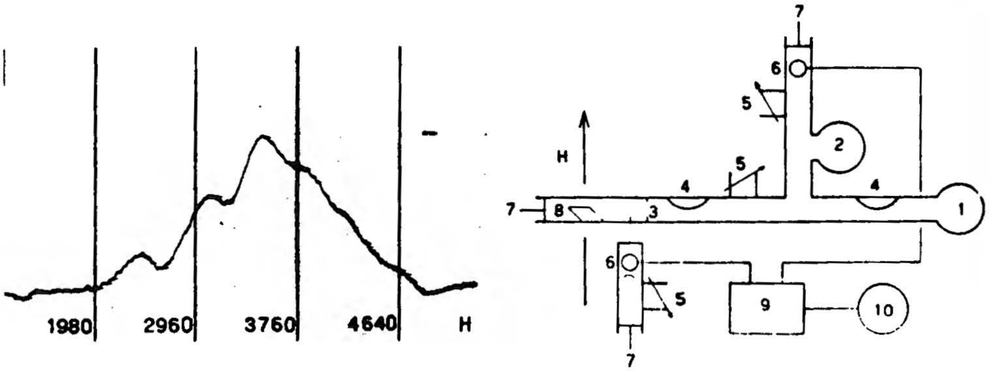


Fig. 5 - The device to study the phase dependence of the NMR signals (Ref. 12).



1, Klystron; 2, Ondametro: 3, Iride; 4, Attenuatori variabili; 5, Pistoncini d'accordo; 6, Cristalli rivelatori; 7, Pistoni terminali; 8, Cristallo in esame; 9, Ponte; 10, Galvanometro di Moll (Periodo 0,2 sec).

Fig. 6 - The apparatus for an automatic recording of paramagnetic resonance absorption and the spectrum obtained in a single crystal of chromum alumen (Ref. 15).

conceptual backgrounds underlying the two discoveries were basically different (8). The magnetization precession and magnetic induction approach taken by Bloch was more or less in preparation for about ten years, in connection with the study and the experiments on the magnetic moment of the neutron. Purcell, who had the rather different picture of magnetic resonance as spectroscopic transitions in a two levels system, had not had yet time to produce a body of research before 1945. Both of them, Bloch and Purcell, were engaged in war-time activities. Purcell was at the MIT Radiation Laboratory working on the development of radar systems, and his resonance absorption of spectroscopic character for NMR was largely laid by that experience on microwave radiation. Bloch was at the Harvard Radio Research Laboratory working on counter-radar measures, thus learning about radio-techniques, noise etc.

a) *The NMR detection in Pavia and the clarification of the phenomenological aspects*

In Pavia, Giulotto became aware of the NMR experiments in bulk matter through Caldirola, who brought to his attention the papers of the Stanford and Harvard groups (34). Giulotto thought that the experiment did not require a great deal of instrumentation and could be set up even in small university laboratories, with little budget. In a way Giulotto also benefited from the war events. Besides some experience in radio telephonic transmission that he got serving the army, in 1946 Giulotto had to resort to the military surplus for electronic hardware, finding a radio receiver at the Senigallia market (the Milano equivalent of Portobello Road), for his NMR experiment. The radio generator could be home-made, taking advantage of the skill in electronic techniques of P. Sillano, an industrial engineer who was partly collaborating with him. Still, the conditions for a rather advanced radiofrequency experiment were really poor in Pavia at that time (9). Giulotto did not even have an oscilloscope or a recorder and when he succeeded in getting the NMR signals he had to *hear* the signals as an extra-noise in a telephonic head-set. (Once he said : "I could hear the signals because of my faith", "*avevo la fede*"). In 1947, with the help of a check by Orazio Specchia, director of the Institute of Physics (a research grant had been provided directly to him by C.N.R., and Specchia was storing the checks in the safe of his office as sacred material (10), an oscilloscope could be bought (Pontremoli, cost 15.000 Lire) and Giulotto and Gigli could finally see the NMR signals, taking a picture and publishing the paper (11). The core of the nuclear inductor (as Giulotto named it) is shown in Fig. 4. The modulating field for sweeping through the resonant magnetic field was provided by the 50 Hz industrial ac current. The first NMR signal seen on the scope were due to the protons of water and were observed to depend in strength on the concentration of paramagnetic salts and on the position of the receiving coil. In a few weeks Giulotto and Gigli realized that the changeover in the shape of the signal caused by slight variations in the position of the receiving coil had to be related to the phase difference between the signal induced by the motion ofthe resonant nuclei and the rf directly collected by the receiving coil from the transmitting one. A simple device allowed them to study more quantitatively this effect (12) (see Fig. 5). The experimental apparatus was quickly improved and other relevant features of the phenomenon, remarkably the saturation effects due to the spin-lattice relaxation, were clarified by Giulotto (13) in 1948: the shape of the signals resulting under various conditions were interpreted on the basis of Bloch's theory (14).

In 1949 Giulotto and Levi Setti (15) set up an automatic microwave apparatus to detect the electron paramagnetic resonance absorption by means of a differential method. Fig. 6 shows the simple device, based on a Klystron and a T waveguide, with an ingenious system for a direct recording, based on a variable electrolytic resistor. The magnetic field intensity was proportional to the angle of rotation of a cylinder where a photographic paper recorded the differential signal. The calibration was obtained by means of proton NMR. The method devised by Giulotto and Levi Setti was a valuable one because a rather precise measure was joined to a fast recording of a wide line.

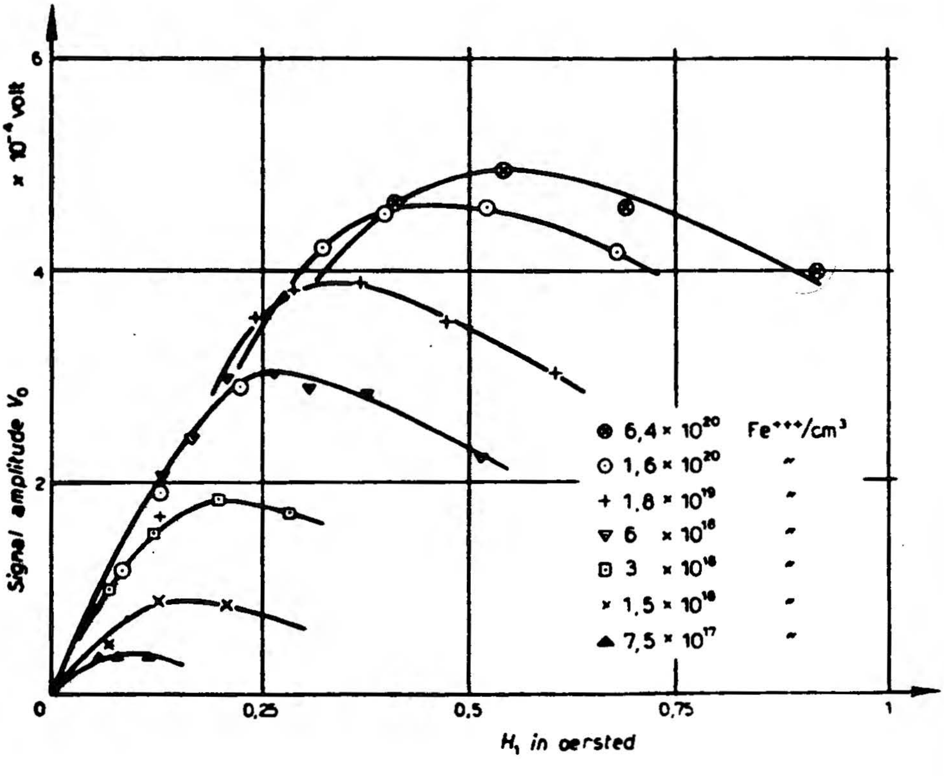
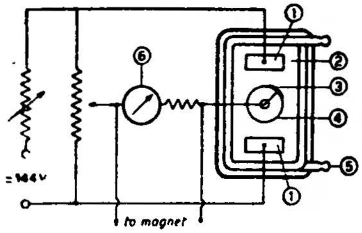
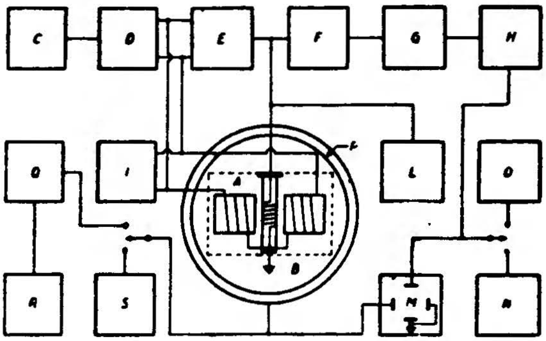


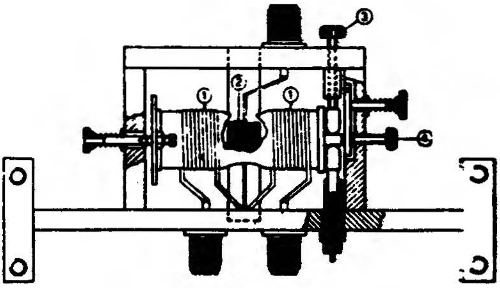
Fig. 7 - Dependence of the amplitude of the proton NMR signals, in water with paramagnetic salts, on the strength of the radiofrequency field (Ref. 20).



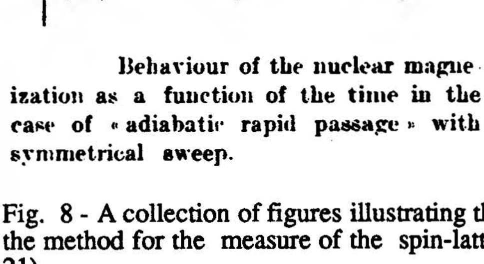
0 -- 20 Hz generator.
(1) carbon electrodes; (2) aqueous solution of $NaHCO_3$; (3) nickel electrode; (4) rotating glass cylinder; (5) glass tube for cooling; (6) galvanometer.



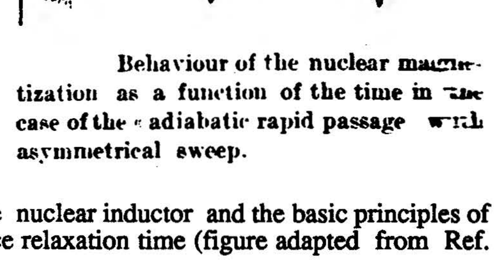
Block diagram of the arrangement. *A* r.f. head; *B* magnet; *C* standard signal generator; *D* r.f. power amplifier; *E* r.f. phase shifter; *F* r.f. amplifier; *G* detector; *H* d.c. amplifier; *I* symmetrical diode voltmeter; *L* heterodyne r.f. voltmeter; *M* oscilloscope; *N* C.R.T. recorder; *O* galvanometer recorder; *P*; modulating coil of the magnet; *Q* audio frequency power amplifier; *R* 20 - 1000 Hz beat oscillator; *S* 0-20 Hz generator.



r.f. head



Behaviour of the nuclear magnetization as a function of the time in the case of « adiabatic rapid passage » with symmetrical sweep.



Behaviour of the nuclear magnetization as a function of the time in the case of the « adiabatic rapid passage with asymmetrical sweep.

Fig. 8 - A collection of figures illustrating the nuclear inductor and the basic principles of the method for the measure of the spin-lattice relaxation time (figure adapted from Ref. 21).

b) *A method for spin-lattice relaxation measurements - The achievement of negative spin-temperatures*

From 1951, in Pavia began the first attempts to devise methods for the measure of the relaxation times (16). From a phenomenological point of view, the spin-lattice relaxation time was defined through the Bloch equations as the characteristic time describing the growth of the nuclear magnetization towards the thermal equilibrium value M_0 when the sample is placed in the magnetic field:

1] $M_z(t) = M_o [1 - e^{-t/T_1}]$;

the spin-spin relaxation time T_2 was defined as describing the progressive decrease towards zero of the components of the nuclear magnetization perpendicular to the external field:

2] $M_{x,y}(t) = M_{x,y}(0)\, e^{-t/T_2}$

The theory of the relaxation processes developed by Bloembergen, Purcell and Pound in 1948 and by Kubo and Tomita in the early 50's (17), had pointed out that microscopically the relaxation times had to be related to the fluctuating dipolar fields. For a random motion modulating the dipole-dipole Hamiltonian the spin-lattice relaxation time can be written (18)

3] $T_1^{-1} = \omega_d^2 \{ j(\omega_L) + 4 j(2\omega_L)\}$

where $\omega_d = \gamma H_d$ (with H_d dipolar field) and $j(\omega_L)$ is the spectral density of the motion at the Larmor frequency ω_L. For the relaxation time T_2

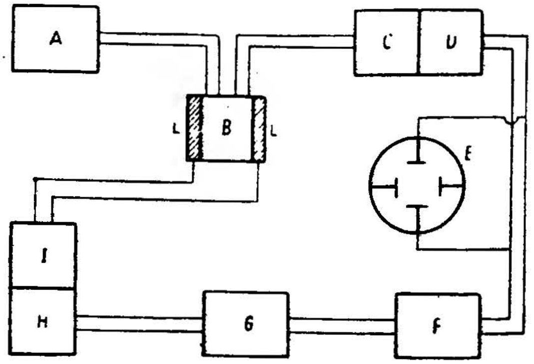
4] $T_2^{-1} = \omega_d^2/2 \{ 3 j(0) + 5 j(\omega_L) + 2 j(2\omega_L)\}$

In the early 50's in Pavia the NMR activity grew with relevant developments. Giulotto, now director of the Istituto di Fisica Superiore, gathered a distinguished group working on NMR in condensed matter (19). Primarily G. Chiarotti, G. Lanzi, G. Cristiani and, later on, L. Tosca, with the technical help of P. Orlandi. After a couple of papers by Chiarotti and Giulotto (20) on the dependence of the NMR signals from the strength of the radiofrequency field, which yields information on the spin-lattice relaxation time, (see Fig. 7) a very fine piece of work was the method for T_1 measurements. The method devised by Chiarotti, Cristiani, Giulotto and Lanzi (see Fig. 8) was based on the continuous recording of the "in phase" signals due to the reversing of the nuclear magnetization. In a system with T_1 and T_2 of the same order, when passing through the resonance in a time much shorter than $T_{1,2}$ and in such a way that a variation of H_0 of the order of H_1 occurs with a rate much shorter than the Larmor frequency in H_1, namely

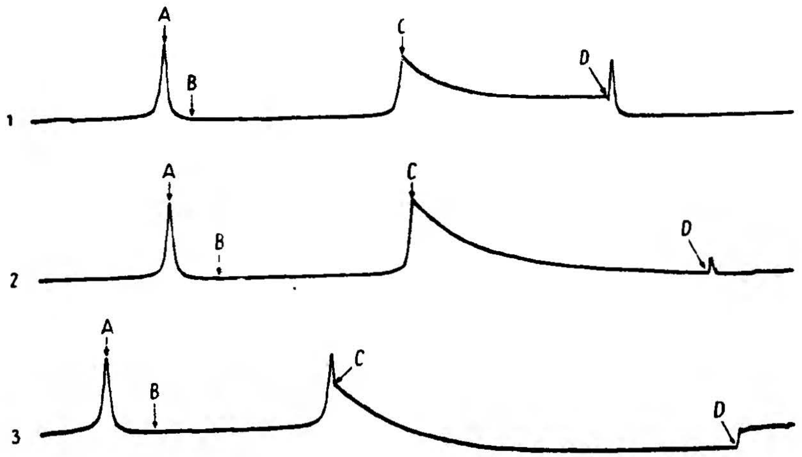
5] $(1/H_1)(dH_o/dt) \gg \omega_1 = \gamma H_1$

then one has a "fast adiabatic passage" and the magnetization is reserved. If the time interva between two successive passages is of the order of T_1, then the amplitudes of the signals depend upon the time interval, resulting alternatively up and down according to the sense of the passage. Two recordings with different sweep frequencies caused a different amount of partial saturation, allowing them (21) to obtain the relaxation time T_1.

This method for T_1 measurements had an implication of enormous relevance, which although it might appear obvious today, in 1953 could be considered heterodox. The total reversing of the nuclear magnetization induced by the fast adiabatic passage implies that the statistical distribution of the nuclear spins between the two levels is described by a negative temperature (population inversion). As is known, this phenomenon is one of the



Blockschaltbild der Apparatur zur T_2 Messung: A, HF Generator; B, HF Spulen; C, HF Verstärker und Detektor; D, Gleichstromverstärker; E, Oszillograph; F, Diskriminator; G, Verzögerungskreis ; I, Modulationsstufe; H, Hemmungsanordnung; L, Modulationsspulen.



Drei typische Fälle von blockierten Signalen: A, Normaler schneller adiabatischer Durchgang; B, Rückkehr (das Signal ist nicht sichtbar); C, Blockierter Durchgang: in 1: vor der Resonanz, in 2: in Resonanz, in 3: nach der Resonanz; D, Wiederbeginn des Durchganges.

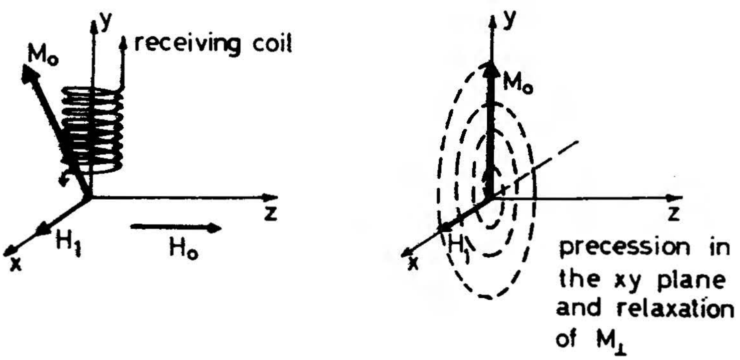


Fig. 9 - Block diagram of the apparatus for T_2 measurements, examples of decay signals in typical cases and illustration of the motion of the magnetization (Figure adapted from Refs. 31 and 32).

basic operational principles in masers or in lasers. At that time, its scientific meaning and the deep consequences could not be easily realized, particularly because the population inversion is not allowed by the time-dependent perturbation theory. However, Giulotto was quite confident about that implication of the method. His confidence in the total reversing of the nuclear magnetization was mostly standing on a classical visualization of the phenomenon based on the analogous behavior of the gyroscope in the gravitational field. This pictorial view and the use of classical equations are also the basis of the geometrical description of the motion of the nuclear magnetization under various conditions that was carried out by Bonera and Giulotto in 1959 with the rotating coordinates approach (see section e)).

c) *Application of NMR and Relaxation Measurements in Condensed Matter Physics*

Since the discovery of NMR in bulk matter and the clarification of its major phenomenological aspects, Giulotto realized the possibilities offered by that new tool in solid state physics. In his view, radiofrequency and microwave spectroscopies had to be pursued because they were very educational (being a synthesis of electromagnetism, quantum mechanics, statistical physics) and they could be cultivated even in small laboratories lacking large budgets. Furthermore, since the experimental techniques as well as the theoretical basis (e.g. coupling of the nuclei with the lattice through dipolar or quadrupolar hamiltonians, paramagnetic and diamagnetic effects, indirect spin-spin coupling etc.) had reached a satisfactory level of understanding, NMR, EPR and the pure quadrupole resonance (NQR), could be used as powerful tools in solid state physics. A Varenna school was organized by Giulotto in 1956, with the aim of favouring the application of those new spectroscopies to solid state physics. The school benefited from the presence and the scientific contributions by Abragam, Gorter, Kastler, Kittel, Kubo, Kurti, Neel, Pryce, Purcell and Van Vleck, a list that makes further comments useless.

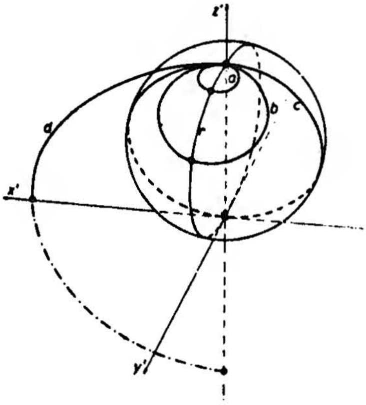
In Pavia, NMR and T_1 relaxation measurements have been used, starting in about 1954, for the study of phenomena in condensed matter physics. Limiting ourselves to the years before 1960, one can mention explicitly the studies on the molecular motions and quasi-crystalline structure of liquids (22-24), on the effects of paramagnetic gases in solution (25) and on molecular associations (26) (27). In particular, the relationship of the spin-lattice relaxation times with the coefficient of viscosity was critically analyzed (28). The discovery of the paramagnetic effect of the atmospheric oxygen in solution in reducing the relaxation times, allowed the Pavia group to re evaluate most of the T_1's in liquids, formerly measured by Purcell group, yielding more significant comparison with the theory of the relaxation processes.

d) *A method for the measurement of the relaxation time T_2*

After the development of the method to measure T_1, the next experimental step pursued by Giulotto and coworkers was towards devising a method for the measurement of the spin-spin relaxation time T_2 (Eq.2). At the AMPERE (29) Meeting in 1958, Giulotto and Lanzi (30) presented a paper reporting on the preliminary attempts to measure T_2 by stopping a fast adiabatic passage exactly at the resonance and collecting in the receiving coil the signal due to the rotation of the progressively decreasing transversal component of the magnetization. The method was subsequently improved and accompanied by a theoretical description (31) (see Fig. 9).

A remark on that method is now in order, which illustrate the unexpected paths of science. Since the rf field H_1 due to the transmitter coil is present during the relaxation process and H_1 is much greater than the line width, what was actually measured, to a large extent, was a longitudinal relaxation time along H_1, rather than T_2. A time constant, $T_{1\rho}$, describing the longitudinal spin-lattice relaxation time of the magnetization (created in H_o) when it is locked along H_1 was introduced later on (and measured by pulse

In the case $T_1 = T_2$ the equilibrium ellipsoid becomes the sphere shown in the figure. The circles *a* and *b* represent two possible paths for the nuclear magnetization during a slow passage through resonance; the circle *c* is the path described by the nuclear magnetization for $H_1 \gg 1/\gamma T_2$. During a rapid adiabatic passage the nuclear magnetization goes out of the equilibrium sphere and reverses itself describing the semicircle *d*.



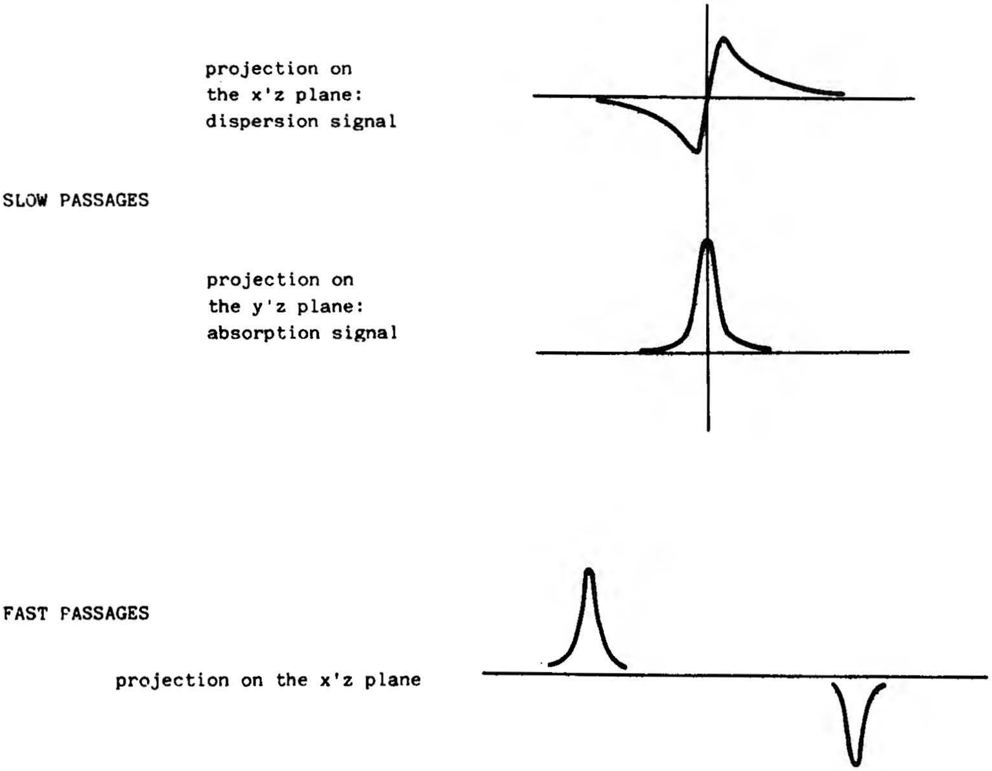


Fig. 10 - Motions of the extreme of the magnetization vector under the various conditions of passages through the resonance and illustration of the relative signals, as deduced with the pictorial description based on the rotating coordinate system (figure adapted from Ref. 33).

techniques). In terms of the microscopic motions modulating the dipolar hamiltonian, the analogous of Eq. 3 for T_1 can be written for $T_{1\rho}$ in the form (18)

6] $T_{1\rho}^{-1} = \omega_d^2/2 \; \{3\, j\, (2\omega_1) + 5\, j\, (\omega_L) + 2\, j\, (2\omega_L)\}$

An inspection of Eq. 4) shows that the spectral density at $2\omega_1$ is involved in $T_{1\rho}$ rather than the spectral density at zero frequency as in T_2. However one can observe that the method was still providing the correct value of T_2. In fact, in liquid-like systems, where this method was applied, the characteristic frequency of the motions are greater than ω_1 (which is typically in the kHz range) and thus for random motions no practical difference occurs between $j(2\omega_1)$ and $j(0)$.

e) *The geometrical description of the passage in resonance by means of the rotating coordinates*

The pictorial visualization of the motion of the nuclear magnetization already used by Giulotto to understand the achievement of the negative temperatures (subsection b)), was also the basis for a geometrical interpretation of the method for T_2 measurements as well as for a nice description of the effects of the nuclear relaxation during the passages in resonance. The geometrical picture, carried out by Bonera and Giulotto (33) had the advantage that it avoided the mathematical difficulties involved in the complete solution of the Bloch equations. The effects of the relaxation on the motion of the magnetization are taken into account by considering its motion during the adiabatic passage in resonance as a succession of equilibrium states for which the precessional rotation rate of M around the effective magnetic field, in the rotating coordinate systems, is compensated by the variation of M induced by the relaxation effects:

7] $dM/dt = (dM/dt)_{prec} + (dM/dt)_{relax} = 0$

This simple relation in the rotating frame of reference substitutes the system of the Bloch equations. From such a physical insight, by looking at the trajectory of the magnetization vector, it was possible (33) to deduce the effective paths of the magnetization during the slow passages and the fast ones, thus deriving the shapes of the signals collected in the receiving coil under the various conditions (see Fig. 10).

IV - *Conclusive Remarks*

As appears from the preceding survey of the research activity in Pavia under L. Giulotto, one should say that until about 1954 that activity was in the forefront of NMR research in the world, although hampered by the lack of general facilities and adequate grants. Later on, when high-power rf pulse techniques were being developed and large companies were engaged in producing resistive and superconducting magnets and advanced (and expensive) spectrometers, one could say that the instrumentation in Pavia began to lose ground, as can be expected.

The entry of large companies (such as Varian and Bruker) in the production of commercial equipments was triggered by the variety of the NMR applications in many fields of physics, in chemistry, in biology and, more recently, in medicine. Giulotto, as well as Bloch, (according to a private comment by himself in 1977) were not aware of the possibility of such an enormous explosion of applicative NMR techniques that were to occur in the forthcoming years.

As regards the scientific appreciation that the NMR activity in Pavia under L. Giulotto evidently deserved, one should say that some of the relevant contributions did not have proper acknowledgments. In particular, the methods for the measurements of the relaxation times T_1 and T_2 as well as the achievement of the negative temperatures are reported in institutional respected books on NMR without appropriate reference. This is also the case for the nice description of the motion of the magnetization during the passages in resonance. Also its possible uses for the interpretation of several NMR experiments when the effects of the relaxation during the passage have to be taken into account do not seem to have been fully grasped by the community of physicists. The authors of the present paper do not want to comment in terms of "lobbies", "political involvements", "propaganda" etc., all things that Giulotto disliked much (judging from the tape of the interview by Giuliani and Galdabini, Giulotto thought that, in part, the under-estimation of those aspects of the NMR in Pavia was due to the little diffusion, in those years, of the journal "Il Nuovo Cimento", where the papers had been published).

On the other hand, we think that the choice of Pavia as the site for this meeting is an implicit acknowledgement of the role that Luigi Giulotto and the Istituto di Fisica Superiore, that he created and ran, had in the birth of modern solid state physics in Italy.

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(9) One should mention that also the U.S., groups did not have plenty of adequate equipment. To give an idea, everything for the Stanford induction experiment, except for the oscilloscope, was home-made. The entire cost of the experiment (450 $) was financed out of the departmental budget (Ref. 8). The magnet used by Purcell (the joke had been fashioned out of an old generator discarded by the Boston Street Railways and used by Stevenson in 1937 around a cloud chamber) was so poorly calibrated that for a long time he had been working above the resonant value (the frequency for the resonant cavity had been fixed at 30 MHz because of the intermediate-frequency amplifier available at thE Radiation Laboratory). Finally frustrated and disappointed, Purcell decided to give up and told his students to turn off the magnetic field. While the field was decreasing and

they were sadly looking at the oscilloscope, they saw the first NMR signal passing through the screen. (private communication).

(10) It might be interesting to recall that also the use of the small workshop of the institute was primarily reserved for the director. Giulotto and Gigli made the metallic boxes for the electronic screening working during the summer, in the absence for vacations of the technicians.

(11) L. Giulotto, A. Gigli and P. Sillano, Nuovo Cimento 4, 201 (1947)

(12) L. Giulotto and A. Gigli, Nuovo Cimento 4, 275 (1947)

(13) L. Giulotto, Nuovo Cimento 5, 1 (1948)

(14) Since 1947-48 Giulotto was corresponding with Felix Bloch, as appears from some acknowledgements of the papers, in which he also mentions the appreciation that Bloch had expressed. This appreciation was confirmed later on, in 1977, when Bloch came in Pavia to be rewarded with the *laurea "honoris causa"*

(15) L. Giulotto and R. Levi Setti, Nuovo Cimento 6, 594 (1949)

(16) In the early times of the NMR discoveries there were rather confused ideas about the relaxation time of the magnetization. Purcell thought that to get the equilibrium distribution of the nuclear spins between the two Zeeman energy states (thus getting a proper magnetization) the sample "had to be cooked" in the magnetic field for about 10 hours (actually the relaxation time of the paraffin used as a sample was found around 10^{-3} sec.). As regards Bloch, there are rumors that he went on a skiing trip while the water sample was "equilibrating" in the magnetic field (Ref. 8).

(17) See, for example, E.R. Andrew, "Nuclear Magnetic Resonance", Cambridge University Press (1956)

(18) For details and for the conditions of validity, see G. Bonera and A. Rigamonti, Gazz. Chim. Ital. 106, 371 (1976). Analogous expressions can be derived for the relaxation process driven by the quadrupole interaction of the nucleus with the fluctuating electric field gradients.

(19) Meantime, another group of physicists was being formed under the leadership of Fausto Fumi, devoting attention mostly to the theory and the optical properties of solids.

(20) G. Chiarotti and L. Giulotto, Nuovo Cimento 8, 475 (1951); Nuovo Cimento 10, 54 (1953)

(21) G. Chiarotti, G. Cristiani, L. Giulotto and G. Lanzi, Nuovo Cimento 12, 519 (1954)

(22) L. Giulotto and G. Chiarotti, Phys. Rev. 93, 1241 (1954)

(23) L. Giulotto, G. Chiarotti and G. Cristiani, J. Chem. Phys. 22, 1143 (1954)

(24) G. Chiarotti, G. Cristiani and L. Giulotto, Nuovo Cimento 1 Suppl. 2, 154 (1955)

(25) G. Chiarotti, G. Cristiani and L. Giulotto, Nuovo Cimento 1, 863 (1955)

(26) L. Giulotto, G. Lanzi and L. Tosca; J. Chem. Phys. 24, 632 (1956)

(27) L. Giulotto, G. Lanzi and L. Tosca, Nuovo Cimento 6, Suppl. 2, 1213 (1957)

(28) L. Giulotto, Nuovo Cimento 9, Suppl. 1 101 (1958)

(29) The Groupment AMPERE is a scientific association of physicists, mostly from European countries, working in the fields of NMR, NQR, EPR and dielectric effects. This association organized general meetings and specialized schools and has had an important role in the European Physics. Among the founders, L. Giulotto from Pavia and A. Gozzini from Pisa.

(30) L. Giulotto and G. Lanzi, Archives des Sciences, Vol. 11, fasc. spec. 250 (1958)

(31) G. Bonera, L. Chiodi, L. Giulotto and G. Lanzi, Nuovo Cimento 14, 119 (1959)

(32) L. Giulotto, in "Hochfrequenz Spektroskopie" Akademic Verlag, Berlin, 1961, p. 49.

(33) G. Bonera and L. Giulotto, Nuovo Cimento 14, 435 (1959);G. Bonera, P. De Stefano and L. Giulotto, Bull. Ampere, Fasc. spec. 9^{e} année 365 (1960).

(34) In 1946, Edoardo Amaldi, just on his return from a scientific trip in U.S., paid a visit to the Pavia group. He, also, brought news on the recent trends in U.S., including NMR (A. Gigli, private communication). The suggestion from E. Amaldi to pursue NMR experiments in condensed matter was collected by Bolle, Puppi and Zanotelli who measured in 1947 the magnetogyri ratio of ^{7}Li through induction NMR signals (A. Bolle, G. Puppi and G. Zanotelli, Il Nuovo Cimento III, 412 (1946)). No further activity of this group in the NMR field seems to have occurred.

MICROWAVE PHYSICS IN PISA IN THE FIFTIES

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In October 1945 I set off on what was then an adventuresome journey from Florence to Pisa to visit Luigi Puccianti, after five years of absence. I found him in his study in the half-destroyed Institute absorbed in a newly published book "Questioni di Fisica" by G. Bernardini and G. Polvani. As I entered the room he raised his eyes from the book, said "ciao Gozzini" and became absorbed again in his reading. After about ten more minutes Bernardini and Carrara entered the study. They too had come to visit their old "maestro" after years of absence. He greeted them with a "ciao Gilberto, ciao Nello" and returned once again to reading the book. After several minutes he got up and left the room leaving us dumbfounded. This was my first encounter, after five years of absence, with my old "maestro".

A few days later I received a letter from him in which he offered me the temporary position of "assistente supplente" in substitution of Prof. Lamberto Allegretti who had not yet returned from his wartime occupation[1].

The Institute's condition after the end of the war was and much the same as that of other Institutes. The building was semidestroyed, the library impoverished, due to subtraction of the books, subscriptions to the journals suspended for years. Instrumentation, already scarse before the war, had been partially removed by the Germans[2].

The teaching staff was composed of the Associate Professors Anna Ciccone, Tullio Derenzini, Cosimo De Donatis and Lamberto Allegretti, whom, as I mentioned above, I had

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[1] It was in this manner that I became a member of the Institute of Physics. I had taken my degree with Puccianti in June 1940 and since that date I had not even touched a physics book. Nowadays endowed and promising graduates who have not been fortunate enough to have had some type of scholarship during those particular years favoured by various "ope legis" agreements, after years of post-doctorate studies, voluntary research work and brilliant publications, do not have any possibility of enrollment in the university. Comparing the latter situation with my own personal experience I may infer that the immediate postwar years were not "gli anni difficili" at least from that particular point of view.

[2] Before leaving Pisa the Germans mined and blew up a wing of the Institute with its tower. Anna Ciccone, the only person present in the Institute at that particular time, refused to abandon it and retired to the other wing of the building. After the mines had been exploded, the Germans withdrew taking with them the best optical instruments. When Anna Ciccone saw that, she precipitated on the soldiers in a fury, as an enraged tigress would defend her offspring, offering the soldiers the alternative of killing her on the spot or renouncing on their removal. Fortunately they chose the latter alternative, so that the best of these (including a Michelson échelon and a diffraction grating autographed by Rowland, now conserved in the museum of Certosa di Calci) had been saved. Whoever knew Anna Ciccone can imagine the scene.

been called on to substitute, by two elderly technicians, by a doorkeeper-carpenter, Otello Serraglini, and by Teresa employed as a cleaner and forever quarreling with an exacting Miss Ciccone. Besides the Professor, this was the roll of the Institute.

In those years teaching and the supervision of the theses of the numerous students, ex-service men, was the unique activity. During those years, amongst others, Carlo Castagnoli, Gerardo Alzetta, Arrigo Battaglia, Ruggero Renzoni, Giulio Chella, Aulio Stura, Silvio Gibellato, and Cesare Marchetti graduated.

A depot of stores had been left by the American troops in the nearby camp of Tombolo. That material was subsequently marketed in the Arar stores, but at that time was sold clandestinely. For just a few lire it was possible to buy marvelous objects, such as klystrons, magnetrons and sophisticated electronic apparata. Puccianti made a small sum available for purchasing such merchandise and we started using it for the degree theses of the majority of those mentioned above[3].

The periodicals, interrupted during the war years were resumed and from this literature it appeared that microwaves had indeed opened up new and promising fields of investigation (microwave spectroscopy, EPR etc.). In the meantime Alzetta, Battaglia and Stura had obtained their degrees and, while waiting to find suitable jobs, they still attended the Institute. We then decided to form a small research group. This only survived for a few months because Battaglia found a position at the Naval Academy, Stura at the Leghorn high school, and Alzetta in industry.

Puccianti retired at about that period and the direction of the Institute was entrusted to Nello Carrara, father in Italy of ultrashort waves. (Among other things during the war years he had constructed a unique specimen of a prototype radar, in collaboration with Prof. Tiberio.) Carrara, together with Toraldo di Francia, Schafner, Checcacci, Laura Ronchi and others, had been organizing the "Centro Microonde" in Florence, now IROE (Research Institute of Electromagnetic Waves). With his arrival the activity in microwave physics received a notable impulse. In those years he performed in Florence a beautiful piece of research on the angular momentum of em waves. That research, as I shall recount further on, inspired a technique for studying non linear processes in E.P.R. In the meantime I had initiated measurements of the dielectric constant of gases (Nuovo Cimento 1951).

In 1948 appeared a work by Wilson and Hull in Physical Review (Phys. Rev. 74, 711, 1948); they had studied the Faraday effect at a frequency of 9 GHz in numerous substances, without finding a measurable rotation except for the case of some manganese salts. Since the effect is inversely proportional to the square of the wavelength, and it is very small at optical frequencies, I perceived that the Macaluso-Corbino effect was involved, that is to say a resonance of the Faraday rotation that manifests itself in the vicinity of an absorption band. A few years before the electronic paramagnetic resonance had been discovered, and the Mn^{++} salts are paramagnetic. The American authors had performed their experiments with weak magnetic field values for which the absorption due to magnetic resonance at that frequency begins to appear. Therefore it could be predicted that the effect would have been much larger with more intense fields, that it would present a resonance character and would provide an interesting technique for studying paramagnetic resonance.

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[3] For several years that material was practically the only modern instrumentation available, which would allow research in a still unexplored region of the em spectrum. The first piece of original research performed in the Institute in that period was the argument of Gibellato's degree thesis, a theoretical and experimental analysis of the evanescent field and of its reflection by a mirror. This study performed at 9 GHz provided a detailed analysis of the phenomenon of total reflection; was published (Nuovo Cimento 1949-ibidem 1950) and taken up again in the field of optics many years later with the advent of the laser. Gibellato died still a young man just a few years later.

After having overcome the difficulties of providing a sufficiently intense magnetic field and of creating a simple apparatus I published the work in 1951. It was a rather special event because it preceded an analogous much more extensive work of Hogan (1952) on ferrites and permitted the realization of non reciprocal devices of great interest for radar technology. But the more important fallout of this work resides in the fact that it interested Prof. Alfred Kastler of the Paris' Ecole Normale who had predicted it. (C.R. Acad. Sci. 228, 1640, (1949)) He wrote to me and came to Pisa, and we established a friendship and a collaboration which have been of inestimable value to me. Kastler suggested investigating also the transverse effect (the Cotton-Mouton effect) which he had also predicted (C. R. Acad. Sci. 231, 1462, 1950) and which we detected some time later (Nuovo Cimento 1953)[4]

These magnetooptic effects turned out to be an interesting field of research. It was taken up by many French and Russian laboratories. In Italy it was extensively investigated by the EPR group of the University of Parma (D'Ascola and collaborators) who also performed research on monocrystals, discriminating effects due to crystalline anisotropy from those due to EPR. In Pisa became the subject of many theses during the next few years (Pietro Bucci and Mario Iannuzzi).

In those same years Carrara had stipulated in Florence a contract between the "Centro Microonde" and the American Airforce related to various studies on the physics of microwaves. Among the other research work prospected were some studies on the dielectric properties of the atmospheric gases and, in particular, on the spectroscopy of O_2 and of water vapour at millimetric frequencies, problems related to radar. Carrara entrusted these to the Pisa group which in this way gained disposal of equipment not yet available commercially, such as millimetric klystrons, and was able to appoint a technician (Gino Ciampi), who very soon became a precious collaborator. In the context of those research projects various apparata were constructed, the most important of which was an instrument for measuring with a high degree of sensitivity and precision small differences between the frequencies and the quality factor of two resonators, by means of a very simple impulsive technique. The instrument, conceived initially as a spectrometer, was later subjected to a great deal of improvement and adaptation in order to measure small variations of whatsoever a physical quantity that could be associated with a variation in frequency or of the Q value of a resonator. Under the terms of the contract we were able to study the spectroscopy of O_2, of great interest because of the particular nature of that spectrum, and of water vapour, and we were able to obtain a precise measurement of the dielectric properties of the atmospheric gases. We were also able to offer hospitality to some foreign research workers, amongst whom Bruin, husband and wife, of Amsterdam, George Boudouris, (presently Rector of Athens Polytechnic), Demetre Ilias and F. Diamond from Paris. In a mutual exchange program some Pisa research workers were able to take advantage of scholarships for abroad. Polacco and Fornaca spent a period in Paris at the Institut H. Poincaré, Battaglia was a guest at the Zeeman Laboratory in Amsterdam, where with Heiniken they reproduced the previously mentioned spectrometer with which they measured the spectrum of HN_3, and Polacco and Ianuzzi spent a period in England at Oxford.

In the early fifties Nello Carrara was called to the chair of "Fisica Superiore" (Advanced Physics) of Florence University and Marcello Conversi was called to Pisa to the chair of "Fisica Generale" (General Physics - the only chair existing in the Institute at that

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[4] In the early fifties Professor René Freymann and Alfred Kastler organized the "Groupment AMPERE" (Atomes et Molecules Par Etudes Radioélectriques) whose activity consisted in the publication of a reference Bulletin and in the organization of a yearly colloquium, the first being held in Paris in 1952. We participated in these meetings and had the opportunity to interact with the leading physicists in the field; Gorter, Townes, Ingram, Bleaney, Abragam, Powles and many others. The membership in the Ampere group was of great importance for the research development in Pisa.

time). In a few years the Institute was reorganized. Administrative offices, an electronics laboratory and a mechanics workshop were created, run by extremely efficient persons[5]. New chairs were obtained and filled, that of "Fisica Teorica" (Theoretical Physics), to which Luigi A. Radicati was called, and that of "Fisica Superiore" (Advanced Physics) to which Giorgio Salvini was called.

Radicati organized theoretical physics research, Conversi and Salvini research on cosmic rays physics. Conversi called two assistant professors from Rome, Giuseppe Martelli and Elio Fabri and Pisa obtained a subsection (and later a section) of I.N.F.N., the National Institute of Nuclear Physics. The Institute saw its importance increase to the extent that the organization of the 1955 International Conference on Elementary Particles was entrusted to it. In those same years it hosted the team of research workers and technicians that constructed the Frascati electron-synchrotron, and later, after the team moved to Rome, it hosted the group that created (on the suggestion by Enrico Fermi) the first large electronic computer in Italy (CEP, the Pisa Electronic Calculator) which was housed for several years in the Institute.

These episodes permitted a rapid reconstruction of the premises that had been destroyed and a notable growth of the technical services. However, the space that previously had been more than sufficient now became critical and all the available room from the basement to the attic was being utilized for experimental research[6].

As far as the microwave activity is concerned, with the return of Alzetta and Battaglia, and the graduation of Erseo Polacco, Giuseppe Fornaca, and Mario Iannuzzi, a permanent group was formed, which was not limited only to myself and an occasional graduating student, and we obtained financial contributions form CNR.

As I mentioned previously, Carrara had performed a beautiful experiment at the Centro Microonde in which he had detected the angular momentum flux associated with the flux of energy carried by a beam of circularly polarized em waves. He directed the incident circularly polarized radiation emitted by a magnetron on a special mirror hung on a torsion wire which reflected the beam thereby inverting the sign of the circular polarization. The mirror was thus subjected to a mechanical torque $2P/\omega$ which was measured by the torsion of the wire[7].

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[5] Amongst others I especially wish to recall Ugo Della Croce (electronics), Armando Pecchi (in charge of the workshop) and the secretaries Miriam Fanucci, Vivetta Della Capanna, Angela Cocchella, Graziella Renzoni).

[6] At one stage some of the rooms were divided horizontally, reducing the height with scaffolding and thereby doubling the available area. At a later stage that problem was solved by renting apartments for some of those laboratories.

[7] A problem which immediately arose was that of the origin of the energy acquired by the pendulum, and it was immediately demonstrated (and besides there was no other possible source of energy) that it came from the radiation, whose frequency is modified when the polarizer is made to rotate about the direction of the beam propagation. A kind of "rotational Doppler effect" occurs, due to the change of sign, rather than of the momentum, of the angular momentum of the light. In the case of reflection or transmission with a change of sign of a circularly polarized beam, the frequency ω of the reflected of transmitted radiation by a polarizer that rotates with a frequency Ω around the direction of the bean is $\omega = \omega_o (1 + \Omega/\omega_o)$ analogous to that of the Doppler effect, where the linear velocities are substituted by the angular velocities of the polarizer and of the light. Alzetta and Polacco verified this immediately bay interposing a rotating half wavelength plate in the trajectory of the polarized monochromatic bean. We communicated this result to Persico, thinking that we had discovered an interesting optical effect of motion, which we had never seen discussed in any book on optics that we had consulted. Persico sent us a reference to a work by Augusto Righi (published in Comptes Rendus

Such a torque is clearly present in all those cases in which the circular polarization of the beam is modified, and in particular when the radiation interacts with a medium that possesses circular dichroism, such as in the case of magnetic resonance. Simple estimates show that theoretically the measurement of the torque associated with the absorption for MR provides a sensitive technique for detecting MR, superior to the radioelectric method in the case of low frequency and high intensity experiments. After various unsuccessful attempts to detect this effect, due to the lack of skill in manipulating thin quartz wires, to the difficulty of eliminating mechanical forces produced by the external field on the magnetic sample, and to the mechanical noise of the environment, Alzetta observed a small effect and the experiment was rapidly realized. The experiment proved to be an important method for investigating non linear effects in EPR absorption. It was later studied accurately by Ennio Arimondo and extended to the detection of paramagnetic dispersion.

In an experiment designed to detect the presence of traces of polar impurities in a non polar liquid, Battaglia and myself saw that a powerful (1 Mw) but brief (1 ms) em impulse emitted by a magnetron was not able to trigger a discharge in a neon tube if this was expose to the pulse in complete darkness[8].

Discussing this result with Conversi, we attributed it to the fact that, in the absence of light and therefore of the photoelectric effect on the electrodes of the neon tube, the probability that there could be a free electron density in the gas sufficient to trigger the discharge in such a brief time interval was practically zero, and we decided to utilize this to make a path detector of ionizing particles. This was constructed (hodoscopic chamber, flash tubes) and was presented at the elementary particle conference (1955) in a communication by Conversi. The hodoscopic chamber has been used extensively in cosmic radiation research and, some years later, the spark chamber was constructed by Japanese physicists using the same principles.

In the second half of the fifties research developed in various direction. In the microwave spectroscopy of gases results were obtained regarding the form and width of spectral lines and on phenomena of saturation, which led (for the first time in molecular spectroscopy) to the detection of two photon transition processes, previously observed in atomic spectroscopy with the technique of optical pumping. Adriano Di Giacomo, who graduated at that time, gave a complete theory of the process in perfect agreement with the experimental results. The latter process became a precious technique in microwave spectroscopy in subsequent years. In the field of the width of spectral lines, besides furnishing a theoretical support to the experimental work, Di Giacomo formed a small theoretical research group which is still in activity. Alzetta and Santucci applied the EPR techniques to the study of various solid state physics phenomena, and with Fornaca we started experimenting using the elegant, simple and powerful optical pumping technique, a field in which it was shown that a magnetic rotatory power is associated with the atomic orientation, an effect which results to be a sensitive non-destructive technique for the detection of the orientation itself, and which has been applied to a number of problems. In the late fifties the group was engaged in organizing two important events which took place in 1960. The first was a

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at the end of the last century), in which he reported that effect. It was utilized many years later in a thesis by Roberto Calabrese "Single photon beats" (Nuovo Cimento 1987).

[8] In this experiment a magnetron pulse was directed on a cell containing the fluid in question exposed to a light beam in order to see whether a strong signal was emitted by the photomultiplier receiving the light scattered by the liquid in coincidence with the pulse. In the presence of traces of polar impurities the dipoles should have produced a local heating under the action of the field with a consequent local variation of the refractive index of the scattered light. Kastler provided us with extremely pure specimens of cyclohesane. The experiment was performed in the dark and since nothing appeared to happen, I and Battaglia checked the performance of the magnetron by exposing a neon tube to the pulse. This lit up when the room was illuminated but not in the dark.

summer school in Varenna, entrusted to me by G. Polvani, the second the IX Colloque Ampère.

The school was held in July on topics of radiofrequency spectroscopy. It was the second to be held on this subject matter, the first having been organized by Giulotto in 1956. As in the latter case, and thanks to the contribution of physicists such as Kastler, Townes, Cohen-Tannoudji, Brossel, Abragam, Skalinski, Shimoda and many others, the event was, as one might say, extremely exciting (among other things, the possibility of constructing an "Optical Maser" was discussed there anticipating its effective realization by a few months). The Proceedings of the school are collected in a volume which has proved to be an extensively used textbook in the sixties, and even today it is still extremely useful. The IX Colloque Ampère was held in Pisa at the Scuola Normale in September. Many more research physicists participated than in preceding conferences. Since then these conferences have gradually lost the pleasant atmosphere of meetings between friends having a common interest and have evolved into the present-day megaconferences.

In December of that same year 1960 the Science Faculty of Pisa University conferred the degree honoris causa in physics on Alfred Kastler to honour his figure as a scientist and in recognition of his contribution to research developments in Pisa. In the subsequent sixties the group increased in size with the aggregation of the then new generation. Franco Bassani was called to Pisa, and research developed in several new directions including Solid State Physics, Biophysics and Atomic Physics. At the end of the sixties two laboratories of CNR were created, one dedicated to biophysics, the other to atomic and molecular physics.

Recalling those years the difference between the possibilities of present-day research activity and what was possible in the immediate postwar period is enormous. Equally great is the difference between the atmosphere in which research was then performed and that which exist nowadays. The scanty facilities, the precariousness of the positions then available, the lack of continuous reunions and bureaucratic obligations, the freedom of initiative and of research all together rendered the atmosphere, in my opinion, relaxed and pleasant. The philosophy of those years was that expressed by the Sicilian cart-drivers song that the Palma's presented as a preface to their contribution to this encounter: "If Good wants and the mule plods on, we will get to the Bivona fair" (in the meantime let us enjoy ourselves). Fatiguing along, the mule proceeded and something has been done. This would not have been possible without the work of a relatively small number of people, mainly of my friends and colleagues Giuseppe Fornaca and Arrigo Battaglia who are no longer with us and to whose memory I dedicate these pages.

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*SOUND WAVES AND PHYSICS OF FLUIDS IN ROME**

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1. Introduction

The C.N.R. Electroacoustic Institute (at present: Acoustic Institute) was created by O.M. Corbino in 1936 as a research Centre on a subject which had grown to a large interest for the development of modern technologies. It turned to be a place where relevant research on the structure of the matter was performed when, after the war, it become more and more evident that the study of propagation of elastic waves could furnished new and valuable information on the nature and properties of the medium in which propagation occurs.

We wish here to give a brief account of the researches in fluids which were conducted from 1945 at the Corbino Institute or were originated there and later carried out at the Institute of Physics of the Engineering Faculty of the Rome University. The period considered has been some how extend over 1960 in order to see clearly the connections with today research.

These researches fall mainly in two lines. The researches of the first line have considered, in numerous contests, the relations between sound propagation and the structure of fluids and have contributed to the development of what is now called ultrasonic spectroscopy: these researches are conducted by making use of low intensity ultrasonic waves. The second line is related to the process of sonic cavitation in liquids and the researches require the use of high intensity waves.

A rather complete bibliography of the contributions is given (arabic numerals): it includes also papers which although not quoted directly in the following presentation, because they appeared successively to the period here considered, are directly connected to the related work.

2. Velocity and absorption measurements

The direct dependence of the sound velocity from the elastic moduli of the propagation medium explains the long lasting use of sound velocity measurements for the determination of the elastic parameters.

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*This paper has not been presented to the Meeting, owing to the fact that Professor Sette was then abroad. However, it is published for sake of completeness. (Editor's note)

Before the war, however, a systematic study of liquids properties by means of sound waves had not started and mainly isolated and uncorrelated measurements were performed.

Such and effort really started after the war, favoured by the great progress occurred in electronics and in ultrasonic techniques, which have allowed the full control of frequencies and intensities of the waves in wide ranges. together with velocity measurements, also absorption coefficient determinations have been brought to high accuracy. The range of frequencies used in measurements extends from the KHz region to many GHz. The methods include resonant cavities, high precision interferometers using either continuous waves or pulses, Bragg reflection and Brillouin scattering of laser light.

Various contributions to the development of methods have been studied in Rome, especially by making appropriate use of the light diffraction produced by the sound waves, taking advantage of a long tradition of the Acoustic Institute on the subject (6) (10) (29) (30). A. Barone (30) for instance has been able to reduce the error in a relative determination of velocity to + 1.5 10^{-4} by optically observing the interference of two sound beams emitted in two liquids (reference and under measurement). Such method is of particular interest in the study of small variations of velocity, as in dispersion investigations.

3. *Sound velocity and chemical structure of liquids*

The measurement of sound velocity (c), allowing the determination of the adiabatic compressibility (β_s)

$$C = (1/\rho\beta_s)^{1/2} \qquad (1)$$

has been frequently used in order to obtain information on the elastic properties of the liquid and on the structural features which determine these properties. Of course these studies were carried on at fixed relatively low frequency (limiting zero frequency), varying some other parameters as composition or temperature. The information gathered in this way were normally analyzed in connection with others, mainly concerning the chemical structure.

On this category of studies belong those conducted by A. Giacomini and various coworkers on electrolyte solutions (1) (1949), in mixtures of methanol-water (2) (1940), ethyl alcohol-carbon tetrachloride (4) (1942), ethanol-water (3) (1941) (8) (1947), in dichloethylene cis and trans (7) (1945).

These studies were extensively conducted in the years '40 and greatly contributed to establish confidence on the possibility of using sound waves for investigating the structure of liquids. A detailed analysis of practically all the existing data on binary and ternary mixtures was conducted in 1949 (11). A similar review concerning pure liquids and, in particular, the relations between sound velocity and structural and molecular properties has been conducted in 1950 (12).

W. Schaaffs (I), at conclusion of a vast analysis of data, has proposed a semiempirical expression for the sound velocity in pure organic liquids which is characterized by two factors: the first one, collision factor, depends on the nature of the collisions between the molecules, while the second one is the ratio between the effective volume of molecules and the molar volume. The collision factor would have the value 4 for completely elastic collisions between hard spheres in Van der Waals theory; in reality it is smaller. the semiempirical Schaaffs formula allows the evaluation of the sound velocity from the knowledge of the chemical structure of the molecules of the liquid. Its interest is evident. In the frame of this theory it has been possible to study the temperature dependence of the collision factor (13), shoving that it can be expressed as an universal function valid for all pure organic liquids by using as variable the ratio between temperature and its critical value.

A particular use of the low frequency velocity in order to extract information on the structural properties of liquids is the study of those liquids which can be easily supercooled. The use of a high precision interferometer has allowed (30) the detection in numerous liquids of variations in the temperature coefficient of sound velocity in the proximity of the freezing point, showing the formation of molecular associations: they are responsible of the behaviour of these systems below the transition temperature.

High precision sound velocity measurements in dilute electrolytic solutions have also been used (33) to discuss the limit of validity of the Debye-Huckel calculations of the activity coefficients of electrolytes based on the hypothesis that the deviation of the behaviour of electrolytes solutions from ideality is exclusively due to Coulomb forces between ions.

4. Ultrasonic spectroscopy in liquids

Having seen the interest of the information that sound velocity at a fixed low frequency can furnish on the equilibrium properties of a fluid medium, it is important to note that the greater importance of the use of sound waves for the study of the properties of a fluid concerns the possibility of extracting information on the non-equilibrium behaviour. Such a study can be performed by the measurements of velocity dispersion and of absorption coefficients.

The molecules in a liquid possess various forms of energy (translation, vibrational, rotational, structural etc.) bound to the various states in which they can exist; a coupling mechanism allows the transfer of energy from one state to another in order to reach the equilibrium distribution. When, however, one of these forms of energy is varied, for instance increased, the re-establishment of equilibrium occurs trough an exponential variation of the energy with a characteristic relaxation time.

The cause of perturbation of the equilibrium can well be a sound wave and the relaxation process leads to particular variations of the sound velocity and of the absorption coefficient as functions of frequency: they can be used through experiment to furnish information on the molecular processes and the dynamical properties of the structure of the liquids.

In order to see easily the type of variations that can be produced, let us consider a simple case.

The molecules receive energy by the wave during compression through the increases of the energy in the translational degrees of freedom and of the related temperature. If the energy can not flow in other degrees, as it is the case of monoatomic gases, the same amount of energy returns as ordered energy to the wave during the decompression and temperature and equilibrium are restored. If, however, the molecules possess other forms of energy, as for instance vibrational energy, and there is a relaxation coupling, part of the translational energy may be transferred to vibrational energy during compression and, as a consequence of the time lag bound to the coupling mechanism, it can not be returned to the translational energy during decompression. This effect produces a decrease of the ordered energy of the waves, i.e. an absorption. The magnitude of the effect depends on the amount of energy which is transferred from one type (translational) to the other (vibrational) and from the relaxation time of the coupling process, compared to the period of the wave. Fig. 1c gives the losses per period (α,λ) in a relaxation process (τ, relaxation time) as

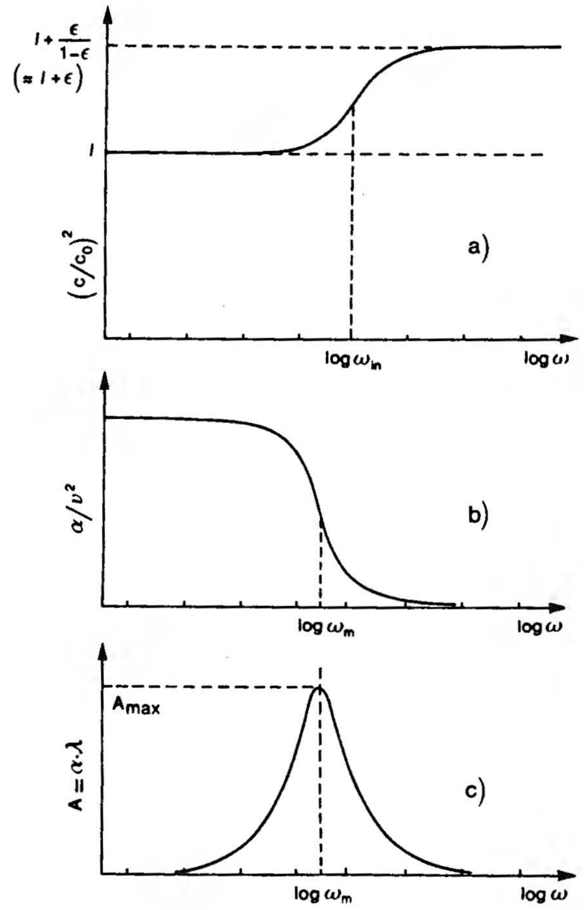

Fig. 1. Dispersion and absorption curves for a single relaxation process: a) dispersion; b) α/ν^2 vs frequency; c) $\alpha.\lambda$ vs frequency.

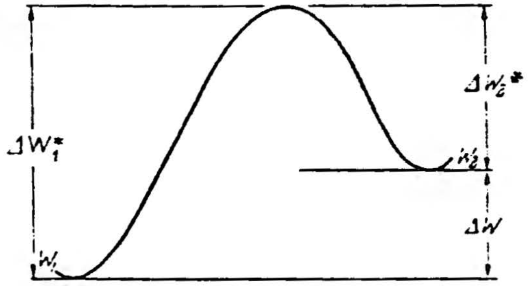

Fig. 2. Diagram for two contigous energy states.

function of frequency: α, absorption coefficient for amplitude, λ wavelength, T period, ν frequency; $\omega = 2\pi/\tau$; $\omega_m = 2\pi/\tau_m$. At low frequency ($T \gg \tau$) the losses are negligible because compression and decompression occur so slowly that the system goes practically through a succession of quasi-equilibria. At frequencies much higher than $1/\tau$ the losses disappear because the compressions occur so rapidly that the coupling mechanism is unable to operate and the transfer of energy from the translational degrees of freedom is blocked (internal degrees frozen). The losses are at a maximum when $\nu = 1/\tau$.

The shape of the curve for $\alpha.\lambda$ is

$$\alpha.\lambda = \omega\tau/(1+\omega^2\tau^2) \qquad (2)$$

Figure 1b gives the corresponding values for α/ν^2, a parameter which is frequently used for comparison with the losses produced by the so called classical absorption coefficient (α_c) due to shear viscosity and thermal conductivity, when α/ν^2 is constant in a very wide frequency range

$$\alpha/\nu^2 = 2\pi^2/\rho C^3\,[(4/3)\eta + (\gamma\text{-}1)\,K_t/C_p] \qquad (3)$$

being η the shear viscosity coefficient, γ the ratio of specific heats (C_p , C_v) and K_T the thermal conductivity.

A velocity dispersion (fig. 1a) is connected with the relaxation process because, when, at high frequencies, the sharing of energy between external and internal degrees of freedom is hindered, the medium appears stiffer;

$$\varepsilon = (C_\infty^2 - C_o^2)/C_\infty^2$$

In order to see more deeply into the types of possible relaxation processes in liquids which can be investigated by elastic waves, let's start by considering longitudinal (sound) waves. A longitudinal stress can be resolved in the sum of a shear stress and a compressional stress. The first one leads to dissipation for the presence of a shear viscosity, the second one causes losses due to the volume viscosity of the liquid, for which many mechanisms may be responsible. The latter losses are the ones in which we are at the present, specially interested.

The sound waves may effect the equilibrium inside the medium by means of the variations they produce either in the pressure or in the temperature; the latter ones are associated to the volume changes.

Relation (1) links the sound velocity to the adiabatic compressibility. When, for any reason, the volume change produced by the wave is out of phase with the pressure, absorption is present and can be accounted by a complex β_s.

The adiabatic compressibility can be expressed by means of the ratio

$$\beta_s = \beta_T/\gamma \qquad (4)$$

between the isothermal compressibility and the ratio of specific heats. A complex β_s can therefore be the result either of a complex β_T or of a complex γ.

Let us suppose that one mole of our liquid is formed by N molecules that can exist in two different energy states and that the transition is regulated by

$$dN_2/dt = N_1K_{12} - N_2K_{21} \qquad (5)$$

being N_1, N_2 the number of molecules in state 1 or 2 and K_{12}, K_{21} the rate constants. The heat of reaction can be expressed by

$$\Delta H = \Delta W + p\Delta V \qquad (6)$$

being ΔW the change of internal energy at constant volume and $p\Delta V$ the work required for the isothermal change of volume, while $p = T(\ S/\ V)_T$ and the entropy.

As indicated before, a sound wave travelling in the liquid produces simultaneous variations of temperature and pressure which may affect the equilibrium and originate relaxation processes

a) <u>thermal relaxation</u>.

A first simple case occurs when $\Delta V = 0$, i.e. no volume change is associated with the reaction . The isothermal compressibility $\beta_T = - (1/V)\ (\partial V/\partial P)_T$ is not affected by the relaxation and $\Delta H = \Delta W$.

An important case is bound to the energy partition between translational degrees of freedom and rotational or vibrational degrees of freedom: the corresponding relaxation processes are of great interest in polyatomic gases and unassociated liquids where the individual molecules act as the basic fluid units. In unassociated liquids few collisions are sufficient to establish the equilibrium distribution between translational and rotational degrees of freedom: i.e. the corresponding relaxation times are very short in comparison with the period of waves with which the experiments are normally conducted: as a consequence, the equilibrium of interest is that between external (translation + rotational) degrees of freedom and the internal (vibrational) degrees.

In this thermal relaxation process the contribution (C_i) of the internal degrees of freedom to the specific heat becomes complex

$$C_{i\omega} = C_i\ [1/(1+j\omega t)] \qquad (7)$$

as well as γ.

For the complex velocity one gets

$$1/[V] = (1/C + j\alpha/\omega) = \rho\beta_T\ [C_2+C_i(1/1+j\omega t)]\ /\ [\Delta+C_2+C_i(1/1+j\omega t)] \qquad (8)$$

were C_2 is the external degrees contribution to C_v and

$$\Delta = C_p - C_v$$

The relaxation time is

$$\tau = 1 / (K^o_{12} + K^o_{21}) \qquad (9)$$

where K^o_{12}, K^o_{21} are the equilibrium values of K_{12}, K_{21}.

Theory and experiment show that in the case of vibrational relaxation in liquids as in gases τ can be expressed by means of the number of binary collisions per second ($\tilde{N}$) and the probability $\bar{P}$ that during a collision a variation of the vibrational quantum state occurs

$$\tau = [\tilde{N}\,\bar{P}]^{-1} \qquad (10)$$

It is therefore evident that binary collisions constitute the mechanism for energy transfer in vibrational relaxation occurring both in liquids and in gases.

Other types of thermal relaxation may occur when the waves alter other equilibria existing in the liquid which depend on temperature, while their variation does not affect the volume. Examples are: the relaxation between isomeric forms and the slow chemical processes. Also in these cases a suitable expression of a complex equivalent specific heat can be used.

b) compressional relaxation.

A second kind of relaxation occurs when the process represented by the reaction (5) is not affected by temperature changes; the pressure variations have instead importance because the two states (1 and 2) have different volumes. In such case $\Delta H = p\Delta V$

A characteristic example is that of water at 4°C when, being zero the thermal expansion coefficient, the adiabatic sound propagation becomes also isothermal: the excess value of the absorption coefficient (over the classical one) can not be due to thermal relaxation.

The compressional relaxation, as suggested originally by Debye, originates in the disturbance, by the pressure variations, of the equilibrium, in the simplest case, between two states having different volumes (V_1, V_2) and different internal energy (fig. 2).

One gets (L. Hall) (II) for the adiabatic compressibility

$$\beta_{s,\omega} = \beta_{s,\infty} + (\beta_{s,r} / 1 + j\omega\tau) \qquad (11)$$

where the relaxing component is

$$\beta_{s,r} = [(V_1 - V_2)^2 / V_o RT] \, \{1/2[1 + \cos (h \, \Delta H/RT)]\} \quad (12)$$

and the relaxation time

$$\tau = h/kT \, [\exp (\Delta W_1^*/RT)] \, / \, [1 + \exp (\Delta H/RT)] \qquad (13)$$

being ΔW_1^* the activation energy for the transition from state 1 to state 2.

The corresponding expression for the sound parameters are:

$$(C/C_o)^2 \approx (1+\omega^2\tau^2) / \{1+\omega^2\tau^2[1-(\beta_{s,r}/\beta_{s,o})]\} \qquad (14)$$

with $\beta_{s,o}$ the static value of the adiabatic compressibility ($\beta_{s,c} = \beta_{s\infty} + \beta_{s,r}$);

$$\alpha = (C/2C_o)\,(\beta_{s,r}/\beta_{s,o})\,(\omega^2\tau/1+\omega^2\tau) \qquad (15)$$

$$\alpha/\nu^2 = (2\pi^2/C_o)\,(\beta_{s,r}/\beta_{s,o})\,\tau \qquad (16)$$

c) <u>Shear relaxation</u>.

A liquid possesses a shear rigidity if stressed at sufficiently high frequencies and ultrasonic shear waves can be used to show that also shear viscosity presents a relaxation mechanism: the effects are of special interest in associated liquids of high shear viscosity (as viscoelastic liquids) where the solid-like structure possesses a characteristic time for the accumulation of energy by a molecules to allow a "jump" in an empty lattice position.

d) <u>distribution of relaxation times.</u>

In the preceding considerations the simplest situation of a single relaxation time process has been considered.

Frequently however various relaxation processes either of the same kind as of different natures, occur in the same frequency region and affect sound velocity and absorption in a more complex way. Aims of ultrasonic spectroscopy are those of using the experimental results in order to deduce the distribution of relaxation times and of trying to identify the molecular processes which are involved.

In such as effort it is of great interest to widen the frequency range of experiment. As it has been already mentioned, the use of the scattering of a beam of light produced by the medium molecules in thermal agitation can extend the frequency range of measurement to 10^{11} H_2; the effective use of these scattering techniques has been made possible by the development of laser light sources with their properties of high monochromaticity and intensity.

5. Ultrasonic spectroscopy research and the group of Rome.

The research on relaxation processes carried out by the Rome group has to be seen in the general lines of the development of the ultrasonic spectroscopy in the years after the war.

As already mentioned, although the research on relaxation processes had already started since the years '30 (the basic theoretical explanation of experiments in gases, was presented by K.F. Herzfeld and O. Rice in 1928 (III)), it was mainly concerned with gases where the experiments can be conducted at a single frequency by changing the pressure (the parameter of importance is the ratio between frequency and pressure). H.O. Kneser (1938 (IV)), however, had already indicated that the process of relaxation between external and internal degrees of freedom could well be responsible of the excess absorption in some liquids.

The available measurements in liquid were, at the end of the war, rather limited and they usually had been not carried out with the intention of using the sound propagation to study the non-equilibrium structural properties of the liquids.

A critical review of the existing data and of the theoretical lines proposed for their interpretation was performed in 1949 (9). It was, of course, concerned with the absorption coefficient and its comparison with the classical one. The dispersion in liquids, in fact, is very small; the frequency range accessible to experiments and the measurement accuracy at the time were not sufficient for the determination of the effect. The review pointed clearly to the relaxation processes as the main effect responsible of the observed excess absorption and to the necessity of considering both thermal and compressional relaxation processes. This review was the first in literature, had a rather large influence on successive work as it has been acknowledged in the literature as well as in successive similar works (J.J. Merkhan, R.T. Bayer and R.B. Lindsay, Review of Modern Physics of 1951 (V)).

In trying to examine the relations between molecular properties of liquids and the sound propagation parameters the group of Rome has very frequently used binary mixtures as the propagating medium because composition offers an added variable which influences, in a controlled way, the properties of the liquid and extends the possibility of gathering information in assigned ranges of variation of other parameters as frequency or temperature.

It would be lengthy and not easy to examine the various researches also because in order to appreciate their value they should be presented in the context of the status of knowledge of the problems and of the available techniques at the time at which they were carried on. We will limit ourselves to give a few indications which will hopefully trace the general lines of the work.

a) vibrational relaxation in unassociated liquids.

A strong support to the hypothesis that the excess absorption in unassociated liquids is due, as in gases, to the time lag in the energy equilibrium between external and vibrational degrees of freedom was given by the results (14,16) of experiments in mixtures of an unassociated low viscosity highly absorbing component (benzene, chloroform) and a component, either unassociated or associated, having a much smaller absorption coefficient (fig. 3). The addition of small quantities of the second component to the first one produces a drastic decrease of the coefficient as a consequence of the increase in the efficiency of the binary collision in the partition of vibrational energy, being different the relative quanta. Such a conclusion was confirmed by the particular behaviour of binary mixtures of two unassociated liquids having similar absorption coefficients (fig. 4) whose molecules do not strongly interact.

A satisfactory theory (15) was in fact developed for this case on the two assumptions of the existence of relaxation processes in the partition of energy between external and internal degrees of freedom and of the higher efficiency of collisions between unlike molecules.

The experimental results are different in the cases where the two liquids have molecules which may strongly interact between themselves: structural effects are present and alter the vibrational relaxation process (16). Figure 5 gives the absorption curves of carbon- tetrachloride-chloroform and benzene chloroform mixtures.

It is possible to justify, on the basis of the molecular structure, why the first system behaves as formed by two unassociated liquids with non interacting molecules while the situation is different in the second system where the high polarizability of benzene molecules produces strong interaction with the polar chloroform molecules.

Carbon disulphide is an unassociated liquid with very high absorption coefficient and it has been very frequently investigated to try to clarify the vibrational relaxation process. A a consequence of the strong effect of impurities, the results of measurements performed by various authors at different frequencies have for a long time, scattered widely.

A problem of interest in the study of the vibrational relaxation process in a polyatomic liquid is that of ascertaining if the process is a single or a multiple relaxation process; in the second case the relation between the processes are to be determined.

Kneser (VI) analyzing the data for CS existing in literature in the range 0.1 - 1000 MHz pointed out that there was not the possibility of clearly determining the relaxation time: this could vary between 5x10^{-9} and 1.6x10^{-9} sec. There was need of measurements conducted with high purity specimens and great accuracy. E. Bauer (VII) had presented an interpretation of the experimental data assuming the presence of multiple dispersion. Bauer's theory considered also the temperature variation of the absorption in CS and, in absence of any experimental data on the temperature coefficient of the absorption, made some assumptions on its value, which seemed reasonable at the time, and used such a theory to support his multiple dispersion interpretation. The accurate measurements of the absorption between -20 and 40 C has however made possible to decide in favour of a single relaxation process in 1951 (19) and this result has been confirmed by later investigations.

b) <u>structural relaxation</u>

Liquids formed by molecules which strongly interact behave differently from unassociated liquids: the energy distribution between external and vibrational degrees of freedom may also occur in the time between collisions and therefore the equilibrium is reached at a much rapid rate: as a consequence, the corresponding relaxation times strongly decreases and this process may loose interest. At the same time, however, molecular structures appear in the liquid and the corresponding equilibria may be altered by the temperature or pressure variations induced by the waves, giving rise to structural relaxation effects.

In the case of pure liquids the equilibria are those between molecular associations characterized by different specific volumes and the relaxation is bound to the pressure variations (complex isothermal compressibility).

The classical example is the already mentioned case of water where two states can exist (ice-like and close packed). In other cases of pure associated liquids different forms of associations are to be considered.

The investigation on the nature of the structural effects present in the liquids can be carried out with advantage in the case of binary mixtures. An extensive work has been carried out in this area. We recall the case of water-alcohol systems where a maximum of absorption at an intermediate composition occurs and has been explained as due to thermal relaxation in the equilibrium of molecular associations. The water-methyl alcohol system which seemed, on the basis of existing data at room temperature, to behave differently from other water-alcohol mixtures, has been accurately studied at sufficiently low temperature

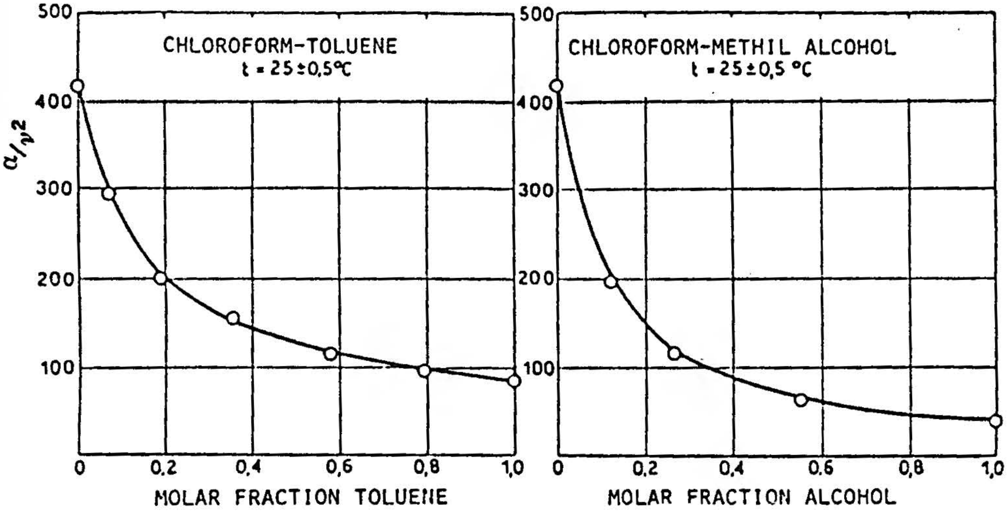

Fig. 3. α/ν^2 vs mole fraction composition in two binary mixtures of an unassociated high absorbing liquid and an (either unassociated or associated) low absorbing liquid (16).

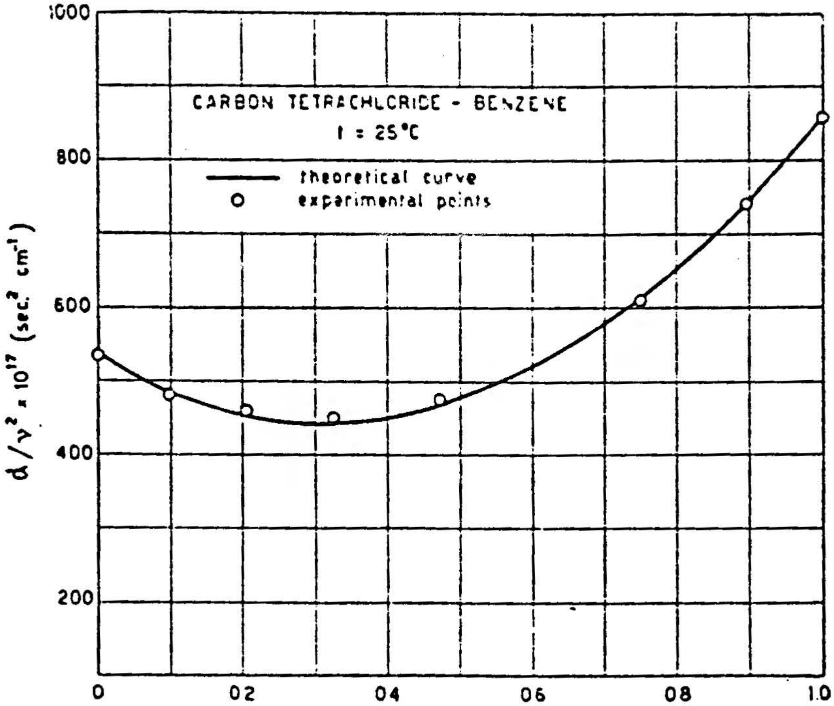

Fig. 4. Absorption coefficient in carbontetrachloride-benzene mixtures (15).

(till -32°C) confirming the presence of thermal relaxation (25). In other cases (aniline-ethyl alcohol, aniline-nitrobenzene) the analysis of the results (31) (43) on absorption coefficients in wide temperature and composition ranges indicates that while the mixtures with low aniline concentration behave as unassociated liquids, the nature of relaxation when aniline content increases turns toward compressional relaxation bound to structural equilibria in the liquid which are perturbed by the pressure variations induced by the waves: the structures seem to be produced by the strong hydrogen bonds between the NH group of aniline and NO_2 or OH groups respectively in nitrobenzene and alcohol.

The study of the appearance of structural effects due to the interactions between molecules can also be usefully carried on by examining the sound propagation in families of pure liquids. such a type of research has been conducted in halogenated methylenes, ethanes, ethylenes, and benzenes (17) (18). One result can be obtained by comparing the absorption in a wide range of temperature in cis and trans-dichloroethylenes: both behave as unassociated liquids; the cis form which has a dipole moment, has a larger absorption than the trans-form without dipole. This result, contrary to what was the existing theory, has been confirmed by measurements in the vapours, as we will see later, and has had influence in the development of the theory for the evaluation of relaxation times.

c) dielectric and ultrasonic relaxation

An interesting aspects of the molecular properties of liquids can be obtained by the comparison of the viscous and dielectric behaviours of a viscoelastic liquid (21). The case of glycerol (5% of water) has been considered by measuring at the same time the dielectric constant and the elastic constant for a longitudinal sonic wave

$$\beta = 1/\rho V^2$$

Both are complex: $\varepsilon = \varepsilon' - j\varepsilon''$; $\beta = \beta' + j\beta''$

Figure 6 and 7 gives a plot of the real and imaginary parts of the reduced dielectric and elastic constants vs viscosity at 30 MHz. The theoretical curves, as indicated by the single relaxation time theory, are also given. The sound propagation in glycerol is associated to relaxation processes of the shear and compressional viscosities. These viscous processes seems to occur with relaxation times very similar, in the limit of resolution attainable, given the existence of a distribution of relaxation times in both processes.

According to Erying a viscous flow requires "translation jumps" of molecules in the pseudo-crystalline lattice and shear viscosity is determined by factors which control the "translational jump" frequency. The dielectric relaxation behaviour depends on "rotational jumps" of molecules in the electric field.

The studies of the two behaviours allows a comparison between the two types of jumps. This study has been the first of this kind and has indicated that the effective relaxation times for dipole relaxation and viscous flow are equal within the experimental error: also the distribution of relaxation times which is detected, appears to be similar in the two processes.

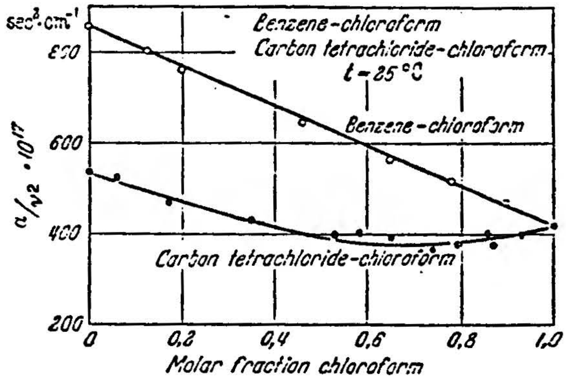

Fig. 5. Absorption coefficient in benzene-chloroform and carbon tetrachloride-chloroform mixtures (16).

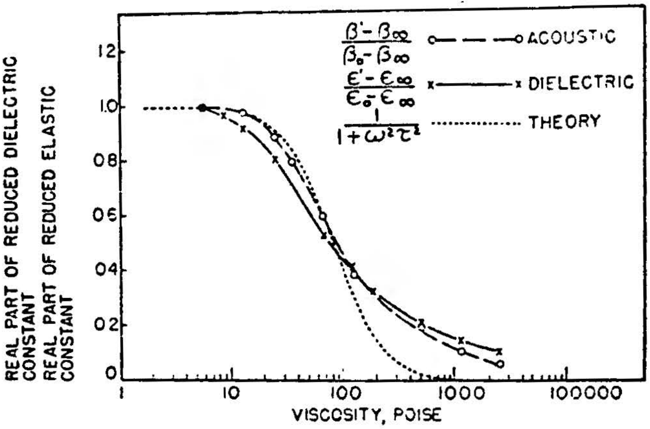

Fig. 6. Real part of the reduced dielectric and elastic constants of glycerol vs viscosity, at 30 MHz (21).

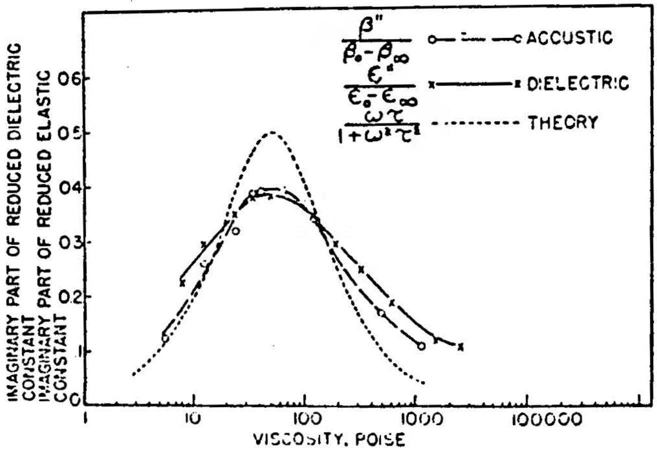

Fig. 7. Imaginary part of the reduced dielectric and elastic constants of glicerol vs viscosity at 30 MHz (21).

d) studies of velocity dispersion in liquids

As already mentioned, the study of relaxation process in liquids is carried on giving attention to the absorption coefficient; the related velocity dispersion is in fact (at difference from the case of gases) usually very small and of difficult experimental evaluation.

It is however of large interest to complement the absorption data with velocity experiments. This has been made in the case of propionic acid by using an interferometer allowing accuracy of 0.5‰ (32).

The total dispersion expected on the basis of the absorption measurement, varies between 3 and 5‰ in the temperature range examined. The results of the dispersion between 2 and 6 MHz agrees with these indications.

6. Sound propagation in fluid critical systems

The use of sound propagation can give, and has given, valuable contributions to the study of critical phenomena. The relevance of the subject has been underlined at various times during the period which has assisted to the rapid development of the field (37, 41, 44).

The low frequency (zero frequency) sound velocity value can be related to the equilibrium thermodynamic behaviour of the medium: in critical systems the measurements at low frequency may become rather difficult in order to avoid disturbing influences, as gravity. Resonance methods have at times been used, where the resonance frequency and the quality factor of a suitable cavity filled with the fluid are determined.

The study of sound absorption and dispersion due to special relaxation processes can give information on dynamic non equilibrium properties of the critical system.

At the beginning of the '50 very few measurements were available (37) in pure liquids as those in Xenon by D.G. Chynoweth and W.G. Schneider (1951-52) (VIII), and in binary systems, as those in aniline-n-hexane by Chynoweth and &Schneider, in aniline-cyclohexane and water-phenol by M. Cevolani and S. Petralia (1952) (IX), in nitro-benzene-n-hexane by D. Sette (1953) (22). Measurements of excess sound absorption in a wide range of frequencies in nitrobenzene-n-exane and water-triethylamine allowed (1955) (26) to indicate the thermal relaxation in the cluster equilibria as the main cause of losses, through an evaluation of the contributions to scattering and viscosity losses introduced by the heterogeneity due to the presence of clusters.

The systems nitrobenzene-n-hexane (40) and aniline ciclo-hexane (39, 42) have received much attention, furnishing valuable experimental results in a period in which new theories have been developed [(M. Fixman (X); K. Kawasaki (XI); L.P. Kadanoff, J. Swift (XII)].

The research has also been extended to consider other aspect of critical phenomena in liquids.

7. Vibrational relaxation in gases

A quantistic theory developed by Schwartz, Slawsky and Herzfeld (XIV) on the transition probability of energy between vibrational states of two colliding molecules, as a

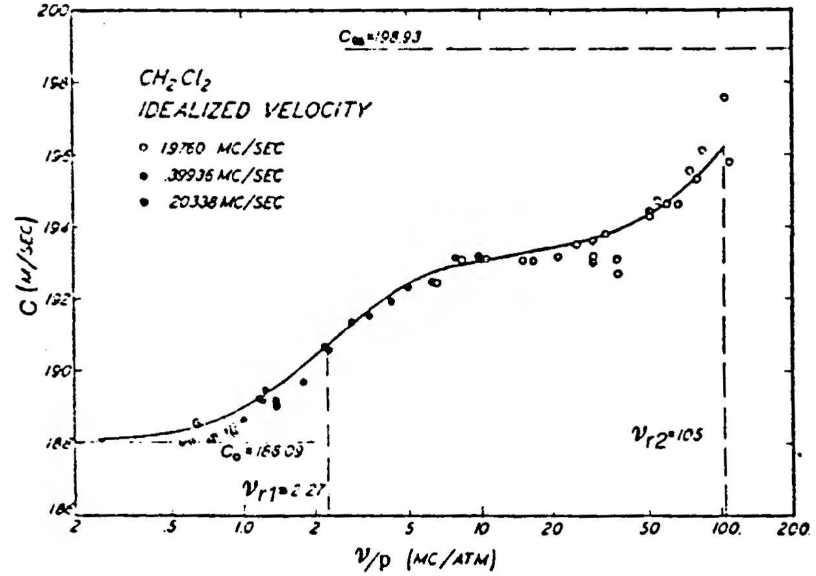

Fig. 8. Dispersion of ultrasonic velocity in methylene-chloride vapours at 30°C (27).

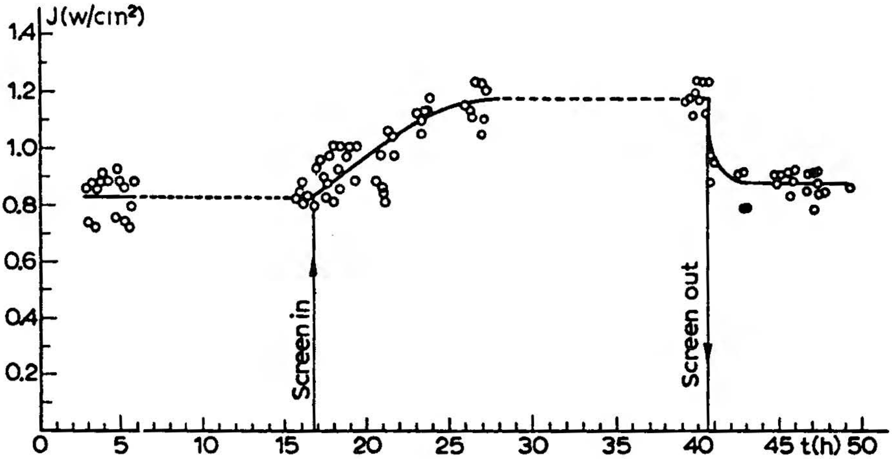

Fig. 9. Cavitation threshold in aerated distilled water at 28°C.

function of the forces between molecules and of their characteristics, has given impulse to investigate experimentally the influence of the variation of forces between molecules by comparing the sound propagation in fluids with molecules having related structures. This research was initiated in liquids (17) (18), but was more clearly carried on in vapours of cis and trans-dichloethylenes, (20).

The measurements in gases were made with high precision interferometers which allow accurate determination of velocity and dispersion.

The examination of the results on dispersion shows that the energy equilibrium among vibrational states occurs quicker in the trans (without dipole) than in the cis (having dipole); the two molecules are very similar in other respects. Such a conclusion, which agrees with the indications obtained in liquid state, was contrary to the preceding ideas: the dipole forces in fact were considered as high effective in increasing the transition probability. The experiment, instead, indicates that the transitions are mainly determined by the short-range forces. The dipole forces could only have an indirect influence by changing the vibration levels of the molecules while they are approaching one another. Such results have been used in the development of the theory for the calculation of the relaxation time, by assuming that the transitions during collisions occur in the repulsive part of the interaction potential.

An important aspect of vibrational relaxation concerns the path of the energy flow from external (translational and rotational) degrees of freedom to vibrational degrees and viceversa. Two extreme cases are possible: in the first one (parallel excitation) each vibrational degree exchanges energy with the external degrees, independently from others; in the second one (series) the energy goes through a vibrational mode to the others. The experiments in chlorinate methanes (28) have allowed to examine this aspect shoving that the more likely path in the energy distribution in these components is the series one through the vibration mode of lower energy: the internal transition times which characterizes the flow into other vibrations are usually very short; they can however become detectable in some cases: the dispersion then occurs in more than one frequency region. The first case of this type in the literature is the one found in methylene chloride (fig. 8). The specific heat relaxation occurs with two characteristic times and it is also possible to determine the vibrational modes involved. These results have been used for theoretical advancements.

Carbon dioxide is a very absorbing unassociated medium. The efficiency of binary collision in producing the energy distribution among vibrational states is very low: 70000 collisions are needed, in average to deexcite a molecule. It is normal that the presence of impurity drastically decrease such a number: 47000 collision are needed to deexcite a CO_2 molecules with Ar molecules. A special effect is however produced by water molecules because the quoted number of collision reduces to 105. Various suggestions had been proposed to explain such an effect: CO_2 and H_2O molecules could associate allowing energy transfer also between collision; the presence of water molecules could drastically change the vibrational state of some CO_2 molecules increasing the efficiency of transition; the possibility could exist of energy exchange between rotational degrees of water and vibrational states of CO_2. In order to examine the latter possibility an accurate study has been performed on the effect produced by the presence of small quantities of H_2O or D_2O. The two molecules differ for the inertial moment and therefore for the rotational quanta. The experimental results can be interpreted on the basis of the Schwartz-Slawsky-Herzfeld theory as due exclusively to the different masses of the molecules and they exclude the possibility of the transition between rotational degrees of water and vibrational degrees of CO_2.

8. Sonic cavitation.

When the intensity of sound waves reaches a sufficient level (threshold) in liquids, specially if gases are dissolved in them, cavities start to form, quickly grow and may violently collapse: the process immediately magnifies causing strong absorption and scattering of the sound beam. The pressures in the gaseous phase during the collapses may reach very high values, intense shock waves originate and chemical reactions are frequently induced.

A special aspect of these effects is the production of intense luminescence. A study (27) was performed in water solutions and organic liquids in order to clarify the origin of the process. The results in water solutions have shown that chemical reactions are occurring at the same time: a quantitative relationship was established between intensity of luminescence and chemical yield, pointing to the process as one of chemi-luminescence.

A research (23) on the relation between cavitation and chemical processes induced by it, has investigated the influence of various dissolved gases on the cavitation threshold of water. Very accurate determinations have shown over 100% variation in bidistilled water saturated with N_2 or SF_6. Strong variations have also been observed when a gas mixture (O_2-N_2; O_2-Ar) is used to saturate the water and its composition is varied.

The negative pressure produced by sound wave (during decompression) at the threshold of cavitation in liquids having dissolved gases, (a few atms), is well below the pressure needed to tear apart the liquid (larger than 10^4 atm). It is necessary therefore to assume that the phenomenon really consists in a growth of bubbles through diffusions in pre-existing nuclei.

It has been of relevance the research for clarifying the process involved. Measurements of sound absorption in an appropriate frequency range have indeed shown the existence of resonance processes and analogous result have been obtained by light scattering. The radius of the microbubbles may go from fractions of 1 μm to about 50 μm.

A difficulty arises in explain the existence of an equilibrium distribution of gaseous nuclei, due to the fact that being the sizes of the nuclei very small they could not remain in equilibrium under the surface tension and the external and internal pressures.

Various suggestions have been formulated to justify the situation: solid particles with concave recesses could host gas nuclei or thin skins of organic greasy material could envelope gas nuclei. A research (24) performed in carbon tetrachloride and benzene (efficient solvents of organic materials which could form the skins) as well as in water solutions containing Ar, prepared with special procedures, has considered such a problem and it has ruled out the skin hypothesis. The possibility of a stabilization mechanism bound to the presence of dust solid particles or of microscopic cracks in the container walls seems the more probable one. It is in any case possible to prove that, in given conditions of a liquid, a dynamic equilibrium of nuclei is established and maintained, as the constance of the cavitation threshold confirms.

A rather interesting problem concerns the processes (nucleation) which may conduct to the production of these microbubbles. Of course they may have been created in various ways during the story of the sample and its introduction in the container: they may also been originated by previous cavitation events. Other processes of nucleation must be assumed to explain experiments. It is possible in fact to change the equilibrium distribution of microbubbles (and the cavitation threshold) by some methods as, for instance, by pressurizing the liquid or in other ways, which we will soon discuss; the equilibrium is however restored when the initial external conditions are re-established. A nucleation mechanism must therefore exist which creates nuclei to restore and keep the microbubbles equilibrium.

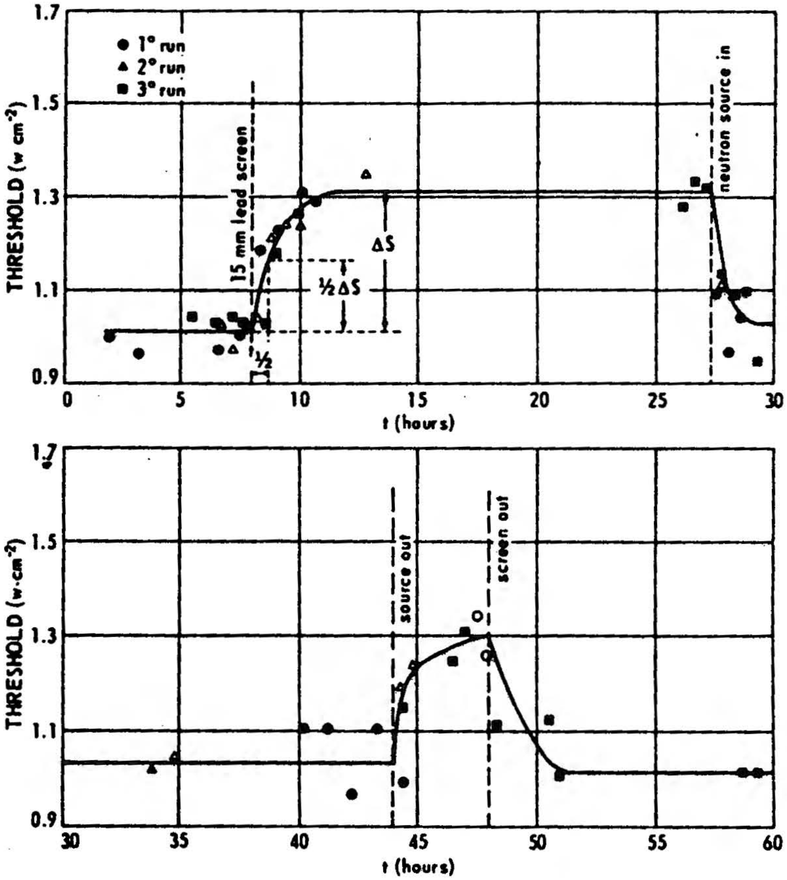

Fig. 10. Cavitation threshold in water: effects of a 15 mm lead screen and of a 10 mc Ra-Be neutron source.

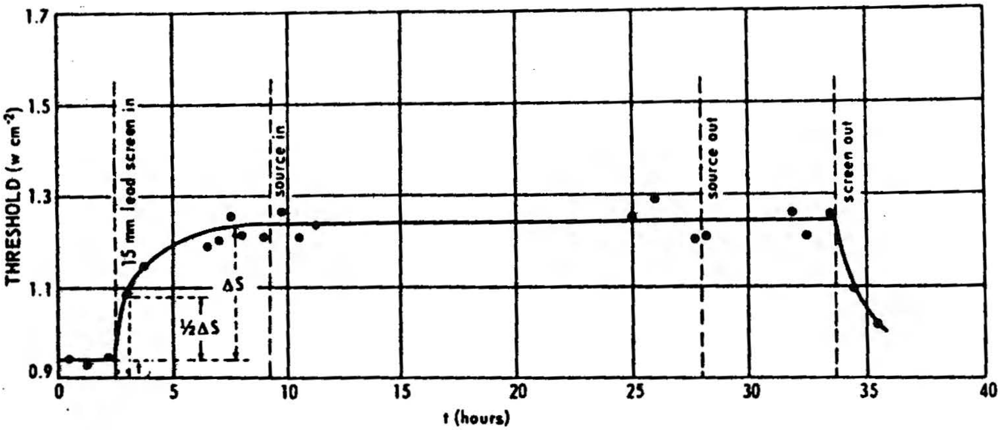

Fig. 11. Threshold in distilled water sorrounded by a 15 mm lead screen and in the presence of a source of neutron with energies lower than 1 MeV.

A fundamental experiment was performed in Rome which did show the influence of cosmic radiation (34). The threshold in normal pure water was significantly increased by shielding the tank from cosmic radiation by means of a lead screen (1,5 cm thick) (fig. 9). at the same Congress in which these results were presented, Lieberman and Rudnick (XIV) examined the occurrence of cavitation events in acetone and pentane in presence of a neutron source: the threshold was drastically reduced without any observable delay from the presence of the source; they concluded that carbon recoil nuclei were responsible for microbubble formation.

In the experiment with water (34) the threshold was found to gradually increase after the screening, with a time constant of the order of hours: the high energy particles of cosmic radiation must be responsible for the creation nuclei and a stabilization mechanism must be present in water.

The action of cosmic rays has been clarified by further investigation (35). Figure 10 give the results of a first experiment. A large distilled-water tank is maintained in equilibrium with the atmosphere and the cavitation threshold is checked for a long time before a leak screen is set around the tank. The screening of cosmic rays produces an increase of the threshold and time is allowed for the threshold to reach the new equilibrium value. At this point a radium-beryllium neutron source is introduced into the liquid; the threshold decreases to a value practically equal to the threshold of unscreened water.

When the neutron source is removed, the threshold increases again and it returns to the original value if the screen is also taken away. The screening of water by lead (or paraffin) decreases the equilibrium concentration of nuclei produced by cosmic rays and makes the liquid sensitive to other nucleation agents; neutrons of 10 to 14 MeV are able to produce nuclei. It seems plausible to assume, therefore, that high-energy neutrons in the cosmic rays are responsible for nucleation in water. The mechanism is the same as that suggested by Liebermann and Rudnick to explain their experiments in acetone and pentane: atomic nuclei are bombarded by the high-energy neutrons and produce the tiny bubbles.

To decide, in the case of water, if both H and O nuclei are able to produce microbubbles, the experiment of fig. 11 has been performed. It is analogous to that illustrated by fig. 10 with the only difference that the neutron source is introduced into the water tank with a paraffin blanket which cuts the energy of the neutrons by a factor of 10. It can be shown that the parameter which is important in the bubble creation by a high-energy ionizing particle is the energy deposit for unit path length, and therefore it is important to consider for a bombarded nucleus the maximum value of such specific deposit during its life in the liquid i.e., when its energy goes from the value received by the colliding neutron to zero. The decrease by a factor of 10 of the energy of neutrons form a radium-beryllium source still allows bombarded protons to receive an energy much larger than that of the maximum specific energy deposit in water. This means that the energy cut of neutron energy does not affect the action, if any, of protons, in creating cavitation nuclei.

The situation is different for bombarded oxygen nuclei in which a strong decrease of the maximum specific energy deposit is produced by the cut in neutron energy. The experiment of fig. 11 shows that no threshold variation is produced by the presence of the screened neutron source. It is therefore concluded that oxygen-bombarded nuclei are the agents which create microbubbles.

Figure 12 gives the threshold in water as a function of lead-screen thickness. The threshold increase to a maximum and then decreases. Such behavior can be explained by taking into account nuclear reactions produced by cosmic rays in the screen material and the production of secondary neutrons.

The body of experiments such as those here quoted leads to the conclusion that nucleation in water under normal conditions is produced by cosmic neutrons through bombarded oxygen nuclei. The energy of neutrons must be larger than 10 MeV.

The proof of the existence of an equilibrium distribution of nuclei allows to examine the cavitation process in a way which seems less crude that the simple consideration of the cavitation threshold, intended as the lower limiting value of the acoustic pressure for the onset of cavitation, defined in a operative way by each experimenter. One can in fact give attention (36) to the concentration and size distribution of nuclei, i.e. of microbubbles with may grow to visibility in a suitable sound field. A study of this kind, of statistical nature, furnishes a deeper insight in the physics of cavitation than the mere determination of the threshold.

It has been possible in this way to examine closer the processes due to screening: a general decrease in the number of nuclei of all sizes present in the liquid, due to the absorption of cosmic rays in the screen, coexist with the creation of nuclei of a particular size. The events of a second type are bound to the possibility of production of secondary neutrons in the bulk of the screen. Such an effect, however, is not sufficient to compensate the general decrease of nuclei produced by the screening, in determining the crude parameter which is the cavitation threshold.

Many other similar experiments have been performed in various laboratories (XV). In particular Greenpann and Tschiegg, as well as C. West and R. Howlett, performing experiments in numerous liquids under neutron irradiation, have proved that a cavitation event follows from the action of a single neutron, i.e. it is not the consequence of a cooperative action of two or more neutrons.

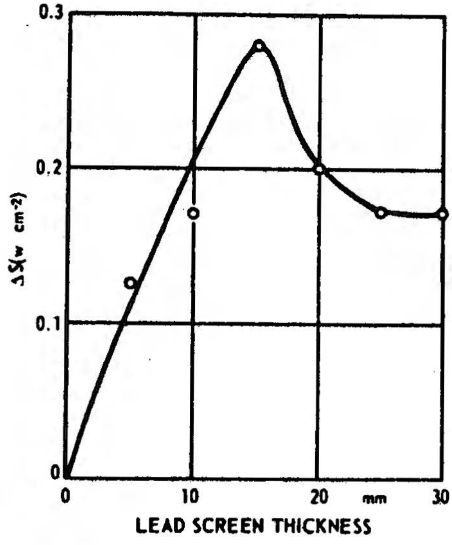

Fig. 12. Threshold variation in distilled water as a function of lead screen thickness.

The nucleation process involved in the sonic cavitation looks in some way similar to the one active in bubble chambers. One must, however, note the great differences in both the thermodynamic conditions of the system and the sizes of nuclei in the two cases: the bubbles chambers operate near the critical temperature and the dimensions of nuclei are of the order of 10^{-7} cm; sonic cavitation is usually observed at room temperature and the nuclei have radii of about 1 µm. F. Seitz (XVI) had developed the thermal spike theory for the bubble chambers operation: energetic neutrons produce recoil atomic nuclei which act as nucleating agents in the liquid. Such a theory may be able to explain the experiments of sonic cavitation in liquids like pentane and acetone (XIV); its fails for water (35): energy deposit as high as 47.000 MeV/cm would be required while the maximum value of this parameter for oxygen recoil nuclei, which are able to produce sonic cavitation nuclei, is about 6.000 MeV/cm.

A different thermodynamic theory has been developed (38) which seems able to explain the experiments. The theory is based on the well known phenomenon (XVII) that an apparently homogeneous thermodynamic phase always contains embryos of other phases which may be stable under suitable conditions. It has therefore been assumed a statistical presence of gaseous embryos in the liquid phase. The mechanism of nucleation by high energy particles appear to consist of two successive stages: the first one is a local variation of thermodynamic conditions favorable to the growth of embryos; the second one is the actual growth of these embryos. The theory is able to explain both the bubble chamber operation and the creation of nuclei for sonic cavitation. In the latter case, at difference from the case of bubble chamber operation, the energy for both processes has to be furnished by the incoming particle.

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LOW TEMPERATURE PHYSICS IN FRASCATI, PADUA AND ROME

(1955-60)

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Up to the early nineteen sixties low temperature physics was one of the major areas of fundamental research in physics. In spite of the two-fluid model, developed by Landau in the forties to describe the strange properties of superfluid helium, several basic questions still remained unanswered. Particularly the wave function properties of the Bose condensate and the microscopic origin of the superconductivity. For these reasons, during the fifties, low temperature physics attracted the attention of some of the major theoretical physicists of the time, such as Onsager, Feynman, Bogolyubov, Yang, Lee, Frölich, Bardeen, and many others. They would attend low temperature conferences and propose new crucial experiments.

It was at this lively and exciting moment that the occasion arose for starting research in this field in Italy, around 1955. The occasion was the need for low temperature facilities by the Italian high energy physics community, in connection with the construction of the first Italian particle accelerator, the Frascati electron synchrotron (1.1 GeV). A small group active in liquid state physics at the University of Rome was the seed for the birth of low temperature physics in Italy and for the growth of a substantial research group: in addition to general cryogenic techniques, this group developed new experimental approaches to investigate the nature of the superfluidity of liquid helium and was soon connected with the scientific mainstream of that time (See Table I).

We shall describe here the major steps of this effort, stressing the historical and social aspects, in keeping with the purposes of this meeting.

1. The beginnings (1955-56)

The decision to build the Frascati synchrotron was taken in 1954 by the community of Italian high energy physicists and was sponsored by the CNRN* (Comitato Nazionale per le Ricerche Nucleari), whose president was Francesco Giordani, and by the INFN (Istituto Nazionale di Fisica Nucleare), under president Gilberto Bernardini.

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* To become CNEN (Comitato Nazionale per l'Energia Nucleare) and, more recently, ENEA (comitato nazionale per la ricerca e lo sviluppo dell'Energia Nucleare e delle Energie Alternative)

TABLE I: key events in the development of the growth of the Frascati-Padua-Rome low temperature physics group in the international community

1956	March: helium is for the first time liquified in Italy
1957	First communication of scientific results at an international conference (1)
1959	First liquid hydrogen targets built for high energy physics experiments
1960	Invited paper to the first international conference on many-body problems (2)
1961	Review paper on the results of the group published on Progress on Low Temperature Physics, Vol 3 (3)

While the design and the construction of the synchrotron was carried out, under the direction of Giorgio Salvini - with all the people crowded in the Istituto Fisico Guglielmo Marconi at the University of Rome - the problem came up of targets for the synchrotron beams. The first, simplest target was to be liquid hydrogen, but then liquid deuterium, liquid ^{4}He and liquid ^{3}He would follow. This meant the need for know-how in cryogenics.

The solution to this problem was notably creative: responsibility for cryogenics was given in 1955 to Giorgio Careri, at that time a young assistant professor at the University of Rome, who was conducting research on condensed matter physics, in particular on problems of diffusion in liquids. The idea was that cryogenic needs could be met by starting a research program in low temperature physics.

Only a few years back a helium/hydrogen liquefier, the well known Collins, developed by professore Sam Collins of MIT and produced by the American firm Arthur D. Little had become commercially available: before then, every laboratory wanting to do research with these cold fluids had to build its own liquefier. Among the few laboratories able to do that in Europe were Cambridge, Oxford, Leiden, and Moscow. Thus the decision was taken to buy one of these new machines, which could be able to liquefy about 15 liters of helium per hour, using two compressors and precooling (one liter of liquid nitrogen per liter of liquid helium); it was also able to produce a smaller amount (7 l/hr) of liquid hydrogen, using part of the same helium gas circuit - the first two stages, equipped with expansion engines - to cool and liquefy hydrogen practically at atmospheric pressure. The order was placed in 1955.

At the same time Careri, who was an expert in condensed matter physics and related techniques (for example, mass spectroscopy), but not in cryogenics, went to Leiden on a CNR fellowship, to learn the fundamentals of this technique. He spent six months there and, in addition to learning basic cryogenics, he made two important acquaintances. The first one was with the brilliant school of condensed matter physics operating at Leiden under the guidance of professors Gorter and Taconis. In particular, he met a young dutch physicist, Jan Beenakker, with whom he had very fruitful discussions. As a consequence, combining his experience on diffusion with the low temperature expertise found in Leiden, Careri proposed an experiment on the diffusion of ^{3}He in ^{4}He in the liquid phase. He also crossed paths with a young german physicist, Jorg Reuss, who was a graduate student at Leiden, having already earned a Bachelor's degree at the University of Freiburg. Reuss already had expertise in cryogenics and accepted the invitation by Careri to follow him to Italy, to help start the new cryogenic plant at Frascati.

Fig. 1 A lunch under a pergola in Frascati in the early days of the Frascati Laboratories (1956). From left: F. Scaramuzzi, A. Bellatreccia, J. Reuss, G. Careri.

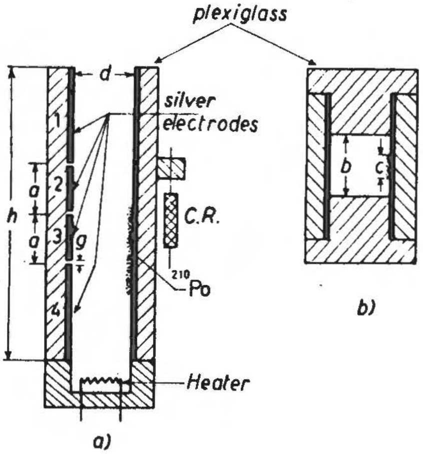

Fig. 2

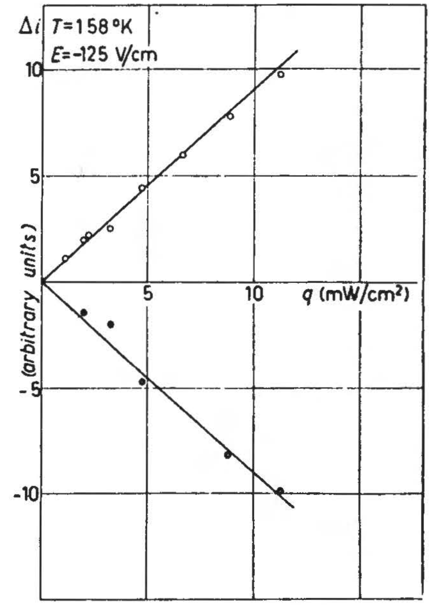

Fig. 3

Fig. 2 Schematic view of the last version of the "heat flush" apparatus: a) side view; b) top view (From il Nuovo Cimento, X, 13, 186 (1959)).

Fig. 3 Plot of the change in current Δi produced by the heat flush vs heat input q, for two of the electrodes: white dots refer to electrode n. 2 and black dots to electrode n. 4 (see Fig. 2). (From Il Nuovo Cimento, X, 13, 186 (1959)).

Soon thereafter Careri was given a position of full professor at the University of Bari, where he went in March 1956. Back in Frascati, the building for the liquefier had just been erected and the Collins had been crudely assembled. In Bari Careri met Franco Scaramuzzi, who had attained a degree in mathematics and physics at that University a few years before and was teaching there as an assistant professor. He was the youngest in the Bari institute, and a bachelor, and he agreed to split his time and energies commuting between Frascati and Bari, i.e., between working at the liquefier and teaching physics.

An experienced technician, Edoardo A. Solinas, who had in the past worked in a navy yard and aboard warships, and was an expert in handling compressors and pressure circuits, was hired; a young student-technician, Alberto Bellatreccia, who was already helping with the diffusion measurements in Rome, was engaged as a part-time helper for the laboratory and completed the staff responsible for starting the first Italian low temperature laboratory.

The Collins was mounted in the only, still unfinished, building existing in the area of the Frascati laboratories, and was tested on March 1956, under the direction of Milton Streeter, a skilled technician from Arthur D. Little (F. Scaramuzzi had not yet joined the group: he would follow in early May).

A few technical details help give a sense of the difficulties encountered in operating the liquefier in those early times. Cooling water for the compressors was provided by pumping water contained in some tanks, which had to be filled by a tank-truck at least twice a week to compensate for evaporation and leaks. On very hot days it was not possible to operate the plant, because of the high temperature of the water. The street connecting the main (Frascati-Rome) road to the laboratory was either dusty or muddy, depending on the weather. Liquid nitrogen and dry ice, needed for laboratory appliances, had to be bought every morning in Rome and brought to Frascati. However, at least one of the inconveniences, the lack of restaurants and cafeterias in the vicinity, resulted in one of the most pleasant aspects of life: a family of neighbouring farmers offered to prepare meals for the people working in the semi-deserted laboratory, i.e., those working at the liquefier and a few masons, who were erecting the synchrotron building. It was very pleasant to have a delicious lunch under a pergola in the open country: in Fig. 1 one of the lunches has been photographed. For the record, the price was 500 lire per meal: including unlimited wine and fruit (which could be picked from the tree).

2. *The early days in Frascati (1956-57)*

The first experiment performed in Frascati at liquid helium temperatures was the measurement on diffusion coefficients in dilute H_2-D_2 and ^3He-^4He mixtures. The experiment, proposed by Careri during his stay at Leiden, was performed with the collaboration of Reuss and Beenakker. It took advantage of the combination of three factors: the previous experience of Careri on diffusion, gained by performing measurements, with Matilde Vicentini and Antonio Paoletti, of the self diffusion coefficient in liquid metals with radioactive tracers: his expertise in mass spectrometry, due to research conducted previously with Giovanni Boato; and the know-how in low temperature physics and techniques contributed by Reuss and Beenakker.

This experiment, aside from producing published measurements of the diffusion coefficient (4), laid the basis for the main research line of the whole group on the properties of superfluid helium. The idea was that, by studying the behaviour of foreign particles, like ^3He atoms, of the same size as the excitations postulated by Landau, it was possible to perform macroscopic experiments able to give an insight into the fundamental microscopic mechanisms of superfluidity. Because ^3He atoms proved to be difficult to handle, Careri proposed to use ^{4}He ions instead. They were much easier to move and detect. Careri's skill in measuring very small electric currents, gained in mass spectroscopy, was a great advantage in this new work.

The first experiment of this type was intended to test the statement, due to Landau and Pomerancuk (5), that in superfluid helium a foreign particle must collide only with the excitations and not with the superfluid phase, provided that the particle moves with a velocity lower than that needed to create an excitation. There was at that time some indirect evidence of the correctness of this statement, from the study of dilute solutions of ^{3}He in ^{4}He (not the measurements just made in Frascati, which were all above the lambda-transition), but there was not a direct quantitative check.

The experiment is illustrated in Fig. 2, where the final version of the apparatus, much more refined than the first one, is shown. The idea is that, if in a narrow channel a heat flow is created by dissipating a certain amount of power at its bottom, it is possible to describe the situation, in terms of the two-fluid model, as a double current: superfluid moving toward the heater and normal fluid away from it. The ions, produced by a ^{210}Po source deposited on an electrode, cross the channel perpendicularly to the heat flow. If the Landau-Pomerancuk statement is correct, they should interact only with the normal fluid, being flushed upwards, away from the heat source (whence the name of *heat flush* for this experiment). The electric current on a series of conveniently placed electrodes, facing the electrode with polonium, could be detected. The current change (Δi) on two of these electrodes as a function of the heat current (q), in Fig. 3, shows a linear dependence of Δi on q: thus the drift velocity of the ions in the direction of the heat current could be calculated. With a few reasonable assumptions it was possible to consider this velocity equal to the normal fluid velocity and to deduce from it, and from the other parameters of the experiment, the mobility of the ions, which at that time was not known for small electric fields. Conversely, when, a few years later, mobility was measured with other techniques, and was found to coincide with the Frascati measurements, the Landau-Pomerancuk statement was definitely and quantitatively verified, both for positive and negative ions (6).

The heat flush experiment was started at the beginning of 1957. Reuss had moved back to Leiden to continue his studies, and an American physicist, Ollie Thomson, who had just gotten his PhD at the University of Illinois at Urbana, had joined the group with a Fullbright fellowship. The experiment was done by Scaramuzzi and Thomson, under the supervision of Careri. In spite of many minor difficulties, which will be briefly recalled later, by early summer preliminary results were obtained and were presented by Careri together with the preliminary results on the ^{3}He-^{4}He diffusion coefficient, under the title *Movement of ions and ^{3}He in liquid helium*, at the Fifth Conference on Low Temperature Physics and Chemistry (LT5) in Madison, Wisconsin, USA (1).

It is amusing to recall a few episodes that give a feeling of the uncertainties and difficulties typical of any activity at its beginning, and also give the flavour of exciting adventure that belongs to these pioneering enterprise.

Though the Collins liquefier was working perfectly, producing the correct amount of liquid helium per hour, there was a complete failure in transferring it into the transport dewars: all the liquid would evaporate and nothing would be left in the dewar. That was the standard way of working: liquefy into the Collins, store by transferring into a transport dewar and, when necessary, transfer from this into the experimental dewar and perform the experiment. In due time (in 1958) a simple reason for this anomalous behaviour was found. There was too much impedance in the evaporation line: it was sufficient to increase the diameter of the evaporation piping to solve the problem! In the meanwhile experiments had to be carried on in a cumbersome fashion. One of the experimenters would wear insulating gloves and hold the experimental dewar, including the brass crosshead, and a transfer would be performed directly from the Collins into the experimental dewar, losing of course all the evaporated helium; the vapors gave to the scene a phantasmagoric appearance, characterized by large intensely white clouds escaping from the dewar. Then, rapidly, the dewar would be brought to the rack and bolted to it and the experimental run would start.

When the decision to study the motion of helium ions was taken, the problem came up of how to produce them. The first attempt was made with a source of ^{60}Co (50 mCi), that would produce gamma-rays, which would ionize everything they found on their path. The idea was that the gamma-rays would ionize the helium in the channel even with the radioactive source outside of the dewar. The inconveniences of this choice were quickly evident. The first was the most important from the scientific point of view: it would have been impossible to discriminate between positive and negative ions, since both species were created in the channel and moved in opposite directions under the effect of the electric field. Another inconvenience was the difficulty in collimating the gamma beam into the region of interest. This meant the presence of spurious currents due to ionization in the gas above the liquid level, where the cables connecting the electrodes to the external circuit passed. The third item was safety: a 50 mCi source of ^{60}Co is quite dangerous and protection for the operator was a problem. A lead brick of the type used for radiation shielding was modified, by drilling a deep hole parallel to the longer side, at the bottom of which the source was place (this served also as a crude collimator). A handle was attached to it at the other end. Each operator, in turn (in order to share unwanted radiation), would irradiate the dewar, aiming the source to it, and the currents would be measured. As a further precaution, a stack of four lead bricks was mounted to make a small wall (5x10x25 cm^3), with a handle, and the operator would keep it in such a position as to protect his genitals before starting his radiation turn. The use of ^{210}Po deposited on one of the electrodes was a great step forward. The 5 MeV alpha-particles of ^{210}Po have a range of 2 mm in liquid helium. Thus a thin layer of plasma would be created close to the source-electrode and the ions of the wanted sign could be drawn out of it by the electric field without any danger to the operators.

Measuring the current also created a few problems. The first instrument used was a ballistic galvanometer, which made it necessary to work in the dark, in order to see the displacement of the mirror image on a graduated scale. Guided by experience in detecting small currents in a mass spectrometer, Thomson in Rome designed and built an electrometer, which was a noticeable improvement over the galvanometer, but still had a high level of noise. Finding a commercial electrometer (it happened in Padua in 1958) was another great step forward. The first commercial electrometer used in the group was english, an EKCO vibrating reed instrument, and changed substantially the life of the group.

Take a moment to imagine the first experiments, with the initial fumbling with the helium transfer, and then the irradiation rite in the dark, while somebody tried to make sense of the measurements made with the ballistic galvanometer!

In 1957 Careri was offered a physics chair at the University of Padua, together with the necessary resources to start a research group in low temperature physics. He accepted and began to look for young collaborators who would join the group. The first one was Franco Gaeta, an assistant professor at the University of Naples, who had his first contact with low temperatures in Frascati in the summer of 1957. In the autumn, Berto Fasoli of Padua, joined the group and spent a little time in Frascati too. By the end of 1957 the experimental group, including Scaramuzzi, Thomson, Gaeta and Fasoli moved to Padua, together with all the experimental apparatus. In Frascati Giancarlo Moneti, an assistant professor at the University of Rome, who was building, with a group of collaborators in Rome, a liquid helium bubble chamber to be used at CERN, took over responsibility for the cryogenic plant and started the development of the Cryogenic Group of the Laboratori Nazionali di Frascati.

3. The Careri group in Padua (1958-60)

The Careri group started its activity at the very beginning of 1958 at the Institute of Physics of the University of Padua. For that time it was a particularly well endowed group, both in the number of physicists belonging to it and in financial and technical resources.

In addition to the four physicists mentioned in the last section, two more had joined: Ivo Modena, who had gotten his degree in physics at the University of Padua a few years earlier and had been working as an assistant professor in the cosmic rays group in that Institute and Mario Santini, who had just gotten his degree in physics at the University of Pavia, with a thesis on magnetic resonance with Luigi Giulotto. In the course of the three years treated in this section other physicists joined the group: Turi Cunsolo, who got his degree in engineering at the University of Padua at the beginning of 1958; Franco Duprè, who came from the University of Rome in 1958; Paolo Mazzoldi, who achieved his degree in physics at the University of Padua in 1959 with a thesis on the main theme of the group, supervised by Careri; and Vittorio Nardi, who started a collaboration on the theoretical aspects of superfluidity. Ollie Thomson, after two years of fruitful research, went back to the USA in 1958, and in 1959 another american physicist, Bill McCormick, who had just gotten a PhD in physics at the Duke University (North Carolina, USA) completed the group. One technician, Ferruccio Marotto, was the only technical help, beyond the general facilities (mainly mechanical and electronic workshops) of the Institute.

The most important among the scientific facilities at the disposal of the group was a big electromagnet, able to produce field up to 2 tesla in a volume where a helium dewar could be placed. It had been used in the past by the cosmic rays group. The magnet made it possible to start a research project at very low temperatures, using the only technique existing at that time, the adiabatic demagnetization of a paramagnetic salt.

Another important device was a high pressure compressor, used to recover the evaporated helium, filling high pressure (120 atm) bottles, to be sent back to Frascati for purification and reliquefaction. This compressor, a german Hofer, was given to the group by professor Semerano, director of the Institute of physical chemistry: it had originally been installed on a German submarine during the second world war, and had been part of the reparations for war damages from Germany to Italy.

The results presented at the Madison conference (1) on the heat flush experiment had been widely noted. In many laboratories around the world it was realized that ions could be particularly suitable probes to study the fundamental excitations in superfluid helium, and research based on this technique had soon started. In the same year (1958) Meyer and Reif at the University of Chicago published accurate measurements of the mobility of positive and negative ions in superfluid helium at low fields, as a function of temperature; they used a time-of-flight technique (7). The reinforced Italian group attacked different aspects of the physical problem, dedicating to it most of its energies; the only other line developed was a measurement of the spin-lattice relaxation time in liquid ^{3}He. We will now briefly review the results obtained under Careri's supervision.

Heat flush and turbulence (Scaramuzzi, Thomson, McCormick). The first effort was to improve the results obtained in Frascati; a new apparatus was built, the one whose sketch is shown in Fig. 2, and whose results have already been quoted (6). But a new interesting feature had appeared: when negative ions were moving across the channel, for values of the heat current higher than a certain threshold values (depending on the temperature), the dependence of Δi on q (see Fig. 3) was no longer linear, but diverged to higher absolute values. A further feature was later found: if the total current was measured - i.e., if all the electrodes were in parallel - a decrease in current was measured at the threshold, as if the mobility of the negative ions was reduced. The hypothesis of the creation of turbulence in the superfluid component was made, and comparison with measurements made by Vinen (8) in a similar geometry, while measuring the attenuation of second sound in the presence of a heat flow, supported this hypothesis. The turbulent superfluid was conceived as a tangled mass of the vortex lines suggested by Onsager and by Feynman, whose cores could exert an attractive force on the ions. The fact that the negative ions would feel the turbulence, while the positive ones would not, was interpreted in terms of the different nature of the two species of ions (see below). A posteriori, it turned out also to be a question of cross section, which is temperature dependent: as a matter of fact, at low enough temperatures, positive ions too would interact with vortex lines. The ions thus proved to be an efficient tool to probe the turbulent state of superfluid helium. A systematic research was performed and the results published (9, 10).

The structure of ions (Fasoli, Gaeta). There had been for many years an argument about the nature of positive and negative ions in liquid helium. The experiment performed in Padua was very simple: a diode, with horizontal electrodes, could be completely or partially filled with liquid helium and could also be filled with solid helium. The current for both species of ions was measured as a function of the applied field. From the quite different behaviour of positive and negative ions in the interphase geometry (partially filled cell) it was possible to deduce that the positive ion is a cluster of polarized atoms surrounding a charged atom, a model already proposed by Atkins, and that the negative ion is a large empty cage where an electron in self-trapped (the bubble model) (11).

Direct measurement of mobility (Cunsolo). Cunsolo developed a new time-of-flight method to measure the mobility of ions in superfluid helium, which was particularly simple when compared with other known methods and has been since then used extensively in Italy and abroad (12).

Mobility under pressure (Cunsolo, Mazzoldi). An extensive measurement of the mobilities up to the melting point showed interesting features; in particular, the behaviour of negative ions supported the bubble model (13).

Mobilities at very low temperature (Duprè, Modena). Using adiabatic demagnetization, the mobility was measured down to 0.2 K, by the magnetic deflection of the ion beam. The values obtained for the mobility were much lower than expected by extrapolating the known data to low temperatures. At these temperatures the mean free path is long and, even with small electric fields, it was conceivable that the accelerated ion acquired enough energy to permit the creation of some sort of excitation, although it could not be a phonon or a roton (14). Eric Mendoza, a guest physicist from the United Kingdom, helped set up the adiabatic demagnetization technique.

Hot ions (Cunsolo, Mazzoldi). By this term we mean ions that are accelerated enough during one mean free path to create excitations in a way similar to that described in the preceding experiment. In this experiment the evidence is more dramatic, since it consisted of a direct measurement of the mobility (by the Cunsolo method) as a function of the applied field, showing a sudden decrease at a certain critical field (15). This subject would be the main research topic of the Rome group after 1960.

Ionic recombination (Gaeta). A simple experiment was performed aimed to study the mechanisms of ionic recombination in liquid helium. The experimental data, taken as a function of temperature, were in quite good agreement with Langevin's theory (16).

Spin-lattice relaxation time in liquid ^{3}He (Modena, Santini). This measurement was performed in the range 1.1 K to 3 K. ^{3}He was the only liquid for which this measurement could be made at low temperatures. The measurements showed that it did not satisfy the BPP (Bloembergen, Purcell, Pound) theory. The most significant result obtained in this experiment was to identify the importance of the contribution of the contact surface between the liquid and the container's wall to the observed relaxation time, as measured in different laboratories. This was most probably due to the catalytic effect of the oxygen adsorbed on the wall. This work was continued later in Rome (17).

The foundation for all these experiments involved certain techniques that had to be set up and were substantially home- made: transfer tubes (made out of double walled glass tubing, which allowed watching liquid helium flow during transfers), thermometers, thermoregulators (the first thermoregulator was a student, named Golzer, whose part-time task was to turn a valve, connected to the pumping system, in one direction or the other, depending on the indication of the thermometer, which he had to look at continuously), polonium sources, vacuum systems, the Toepler pump for handling ^{3}He (usually called *signora omicidi*), and so on and so forth.

The atmosphere of the group in those three years was uniquely happy, probably because of a combination of many factors: the youth of everybody, the exciting sense of exploring a completely virgin territory, and the thrilling feeling of succeeding in obtaining results of international importance.

During 1960 Careri was offered a physics chair at the University of Rome and Scaramuzzi was offered responsibility for the Cryogenic Group at Frascati, since Giancarlo Moneti had planned to spend a sabbatical year in USA. Both accepted and the whole group, with the exception of Fasoli, who preferred to stay in Padua, and Gaeta, who accepted a one-year fellowship in the United Kingdom, moved to the Rome area. Scaramuzzi, Modena and McCormick went to Frascati, all the others to the University of Rome.

4. The cryogenic group in Frascati (1958-).

The cryogenic group of the National Laboratories in Frascati had two main objectives in the first years of its life: production and supply of liquid helium and liquid hydrogen and construction and operation of the first liquid hydrogen targets. It also supported construction and testing of the Rome liquid helium bubble chamber (18). The group, headed by Moneti, was enriched in those years by one physicist, Vinicio Montelatici, who had participated to the construction of the synchrotron, and by a group of high level technicians, who joined Bellatreccia and Solinas; their names were: Remo Bolli, Pietro Cardoni, Italo Cenciarelli and Luigi Siracusano. There were also two very young helpers, Franco Campolungo and Enrico Gazzellini, who would prove their value in due time.

We have already mentioned how the problem of transferring liquid helium from the Collins to the transport dewars had been solved: that had to be done in order to supply liquid helium to the Careri group in Padua. When time came to start the supply, transportation was one of the main problems. Scaramuzzi, who was at that time commuting between Bari and Padua, with occasional stops in Rome, was empowered to get in touch with the Italian railway authorities, in order to find a safe and fast means to transport a liquid helium dewar from Rome to Padua. There were two main problems: the first was to convince the authorities that the smoke puffing tank was safe to have on a train; the second was to be able to employ the shortest possible time for transportation. The last demand excluded the use of the traditional freight trains, which could take more than a week. An empirical solution was found, consisting of using the freight-wagon of a passenger train, with the condition that an expert would be available on the same train to deal with any problem that might come up. Scaramuzzi was the expert on most of the first trips: he would arrive from Bari during the afternoon, take charge of the dewar at Rome Termini station,

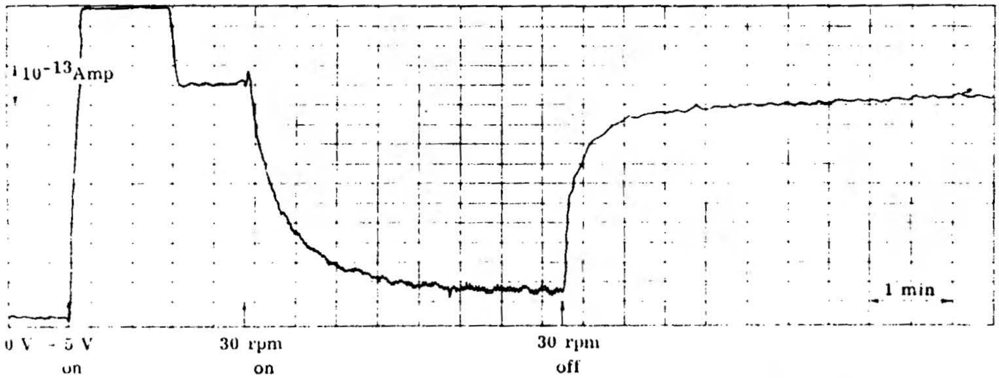

Fig. 4 The dramatic change in current due to rotation in a rotating helium experiment. This is a copy of a recorder trace; the negative current is shown as a function of time. Temperature is T = 1.38 K; the applied potential is -5V. The initial out of scale value of the current is a transient due to induction effects. (From Phys. Letts. 1,61 (1962)).

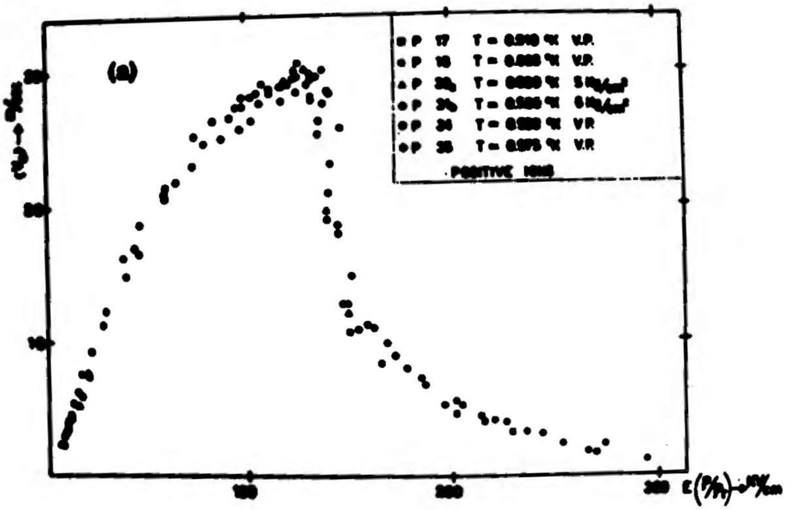

Fig. 5 The sharp change in the drift velocity v_D of ions as a function of the reduced electric field $E(\rho/\rho_r)$, the *gran calata* (ρ_r is the roton density); many different runs with positive ions contribute to this graph. (From Phys. Rev. Letts. 15, 392 (1965)).

and escort it to Padua overnight. Everything worked perfectly; after a certain time, the transportation was officially allowed without the expert. However, years later, when the research activity with liquid helium had moved back to the Rome area and nobody was using this transportation facility, this rule was canceled and never restored.

The Rome helium bubble chamber was mounted and tested satisfactorily, with contributions from the whole group; among the physicists and technicians from the Institute of Physics of the Rome University, who participated in this enterprise, were Enrico Di Capua, Ubaldo Dore, Giancarlo Gialanella, Paolo Guidoni, Ilka Laakso, Alvaro della Ciana and Fulvio Cerquitella. The chamber was eventually transferred to CERN, where it was used extensively.

The need for liquid hydrogen targets began at the end of 1959, when the synchrotron started to operate. The first type of target, designed by Montelatici, was very simple: the thermally insulated cell to be filled with liquid hydrogen ended in a thin-walled stainless steel tube immersed in a transport dewar containing liquid hydrogen. The volume above the free level of the liquid in the dewar was sealed and could be pressurized. The hydrostatic pressure pushed the liquid up into the cell, and an automatic system kept its level constant. One of the main requirements was to use very light and very thin materials as the walls of the cell and of the surrounding vacuum tank, in order of reduce to a minimum the unwanted scattering of the gamma rays coming from the synchrotron. This required solving a series of difficult technological problems. Target technology, which would become very sophisticated in the ensuing years, was being initiated in Italy.

During 1960 first Scaramuzzi, then Modena and McCormick joined the group, coming from Padua. The agreement that Scaramuzzi had made with Salvini, director of the National Laboratories, was that, provided that the service activity - i.e., supply of cryogenic liquids, production and operation of targets - was satisfactorily accomplished, the physicists of the group could conduct fundamental research in low temperature physics. That began a fruitful period of service, and technical and fundamental research, which we now outline briefly.

As far as fundamental research is concerned, Scaramuzzi and McCormick, in cooperation with Careri, performed an experiment that was the logical continuation of the turbulent heat flush experiment. In order to test and to study the interaction of ions with vortex lines, it was decided to create the latter in an orderly way, rather than in the disordered fashion characteristic of heat flush. Onsager (19) and Feynman (20) had each postulated that quantized vortex lines would be formed in rotating helium. Such a hydrodynamic condition should produce an anisotropy in the system with respect to the axis of rotation. The experiment done in Frascati showed that, when the (negative) ions moved parallel to the rotation axis, no attenuation of the current was detected, while a dramatic change in current (See Fig. 4) was measured when the ions moved perpendicularly to the axis of rotation. Further information was obtained by using a very intense polonium source, thus creating the condition of full space charge limitation: for this condition, in the absence of vortices, the current is proportional to the square of the applied voltage. Comparative analysis of the i vs V^2 plots, with and without rotation, led to the conclusion that the change in current could be attributed to an uniformly distributed stationary space charge. It was a natural conclusion to think that the negative ions were trapped by the vortex lines and created such a space charge. It was also possible to evaluate the number density of the space charge (21, 22). This experiment was later cited by Onsager as the most convincing experiment proving the quantization of circulation in superfluid helium. The full space charge limited condition was later proposed by Scaramuzzi (23, 24) as a very convenient method for measuring mobilities.

Modena started the construction of a ^{3}He refrigerator, which was at the time a pioneering technique for reaching temperatures down to 0.3 K. He designed a sophisticated apparatus with which he could measure the mobility of ions in ^{3}He as a function of temperature down to 0.38 K and as a function of pressure up to 20 atm (25, 26, 27).

In the ensuing years research on liquid ^{3}He and liquid ^{4}He was continued (Modena, Savoia, Scaramuzzi) and research on double polarization was started (Baldacchini, Montelatici). The service activity had quite a large derivative in its first years, since requests for more and more targets came from the many experimental groups operating at the synchrotron. Synchrotron time was so valuable that the need to reduce cryogenic operations in the experimental hall was imperative. It was then decided that a different type of target would be developed, one with a reservoir of liquid hydrogen and a reservoir of liquid nitrogen (as a radiation shield). Furthermore these target could use either liquid hydrogen or liquid deuterium in the experimental cell (whence the name HD for this type of target). The performance of these targets, designed by Montelatici (28, 29), was very satisfactory: once filled with the cryogenic liquids, they would work unattended for more than a week. A special target, using liquid ^{3}He or ^{4}He was later designed by Modena (30), the first in the world. In addition, a cryostat where solid deuterium could be extruded, so that a pellet could be exposed to a laser beam, was designed by Modena, and was the the heart of one of the first experiments on fusion research by inertial confinement (31).

One of the activities of the group that is worth mentioning is the technical support given to other growing cryogenic groups in Italy, in the universities and in the research centers. Particularly worth mentioning are a group from the University of Genoa that performed measurements on the liquid-vapour equilibrium in isotopic mixtures of simple liquids (G. Boato) and a group from the University of Rome that measured the diffusion coefficient of neon and helium in liquid hydrogen (F.P. Ricci, G. Castagnoli Cini, G. Pizzella, A. Giardini).

5. *The low temperature physics group in Rome (1960)*

Since this activity exceeds the time period covered in this meeting, we shall limit ourselves to a brief review of the initial work only. On the basis of the experience gained in Padua, work was mainly concentrated on the study of quantum vorticity in liquid helium by the ion technique. These results have been reviewed in 1965 in an invited paper presented by Careri at the Sussex University Symposium on Quantum Fluids (32), and will be only briefly outlined here.

Periodic discontinuities in ion mobilities (Careri, Cunsolo, Mazzoldi, Vicentini). The occurrence of periodic discontinuities in the drift velocity of positive ions at 1 K was first noted in a time-of-flight experiment in 1961 (15), and later substantiated and extended to negative ions in 1964 (33). The presence of this strange phenomenon has been confirmed in a heat flush experiment in Rome in 1964 (34) and later with different techniques by other authors. The presence of these periodic discontinuities was not easy to explain, in spite of the theoretical work by Carlo di Castro in Rome in 1962 and by K. Huang and A.C. Olinto at MIT in 1965. The problem has been revisited by Careri in 1982 (35).

Charged quantized vortex rings (Careri, Cunsolo, Mazzoldi, Santini). In experiments carried out at 1 K the formation of charge vortex rings (the stable coupling of an ion to a quantized vortex ring) was identified in 1965 with the sharp transition at which the giant discontinuity (*gran calata*) occurs, as shown in Fig. 5. The condition for the existence of a charged vortex ring of one quantum of circulation is then obtained by writing the balance of the electric and dissipative forces. Together with experiments carried on in Berkeley by Rayfield and Reif in 1963 and 1964, these experiments provided detailed evidence for the conditions of stability and for the behavior of these strange objects in low

Fig. 6 A group of participants to the Varenna Conference in 1957. From left: G. Uhlenbeck, J. Mayer, G. Careri, S. De Groot, L. Onsanger, J.A. Prins.

Fig. 7 A group of Italian physicists at the Varenna Conference in 1957. From left: F. Scaramuzzi, A. Paoletti, M. Vicentini, F. Gaeta, G. Castagnoli Cini, G. Careri, G. Boato.

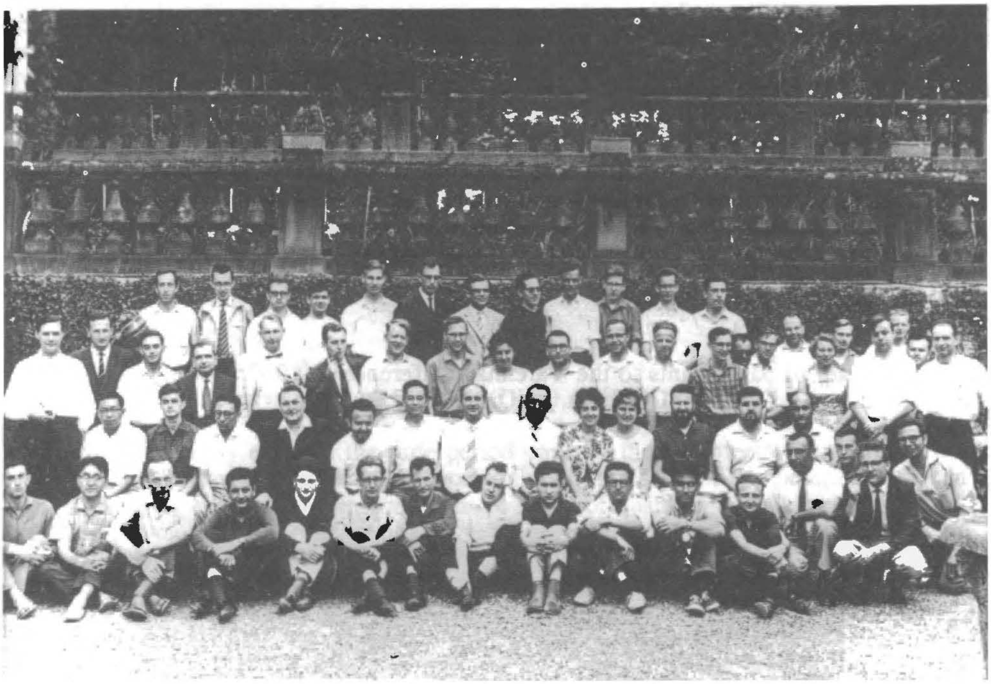

Fig. 8 The official group picture of the participants in the Varenna summer school in 1961.

temperature physics. The interested reader is referred to the lively discussion on this subject at the Sussex symposium (36).

Some other activities were started at that time such as the spin-lattice relaxation of ^{3}He adsorbed on zeolite (Santini, Giura, Signorelli), light scattering from superfluid helium (Signorelli, Mazzacurati, Lacucci) macroscopic vortex rings and Josephson junctions (Cerdonico) and the behavior of very hot ions in liquid helium (Bruschi, Maraviglia, Mazzoldi). Several visitors came to Rome to visit the group on sabbatical leaves, notably B. Adler (Berkeley) E. Gross (Brandeis), M. Cohen (Chicago), F. Moss (Lousiana), J. Rosenshein (Florida), and D. Goodstein (Caltech).

6. Conclusions

Before ending this review we want to recall three cultural events that had some influence on the international scientific community.

In September 1957 an International Conference on Simple Systems was held in Varenna, organized by Careri, under the auspices of IUPAP (International Union of Pure and Applied Physics), of SIF (Società Italiana di Fisica) and of CNR (Consiglio Nazionale delle Ricerche). About one hundred theorists and experimentalists participated from all over the world. The purpose of this meeting was to bring together physicists expert in classical liquids and physicists working on liquid helium. Among the presentations we recall especially those by Onsager, Kirkwood, J. Mayer, De Boer, Montroll, Prigogine and on the experimental side, of Mendelsshon, W. Fairbank, Torrey and Brockhouse. Careri reported on the first experiments on ^{3}He-^{4}He diffusion and on heat flush with ions in superfluid helium, performed in Frascati with Reuss, Scaramuzzi and Thomson. Among the many italians present, Franchetti and Giulotto presented communications (37). In Fig. 6 and 7 two pictures of the participants in the meeting are shown.

In summer 1959 Van Hove organized in Utrecht the first International Conference on Many Body Problems. This conference was predominantly theoretical, but three experimentalists (Careri, W. Fairbank and Kramers) were invited to present the state of the art on superfluids. On that occasion Careri had to defend the ideas of Onsager and Feynman on the quantization of the circulation, which at that time met the skepticism of physicists at the level of Yang and Lee: he did so also on the basis of the experiments in course in Padua (2).

In July 1961 Careri organized in Varenna a summer school on liquid helium, with the participation of well known theorists (among whom were Chester, De Boer, Lin, and Pines) and experimentalists (including W. Fairbank, Vinen, Hall, Hammel and Taconis). The central subject of the school was the debate about the very recent experiments on the quantization of the circulation that were performed at Cambridge, Stanford, Rome and Frascati. On that occasion Careri presented a review of the - by now numerous - experiments of the Italian groups on liquid helium. Many young italian physicists working in low temperature physics and many young foreign physicists participated, some of which we like to remember here: Baym, Hohenberg, De Bruyn Ouboter, Mermin (38). Fig. 8 shows the official group picture of the participants at the school. We want to end this review by acknowledging stimulation and encouragement given us by Lars Onsager, mostly during the Padua period, both on the occasion of his visits to Italy and in encounters in the USA. It was Onsager who suggested to Careri at the Varenna Conference in 1957 the possible structure of the negative ion (electron) in helium, with the obscure words *like sodium in ammonia*; that structure was then proposed independently by Feynman to Careri in 1958 in Leiden, during the conference held there to celebrate the 50th anniversary of helium liquefaction.

For an up to date review of the main scientific aspects of the work reported here we suggest the text *The Physics of Liquid and Solid Helium*, edited by K.H. Bennemann and J.B. Ketterson; in particular the chapter by A.L. Fetter on *Vortices and Ions in Helium* (39).

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RESEARCH ON COLOR CENTERS AND SEMICONDUCTORS IN PAVIA

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"*Omnium rerum principia parva sunt*". Cicero.

At the end of the forties and beginning of the fifties, when I was a student at the University of Pavia, solid state physics was almost unknown in Italy. It did not appear in any of the courses taught at the Universities and it was probably considered at best as a branch of atomic or molecular physics. Concepts like bands, phonons, defects, semiconductors were absent from the language of the students. We had some superficial idea of Sommerfeld theory of metals, mainly considered as an application of Fermi-Dirac statistics and we knew of superconductivity simply because of its outstanding electrical properties and because it resisted the efforts of interpretation of so many famous theoretical physicists of the time.

We were taught on physical principles and we firmly believed that that was enough to solve any problem. In a way, solid state physics, being considered mainly as an application of known principles did not interest many of us.

The teaching of physics at the University of Pavia, in those days, was by no means of a low standard: we were presented with two years classical physics, two years theoretical physics (including quantum mechanics, special relativity and statistical physics), one year atomic and nuclear physics, some spectroscopy, some electronics, three years chemistry (including laboratory experience), three years practical physics and a great deal of mathematics.

Among the Professors, only two were engaged in modern research: Luigi Giulotto and Piero Caldirola. Giulotto was a spectroscopist who had recently (1947) given an important contribution to the knowledge of the structure of the H_α line of Hydrogen (in a way anticipating the discovery of the Lamb-shift). At that time, among the first in Europe, he set up an apparatus to investigate Nuclear Magnetic Resonance (NMR) only recently discovered. Caldirola, who had just moved to the University of Milan but was still teaching in Pavia, was a theorist with broad scientific interests focused on the principles of quantum and statistical mechanics, on field theory and cosmic rays. Both Giulotto and Caldirola did much to remove the somewhat provincial atmosphere that had covered the Physics Department since the long period of inactivity during the war. The students saw the novelty and the great majority wanted to do their thesis work with them.

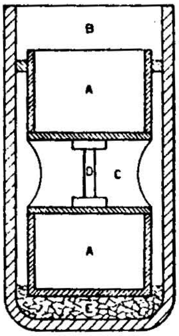

Fig. 1 The cryostat for making the absorption measurements at the liquid air temperature: A) Brass vessel containing the liquid air. B) Dewar vessel. C) Horizontal tube for passing the light. D) Crystal. E) Dessicant. (After Ref. 1).

We were very few (when a freshman I was the only student of Physics), most of us Alumni of the Collegio Ghislieri but we were very motivated and some of us had to play a role in the development of solid state physics in Italy. I shall mention: Franco Bassani, Roberto Fieschi, Paolo Camagni, Mario Tosi all active in Pavia around 1950.

In the Summer 1951 I was doing my thesis work under L. Giulotto on NMR of protons in water. I attended an informal seminar by Fausto Fumi, a young theorist who had spent some time in the U.S. working with Seitz in Pittsburg and at the University of Illinois and just come back to Milan in Caldirola's group. The seminar was delivered in the office of Giulotto and we were listening at leisure on a sofa. Fumi was talking of defects showing to our surprise that many of the properties of solids depend more on defects than on the regularity of the lattice. The subject of the seminar was on color centers, a thing we had never heard about: Fumi was elucidating some of the models that were at that time proposed by F. Seitz for the various centers and that, in principle, could be verified by simple spectroscopic experiments. Giulotto grasped immediately the interest of the field but even more the possibility of exploiting the remarkable optical equipment possessed by the Department and that was not in use since Giulotto had started working on NMR.

So he asked me to work part-time on the problems Fumi had suggested (the remaining fraction on my time I spent continuing my work on NMR).

The prediction by Giulotto that the equipment was easily available was unfortunately, at least in part, not correct. The Department had many high resolution spectrographs, all equipped with photographic plates and several with interferometric attachments. They were not suitable for detecting the broad absorption bands of solids. In fact we had an old spectrophotometer of the type of Lummer and Brodhun in which light beams coming from two slits (one of which had in front the sample) were superimposed, in a complicated figure, in the field of the ocular: one had to change the width of one of the slits until the two fields appeared equally illuminated.

When I succeeded in growing the first KCl crystals with a rudimentary Bridgman technique and had them colored with X-rays, I tried the Lummer and Brodhun photometer for detecting the F-band. During the measurements I realized that the absorption band looked much more asymmetric than it should and I soon found out that the crystal was almost completely bleached by the white light impinging on the slit!

All other plate spectrographs suffered from the same incovenience so I decided, quite independently, to build a spectrophotometer by my self. With the consent of Giulotto, I commandeered from the students' laboratory a reflection prism spectroscope and substituted the ocular so that it gave a real image. I equipped it with a fixed external slit made of two razor blades and with a photovoltaic cell I found in one of the cabinets of the Department. As a light chopper I used a fan and as an amplifier a wave analyzer which I borrowed from the NMR laboratory. The home-made spectrophotometer was ready in a few days, worked very well and remained in use afterwards for several years.

A second episode that shows the type of pioneering work we did at that time is the following: during the work on the F-Z_1 conversion in KCl:Sr (done in collaboration with P. Camagni in 1952-53) it became evident that in order to separate the two ìbands in a reasonable way, low temperature was required. Liquid Nitrogen was not available in those days in Pavia. Liquid Air could be obtained in Milan and was usually carried to Pavia, four liters at a time, in a wooden box containing four commercial Dewars. That wooden box always called the attention of the municipal police. At the time Italian cities charged duties on imported goods, specially on alcohol, a remnant of the medieval subdivision of Italy into city-states. Once that I did the transportation myself I was stopped at the railroad station by two policemen who inquired of what was in the wooden box. I said naively: "liquid air". "You aren't going to fool anybody" they replied. And only when I told them I was an Assistant at the University and they had smelled at length the fumes of the Dewars, they let me go.

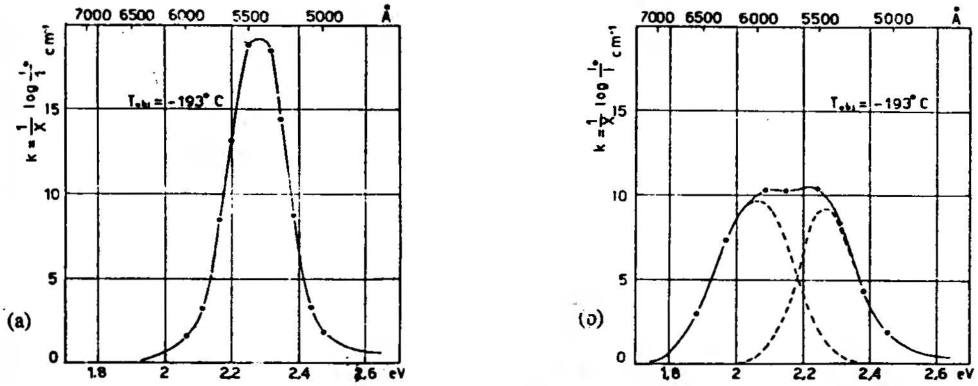

Fig. 2 Optical absorption spectrum, in the visible, of a KCl crystal containing Sr impurities (5.5x10-5 mole fraction immediately after additive coloring (a) and after a long exposure to F light at room temperature (b). Measurements done at liquid air temperature. (After Ref. 1).

Liquid air was easy to obtain, the cryostat was not! It was not possible to build it in the mechanical workshop. There was only one technician in the workshop of the Department until the end of 1952. Moreover, I knew he was often engaged in building for his own devices to cork wine bottles though I did'nt dare to tell the head of the Department since I was so dependent on his work.

At that time money was also very limited. The chair of Giulotto was endowed with a budget of approximately 200$ per year! Giulotto showed us a cylindrical Dewar on which the Al coating was removed in correspondence to two long opposite slits so that light could pass through them and through the immersed crystal. Unfortunately liquid air is slightly blue colored so that its absorption should be subtracted out. Moreover it boiled quite strongly (probably because of deteriorated vacuum in the Dewar) thus increasing the noise of our photoelectric detector. So the rudimentary "cryostat" shown in Fig. 1 was built: a cylindrical brass vessel with a transverse tube, in which the crystal was held by means of some insulating material, contained the liquid air. Because of the different thermal conductivities, the brass cooled down much more quickly capturing all the moisture and leaving the crystal clear. The presence of air at atmospheric pressure insured cooling of the crystal in a reasonable time. Our one-dollar-worth cryostat together with the home-made spectrophotometer did an excellent job as shown by the accuracy of the results of fig. 2 obtained in 1953 (1).

Color Center research had known, in the years around 1950, a great revival. Frederick Seitz published two famous review articles on Review of Modern Physics of 1946 and 1954 (2) (A draft of the article of 1954 was however available to us already in 1952).

The articles stressed the importance of a unified picture of electronic and ionic defects in alkali halides, proposed microscopic models for the various centers and suggested model-dependent properties and effects. In this sense, quite independently of the validity of the models, they were of utmost importance for the development of the field. For us they had the additional merit of requiring, because of the generality of the arguments set forth to support the various models, a broad knowledge of the entire field, so that they introduced us to the complexity, diversification and beauty of solid state physics.

The subject fascinated us. We were often talking of our scientific problems and results. A new technician, hired by the University in those days, Pietro Orlandi, was very unfavorably impressed by the futile discussions of scientists during their work. Afterwards he confessed that for a time he had thought that the main subject of our conversation was "holidays". In fact, in Italian, "holiday" and "vacancy" are expressed by the some word: "vacanza". We were talking of vacancies all the time!

Stimulated by the work of Fumi and Bassani and later on by Tosi on the formation and activation energies of vacancies and impurity-complexes we had come to the decision (1952) to study alkali halides doped with divalent cations or in the language of color centers to study the so called Z-bands (Zusatzbanden). As is known, divalent cations enter substitutionally alkali halide crystals introducing, at the same time, an equal number of positive-ion vacancies. When the crystals are colored (either additively or by X-rays) the various complexes containing divalent impurities and/or vacancies capture electrons giving rise to various absorption bands.

Under certain circumstances it is possible to bleach the F-band, transforming part of it into the so called Z_1-band. In our first article on color centers (1) we determined the quantum yield of such a transformation and from its dependence upon the number of F (or Z_1) centers we were able, by simple kinetics analysis, to determine the relative cross sections for electrons of F and Z_1 centers. We found them approximately equal. This seemed to us a very convincing proof of the validity of Seitz's model of the Z_1 center (namely an isolated divalent impurity with an excess electron) since both, the F-center and the divalent cation, possess, at large distance, the same Coulomb field and we conjectured that the capture of an electron occurs in some excited state, i.e. at large distance. Of course Physics is not that simple and other more direct techniques developed much later (1965) showed that the model had to be modified.

However, this work gave us stimulus for further research, brought us into correspondence with many distinguished physicists of the field and gave us the impression of taking part in the fast growing process of past-war solid state physics.

The experimental situation was still rather difficult. In order to measure the quantum yield of the F-Z conversion we had to determine the number of photons impinging on the crystal, a delicate measurement even with modern techniques. At the time we had an old pyroheliometer, already used by Giulotto in 1935 during his campaigns to measure the solar constant in the eastern Alps. The pyroheliometer, designed by Amerio, a former professor at the Polytechnic of Milan and manufactured in Milan by Allocchio Bacchini, consisted essentially of a very thin manganine strip, blackened on one side and having a thermocouple soldered on the opposite side. The thermocouple measured the increase in temperature caused by the absorption of radiation and could be calibrated by passing a known current through the strip. The pyroheliometer worked very well, giving accurate results that later on were checked by comparison with a calibrated bolometer.

Two years later (1954-55) a girl student was doing her thesis work in our group. To teach her some of the Laboratory techniques and keep her busy until the thesis subject could be defined, I had her using the pyroheliometer to measure the intensity of a light source. As all beginners she was very enthusiastic, motivated and ... inexperienced. In calibrating the instrument she passed to great a current through the manganine strip and burned it down. She was frightened for what she had done. The instrument could not be repaired by our workshop. Allocchio-Bacchini had gone out of the business of scientific instrumentation and had become a comparatively larger firm manufacturing radio and TV sets. Nevertheless I suggested the student should take the pyroheliometer to Milan to see if some of the older workers that I knew were still at the factory could do the repairs. She did her job with patience and persuasion and moved the director of the factory telling him she would not be able to graduate if the instrument could not be repaired! So we had our pyroheliometer repaired with no charge! However, the old worker who did the job was a wise man. He figured out that we were rough experimentalists and decided to substitute a much thicker manganine strip to protect the instrument from our careless behaviour. The sensitivity and accuracy of the pyroheliometer were then considerably reduced so that it has not been used since!

Coming back to Physics, I recall that while we were investigating the thermal stability of Z_1 centers, we found out that, in the dark, a reversible reaction took place between the - F-centers and the so called (at the time) Z_2 centers (3). The ratio of the number of F and Z_2 centers is a function only of temperature and is the same in crystals containing different initial concentrations of color centers. The experimental points (fig. 3) fit very well the equation:

$$\ln (k_F/k_Z) = C/T \qquad (1)$$

where k_F and k_Z are the absorption coefficients at the maxima of the bands present in equilibrium and T the absolute temperature. Eq. 1 seems to imply a first order reaction in which F-centers combine with something essentially independent of temperature to form Z_2 centers. Again Seitz's model seemed to be confirmed by our experimental data. Great was then our surprise when electron paramagnetic resonance failed to detect a signal from Z_2-centers (implying a center with two electrons) (4). Several people shared our surprise since both experiments seemed well founded and very clear. Our experiments were repeated by several groups, (5)(6) perhaps with the aim of disproving them, though by accurate and painstaking measurements it was recognized that our results were absolutely correct so that the puzzle given by the kinetics of the equilibrium reaction of F and Z_2-centers is still open.I recalled such an example to show that, despite very little financial support and a rather rudimentary instrumentation, the results of our group in Pavia were, for the time, of standards comparable to that of more established (and supported) laboratories.

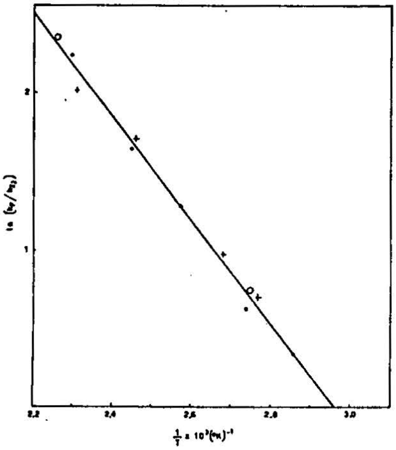

Fig. 3 A logarithmic plot of the equilibrium ratio between the heights of the F and Z_2 bands, as a function of reciprocal temperature. The experimental points refer to three crystals containing the same amount of Sr (2.5x10-4 mol. fract.), but different concentrations of color centers: o) 2.7x1016 centers/cm; (+)4.7x1016 centers/cm (o) 6.6x1016 centers/cm. (After Ref. 3).

Our work in solid state physics was not limited to color centers. Following a suggestion by F. Fumi and through the indefatigable and accurate work of one of our students, Luigi Zanotti, we observed the Kirchendall effect in the couple KCl, (K,Rb)Cl, a work still quoted in literature after more than 30 years (7). We investigated also plastic deformation of alkali halides (8), ionic transport after deformation (9), excitonic transitions at defects (10) etc.

In the middle of the fifties many of us spent some time in the U.S. (at the University of Illinois) or in England and were exposed to a much wider horizon and a most stimulating environment.

When, at the end of the fifties, we all were back in Pavia: Giulotto, Fumi, Bassani, Tosi, Camagni and myself, together with a number of brilliant students (V. Celli, A. Frova, A. Stella, A. Balzarotti, G. Giuliani, U.M. Grassano, G. Samoggia, A. Manara, F. Ceresara and others) it was clear to all of us that a new effort was needed, in order to bring solid state physics in Pavia to a level significant of the development of the country.

It was a time of great enthusiasm. Nuclear energy was beginning to be exploited in Italy and money for research (especially on defects and radiation damage) was flowing more liberally.

In 1957 the first italian enterprise on semiconductors, S.G.S. (Società Generale Semicondutori) was founded in Milan, first as a branch of Telettra, a firm that manufactured radars and radio bridges. Now SGS is one of the two largest semiconductor manufacturers in Europe, but at that time it was very small and there was no space for research, at least for that not directly connected to the manufacture of devices. We signed an agreement by which we were committed to do research in semiconductors in Pavia. On Saturday morning, when both the factory and the University were closed, we met at the Physics Department (G. Della Pergola, G.P. Bolognesi, N. Formigoni, F. Forlani and others from the industrial side) to discuss the new developments in the field, to plan semiconductor research in Pavia and at SGS, and to actually carry on some experiments on the effect of the gas-environment on the distribution of traps at the surface of Ge and on the method of decoration of dislocations by diffusion of Lithium in Silicon.

I doubt that our results had any less than marginal significance for the industrial development at SGS. However, such an experience had two important consequences:

- to our industrial partners, it gave the possibility of following research not directly connected with the problems of industrial production and competition and to keep contact with the great developments of those years. We discussed at length the problem of connection between industry and fundamental research, trying, however, an answer based on practical work instead of on panel discussions as is customary nowadays.

- to us it gave access to materials and technologies that were not easily obtained at that time and allowed us a shortcut toward research in semiconductors.

Our work in surface physics - that some of us still carry on - started in that connection. Our attention to surfaces was perhaps stimulated by our frequentation and friendship with Robert J. Schrieffer who visited us several times in Pavia in those years and who, before his famous work on superconductivity (his Ph. D. Thesis) had written and appreciated contribution on the reduction of mobility of carriers moving in the space charge layer at the surface of a semiconductor (11).

In fact one of our first published works on semiconductors (12) (with A. Frova and A. Balzarotti) concerned the so called field effect in which the change of conductance caused by the application of an electric field perpendicular to the surface gave information on the spectrum of surface states.

My familiarity with optical techniques brought us soon to attempting the optical detection of surface states. Since their number is extremely small (10^{12} cm^{-2} on real surfaces) we used on ingenious technique derived from field effect. Application of an electric field perpendicular to the surface originates a change of band bending and therefore a change of the population of the surface states. Any transition starting from (or ending in) a surface state was modulated by an a.c. field and could be detected with great sensitivity by the use of phase sensitive amplifiers.

The results in Ge (13) confirmed the distribution of states that was already known. They are important, however, because, together with a similar and independent work by N. Harrick on Si (14) (both of 1962), they started the field of modulation spectroscopy that knew a great success and diffusion in the years to come.

For us, however, it was even more important since it brought us into the study of optical properties of surfaces, a field in which we obtained significant results and gained widespread reputation.

At the end of the fifties, the activity of research in condensed matter in Pavia was then of high quality, rather diversified (N.M.R. in liquids, defects, semiconductors, surfaces) and very promising. The concentration of scientists, many of them with international experience, quite considerable. The flow of money, especially through contracts with the Italian Atomic Energy Commission (CNRN), the Air Force Office for Scientific Research, and the SGS reasonable. There was a great enthusiasm and a feeling of doing something important for our society.

Unfortunately things did not go as we had envisaged. By 1962 most of the people I have mentioned before were again scattered, in our country and abroad.

This had a strong consequence on the development of solid state physics in Italy since it emphasized its polycentric origin, that this Meeting has already stressed.

Among the positive consequences I shall mention the capillary diffusion of condensed matter physics in all Italian Universities and Laboratories and the great efforts of aggregation and collaboration in multipolar programs developed in successive years. Among the negative ones, I shall mention that we missed the opportunity of establishing a center that for its dimension could play a role for the development of applied physics, where the concentration of instruments and technologies is essential.

It might be interesting, for the people professionally involved in the history of physics in Italy to reconsider that period that was so important for our success and for our difficulties.

"*Omniun rerum principia parva sunt*". If I go back to our beginnings I found them very, very small. However, it was a seed, a strong seed, it was our history!

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"THEORETICAL RESEARCH IN THE PHYSICS OF SOLIDS"

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Abstract

Topics of solid state on which research was started in Italy during the fifties are briefly reviewed. Determination of crystal tensors are first mentioned, then the theory of ionic crystals and point defects, finally band structure calculations on semiconductors and the early ideas on pseudopotentials.

We shall not attempt to present a full review of the research in the theory of solids that took place in the fifties in Italy, because to place many different contributions in the proper perspective would be quite difficult.

We shall rather try to give some recollections of those years and of the problems we were facing, hoping to bring back nice memories to some of you and to say something useful to younger people, who may be facing similar problems.

When we were starting our theses in the early fifties, the main problem for us was the absence of an established School, which could provide guidance and perspectives for future work. With the departure of most of the leaders of the preceding generation (suffice it to mention Fermi, Wick, Fano, Racah, Rossi and De Benedetti), theoretical research had become somewhat scattered and individual. The lack of a clear line of thought, where young people could find their humus, was certainly felt.

Piero Caldirola was our professor of theoretical physics and had a clear perception of this situation. His main interests were in the foundations of quantum mechanics and of statistical physics, which he pursued also later on, but he felt that this field was too specialized and too difficult to nourish a new generation of young physicists, who were coming up in Pavia, mostly at Collegio Ghislieri and Collegio Borromeo, and in Milano. Caldirola had a wide culture and knew many aspects of physics. He had been in the Fermi group for a short time, just before the war, and was very familiar with the work of that group in atomic and molecular physics; he knew well the book by Fermi on "Molecules and Crystals". One of us (F.B.) remembers vividly that during his examination of theoretical physics, when he was trying to prove the Bloch theorem in the way reported in the textbooks of the time, Caldirola interrupted him and showed how the proof could be easily obtained by applying to the wave function the translation operator $T(\underline{\tau})$ and showing that its eigenvectors could only be the exponentials $e^{i\underline{k}\cdot\underline{r}}$. His assistant Loinger asked Caldirola how he had found such an elegant proof, and he replied that he had learned it at one of Fermi's seminars in Rome.

When we went to Caldirola to ask for a thesis topic, he said he had in mind to favor research in Solid State Theory, but that - himself not being an expert in the field - the candidates should wait for the arrival of Fausto Fumi, whom he had invited back from the United States to be a Contract Professor at the University of Milano. We did not know anything about Solid State Physics, so we were given to read the book by F. Seitz, "Modern Theory of Solids"; it was too difficult and vast for us at the time, but it became later our Bible.

Fausto Fumi finally arrived, and he felt that we should not follow him closely on his current line of research, but should rather start in a new field, more strictly connected with the experimental activity on "color centers" and ionic crystals, which was then starting in Pavia with G. Chiarotti and P. Camagni, and was to continue also in Milano in the following years, as R. Fieschi and G. Chiarotti will describe in their recollections.

The current research of Fumi in those days was leading to exact results on the independent elastic constants of all crystals and on the tensorial properties of crystals, as obtained from group theory. These results, which are reported in a number of publications appeared in The Physical Review, Acta Crystallographica, Il Nuovo Cimento and Physica (1) (2) (3) (5) have entered into all text-books on elasticity. They are very elegant and they filled a void in the literature of that time (4). We quote as an example the matter tensors obtained from the fifth order coordinate products for the different irreducible representations of D_{6h} (Table I of ref. 4). Fieschi continued work on transport tensor properties using the methods of the thermodynamic of irreversible processes in Utrecht and in Leida with de Groot, and obtained a Ph.D. from Leida in 1955 (6) (see c.g. Ziman's book of 1960).

However, a group could not continue for long on that line, necessarily complete in itself. R. Fieschi was already involved in it; it was felt that an area in a state of expansion was needed for other theorists, and the study of ionic crystals and color centers seemed appropriate. We were disappointed in the beginning, for young people, then as now, like results that are mathematically proven, clean and final, much more than approximate theories based on simplified models. This instead was precisely what was needed for color centers and ionic crystals.

The field had started in Germany in the School of R. Hilsch and R.W. Pohl in the thirties; at the time it was being actively pursued at the University of Illinois in the groups of F. Seitz and R. Maurer, and in Germany in the group of R. Pick and W. Martienssen. The theoretical understanding did not match the wide experimental knowledge and the most appealing theories had failed. It had been found for instance that the beautiful Landau model of the self-trapped polaron (an electron bound by the polarization of the lattice due to the induced ionic displacements), so elegant and pleasing, had no relation to the F center, which was instead an electron bound to a negative ion vacancy. Other color centers were certainly associated to impurities and vacancies bound to them. Crystals were not ideal, and imperfections were essential for understanding their optical and transport properties. So the problem seemed first to understand point defects in ionic crystals and their origin and their interactions, then the optical properties due to them, and in particular the absorption peaks (color centers).

In the case of semiconductors these problems can now be treated with full quantum mechanical calculations of total energy, but in the case of crystals formed by closed shell atoms or ions, even now the best approach is to express the crystal energy as the sum of pair interaction energies between ions or atoms. The Lennard-Jones potential is good for neutral atoms, like He and rare gases. For alkali halide crystals the Born-Mayer interaction is the most appropriate: a long distance Coulomb interaction and a short range repulsive exponential interaction of the type $C_{12}b \exp[(r_1+r_2-r)/\rho]$, where r_1 and r_2 are ionic radii, C_{12} is a numerical coefficient which depends on the charges, and b and ρ are appropriate constants defined for a whole class of materials. Alternative sets of these parameters, as determined from crystal data both in the original work of Born and Mayer and in the subsequent work of Mayer and Huggins, were available, and it was soon apparent that the results of defect calculations were very sensitive to this input. In addition, an electric field is set up around vacancies or charged impurities, and the surrounding ions are displaced and polarized. These effects had also to be taken into account. Our early work in this area led to good estimates for the formation energies of vacancies, the association energies of impurities and of vacancies at various distances, and the association energies of vacancy pairs, which were published in a series of papers by Fumi and both of us (7) (8) (9).

Fumi and Tosi were the main contributors to the theory of ionic crystals for a decade. They brought the theory to a high point of sophistication, in particular through new determinations of the ionic radii, which they were able to relate to independent evidence on X-ray maps of the electron density in ionic crystals and on ionic polarizabilities for ions in crystals. Great stimulation to this work came from an invitation by F. Seitz and D. Turnbull that they should prepare a review article on cohesion in ionic crystals for the well-known Solid State Physics series of volumes. As it happened, however, the write-up of the article was being continually interrupted by work on new problems which kept arising during the examination of the literature. This collaboration continued into the first half of the sixties, leading to a series of articles on crystal potentials, thermodynamic properties, structural phase transitions, and interionic forces in ionic crystals (10-18). The Solid State Physics article was finally completed and published by Tosi in 1964. The interionic potentials determined by Fumi and Tosi found later a number of very useful applications, when attention became focused in the seventies on the molten state of ionic systems. New experimental developments, based principally on refined techniques of neutron scattering as applied to molten salts, then began to stimulate studies of these liquids by microscopic computer simulations in various laboratories. These relied to a large extent on our early results for their choice of interionic force models, and, in conjunction with the experiments, have brought detailed understanding of the main physical properties of dense ionic liquids.

Returning to the work on defect calculations in the late fifties, also M. Asdente, G. Airoldi and R. Guccione contributed to its development, (19) (20) making it probably the largest theoretical effort in Solid State Physics by an Italian group in those early years. The computational work was considerable: only hand calculators were available at the time, but this did not stop us from carrying out detailed calculations on many substances, which were needed to assess the accuracy of the theory and to obtain results useful for the interpretation of experimental data. In fact the theory, as improved with coherent choices of ionic radii and ionic polarizabilities, produced results of adequate accuracy to interpret a number of experimental results: ionic conductivity, thermoelectric conductivity, paramagnetic resonance of magnetic impurities, and color center formation (up to a point, because the lattice instability around the excited state was not taken into account at the time).

Dislocations had become well-known in the fifties, and, when one of us (F.B.) went to Urbana after his graduation in 1954, F. Seitz suggested that he use his experience with the theory of ionic crystals to explain the hardening of such crystals by impurities as being due to pinning of dislocations.This worked out very well; R. Thomson and Bassani found that positive ion vacancies and impurity-vacancy complexes had a definite binding energy with a dislocation and this impeded their motion (21). A few weeks ago, in Toulouse, one of us (F.B.) had the pleasure of seeing and electron microscopy picture of dislocation motion at the surface of an ionic crystal, and of visually observing the pinning of some dislocations between two lattice points.

The theory of point defects and dislocations was not sufficient however to explain the optical properties of ionic crystals and color centers, though it provided the basis for it. Quantum mechanical calculations of the electrons in the perfect crystal and in the defect potential field were needed, and would be partially carried out later on. The problem of the short range part of the electrostatic potential is still a stumbling block. However, the simplified theory of interionic forces allowed a quantitative exploitation of the model of the exciton, formulated by A.J. von Hippel, by which the electronic excited state of the crystal is due to the transfer of an electron from negative ion to a nearest positive ion ("transfer exciton"). The excitation energy of this process could be computed in this model by an appropriate cycle which involves extracting the ions from the crystal, transferring an electron from the cation to the anion at infinity, and putting the neutral atoms back into the crystal. While some problems occur if one wishes to compute the exciton energies, it turned out (22) that this model could explain quantitatively the energy positions of the α and β bands, found by Delbecq, Pringsheim and Yuster on the low energy tail of the exciton absorption. Their energies correspond to those of "transfer excitons" created near negative ion vacancies and F centers, provided lattice displacements are not considered in the calculation of the cycle, which shows the validity of the Franck-Condon principle in crystal excitations.

The study of defects was not limited to ionic crystals; Fumi during an extended stay in Cambridge (U.K.) also reconsidered the problem of vacancy formulation and migration in metals, initiated by Huntington and Seitz. The results obtained (23) were instrumental in promoting the experimental research of Simmons and Balluffi in Urbana and of A. Ascoli, M. Asdente, E. Germagnoli and A. Manara (24) in Milano on the role of vacancies in electrical resistivity and self-diffusion.

Another line of research, which we only mention because it was not further pursued by us, concerns the electronic states of diatomic molecules, in particular optical transition energies between ground and excited states (25) (26). With the advent of computational facilities this field was taken up by quantum chemists. Similarly, one of us (M.T.) was involved during an extended stay in Bristol with the exciting studies developed there on the mode of crystallization of long-chain polymers (27).

We would rather like to discuss in some detail the beginning of the theory of band structure in Italy in the late fifties, because so much work is still going on in this field in Italy and abroad. We will show how the early ideas of those days led to the formulation of the pseudopotential methods, in their various connotations.

Fred Seitz had given a course on group theory in 1956 in Urbana; the book adopted was the photostatic copy of Wigner's book "Gruppentheorie und Wellenmechanik". Not many books on group theory were available at the time; besides, the language was not a real obstacle and we could learn the usefulness of symmetry in defining general properties of quantum states. F. Seitz had previously given a course on the electronic structure of solids, and had invited Truman Woodruff to give a lecture on the Orthogonalized Plane Wave Method, which was just beginning to be used by F. Herman and T.O. Woodruff. Putting the two things together, one of us (F.B.) was vaguely feeling that symmetry could be the dominating element in the band structure of solids, and this could probably be seen with the O.P.W. method. The method consist in expanding the Bloch functions in plane waves, but imposing the condition that the wave functions be orthogonal to the inner states (core states). Seitz read Bassani's mind and came up one day to suggest that the latter should study hypothetical crystals of diamond symmetry made with metallic atoms. The idea was to show that the band structure is the same, but the cohesive energy favors a different symmetry for metallic crystals. The ambitious result could have been to explain why atoms choose a given crystal symmetry, independently of the fact that the band structure depends very little on the type of atom considered. Seitz was very busy at the time and many associates worked in his group, but it was typical of him to appear at the right moment, when he felt that a suggestion could be useful. He knew what anyone of us was doing, and maybe also what he was wondering about.

The O.P.W. method was first tested on silicon to check its power, then on lithium atoms in a diamond lattice and on sodium atoms in a diamond lattice. The calculations on Si were the first to give basically the correct band structure, without any parameters or adjustments (28) (29). Frank Herman had already shown that in Ge the correct band structure was obtained with this method. This was a considerable achievement at the time, because other methods had failed to give and energy gap and had predicted metallic structures. The tight binding method, which requires expanding the Bloch function in atomic orbitals, failed because of the large overlap between functions on different sites. This produced the overlap catastrophe with totally unreliable values for the conduction bands. Instead of atomic orbitals, Slater had proposed to use Wannier functions, which by definition are orthogonal on different lattice sites; this would avoid the overlap catastrophe, but since Wannier functions are not available, the two-center integrals have to be taken as adjustable parameters to fit more precise calculations at symmetry points. This is what Bassani did in silicon, but the number of parameters used was 12, and it still seemed insufficient (28).

The calculations on pseudocrystals with metallic atoms showed that, given elements with the same core states and obeying the diamond symmetry, the band structure was basically the same when computed with the O.P.W. method (30). The calculations on total energy were not accurate enough to explain why b.c.c. symmetry was preferred for simple metals and the diamond structure for group IV elements, but the investigation about the reason why the sequence of energy levels was determined by symmetry led very far.

The basic reason was that the crystal potential acted as a small perturbation on the "empty lattice", i.e. a free electron band structure whose states are classified according to crystal symmetry. In reality the crystal potential is very strong; its Fourier transforms can have values of more than 1 Ry., much larger than interband separation. The fact that the crystal potential acts as a small perturbation was found to be due to the cancellation brought about by the orthogonality to the "core" states. It turns out that the orthogonality condition is equivalent to a repulsive-like potential which cancels the crystal potential, the cancellation being more effective the larger the reciprocal lattice vector of the Fourier transform (31). A total effective potential results, later called "pseudopotential" by Morrel Cohen. The idea of using pseudopotentials had first been introduced in the thirties by Fermi and Amaldi for studying atomic levels, but in this case a rigorous and general formulation was given.

Phillips and Kleinman used this idea to interpolate the band structure between symmetry points with many parameters, which were the matrix elements of crystal potential plus core orthogonality repulsive potential between plane waves, and obtained a good interpolation. Celli and Bassani reduced the number of parameters to three, by assuming complete cancellation for large reciprocal lattice vectors (31). The values of the parameters were easily estimated case by case, either by direct calculations or by fitting. It was not a completely justified approximation, because the orthogonality potential was nonlocal and varied slightly with $\underline{k}$. However, it worked! It gave a good interpolation scheme for valence and conduction bands, and later on it allowed very accurate band calculations (probably the most accurate available) for all group IV semiconductors and III-V compounds. This with only three parameters (a fourth one for III-V), the others having negligible values by cancellation between crystal and "core" potential.

More subtle justifications of the pseudopotential concept have been suggested, using the overcompleteness of the expansion set (plane waves plus core states), but the reason for its validity resides in the nearly perfect cancellation that has been described. It is essentially an approximation that works particularly well in cubic semiconductors.

It may be of interest to recall that the method was controversial for some time. At the Semiconductor Conference of 1958 in Rochester objection were voiced by W. Kohn, who asked J. Phillips informally whether he was doing physics or magic. A few years later, in 1961, E. Ehrenreich told one of us (F.B.), after a seminar in Schenectady at G.E., that he was on the Program Committee of the Semiconductor Conference of 1958 and could not figure out what Phillips or Bassani were trying to do with such strange approximations; "but now you have been vindicated", he added. As late as 1965 G. Dresselhaus, who was still struggling with the tight binding approach, in the course of an informal conversation at the Varenna School said that he was convinced that the pseudopotential method would fall on its face.

That has not happened yet, and, in spite of modern computer facilities, the pseudopotential method still gives the most accurate results and is generally adopted. Nowadays better calculations are done, and we have reached the point where total energies can be computed with sufficient accuracy to answer the original problem started in the fifties: why is band structure essentially given by symmetry, and why do atoms still choose different symmetries to form crystals, and not necessarily the one with the lowest Fermi energy?

Looking in retrospect at those years now far behind, it seems that things have not changed so much in our basic understanding of the electronic structure of solids. The big changes arise from the availability of new materials: crystals which do not exist in nature, like superlattices, quantum well structures, and ceramics. The bases for understanding these materials are still those laid down in the thirties and developed from then on. However, new approximations will have to be made and new ideas are required as the complexity of the new materials increases.

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ELECTRON PARAMAGNETIC RESONANCE IN PALERMO

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1 - Foreword

.... e si Diu vôli e la mula camina cci hamm' a jicari a la Fera a Bivona ... (if God so wants and our mule proceeds we have got to attain to the Fair in Bivona) - from an old sicilian cart-driver song.

It was in Washington D.C., in the occasion of the APS Spring Meeting, in 1954. One evening we found ourselves standing in a corner with Bruno Rossi (whom we had met a few months before, at M.I.T.), and Edoardo Amaldi, encouragingly inquiring about our plans for the future. Bruno was listening, very intense and meditative, as usual. Yes, we answered, we were planning to go back to Palermo and to resume with renewed strength our efforts of establishing there some research activity in Solid State Physics, initially by means of EPR. We did not have to provide explanations, and the next, no longer philosophical question came: how much do you think you will need to begin with? We ventured a "hardly anything different from 20 Million lire, perhaps in two years".The statement was based on a rough estimate we had done with scarce hopes. It was received very matter-of-factly.

This was the first of the key episodes that helped establishing EPR and, in fact, re-establishing a research activity in Physics in Palermo. After all, it was not many years that people like E.Segre' and G.C. Wick had been actively working in Palermo: it was the devastation of wartime, the ravaged laboratory, and people who had gone that made that time look as a distant era. The episode is singled out here to acknowledge the role that people who had so strongly contributed to Physics, and were to continue their outstanding work, had in favoring the start of new activities, in novel areas and in small places, where they felt they were going to be needed most. When our conversation turned to its end, the words "Paramagnetic Resonance" were overheard by one of the people around. He had a respectable reputation in sub-nuclear physics and "...gee, is that any physics?" he asked. By contrast, here were two outstanding physicists investing in that field and in a couple of young people (of 27 and 24, respectively). The young people had no achievements or facts to produce, except for being an unlikely "fluctuation" coming from the middle of nowhere and wishing to go back there.

Some 13 years later, Walter Gropius visited Sicily, and Palermo.He wanted to know in depth not only about Art, but also about Palermo as an historical city, and our own work and life there. Upon his return to Harvard, he sent one of his books(1), asking us to read the following passage:

> ..... In the course of our searching through old files, we came upon a diary my wife had kept throughout the last six years in Weimar and Dessau and which we had not reexamined since. I began reading it, and the further I proceeded the more I became depressed, for it became perfectly clear to me from the text that of all the tremendous effort put into that enterprise, 90 percent had gone toward fighting the hostile forces of the local and national environment, and less than 10 percent had been spent on creative work.....

The proportion applied to our case as well. However, despite his good propos of encouraging us and letting us feel like him, Gropius reached the opposite result, as it was most obvious that his 10% of successful effort had set an historical wave, while our own 10% was only generating a small ripple. C'est la vie.

This account of the establishment of EPR-based research in the 1945-60 period in Palermo factually coincides with that of a re-establishment of the tradition of research in Physics there. As we shall see in the following sections, this endeavour did not start before the 1950-51 years. About one half of this delay was recovered *en route*, so that our relevant period should comprehend the very early sixties. Most obviously, this account suffers from strong personal bias and more or less selective forgetting(2). Even worse, it suffers from being inextricably interweaved with our own family story.As we could hardly help with that, we wish to give an explicit warning to the reader and ask for his/her understanding.

Palermo: the early scenario

2.a - The environment.

The start was from scratch. The town had been heavily bombed (Pl.1) and the Istituto di Fisica ravaged by the German army. They had taken anything that could have a practical use or a commercial value, leaving some antique (and very valuable indeed) instruments. The beauty of Hellenist temples, Roman theaters, Norman Romanesque churches, orange and olive grows, was still there, ignored by assuefaction. The hinterland was as timeless as ever (Pl.1) under the seizure of short-sighted local power, needing no technology, and in fact refusing it (Pl.1). The elite part of the town tried to recover its previous style of life: much more of an exclusive Club ("Palermo Felicissima") than a town in Lewis Mumford's sense of constructive, productive, charismatic aggregation of people(3). And yet, Palermo with its submerged world, with its hungry, barefeet, imaginative, smiling children, had an obvious potential for much to be done, despite of the very little that happened to be done, and the very much that was in fact occurring, and observable. This potential had its reservoir in the deep hinterland, where a culture of resilience against hardship and hunger was based on the illimitate capacity of work that characterizes all truly paysant societies.

As to our University, soon we had a "Magnifico Rettore" much less interested in culture and education than in having a strong role in financial and economic affairs. He belonged in the visible part of a structure which at the time included even the Cardinal of Sicily and the sicilian Ministry for Internal Affairs in the Central Government. They were interested in maintaining the status quo. The only Professor of Physics at the University of Palermo, E.Medi, was himself totally absorbed in political activity as a Member of the Parliament, and hardly interested in culture and science. In fact, he acted as a powerful damping force against any research initiative. Any realistic project of action and enterprise

Pl 1a.

Pl 1b.

Pl 1c.

Pl 1d.

Pl 1a. Downtown Palermo, 1945

Pl 1b. In the sicilian interland, circa 1948

Pl 1c. Agricoltural technology. The thrashing having been accomplished, the grain was collected by hands. Note, at the right, the neat, step-fronted, heap of husks and stalks that a skilled exploitation of the smooth summer wind caused to deposit leeward of the thrashing circular area. This heap resembled a dune and was called in very old dialect 'mbaraguni or 'mbaragunata. (compare with the mahgrebian name of a dune's steep side: barcha'n). Many a love stories blossomed under the lee of a 'mbaraguni

Pl 1d. Agricoltural technology. Stragula, a beautiful latin (and sicilian) name for a carriage having no wheels, to carry sheaves or other weights through uneven fields. The sicilian verb (ignored by new generations) describing this transportation of sheaves through the fields to the purpose of spreading them on the thrashing ground, was stragulia'ri. (Compare with the english expression to struggle one's way through).

would require a strong motivation, and a very long timescale. In short, it was a "love it or leave it" affair.

2.b - 1948-1952

Our account of the post-war period starts in 1948. Some young people and some high-school teachers had been temporarily appointed, to help with the heavy teaching (laboratory courses, etc.) for students of Engineering who were back as war Veterans. Among them, A. Averna (now Professor of mathematical Analysis at the University of Perugia), G. Germana' who was later, for a long time, the Secretary of the Italian Physical Society, and Anna La Rosa, who later was to marry Gaetano Riccobono. Donato Palumbo had just graduated in Palermo, having had his full curriculum in Pisa, Scuola Normale. He divided his interests and great capabilities between physics and mathematics, and had already spent a year in Paris, working with Hadamard. Gaetano Riccobono and Ugo Palma, the first post-war physics graduate (1946 and 1947, respectively), had been essentially self-taught fellows. By 1948 a small number of Physics students were around. Among them, G. Epifanio, M. Curatolo, L. Barbera, and Clelia Cuccia who soon married Donato Palumbo. The relevant personalities in the teaching staff and faculty were the two exceptional junior Assistants Palumbo and riccobono. With much good will and capability, they attempted to encourage these students to start actual research work in a couple of fields. The Physics Building had just been repaired, and it looked clean and empty (P1.2).

In 1949, Beatrice Vittorelli (who was to get married to Palma in 1952) contacted Palumbo for her thesis. The problem was focussed in Palma's small Fiat, on the way back home. With great insight Palumbo suggested that we should work as a group, and should choose a field requiring small-sized equipment and manpower, promising enough for future developments, and sufficiently new to make sure that we would not be cut out by lack of tradition and of experience. (Not even Palumbo, personally inclined towards theory, considered avoiding the difficulty of building a laboratory by concentrating on theoretical work). Having studied by ourselves classical Spectroscopy, we were fascinated by possibilities offered by the combined use of microwave techniques and magnetic fields, allowing unprecedented, direct access to very precisely measurable differences between close-lying energy levels in a variety of systems(4). Wide spaces were so open to research and, even if it was to take three years to build a laboratory, the field looked so new that we did not need to fear to be late-comers.A few days later we had chosen to start working in Electron Spin Resonance(5)(6). It so happens that most paramagnetic substances are solids. The possibility of using ESR and magnetic probes as a general tool in Solid State Physics (and, more in general, in Physics of Condensed Matter) became clear only later.

We could initially use an old electromagnet available in the Laboratory (perhaps too heavy for having been stolen away in wartime) and power it with an existing bank of batteries. We could learn microwave techniques at the new Microwave Center of CNR, in Firenze and we could hope in helpful contacts with L. Giulotto, who had started nice magnetic resonances work in Pavia, and with A. Gozzini who was using microwave techniques for his imaginative work in Pisa. On the theoretical side, there was not such a vaste literature to digest, apart from Van Vleck's treatment of crystal field theory; the Abragam-Pryce-Stevens series of papers had not yet come, and correlation/relaxation times were another land still to be explored.

The occurrence of a turning point in 1950-51 is marked by several events. Mariano Santangelo came back to Palermo, initially on a provisional basis, as (contract) acting Professor and acting Institute Director. Here he had been an assistant to Emilio Segre'. His role will become more clearly evident in the following. It should, however, be stated since the very beginning that he brought an atmosphere previously unheard of, encouraging friendship, discussions, and hard work. He made room for any activity or project having chance to progress. His presence opened a decade of great stability, instrumental to all further de-

Pl 2a. The vacant Istituto di Fisica, 1949

Pl 2b. The staff, in 1949. To the left, Gaetano Riccobono and Donato Palumbo

velopments. Six years had elapsed from the end of the war. Under E. Medi, these had been six blank years for the Istituto di Fisica, a delay difficult to overcome. All the worst, those years were perhaps crucial in preparing the future decisions of Donato Palumbo and Gaetano Riccobono, of leaving Palermo. They were initially motivated to stay, and their presence would have given a different pace and breath to the whole story. In 1951, a young and already respectable biologist, Alberto Monroy, came back to Palermo (his town) as one of the very few full Professors (soon to become Dean) of the Faculty of Science. Many of the future developments of Science in Palermo were due to him. A warm friendship developed soon, which went along with a frank, outspoken attitude whenever the case called for it. Interests in biology-related physics shared today by many people in Palermo, have some of their origins in Alberto's cultural charme.

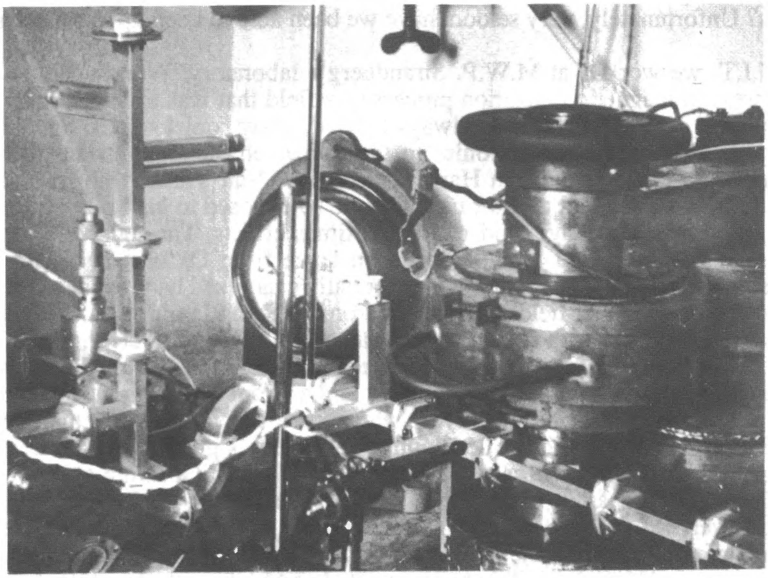
In 1950 il Cavaliere Russo retired. This was the end of an era. A charming person and a gifted machinist, he used a pedal lathe, and cultivated quite personal views of electrostatics. He had been the technician of Augusto Righi and had known as a student O.M. Corbino (the originator and tutelary saint of E. Fermi's group in Roma). In the same year our project received the first grant: 400,000 lire from CNR. Among other things, this allowed Palma to spend several weeks in Firenze, to learn microwave techniques. Nello Carrara, the Director of the Microwave Center, took a warm interest in our efforts, and an enjoyable and fruitful acquaintance started. For the first time we detected and measured an EPR spectrum (7) using a provisional apparatus, yet not inadequate for the time (P1.3).

In 1952 the first paper on EPR from Palermo was completed(8).In the same year we married and both of us applied for scholarships to M.I.T. To our amazement we were soon notified that two of the very few available italian scholarships had been awarded to us. Although we could not trace how it actually worked, this could hardly be due to chance.

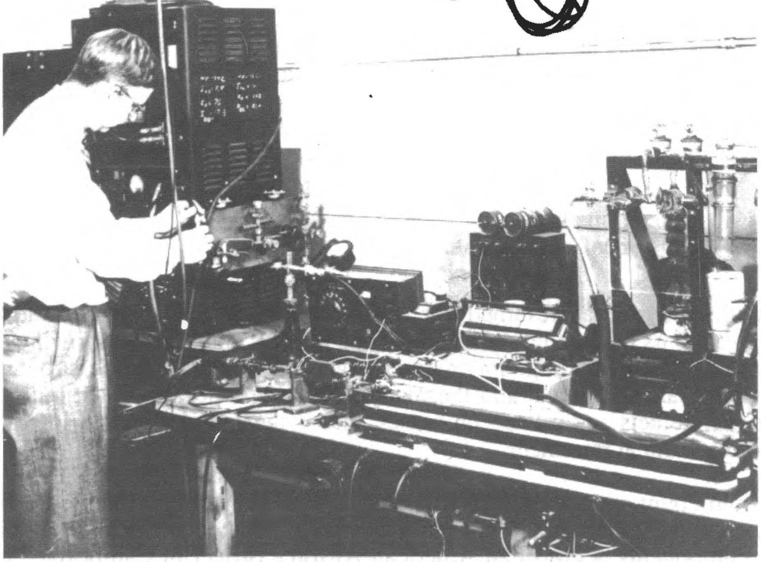
3 - Cambridge, Mass

In Palermo we had studied hard, in the attempt to get culturally fit for this much expected experience. MIT and Harvard made it clear to us, however, that our primary goal prior to our return to Palermo was to expand our cultural background and make it solid. Also, we had to gain a clear insight of where the action was going to be next. If we wanted to combine that with a full-time involvement in one of the vigorous research activity, we had to postpone our start in Palermo. If so, however, we feared that the delay already accumulated would grow beyond a manageable size. Right or wrong, this argument convinced us that it was impossible to postpone our return. Of course, we were involved in research, and to get acquainted with cryogenics and state-of-the-art electronic instrumentation, but we devoted the largest part of our efforts to our primary goal.

The most vigorous and unexpected help came from Bruno and Nora Rossi. Discovering them was breathtaking from start. We were well aware, of course, of Bruno's eminent scientific stature, but we did not know, then, how strong would have been his impact in the development of Physics in Palermo, and in the extension of its scope to areas so different from EPR. Nora was an ideal trait-d'union, well acquainted with our place. As a teen-ager, the daughter of a Professor Lombroso of the dinasty, she had been one of the catalysts of a famous group of artists in Palermo. We had several common friends and acquaintances. She offered quick and deep insights in our problems, as viewed from a highly sophisticated international "observatory". This, and Bruno's unique capability of getting straight to the philosophical and operational cores of problems, so well harmonized with the extraordinary human warmth of both, was just we needed. Bruno introduced us to the top people who could possibly help us in our planned background study. And they did. Bruno was constantly using every single occasion for attempting to teach us in his direct, understated way, the philosophy, the method, and the enjoyment of research and, above all, his taste for a



Pl 3a. The first EPR equipment, used for the work of refs. 7 and 8.



Pl 3b. M.W.P. Strandberg at MIT, 1954

continuous search for harmony between stringent logics and the clinamen of imagination. Bruno and Nora's friendship so became a cornerstone in our life. At every turning point of our life we have posed always the same question: how would Bruno behave in these circumstances? Unfortunately, very seldom have we been able to keep up to their standards.

At M.I.T. we worked at M.W.P. Strandberg's laboratory. Woody (Pl. 3) had a pioneering interest in magnetic relaxation processes, a field that was to have much to do with the development of Masers. He was always hurried, sharp, quick-witted and imaginative, knowledgeable all-over from electronics to theoretical physics and statistical mechanics. Also, we had very close contacts at Harvard, with J.H. Van Vleck, who for some reason, and to our delight, he decided to tutor us. We were so exposed to his basic crystal field theory, and to motional, exchange, and relaxation times effects. Through Van Vleck we became acquainted with K.W.H. Stevens (then on leave from Oxford) and with R. Pound. From Stevens we learned how mature and essentially canonized had just become the theory of EPR based on the crystal field approach and on the Spin Hamiltonian formulation. His most recent review article with B.Bleaney(9) was making this point clear. The most vigorous efforts in the field of ESR had been conducted at Oxford, thanks to a lucky coincidence of competence in microwaves (from war times) and a strong tradition in low temperatures, and to the appointment of M.H.L. Pryce, who turned out to have a remarkable gift for talking to experimentalists, and for developing Van Vleck's pre-war crystal field theory to the needs of EPR(10). Soon it became clear to us that EPR had a future as a unique tool to solve problems encompassing many aspects of physics of the condensed matter. To this purpose, however, we had to develop a state-of-the-art instrumentation, capable of letting us work competitively, despite the necessarily slow pace allowed in Palermo. Our study of the EPR spectrum of Vanadyl Sulphate was started at M.I.T. with the philosophy, already, of a compound vision of EPR, optical, and solid-state properties (11-14). It anticipated our future interest in optical spectra of magnetic crystals, and our collaboration with Maurice Pryce (see Sect.5).

At the end of 1954, we were back in Palermo. Before coming back, we had spent a short period in Berkeley (for an experiment that did not work), and had established direct contacts with Kittel, Kip, Portis, and their young students George Feher and Arnie Honig. There, we were happily surprised to lunch by E.Segre'. He said he had heard something, if small, was on the go in Palermo. However, he said..., and to our great amazement he asked if and how a few, very specific problems of the Istituto di Fisica were being handled. Only when we told him how those problems had been or were being solved, he approved. The detail of his past memories and present information made us meditate. On our way back we had a stopover in Oxford, where Stevens had introduced us to Bleaney and his group.

4 - Palermo: progress

Early in 1955 we had resumed our work at the Istituto di Fisica. It had become increasingly clear to us that the lesson of solid state physics consisted in showing the need for a comprehensive understanding, encompassing geometric and dynamic structure, electric, magnetic, statistical mechanical and thermodynamic properties, and (last but not least) all kinds of crystal defects and related processes, that is their evolution and interaction under thermal and mechanical treatment.

We could count on: our first CNR fundings (see Foreword and Table I); two machinists (P. Vacca and F. Punzo) sharing one reasonable lathe; two conspicuous cases full of microwave components, a gift of an American Airforce officer in Cambridge, to whom we had been addressed by Nello Carrara; collaboration with Donato Palumbo and, to the extent permitted by his administrative and teaching burdens, with Mariano Santangelo who was the senior Faculty member, while we were still in a very junior, untenured position.

TABLE I

Funding and main expenses (in Kl. it.)

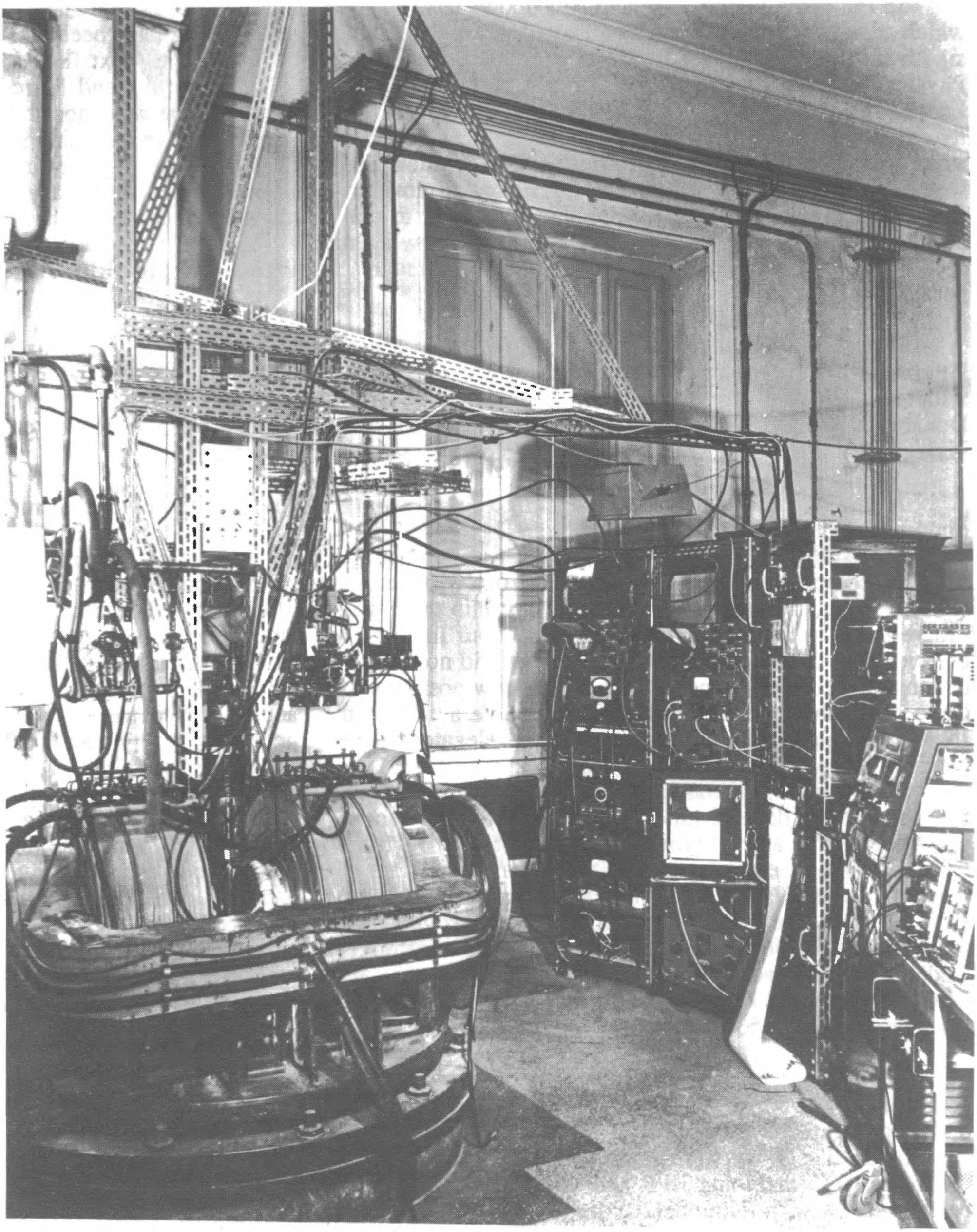
Year	Institution	Contribution	Main expenses related to EPR activity	
1952	CNR	400	M.U. Palma at CNR Microwave Institute in Florence (only part of the contribution)	
1953-54	M.A.E.	Scholarship	M.U. Palma at M.I.T.	
	M.P.I.	Scholarship	M.B. Palma-Vittorelli at M.I.T.	
1955	CNR	12.500	Electromagnet and microwave instrumentation	
1956	CNR	7.500		
1957	CNR	6.000	Nitrogen liquefier	
1958	CNR	7.500	Beckman spectrograph	
	CNR	1.200	Scholarships (L. 50,000 per month) for Ciccarello and Garofano	
	CRRN	50.000	Library, Chemical Lab., X-rays	15 Mil
		(Una tantum)	Lecture Hall	17 Mil
			Helium liquefier (1st installment)	18 Mil
	CRRN	28.000	Chemical Lab.	9.5Mil
		(ordinary)	Library and machine-shop	5 Mil
			Helium liquefier (2nd installment)	10.5Mil
1959	CRRN	25.000	Helium liquefier (3rd installment)	3.7Mil(1)
	CNR	7.500	Others, for cryogenics	10 Mil
			Other laboratory equipments	5 Mil.
1960	CRRN	29.000	Mechanical and Electronic machine shops	12 Mil
	CNR	7.500		
			Others, for cryogenics	5 Mil.
1961	CRRN	30.100	Air liquefier, wide-line NMR	22 Mil
	CNR	7.500	Ciccarello's lab. (first installment)	10 Mil

(1) The total cost of helium liquefier was about 32.2 Mil.

We had no more than two years for developing our novel instrumentation, for purchasing and putting to work a commercially available spectrophotometer, updating our library, establishing from scratch a modern machine and electronics shop, and for moving fast towards a low-temperature laboratory. Also, we had to provide full support to M.Santangelo in establishing good teaching standards, essential if we wanted to grow a good research group in a short time. Finally, on a personal basic, we wanted at least our first child. We attacked all these problems simultaneously.

As to the new EPR spectrometer, several novel features made it competitive: the large electromagnet entirely designed by us, ensuring excellent field homogeneity despite the large gap needed for low-temperature work. It had the feature, at that time unique, of being rotatable, and of accepting an optical self-collimator, orthogonal to the rotation axis of the magnet. In this way and by means of a purposely devised method (15), all parameters of the spin Hamiltonian could be determined by EPR spectral data taken in one single run along three mutually orthogonal, and otherwise arbitrary planes. This permitted EPR studies in crystals of unknown structure, and orientation and (not bad) savings of criogenic fluids and measurement time (15)(16). It was only one or two years later that the first commercial rotatable magnet was marketed (by Varian). We choose (against the then current trend) to have a low-voltage high-current magnet, and to control the field itself rather than the current. The entire, feed-backed current was passed through a bank of 96 Philips EL 34 big tubes. In this way the magnetic field stability was improved by an order of magnitude over current standards. The frequency-stabilized microwave bridge was followed by a very sophisticated signal-processing unit, based on the work we had done (together with D. Palumbo) on the mathematics and thermodynamics of Phase-sensitive (synchronous) detection(17)(18). We achieved an exceptional sensitivity(19), that even several years later could allow us to study problems that other laboratories could not tackle (see Sect.5). All the complex electronics and precision mechanics were home-made (Pl.4). Despite all this work and a burden of some 15 hrs per week of teaching activity, we were keeping on schedule, at the very sustained pace that had to be maintained for another decade and more, to make good use, before its obsolescence, of the instrumentation we had built. The manuscript describing the working EPR equipment was submitted for publication in August, 1957 (19) shortly after the phase-sensitive detector paper (18). The mule kept going!.

Many other events and facts crowded those two years. At the close of 1955, Mariano Santangelo was appointed a full professor and Director of the Istituto di Fisica Sperimentale, to become soon afterwards Istituto di Fisica. In January, 1956 Fausto Fumi was appointed full Professor of Theoretical Physics. He was followed in Palermo by Mario Tosi and, by Franco Bassani, both with temporary, junior faculty appointments. There was at last a more widespread and vivid atmosphere of interest and action in research, in teaching, in thesis subjects offered to our still few physics students. The first students (all of them gifted experimentalists) were, in the order, Ignazio Ciccarello, now Professor of Physics and Institute Director; Pippo Vaiana, now Professor of Astronomy and Director of the Astronomical Observatory (he came after he had got an Engineering degree, together with Ivan Angelo, now Associate Professor of Electronics); Renzo Cordone, now Professor of Physics and head of one of the Biophysics groups; Dino Bellomonte, shy, now Associate Professor of Solid State Physics and, last but not least, Franco Persico, who soon shifted to theoretical work and is now Professor and Head of the Theoretical Physics Group. We shall return to them in the next section. Other good students, working in EPR or closely related subjects were Giusi Agnetta, Tony Orlando and Piero Messina. Fumi, Bassani, and Tosi also took on their shoulders the reorganization and updating of the Library (that we had only started). Also, Fausto took great care with Mariano Santangelo in smoothing to the extent that it was possible our image to the eyes of the still old-styled Faculty of Sciences. (At that time, we had pasted very conspicuously in the EPR laboratory a cartoon from "Punch", showing an angry Dean shouting to the young clergy "young man, will you please stop referring to the Congregation as to the Opposition?") Unfortunately, in a couple of



Pl 4. The home-built E.P.R. equipment (from ref.19).

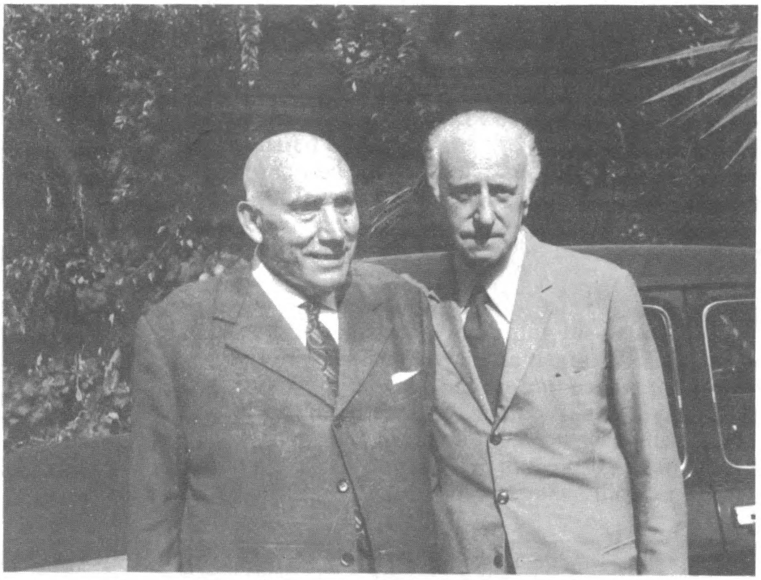
years Fausto Fumi, Franco Bassani, and Mario Tosi left, the Istituto di Fisica missed such an important "fluctuation" of human and scientific resources.

In the same period, Gaetano Riccobono left for good. This, too, was a great loss, which added to the damping of another extraordinary fluctuation that could have been most significant. For a period, in fact, there were at the Istituto di Mineralogia (next floor to Physics) three exceptional young people: Marcello Carapezza, Nino Sgarlata and Marco Leone. They had deep interests in Crystallography and Solid State, and a fantastic possibility could open if the Faculty of Science had decided to grab the occasion, encouraging instead of stopping, as it did, the fruitful collaboration already initiated. After all, the time when E. Segre' and mineralogist C. Perrier had discovered Technetium in Palermo was not so far. Later, it was fortunately possible to recover to our Faculty of Science Carapezza's and Leone's vigorous contributions. Sgarlata is now a Professor of Mineralogy in Rome. Sadly, while this paper was being written, both Marcello Carapezza and Tanino Riccobono passed away.

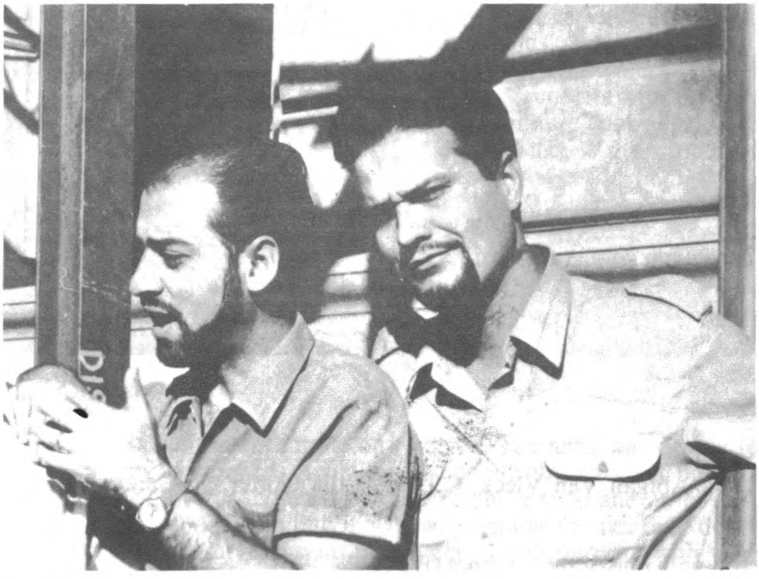
If not very enthusiastically (but this is just an aspect of his fascinating personality), Palumbo went in the same period to Bristol where Pryce had moved, to do theoretical work with him. We were very much looking forward to his return, but unfortunately for Palermo, Donato instead moved to Bruxelles, where he had for some 25 years a central role in devising and actuating Euratom's strategies on plasma and fusion physics.

A new achievement was the appointment of two electronic staff members (tecnici diplomati): Piero Chiricò and Pino Sgroi. This was a long-sought addition to our technical staff, consisting of Pasquale Vacca, a sweet person and a general technician with ample if not deep competence, and Ferdinando Punzo, a wise and witty, solidly competent machinist (Pl.5). Piero and Pino went enthusiastically into their work, and contributed greatly to its progress and to the feeling (to be shared by our first physics students, who were growing) of belonging in one committed group. They did not fail to perceive the sociological implications of their commitment. Soon, when new positions of technicians and machinists became available through Mariano Santangelo's action in the Faculty of Science and with INFN (see below), Chiricò and Sgroi were delegated to do the necessary scouting and find the right people, and take care with <u>i cavalieri</u> Punzo and Vacca of their training. In this way, the technical and machine shop supports grew harmoniously and with great enthusiasm for about a decade. Later, with the 1968 wave (and its lights and shadows) the spell was gone. Fortunately, Sgroi and Chirico' (today Dr. Sgroi and Dr. Chirico') did find different outlets to their rich personalities. Other technicians gave later a strong contribution to the revival of the Istituto di Fisica: Vincenzo Greco, Giovanni Gambino, and Francesco Ficarra. It should be clearly understood that no progress would have been possible without those committed people. By contrast, when at one of the very early meetings organized by students in 1968 we proposed that professional technicians (rather than Faculty and students only) should be involved in technical decisions, our proposal was discarded by a "progressive" 14 to 53 vote. We did not need to attend any more meetings.

A pleasant and most profitable "<u>intermezzo</u>" in that intense period was the Varenna course in July 1956, so well organized by the late L. Giulotto (Pl.6). This gave us a general updating, together with a view of most italian groups working or planning to work in related fields. There, we were again with Van Vleck, and we started discussing with Pryce the interest of combining EPR and vibronic spectral measurements. This was to result in collaborations with Palumbo(20) and ourselves (see next section). Contacts were revived with C. Kittel. They were to take our first student, Ignazio Ciccarello, to Berkeley for a few years. Finally, we had with J.C. Gorter discussions leading, later, to another collaboration (see Sect.5). Shortly after, Gorter also helped us a great deal, by allowing the excellent glassblowing shop of his laboratory to build a series of cryostats purposely designed for our EPR and optical spectrometers, and for the operation of our temperature controller. We had taken to Varenna our first baby, 6-week old Manfredi. So, as Giulia Gozzini was there



Pl 5a. F. Punzo and P.Vacca, the two technicians of the Istituto in 1950, in their late age (Photograph of circa 1980).



Pl 5b. P. Chiricò and P. Sgroi. To the left is also F. Ficarra, another of the technicians who contributed most to the work here described.

Pl 6a.

Pl 6b.

Pl 6c.

Pl 6a. J.H. and Abigail Van Vleck, C.J. and Lilla Gorter, G. Careri, P. Brovetto and the Authors.

Pl 6b. Gozzini with one of the Authors (B.P.)

Pl 6c. An official photo of the Varenna School of 1956, beautifully organized by L. Giulotto.

along with Adriano, our friendship started becoming a family affair. In the next 30 years, this friendship was to become a reference frame in our lives. Giorgio Careri was there, too. He and Gozzini (in Roma and Pisa, respectively) had already established groups doing fine work in Physics of Condensed Matter.

Last but not at all least, in August 1957 a new Sicilian Regional Government, with great insight, approved a law establishing and funding a Regional Committee for Physical Research (CRRN now CRRNSM). The balance was not bad (150 Million lire to begin, and 100 Million lire per annum, to be shared between Palermo, Catania, and Messina). The law was very advanced and in fact it preceded a similar national law, which proves that good will pays even in unlikely conditions. It had been fostered by Renato Ricamo, a low-energy nuclear physicist having high organizational spirits, who was a full Professor in Catania, following the Cocconis' departure and had an important role in re-establishing research there. In addition, it so happened that the elected Sicilian Representative in charge of preparing and relationing on the law had been for long years a schoolmate of one of us. It was only natural for him to ask for advice and help in writing the actual text. The law was so written in less than 24 non-stop hours, and approved the next day. This was an interruption, in the August canicola of Palermo, in the preparation of the manuscript describing the working EPR instrumentation, which was submitted two weeks later(19). Another week later, Laura, our second child, was born. In November, Ignazio Ciccarello (our first student) obtained his Laurea. We arranged for him a stay in Pisa, to expose him to Gozzini's unique style of research. A week of mutual silence was enough to make them enthusiastic of each other.

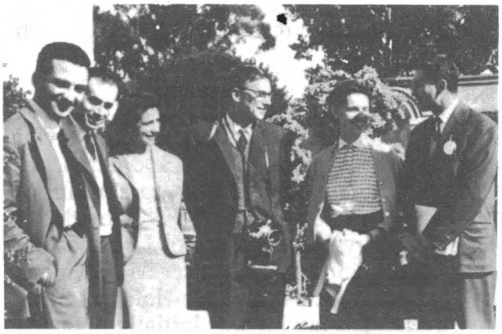
Santangelo and Ricamo did a good job in involving the Istituto Nazionale di Fisica Nucleare (INFN) in the operation of CRRN. Ettore Pancini and soon after Giorgio Salvini came as INFN delegates. They discussed our work with unexpected interest and depth. An official agreement was soon established, whereby INFN contributed six full-time positions for technicians and several paid research collaborations. In this way, INFN provided a strong contribution to the development of non-nuclear physics in Palermo. Long-lasting friendships were also established with E. Pancini, G. Salvini and soon after M. Conversi while Amaldi kept his encouraging attitude. By the end of 1959 a Collin's Helium Liquefier was in operation. It had been purchased on CRRN funds, and it was initially operated by Cordone (at that time still a student) and Sgroi. Further, a Beckman DK-2 UV-visible spectrograph had been purchased. We equipped both spectrometers with cryostats, and designed and built (with Vaiana and Angelo) a precise temperature controller offering for the first time the possibility of bridging the "forbidden gaps", that is the temperature regions that could not be reached by controlling the vapor pressure of cryogenic fluids. A description of the apparatus was delayed by the priority given to experiments until 1967 (when it was still very innovative) and was published on the J.Sci.Instr. The apparatus is up to now working very satisfactorily. In none of those years we had missed the extraordinary, pervasive intellectual stimulus of Bruno and Nora Rossi (Pl. 7).

5 - Science, in the new scenario

At last, it was possible to concentrate on research. The need was deeply felt, and the enjoyment had been long postponed. Actually, along with the effort of building the EPR machine, and altogether a new Laboratory, with a machine shop and an electronics shop, and getting everything to work (including a 50 Kw generator to take over during frequent electric mains failures, and a large system to serve a similar purpose with water supply), some science had been done. This was an analysis of the mathematics and thermodynamics of phase-sensitive detectors(17)(18) needed for our high-quality signal processing, a new method for EPR spectroscopy(15) embodied in our new machine(19) and perhaps the first combined EPR, X-ray and Optical study of a magnetic crystal(13)(14).

Pl 7a.

Pl 7b.



Pl 7c.

Pl 7d.

Pl 7a. Bruno and Nora Rossi, near Palermo, 1957

Pl 7b. M.H.L. Pryce in Sicily, with Isabel Powell and Beatrice Palma. The children are Augusto Cacopardo and Manfredi and Laura Palma. (1959).

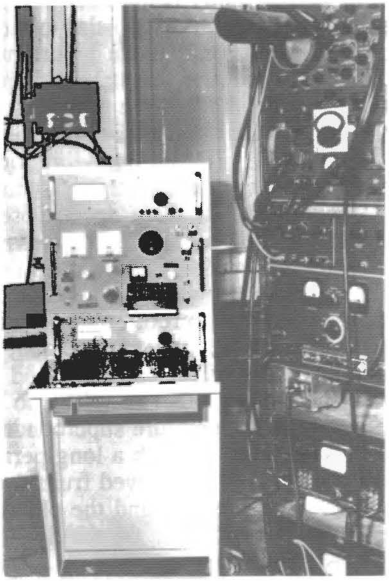
Pl 7c. M.U. Palma, G.F. and Pupa Chiarotti, J.W. Mitchell, Beatrice Palma, and F. Bassani, Agrigento, 1958.

Pl 7d. J.H. and Abigail Van Vleck.

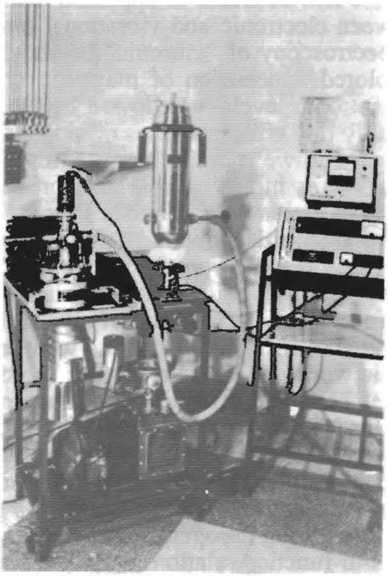
The existence already of a group of young, very capable eager students, made it possible and desirable to approach many problems at one time. The study of interactions between electronic and vibrational transitions in magnetic crystals was started using optical spectroscopy of "vibronic" bands. It was being realized at that time that the recurrently colored appearance of magnetic crystal is due to transitions between crystal-field-split electronic levels, as allowed by interactions with lattice dynamics. We were equipped to study this effect in slices of single crystals, wherever the best-suited range of temperature was, and we started doing it with G. Agnetta and T. Garofano(21) (Pl.8). The vibrational structures including so-called precursor lines were nicely resolved, and interpreted, in a collaboration with Maurice Pryce planned already in Varenna. Bands were decomposed, and precise data obtained, allowing one of the first quantitative checks of the correctness of the theoretical approach. A more complete report was published in 1964 on Philosophical Magazine. In addition, the method and the novel instrumentation allowed a detailed study of the thermal excitation of crystal dynamics, continuously from 4 K to room temperature, and above(21) (Pl.8). These were among the very first studies of this type. An account of this work and of its relevance in connection with the Jahn-Teller effect can be found in Ref.22. The potentiality of our approach attracted in Palermo, among other people, also K. Alex Muller who was much later to contribute so largely to high-temperature superconductivity. Collaboration with Pryce on lattice dynamics continued later, through a long period spent by Dino Bellomonte with him. The potentiality of the method has proved fruitful up to these days, as Renzo Cordone's group is using the very same method and the old and still working cryogenic temperature controller, to obtain basic information on the dynamics-to-function relationship in proteins (see below, Table II and References therein).

With Ignazio Ciccarello at the beginning, and later with Renzo Cordone and Dino Bellomonte, we decided to study the standing problem of the primary photographic process in the volume of large silver halide crystals. In a very pure and annealed AgCl crystal, photoliberation of electrons results in electron-hole recombination, and no photographic effect is observed. The latter occurs, however, in crystals doped e.g. with Cd or Cu ions. Upon low-dose UV irradiation, a "latent image" (that is, a collection of essentially invisible, colloidal "specks" of few silver atoms) is formed in these crystals. The silver specks had to be formed upon migration and condensation of silver ions and photoliberated electrons, but why did the latter not recombine with their counterpart, that is photoliberated holes? Also, how could there be silver ions at interstitial positions if much more than their equilibrium population are metalized in the photographic process, and a correspondingly great excess of vacancies is present? Both electron deficiencies and vacant Ag lattice sites had to be taken care of, as J.W. Mitchell did not fail to emphasize in his model. The situation was not clear, and the same was true for the mechanism (and free energy) by which the silver specks make room for themselves in the otherwise quasi-perfect crystal. A number of processes were certainly involved, and we were looking for processes.

Mario Tosi came to us saying that in his opinion, EPR of Cu doped crystals could help solving part of the problem: since Cu sensitizes the crystal for photographic effect, the photoliberated holes should be trapped at copper ions, and convert them into paramagnetic Cu ions, detectable by EPR. As we started studying the current literature, N.F. Mott's strong role in the field appeared evident, but it was also evident to us that much of the folklore, perhaps its crucial part, was not found there. In those days, Jack Mitchell and his group in Bristol were providing beautiful, cut-and-dry evidence of helical dislocations formed to make room to photographic silver specks in AgCl crystals(23-24). Also, they were providing the first important support to Mitchell's model of photographic sensitivity (25-27). They had a method for preparing the purest available crystals. After all, the photographic effect, was at home in Bristol, with so-called nuclear emulsions, with C.F. Powell, N. F.Mott, and J.W. Mitchell there. In those days Fumi was in Bristol, and Pryce had moved there from Oxford. Contacts were thus easily established with Mitchell, who soon afterwards came to Palermo, in the occasion of the SIF Annual Meeting, 1958 (Pl.7). One of us (U.P.) followed him in Bristol and after a few weeks, through his and Ernest



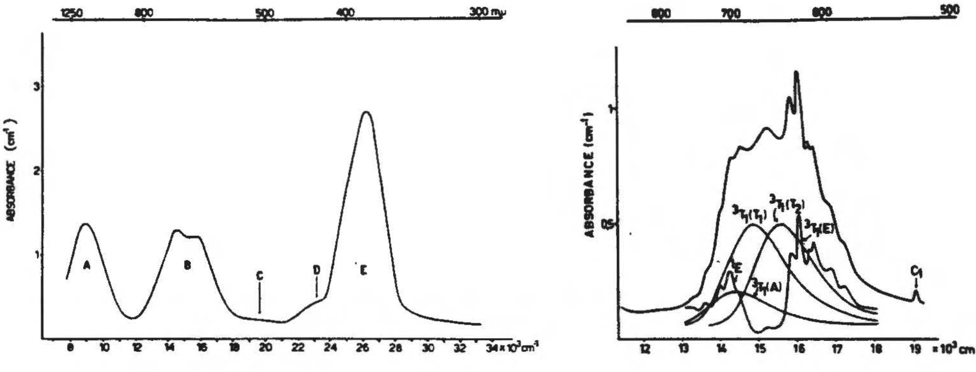
Pl 8a.



Pl 8b.

Pl 8a. The temperature controller working in the 4-400 K range used eversince.(This is the somewhat later version described in ref.18 and used e.g. in the work of refs. 77-80).

Pl 8b. The temperature-controlled Dewar used for vibronic spectroscopy.



Pl 8c. Phonon-electronic (vibronic) coupling (Nickel fluosilicate crystals). Left: at room temperature. Right: one of the bands, disentangled at liquid helium temperature, and its decomposition, evidencing the vibronic coupling.

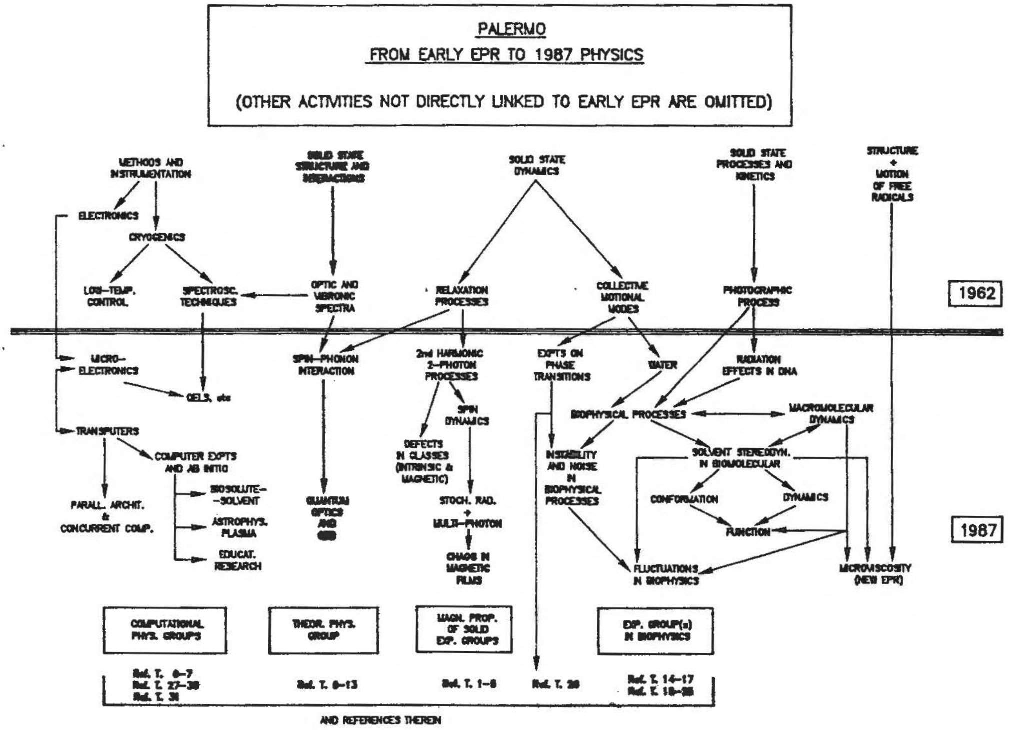

PALERMO
FROM EARLY EPR TO 1987 PHYSICS
(OTHER ACTIVITIES NOT DIRECTLY LINKED TO EARLY EPR ARE OMITTED)
METHODS AND INSTRUMENTATION
SOLID STATE STRUCTURE AND INTERACTIONS
SOLID STATE DYNAMICS
SOLID STATE PROCESSES AND KINETICS
STRUCTURE + MOTION OF FREE RADICALS
ELECTRONICS
CRYOGENICS
LOW-TEMP. CONTROL
SPECTROSC. TECHNIQUES
OPTIC AND VIBRONIC SPECTRA
RELAXATION PROCESSES
COLLECTIVE MOTIONAL MODES
PHOTOGRAPHIC PROCESS
1962
MICRO-ELECTRONICS
GELS, etc
SPIN-PHONON INTERACTION
2nd HARMONIC 2-PHOTON PROCESSES
EXPTS ON PHASE TRANSITIONS
WATER
RADIATION EFFECTS IN DNA
SPIN DYNAMICS
BIOPHYSICAL PROCESSES
MACROMOLECULAR DYNAMICS
TRANSPUTERS
COMPUTER EXPTS AND AB INITIO
DEFECTS IN GLASSES (INTRINSIC & MAGNETIC)
INSTABILITY AND NOISE IN BIOPHYSICAL PROCESSES
SOLVENT STEREODYN. IN BIOMOLECULAR
BIOSOLUTE--SOLVENT
PARALL. ARCHIT. & CONCURRENT COMP.
ASTROPHYS. PLASMA
EDUCAT. RESEARCH
QUANTUM OPTICS AND
STOCH. RAD. + MULTI-PHOTON
CONFORMATION
DYNAMICS
FUNCTION
1987
CHAOS IN MAGNETIC FILMS
FLUCTUATIONS IN BIOPHYSICS
MICROVISCOSITY (NEW EPR)
COMPUTATIONAL PHYS. GROUPS
THEOR. PHYS. GROUP
MAGN. PROP. OF SOLID EXP. GROUPS
EXP. GROUP(s) IN BIOPHYSICS
Ref. T. 6-7
Ref. T. 27-30
Ref. T. 31
Ref. T. 8-13
Ref. T. 1-5
Ref. T. 26
Ref. T. 14-17
Ref. T. 18-25
AND REFERENCES THEREIN

Table II.

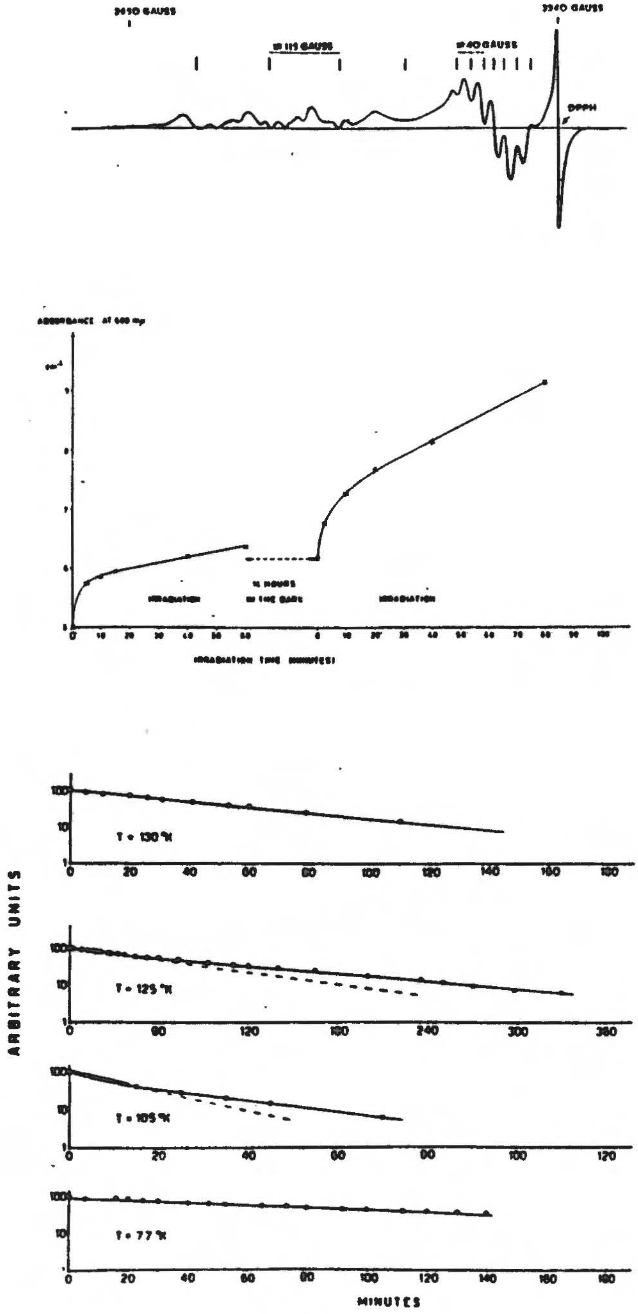


Fig. 1. Some results of work on the photographic process. From top to bottom: EPR spectrum of Cu++ in illuminated and quenched copper-doped AgCl ; darkening curves, showing the reversible operation of Cu+ ; the decays (at somewhat higher temperatures) of the "permanent" photo-current, in Cd++ doped AgCl.

Braun's collaborative and friendly attitude, came back with some pure and Cu doped crystals, and experience concerning their preparation and handling.

The EPR experiments could be started, but as we read in a recent paper that Fausto had perhaps sent to us in pre-print(28), Cu sensitized crystals had been found to show no sign of the presence of Cu ions upon irradiation at room temperature, as well as at liquid nitrogen temperature. Mitchell, however, had told us that a faint and quickly disappearing blue hue was perhaps observable in those crystals upon irradiation. If true, this indicated a cascade of processes. It was necessary to stop the cascade at the appropriate stage. Quenching the crystal into liquid nitrogen after irradiation could be too late, so we started irradiating at room temperature, and dropped the crystal into liquid nitrogen, under irradiation. It was not easy, but eventually we hit the appropriate timing, and an EPR signal appeared(29). In the very moment when the first signal appeared, Franco Bassani had stepped in the Laboratory. Together, we worked out the theory that he brought good luck.

This was the start of a long story. First, the EPR "signature" of the Cu ion was to be obtained, and the AgCl crystal had to be properly oriented. X-rays could not be used to this purpose, as they would originate their own photographic process. The possibility offered by our EPR spectrometer of rotating both the crystal and the magnetic field at right angles solved this problem, and the wanted "signature" appeared (Fig.1). Similarly, the possibilities offered by our cryogenic temperature controller played an important role in eliciting the different processes. To make a long story short, our studies provided a very ample support to Mitchell's model, and further showed unsuspected effects. Among other things, our time-resolved studies showed that(29-32):

- At room temperature a first temporary trapping occurs(29). Sensitizing impurity centers (as in the typical case of Cu sensitization), or extra vacant lattice sites (as in the typical case of Cd sensitization) act as such temporary traps(31). Lattice relaxation follows, and it prevents electron-hole recombination, as predicted by Mitchell.

- In this way, photoelectrons are free to migrate and condensate at appropriate dislocation sites with Ag ions, to form (as observable) silver specks. Vacancies left behind increase in number. When time and temperature allow them to migrate, their migration, and that of holes which can be released to reach a more favourable state, results in a condensation causing the formation of a "complementary photographic image"(31)(32). As shown in later work, published in two Phys.Rev.Letters and in Suppl. Nuovo Cimento this consists of microcavities (nearby or at dislocations) containing Cl, that is just the counterpart of metallic silver specks (several other steps, too long to be recalled, are involved in between).

- The disappearance of the excess vacant Ag lattice sites allows the number of interstitial Ag ions to increase again. This explains how the number of metallic silver atoms formed under repeated illumination can exceed by several orders of magnitude the number of naturally occurring interstitial, free to migrate, Ag ions. Also, it explains the paradoxical sensitization due to Cd at the surface and not in the volume of crystals(30).

- When e.g. Cu ions have released the temporarily trapped holes, they are ready to repeat the process. Also, the growing specks of metallic silver leave behind more and more Ag vacancies. The growth of the specks itself generates dislocations providing more and more condensation sites for both the regular and complementary "images". Altogether(31)(32), this explains very well not only the cyclic action of sensitizers, but also the increase of "final sensitivity" upon prolonged irradiation (Fig.1).

In the following, by playing with doping and temperature, we could let the two complementary images destroy each other in a controlled fashion. Or we could prevent migration of Ag ions while photoliberated holes were being trapped and corresponding electrons remained free. In this way, it was possible to have some kind of "diluted metal" having the

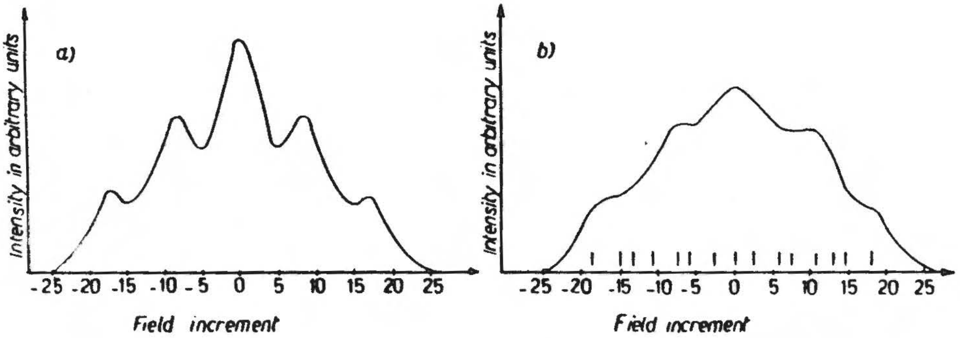


Fig. 2. EPR spectra of two chemical derivatives of a free-radical.

wanted concentration of free electrons. These latter studies were initiated and pushed forward by Cordone, and later also by Stefano Micciancio and Sandro Fornili, who was, to our delight, to join our group from Milano and who is now Professor of Physics and head of the Computational Physics Group at the Istituto di Fisica (see Table II and References therein). Results used techniques different from EPR. Their studies are not reported here in detail as they fall just off the date at which this report ends. Results were published in Phys.Rev.Letters. in the Proceedings of the International Congress of Photographic Science of Moscow. Cordone and Fornili had to extend several years later their studies of photoinduced processes to radiation damage in DNA, and produce a series of clarifying papers on this subject.

At the same time, Ciccarello, Santangelo and Garofano were engaged in another project concerning EPR of Free Radicals. Paramagnetic properties, hyperfine interactions, and lineshapes as affected by thermally excited dynamics of these radicals in the solvent were far from being precisely understood. By EPR spectrometry they studied the charge localization and transfer of a group of chemical derivatives of a free radical (33-35) (Fig.2). These were essential for understanding fine and hyperfine structures, and, later, the EPR spectral modifications due to motion. Free radicals had to prove later as very useful spin labels and probes, and in present days we are in fact making use of a new EPR spectrometer for spin-probe studies of viscosity on the Angstrom scale, as determined by biomolecule-solvent interactions (see Table II). Unfortunately, this very promising line of work could not be continued: by the end of 1961 Ciccarello went to Berkeley to work in Kittel's and Kip's groups (actually with K. Dransfeld, a collaboration to be continued over the years). Not much later, as we shall see shortly, Santangelo moved to Modena. Garofano himself left in succession, and this work was interrupted.

Another problem, bearing on crystal dynamics, was being studied by EPR with Franco Persico and, initially, with Dino Bellomonte(36-40). Actually, although we were looking for problems involving dynamics, the start of this particular one was not specifically focused on dynamics. EPR theories based on crystal field splittings had been tested on magnetic ions taking part in hydrated-salt crystals. In these cases, the crystal field experienced by the magnetic ion is mainly due to hydration water molecules surrounding it. We knew, on the other hand, of the existence of a class of cubic crystals (metal halides such as NiCl) embodying six NH molecules per ion, arranged in apparently perfect octahedra. We reasoned that crystal field, and exchange and superexchange behaviors might be interestingly different. Also, the apparently strict cubic symmetry was suggestive of the occurrence of subtle Jahn-Teller-like dynamic effects, that our cryogenic temperature controller could allow us to study carefully. First of all, however, we had to check the general behavior of these solids down to liquid helium temperature. In the summer of 1959 while our Helium liquefier was scheduled to reach Palermo, Gorter, gentlemanly and friendly as ever, invited us to do the first experiments at the Kamerlingh-Onnes Laboratorium in Leyden. We had two of his collaborators, Drewes and Koerts, working with us(37). There was plenty of cryogenic fluids available and, even if their EPR setup had not yet been renewed, we could at least perform measurements in the liquid Nitrogen, Hydrogen, and Helium regions and also measure static magnetic susceptibilities in those regions. The very first crystals were kindly prepared by Franco Maggio (a young chemist and a good friend and now also a respected colleague as our Faculty Dean). Subsequently, preparations were taken over by Garofano. The EPR spectrum at room temperature showed one rather narrow line only. Below a characteristic temperature, different for each halide salt, the line appeared enormously broadened. In Leyden we could only study the iodide, whose transition temperature luckily falls in the liquid hydrogen range. But it was enough to start. Static magnetic susceptibility showed to be not affected by the transition, while an anomaly in the specific heat was measured(37). Then, there was a transition, but it was not magnetic. The collaboration with Leyden was continued and further work was published in Physica.

By November of the same year, the Collin's liquefier was in Palermo, and by January it produced regularly and we were already collecting experimental data. Now, our controller allowed us to explore anywhere from room to helium temperature, and our EPR spectrometer allowed precise linewidth measurements. We studied the entire series of halides(38)(40). Experiments with NH_3 an ND_3 gave conclusive evidence for the motional nature of the transition(40), and elucidating the basis and the ampler implications of its remarkable cooperativity. In short, the following was found. The EPR linewidth detects a very sharp, cooperative, hysteretical transition in the motional state of ammonia molecules. The latter start to interlock and quickly become blocked in their rotations as temperature decreases below a well-defined value. This generates a distribution of crystal-field splittings. This line of work was actively and profitably continued. Already in 1964 it was shown (in a paper on Phys.Letts.) that up re-heating, the ammonia molecules resume their vapor-like state (as far as rotations are concerned) at a hysteretically higher temperature, not so sharply defined as in the decreasing-temperature case. As we could accurately measure the percentage of blocked NH_3 molecules,the correctness of the motional interpretation could be checked in various ways. Experiments with NH_3, ND_3 and with various proportions of NH_3/ND_3 (with exchange providing also NH_2D and NHD_2 species) measured the extent of cooperative interactions. A final report, including dielectric properties, was published later on Collective Phenomena.

It so became clear that this novel transition was based upon a very simple, yet not understood phenomenon having implications also in distant fields. This is illustrated in Fig.3. Here we see how a potential well, experienced by one particle as generated by nearby particles, is effectively washed out if those particles that generate it are not kept in fixed positions and are in rapid motion. This mechanism explains all the observed phenomena (the transition, its sharpness, its hysteresis, its being sharper at decreasing temperatures, the ample collective character of its isotope effect). Also, as shown in a series of papers from 1973 to 1987, by the authors and their colleagues, it appears to be involved, through its operation in solvent water, in both stability and function of biomolecules.

The beginning of the sixties was marked by an unpredictable episode, occurred just in 1960. A distinguished old couple appeared one morning at the Istituto di Fisica, asking to meet the Director. Mariano Santangelo was away with Ugo Palma, and somebody took the old couple to Beatrice, who asked them to wait in the hall, please, because she was very busy. Not before the gentleman produced his card, several minutes later, and again mum-

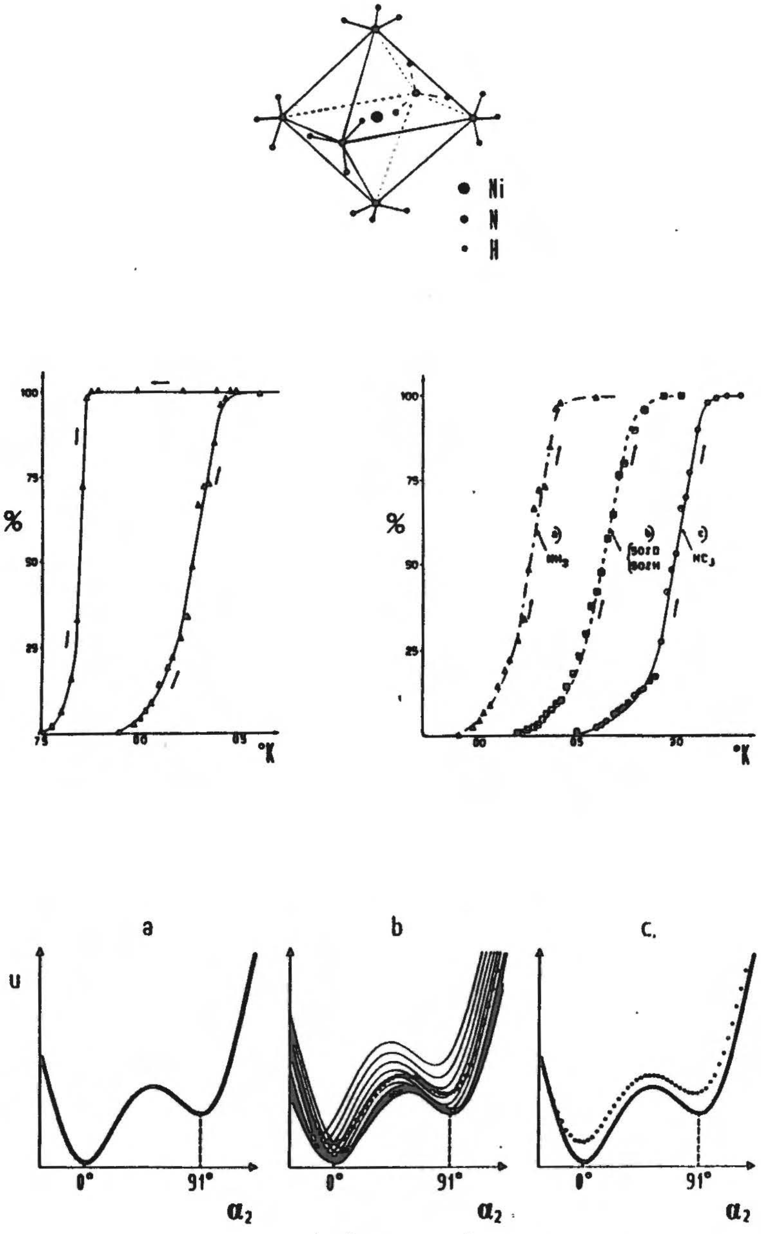


Fig. 3. Collective freezing and excitation of proton dynamics (hexammine nickel halides). Top: the structure of the crystal octahedral unit. Center: the number of octahedra in which NH_3 groups are rotating, as obtained from EPR spectra; left: the hysteresis cycle; right: the isotopic effect. Bottom: a recent illustration of the same dynamical cooperative mechanism, also operating in H_20, and thought have a biophysical relevance (ref.85).

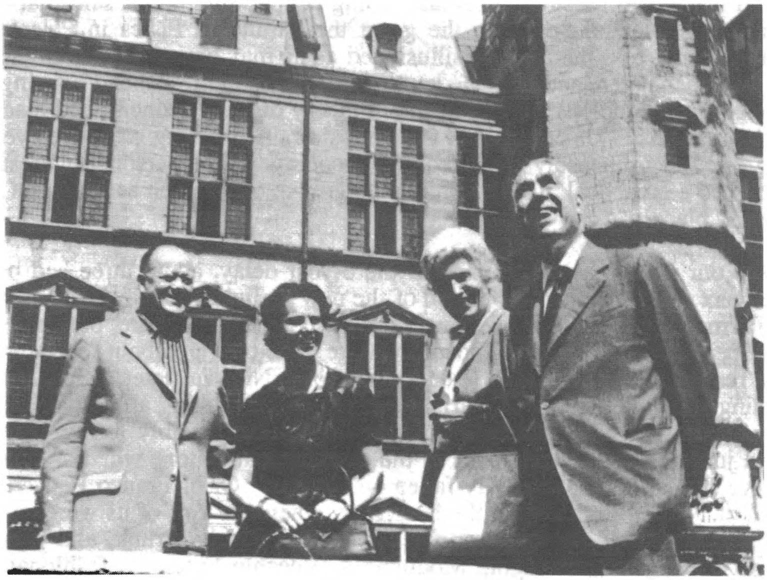
bled his name, was Beatrice aware that she was in front of Niels Bohr! Th e Bohrs stayed a few days and wanted to meet students and young people only. Bohr said that "his spies" had told him that something was on the go at the Istituto di Fisica in Palermo, and he wanted to know how true this was. Disillusioned as he may have been, he invited us for a week or so in Copenhagen, and there he kept taking us around (Pl.9) and tutoring us with a heap of thoughts on complementarity, quantum theory of measurement, and inadequacy of logics to human needs. This certainly was the most brain-storming week we ever had, and the whole group felt immensely rewarded and encouraged. The personal interest of such a great man helped a great deal in a reinforcing the growth of research activity in a novel area and in far-away place.

In 1963 our story reaches its end. Of the 6-year delay, about three had been recovered. The climax of the charismatic period of the new "religion" of Physics and of its sociology in Palermo was over. It was a new era, for the better to be sure, but some cherished aspects -and people, and a whole atmosphere were gone or were about to go. Nice memories though, remained, as of Matilde Zalapi' and Sonia Nicosia (later, Mrs. Chirico') who were providing very intelligent secretarial help, and kept laughing at how a vacancy could be filled by a hole. Or of Renzo Cordone who could not possibly refrain from entering shouting and jumping and telling jokes in the darkened laboratory where a most valuable photosensitive crystal had incidentally fallen on the floor. Or of Franco Persico appearing at 11.45 PM of New Years's eve in the laboratory where the two of us were still working. Very distinguished in his most appropriate tuxedo, yet totally drunk, and presenting his New Year's Greetings while singing Modugno's "Vecchio Frack", a fashionable song at that time. Or of Dino Bellomonte writing as a second year student his famous essay on electrolytic generation of hydrogen gas for his instructors, Pippo Vaiana and Ivan Angelo. It was this the time when Ignazio Ciccarello developed and taught his distinct philosophy. This was to ignore experimental approaches and strategies planned together with us, and follow new ones, teaching the younger Persico, Cordone and Bellomonte that "not always have we to do what <u>they</u> say". Very often he was damn right. No wonder if a generation of wildly independent, if considerate, individuals grew that way!

More or less at the time when this account terminates, Santangelo had good reasons to move to northern Italy with his family, to which he was deeply attached. Before leaving, he had an important role in decisions concerning further action and expansion. His photos in Pl.9 and Pl.10 were taken on the day of his official departure. Sadly, after few years in Modena, he died of cancer. In these years he kept visiting us. He went around in the Laboratory, sitted at "his" desk in "his" office which we kept at his disposal, and followed with great, affectionate interest what was going on. His premature departure was deeply felt by us all.

6 - 25 years later. 1987

The strategy developed with Santangelo was to enlarge the scope of scientific research in Palermo through the policy of sending the younger people abroad, trusting that they will come back motived to stay and to start new, diversified activities of their own. This was upstream swimming, as we had to miss the contribution of the young people, as soon as they had reached a productive level. However, we felt with Santangelo a responsibility for the cultural expansion of the Istituto di Fisica. We had already experienced that there was, at that time, scarce hope of attracting fine people in Palermo, on a long timebasis were likely to result in frustrations for the younger people. The strategy was gradually actuated in the following years and the results, after a 25-year span, are illustrated in Table II and references therein. Many current activities are not found in the Table, for reason that will be made clear below.



Pl 9a. With the Bohrs, and the Curator of the Kronborg Castle (1960).

Pl 9b. The farewell-and-come-back-soon salutation to M. Santangelo (1963).

Pl 10. M. Santangelo, at the front-door of the Istituto di Fisica, in the day of his departure (1963).

Ciccarello spent more than two years in Berkeley, where he did excellent work. This was published in several papers in Phys.Rev., in collaboration with K.Dransfeld et al. and it marked a shift from EPR to spin-phonon interactions and to non-linear interactions. Prior to his return, and at his specifications, all the equipment for a new laboratory for him. The group is now well diversified and their work in very well known altogether. (See Table II and Refs. T 1-5 there).

Less than two years later, Pippo Vaiana and Ivan Angelo, accepted at Harvard with van Vleck's reference and with CRRN scholarships, had modified their programs. Angelo moved to the Brooklyn Polytechnic Institute, and Vaiana went to work with Riccardo Giacconi, with Bruno Rossi's blessing. So, he joined the imaging X-ray Astronomy adventure, leading soon an active group and doing his frontier work there. Long before his return, he started in Palermo what rapidly became a strong and respected group in Astrophysics. His first collaborator (S.Serio) holds another chair of Astrophysics here and we have with their entire group common motivations and plans. Apart from refs. T-6 and T-7, relative to Astrophysical plasma as simulated by the "Palermo-Harvard numerical code", falling under "Computational Physics", their work is omitted from Table II because their activity could hardly be labeled as a filiation of early EPR. This is also the case of other omissions from the table. As a consequence of this limitation to EPR-derived expansions, Bruno Rossi' role in the cultural expansion of the Istituto di Fisica of those days (now comprehending both culturally and operatively the Ossservatorio Astronomico) is not explicitly evidenced. So, it is less than fair to state here that not even one step of this cultural extension would have been undertaken, had the Istituto missed Rossi's inspiration and intense help.

At that same time, we arranged for Persico to work in Theoretical Physics with K.W.H. Stevens, on spin-phonon interactions(41)(42). Reports from Stevens were enthusiastic as to Persico's capabilities and productivity, but..... he said, Franco works too much, he will destroy himself..... On the other side, Persico wrote: "here life is very enjoyable, and everybody helps me to relax and to let my subconscious insights to physical problems develop by playing tennis". In a very short time, with Stevens' and, later, Ziman's help Persico could start a group doing fine and much respected work in Theoretical Physics. The group is now well diversified and well known altogether (see Table and Refs T 8-13, and further references therein).

Soon afterwards, Dino Bellomonte went to work with M.H.L. Pryce on localized excitations in solids. The resulting, well-known of papers is in Proc.Phys.Soc. Renzo Cordone was encouraged by Alberto Monroy and by us to shift his active interests in radiation effects, from Silver Halides to DNA. Monroy himself found support for Cordone's stay in Bruxelles, at R. Thoma's and M. Errera's Laboratories and so a new story started. We, too, were soon attracted towards the physics of biomolecules and biosystems, by Monroy's and Cordone's cultural charme and enthusiasm. Now Cordone's well known and distinguished group is active in the field of biomolecular dynamics and of its relation to function (Table II and Refs. T 14-17). The same table, and Refs. T 18-25 show the interests and activities of our own groups.

Times were indeed mature for cultural expansions and new initiatives. Ricamo from Catania asked us to introduce one of his good students, Emanuele Rimini, to solid state and EPR, and optical spectroscopies. Ricamo knew we were going to be in difficulties, having planned to send most people abroad, and proposed as a gentlemen's agreement that we wouldn't attract Rimini in Palermo. Indeed, Rimini did not fail to ask to remain in Palermo, but we outspokenly honored our agreement, and he went to Catania where he started a now flourishing group, being a Professor of Physics there. Much time, and many events, have intervened since. The new atmosphere may have been felt by students of Engineering, taking Physics courses with us: Vincenzo Daneu and, shortly after, Stefano Riva-Sanseverino, had a go at the Faculty of Engineering, where they started basic thin-film research using Laser sources. In succession, we could help them spend some long periods at

MIT and Bell Labs, where both did excellent work, soon becoming full Professors in Palermo (Faculty of Engineering) and establishing a strong and respected group there, and at CRES, in Palermo.

While the first generation of former students was abroad or was starting new activities, another generation worked in EPR and closely related research. Some of them found a rewarding way elsewhere. Among them Piero Indovina (now Professor of Physics in Napoli and responsible for a very active group at Istituto Superiore di Sanita' in Roma), and Pietro Cosentino, now Professor of Earth Physics at our Faculty of Science. Many of them continued successfully, being very committed in stabilizing "the fluctuation". Their work and names are only in part reflected in Table II. There, references concern latest developments only, and should be intended to be quoted "with references therein", and the Table itself reflects only those activities that descend directly from the early ERP (and related instrumentation) work. Microhistory, as it has been realized, helps understanding history. The present article is a contribution in that sense.

7 - Conclusions

Invigorating, wasn't it? Even if we didn't reach to the Fair (lejana y sola).

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SOLID STATE PHYSICS AT CISE UNDER ELIO GERMAGNOLI

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Summary

Solid state physics research started at CISE when it was realized that the solution of several problems pertaining to the development of nuclear technology (cladding, heat removal, radiation damage, surface stability of components, etc.) was to be grounded on an appropriate knowledge of the intimate structure of solid materials. Hence, a Solid State Physics Laboratory was founded, under the young, creative leadership of Elio Germagnoli. The group soon became immersed in the study of fundamental Solid State Physics.

1. Introduction: young CISE and its technology laboratory

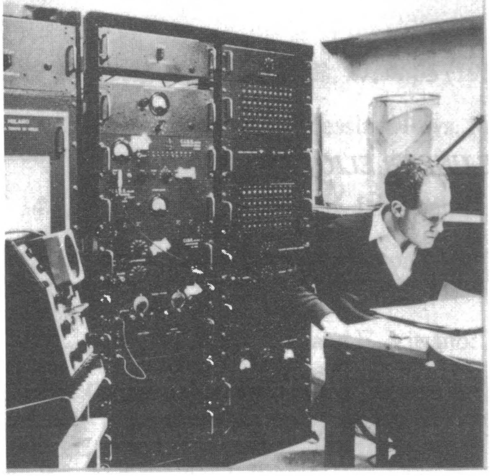
CISE (Centro Informazioni Studi Esperienze) was founded in 1946 by some electrical, chemical and mechanical industrial Corporations concerned, right after the end of the war, about the need for creating a national capability in the field of nuclear technology.

Some tens of young enthousiastic researchers clustered around Giuseppe Bolla, a full Professor at the University of Milan, to cover, in the new Organization, the fields of low-energy nuclear physics, nuclear reactor physics, nuclear engineering, isotope separation for heavy water production, nuclear chemistry, uranium metallurgy, nuclear electronics. Several well reputed physicists encouraged the newly born research centre with frequent visits, scientific interactions, advice: among them Edoardo Amaldi, Bruno Ferretti, Giorgio Salvini, Enrico Persico.

The seat, humble and makeshift (the cellar of the trade-unions club of Edison Corporation) seemed to stress the enthousiastic engagement of the young researchers.

A national reactor design, intended for reactor physics studies, was laid out: a natural-uranium fueled, heavy water moderated reactor to be located in a suitable research campus.

Not many people remember that the Ispra estate (now CCR Euratom) was selected, bought and addressed to research by CISE, which also carried out its former mapping and building. In those years, early fifties, CNRN (subsequently changed to CNEN, now ENEA) had not been founded yet and CISE was the only Italian agency to deal with the peaceful applications of nuclear energy. As soon as CNRN was established (1956), the Ispra research centre passed under its responsibility, but CNRN privileging a research campus near



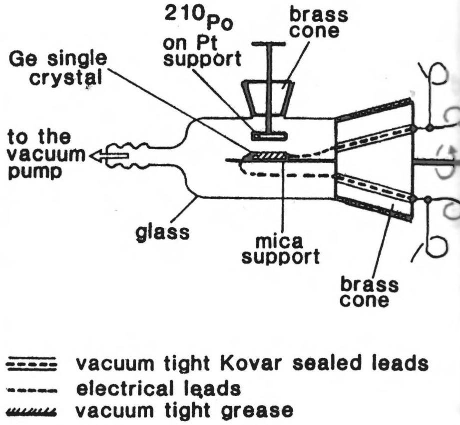


Fig. 1

Fig. 2

Fig. 1 - Dr. Elio Germagnoli working at the 80-channel time-of-flight neutron spectrometer (courtesy of CISE Tecnologie Innovative S.p.A.).

Fig. 2 - Sketch of the irradiation facility. Irradiated sample: germanium single crystal; α-particle source: ^{210}Po on platinum support (6).

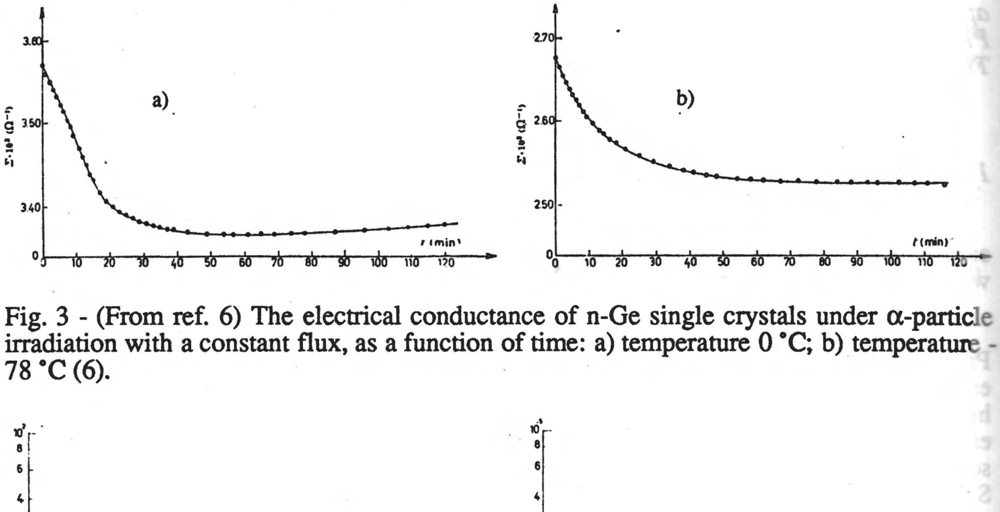


Fig. 3 - (From ref. 6) The electrical conductance of n-Ge single crystals under α-particle irradiation with a constant flux, as a function of time: a) temperature 0 °C; b) temperature -78 °C (6).

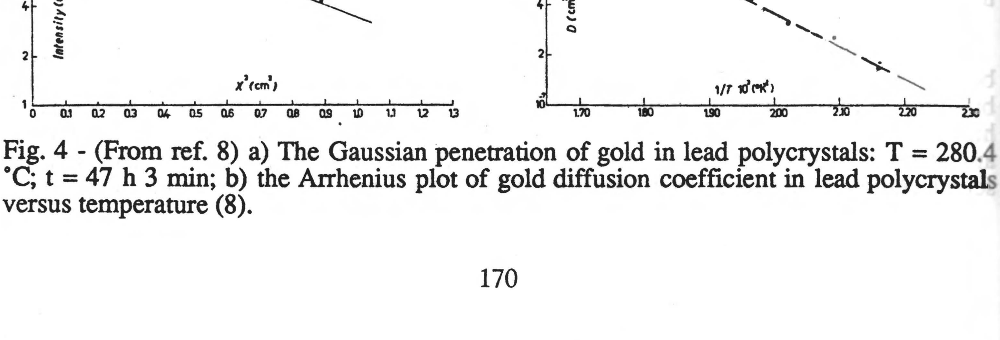


Fig. 4 - (From ref. 8) a) The Gaussian penetration of gold in lead polycrystals: T = 280.4 °C; t = 47 h 3 min; b) the Arrhenius plot of gold diffusion coefficient in lead polycrystals versus temperature (8).

the Capital, the Casaccia centre was built in the outskirts of Rome, and the Italian government donated the Ispra centre to Euratom. Therefore, the history of the by far largest community research establishment goes back to CISE. But let's return to CISE in the early fifties.

The material problems for the CISE-designed research reactor being put under proper control by means of satisfactory uranium metallurgy, of the adoption of a heavy-water moderated reactor design, which by-passed the need for uranium enrichment, and of the set up of a proper process for heavy-water production, the reactor-component fabrication was to be faced, and first of all that of the fuel element, with its canning and/or cladding issue for uranium protection from chemical reaction with water, yet ensuring an efficient heat removal.

The problems of measuring the thermal contact resistance between uranium and aluminium, and of studying the intermetallic diffusion (to ensure a stable fuel-cladding bond) were committed to Elio Germagnoli, a young nuclear physicist who had already proved his scientific maturity and had recently gained reputation thanks to a lucky strike: the measurement of the total cross sections for slow neutrons in Ni, Cd, U (carried out by Germagnoli and Ascoli, who at that time was still undergraduate) with the 80-channel time-of-flight spectrometer set up by Emilio Gatti and the 400 keV Cockcroft and Walton accelerator set up by Giovanni Perona.

Incidentally, the first-in-the world publication of those cross section values by the CISE team (1) hit the jack pot, causing declassification, at the first Geneva Conference (1955), of the up-to-then strictly classified American and Soviet data. Fig. 1 is a photograph of Elio Germagnoli sitting at the 80-channel time-of-flight neutron spectrometer.

A "Laboratorio di Tecnologie" was, then, set up at CISE at the beginning of 1955, to house heat-flow, intermetallic-diffusion and also corrosion experiments, under the responsibility of Elio Germagnoli. It is now well known that, in 1943, only a few months after operation of the first Fermi pile in Chicago, Wigner had predicted the storage of considerable amounts of energy in the lattice of solid components inside the nuclear reactors, and the subsequent release of that energy, now known as "Wigner release". More generally, Wigner had predicted the complex phenomenology which would later be defined as "Wigner effect" or radiation damage, and a comprehensive approach to this problem was published by professor Seitz on Discussion Faraday Society in 1949. The Windscale accident (October 10, 1957) shocked the scientific community with a first dramatic experimental confirmation of Wigner's predictions; little later the "Laboratorio di Tecnologie" had been set up at CISE so that the study of radiation damage was undertaken and implemented in that laboratory.

Notice that, at that time, Italy enjoyed a paramount tradition in nuclear physics (on the wake of the famous "via Panisperna" school of Enrico Fermi), but a cultural tradition of similar span was not available yet in that field of physics that Seitz first named "the modern theory of solids" in his book of 1940. This explains why CISE, though headed and flanked by brilliant physicists, did not immediately approach those problems through the set up of a Solid State Physics Laboratory, but, instead, through the set up of a "Technological Laboratory", and manned it with (besides Germagnoli) a newly graduated engineer, though with a strong inclination for Physics (A. Ascoli), for thermal measurements, with a newly graduated physicist (M. Asdente) for radiation damage, and with a chemist (L. Mongini) for diffusion and corrosion problems.

The first results obtained by this team were the measurements of the thermal contact resistance between flat surfaces of uranium and aluminium (2). To show how a correct physical approach can be influential also in an experiment of classical thermokinetics, let us point out that this experiment was judged by Emilio Gatti (3), "a model of elegance and accuracy, whose results are still a reference point".

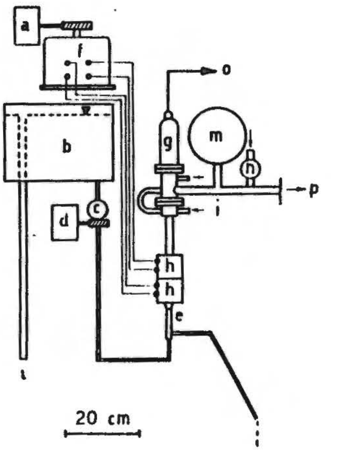


Fig. 5

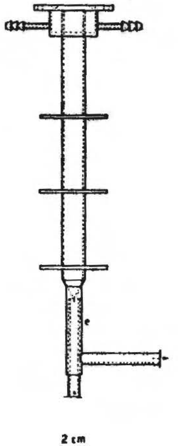


Fig. 6

Fig. 5 - Lay-out of the apparatus for growing metal single crystals from the melt (9).

Fig. 6 - Cross section of the crucible-container in the furnace of the modified-Bridgman-method apparatus by Ascoli and Germagnoli (9).

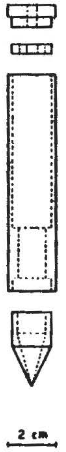


Fig. 7

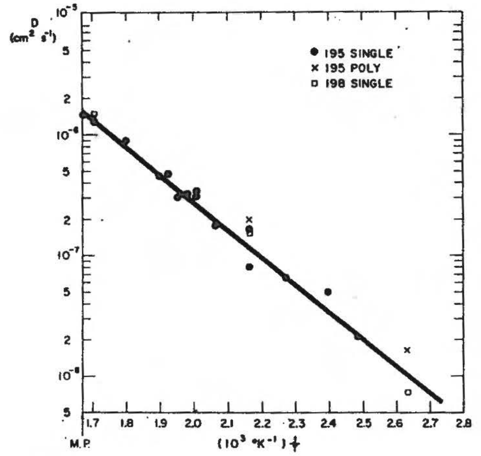


Fig. 8

Fig. 7 - Exploded view of a graphite crucible for the apparatus in Figures 7 and 8 (9).

Fig. 8 - Description of the dependence of the gold-diffusion coefficient in lead by a unique Arrhenius law: ^{195}Au in lead single crystal, ^{195}Au in lead polycrystals, ^{198}Au in lead single crystals (11).

But, as soon as the team tackled the problems, it became evident that any insight into them would depend on an in-depth knowledge of Solid State Physics, so that the entire group settled on the new discipline. Only few months later, the importance of Solid State Physics as the basis for the understanding of any material science problem was fully recognized at CISE, and the Germagnoli group was named the "Solid State Physics Laboratory" of CISE while a new Technology Laboratory was set up to deal with the most immediate technological issue.

2. *Early research activity of the Solid State Physics Laboratory*

In the same years in which the "Technology Laboratory", subsequently termed "Solid State Physics Laboratory" was started at CISE, as described in the previous section, the Milano Polytechnic set up and advanced course in nuclear engineering, calling on CISE researchers for specific teachings. Germagnoli and Asdente were given the responsibility of teaching the first Radiation Damage course in Italy, and they wrote the first notes for Italian students on this subject (4). Ascoli joined them two years later, when the first notes were substantially implemented into a textbook (5). The review articles by Slater in Journal of Applied Physics, by Dienes in Annual Review of Nuclear Sciences, by Glen in Advances in Physics, and by Kinchin and Pease in Reports on Progress in Physics, together with the already mentioned article by Seitz, were the early sources of those lectures and textbooks.

The preparation of the lectures for these postgraduate courses had a strong beneficial influence on the penetration of the Group into the new discipline. For sure, the benefit of the interaction between research and teaching was mutual. Of course the choice of the first research subjects of the new Laboratory was determined by the technological long-distance goals mentioned in section 1, the nuclear physics culture of Germagnoli, and, needless to say, the extreme poverty of facilities: no reactor for a radiation damage experiments, no electroprobe or other sophisticated surface analysis techniques available for low-penetration diffusion profiles.

It thus occurred that, while Germagnoli and Ascoli attended to thermal contact characterization (2,3), Germagnoli and Asdente devised and experiment of α-particle bombardment of germanium single-crystals. The α-particles were emitted by a 210-Po source, and the electrical resistance of Ge samples was measured as a function of fluence. But the measurements required heavy round-the-clock shifts so that the bachelor Ascoli joined the team for night shifts (and to engineer the experiment). Fig. 2 is a sketch of the very simple but perfectly efficient "irradiation facility" and Fig. 3 is an example of the excellent experimental results (6), which were commented by Professor Seitz in a letter to Fumi as follows:

"The paper looks very good to me, and I have no critical comments to make. About three months ago, Fan showed me a manuscript containing data for specimens of germanium having various values of E_f. The results confirm the general conclusions of your group for alpha particle bombardment. Using electron bombardment, the Purdue group found discrete levels, which shows that the effects of electron irradiation are much simpler. You might write to Fan about this."

An exact calibration of the α-γ branching ratio of the 210-Po source, that is, a prerequisite to the accomplishment of the quantitative experiment, was carried out on purpose (7). Here below, Dr. Mann's (of NBS) comments on the result intercomparison: "Dr. Hayward, Mr. Hoppes and I were very interested to note, in Nucl. Sci. Abstr., the very close agreement obtained by you and your colleagues with ourselves in determining the α-γ ratio in the decay of Po 210. I have pleasure in enclosing, herewith, a copy of our paper for you and each of yours colleagues, and we would be most grateful if you would also spare us three reprints of your paper".

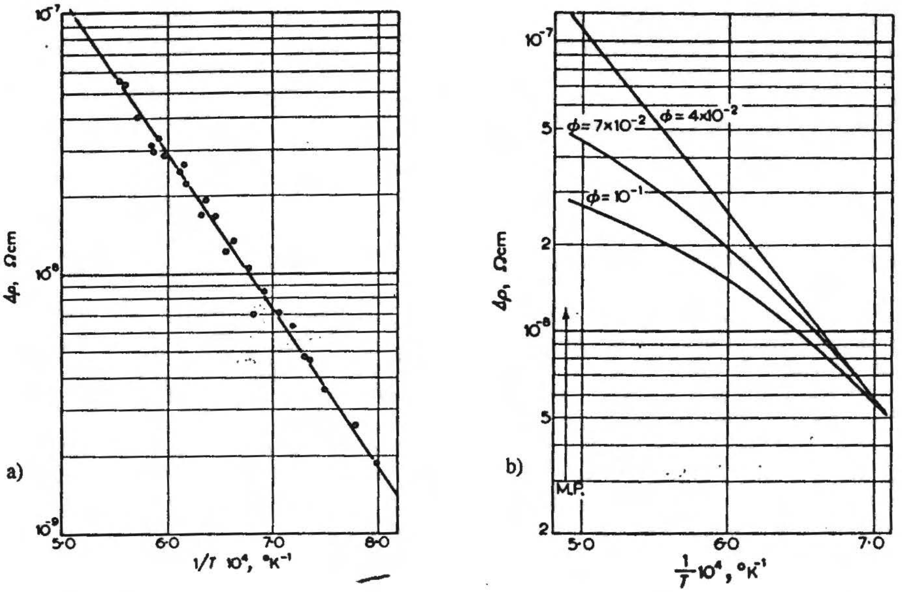


Fig. 9 - (From ref. 12) The quenched-in electrical resistance of platinum wires: a) water quenching, 0,10 mm diameter; b) air cooling, 0,10 mm, 0,01 mm and 0,04 mm diameters (12).

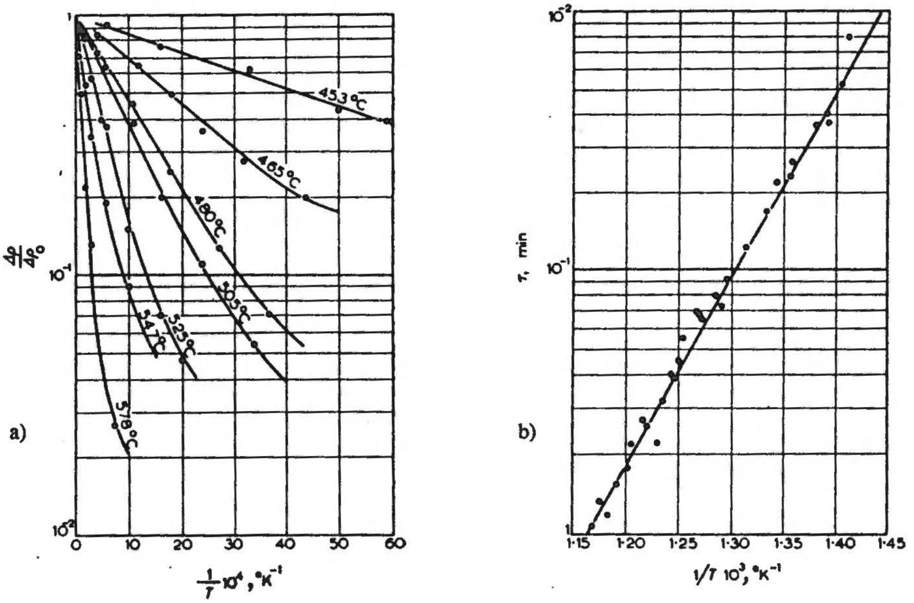


Fig. 10 - (From ref. 12) Isothermal annealing of quenched-in resistivity in platinum: a) the decay of the quenched-in resistivity as a function of annealing time; b) Arrhenius plot of the relaxation times obtained from the isothermal annealing curves (12).

Quite simultaneously, Germagnoli, Ascoli and Mongini were setting up a method for detecting diffusion penetration profiles: needless to say, using a radioactive tracer technique. Fast diffusing gold in lead polycrystalline samples was chosen as a system for a quick approach to the field. Fig. 4 is an example of the neat penetration profiles and Arrhenius plots which were obtained (8).

In the following year, Fausto Fumi became a consultant to CISE for the Solid State Physics programmes. He suggested that the gold-lead diffusion experiment should be repeated in Pb single crystals to separate the possible contribution of grain boundary short circuiting paths. This was done. Ascoli and Germagnoli set up on original modification of the Bridgman method for growing metal single crystals from the melt in a vertical crucible (9), which gave 100% of excellent-quality, low-dislocation-content lead, tin, zinc, silver, gold, copper single crystals, both pure and doped on request, from 5 N pure to Cu_3Au alloy composition. Figs. 5,6,7, are sketches of the apparatus, furnace and crucible, and show examples of Au-doped Pb crystals, of dentritic or cellular morphology obtained by controlled constitutional supercooling (10). Most common size of the crystals was 1.2 cm diameter by 3 cm length, but low-mosaic-spread Pb and Cu single crystals (to be used as monochromators in a neutron spectrometer) up to 28 pounds were also grown by the team. Ascoli repeated the gold diffusion experiment in lead single crystals, showing that the grain boundary contribution, if any, was negligible (11). Since we are at the Collegio Ghislieri, let me recall that one experiment of this series was published in Studia Ghisleriana. Figgs. 8 and 9 compare the single crystal experiment with that performed on polycrystals.

Airoldi and Manara joined the group, while Mongini left it to take the responsibility of the Spectroscopy Laboratory of CISE. At that time Fumi, back from Urbana, suggested a coordinated set of experiments: the measurements of the vacancy formation energy in noble metals by quenching experiments, of migration energy in the same defects by annealing experiments, and of self-diffusion energy by radioactive tracer penetration in single crystals (Au, Cu, Cu_3Au) or polycrystals (Pt, where high temperature expectedly ruled out grain boundary contributions).

This was definitely the most exciting period of the scientific production of the group, because every one was engaged in one experiment or in two, but the results were systematically cross-checked in a unitary frame.

Ascoli, Asdente, Germagnoli and Manara started the quenching and isothermal annealing experiments on Pt wires (12) (Fig. 10), while Airoldi and Germagnoli studied self-diffusion in silver (13) and, as a by product of preparing a very sophisticated self-diffusion experiment in Pt (which would then be performed by Cattaneo, Germagnoli and Grasso in 1962) (14), set up a very sensitive method for quantitative measurement of iridium content in Pt (15).

In the Summer of 1957, the V Course of the International Varenna School for Physics was devoted to Solid State Physics. Fausto Fumi was the Director, and Professors Seitz, Fan, Harvey Brooks gave the basic lectures. Germagnoli, Asdente and Ascoli took part in the school as students. All "students" were to take notes of the lectures of one of the teachers in teams of three students for each teacher under the iron-hand organization of Bassani and Tosi; all students but Ascoli, who complied with the requests of both Fumi, who wanted him to take the notes of George Bush's lectures on single crystal growth (16), and of Germagnoli, who wanted him to take the notes of Ron Smoluchowski's lectures on radiation damage (17); thus Ascoli ended up by spending all his evenings on editing notes, while all the other "students" enjoyed free time. Ascoli even missed the last-evening good-bye party, to honour the promise that he would deliver edited notes prior to the closing date of the school, but he never regretted the experience, which was anticipating a good deal of his subsequent scientific engagement.

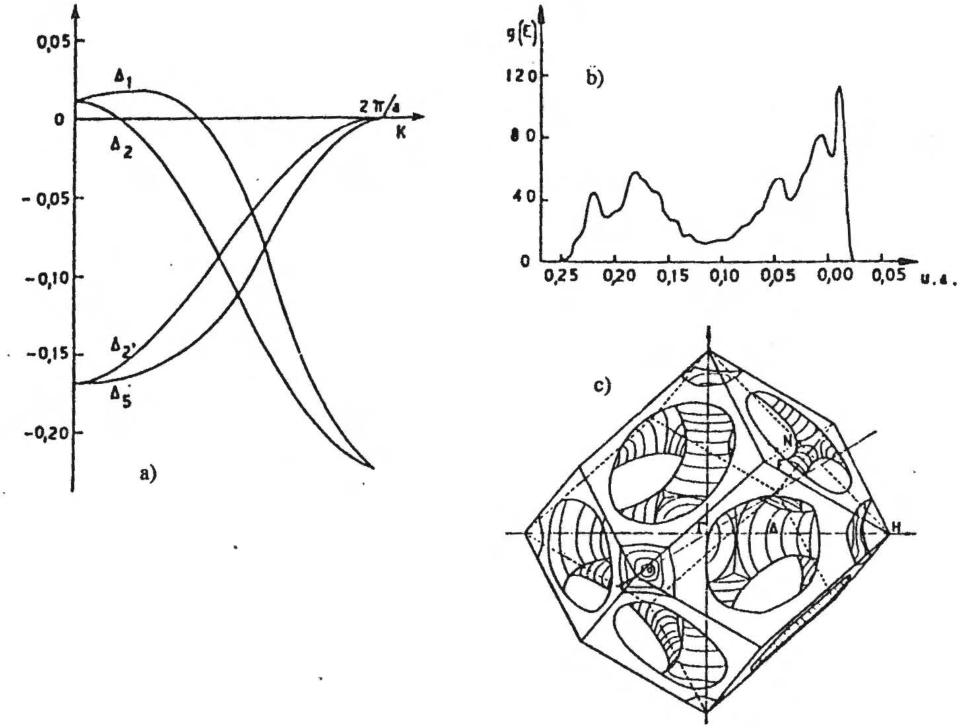


Fig. 11 - (From ref. 22) The electronic structure of bcc Cr: a) energy as a function of the wave vector k in the (100) direction of the reciprocal lattice; b) the density of states g(E) as a function of energy; c) Fermi surface (small electron "pockets" along the Δ line and the spherical surface of s-electrons around the T point are not reported in the figure, to preserve clarity) (22).

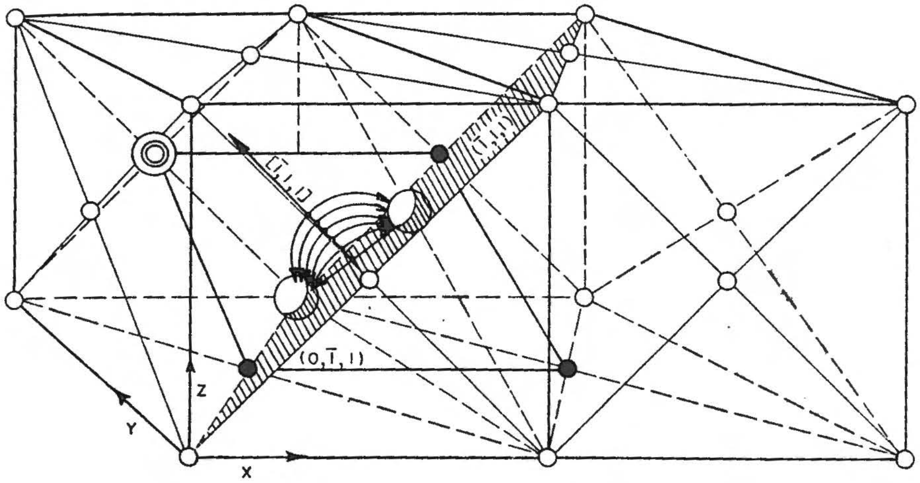


Fig. 12 - (From ref. 26) The calculation model of the migration energy of a vacancy near an impurity atom in copper (26).

Back to the Laboratory, Bacchella joined the team to replace Mongini, and the quenching experiments were continued by Airoldi, Bacchella and Germagnoli (18) on copper, and by Bacchella, Germagnoli and Granata on the kinetics of quenched-in lattice vacancies in Pt (19) (Granata was a student).

Asdente followed Fumi for a stage at the University of Palermo, where she realized her wish for a turning-point towards theoretical physics, by engaging with Tosi on ionic crystals, by calculating the vacancy migration energy in KCl (20). Bacchella's cooperation with the group was instead short-lived, since he never came back from a similar stage at Saclay.

Back from Palermo, Asdente left for Paris to quench her thirst for theoretical culture at Friedel's well. In Paris, Asdente laid down the basis of her subsequent studies on electron behaviour in metals, starting with a study on the "Calcul de la résistivité des cavités sphériques dans le cuivre" (21). The collaboration between Friedel and Asdente was continued after her return from Paris, through systematic calculations (comparing the results obtained with different approximations) of the electronic structure of bcc Cr (Fig. 11) and Fe (22).

As you see, we are up to 1959. It's time for Ascoli to leave for a stage, so that he leaves to spend 18 months at Brookhaven. At last it is a radiation damage experiment with a graphite reactor! Ascoli measures the resistivity change of a Cu-Ni alloy as a function of neutron fluence (23) and, with subsequent isochronal annealing experiments, Ascoli and coworkers (Belloni, Bollani, Queirolo) manage to separate the annealing of vacancies from the randomization of segregated atoms (24), and to give the first directs experimental proof of the existence of a miscibility gap in Cu-Ni solid solutions (25).

But, Ascoli being an electrical engineer, he did not want to accept a theoretical-culture gap, thus at Brookhaven he carried out a theoretical work with Arthur Damask: they calculated the migration energy of a vacancy near an impurity atom in copper (26), using a Morse potential function (see Fig. 12) suggesting that the low diffusion energy measured for Au in fcc Pb might be explained more easily with a deviated-path vacancy mechanism than with an interstitial mechanism (as Nachtrieb and Le Claire had suggested) which did not seem likely in a fcc crystal.

Before Ascoli left for Brookhaven, Germagnoli gave a wonderful internal seminar on positronium. Amazing was the clarity of his explanations, and he must have noticed in Ascoli's eyes how charmed he was left, so that he reacted by donating him his four pages of notes for the seminar: Ascoli never threw them away. They are so clear that Ascoli could use them to give an introductory seminar on positronium any time, although he never worked on positronium.

When Ascoli came back from Brookhaven, he found that Germagnoli had turned that early seminar into a new line of activity of the Laboratory, by publishing papers on positron lifetime in anthracene (27) and on the influence of disorder on the positron lifetime in anthracene (28), together with Cottini (an electronics researcher), Emilio Gatti (there is a lot of electronic equipment in a positron experiment) and Fabri (then a student, now a Central Director of Italtel); and on positron annihilation in neutron damaged anthracene (29) (Fabri, Germagnoli).

Around 1960 the activity lines of the Laboratory started to physiologically diversify: Germagnoli started Mössbauer experiments (30) (with Fabri, Musci and Randone); he also studied electrical resistivity changes in annealed Cu_3Au above the critical temperature (31) (with Damask and Fuhrman, then another student). Asdente continued to study the behaviour of electrons in metals and alloys, mainly from a theoretical approach, but keeping her experimental origins in mind: e.g., with Airoldi and Rimini (then a student, now a full

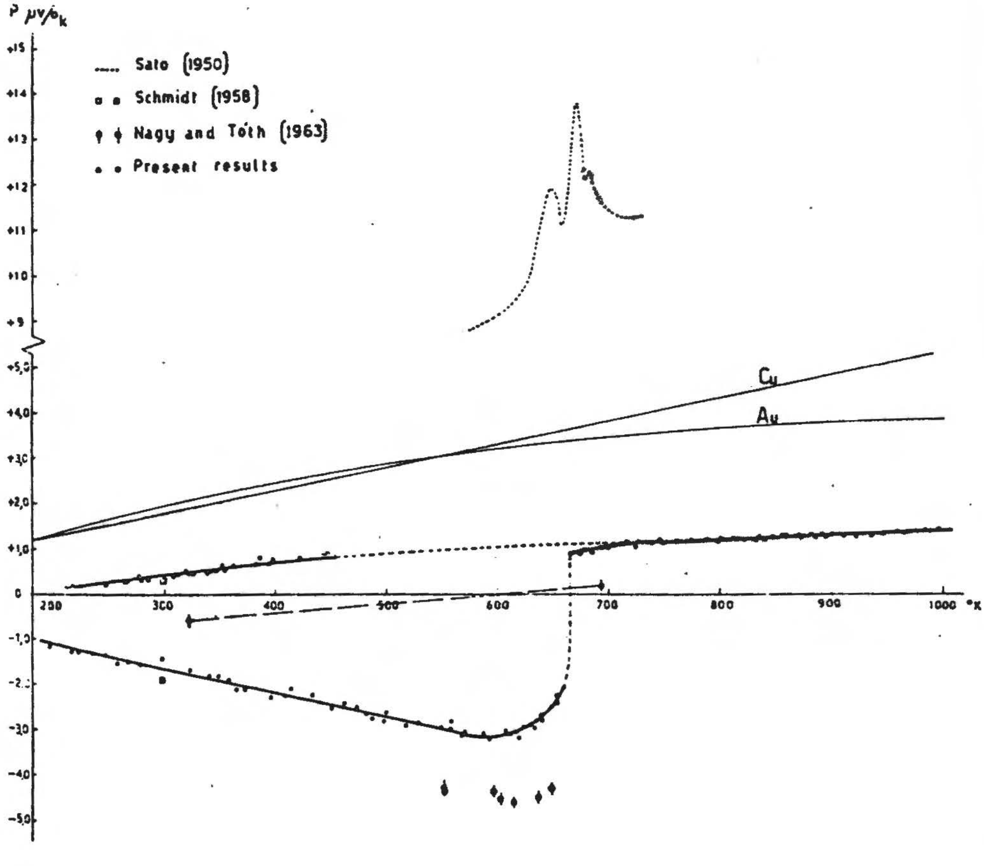


Fig. 13 - (From ref. 32a) Thermoelectric power of the Cu_3Au alloy as a function of temperature. Solid symbols refer to samples at equilibrium. Open symbols refer to samples disordered by quenching. Other authors' data reported in this figure are taken from references quoted in (32).

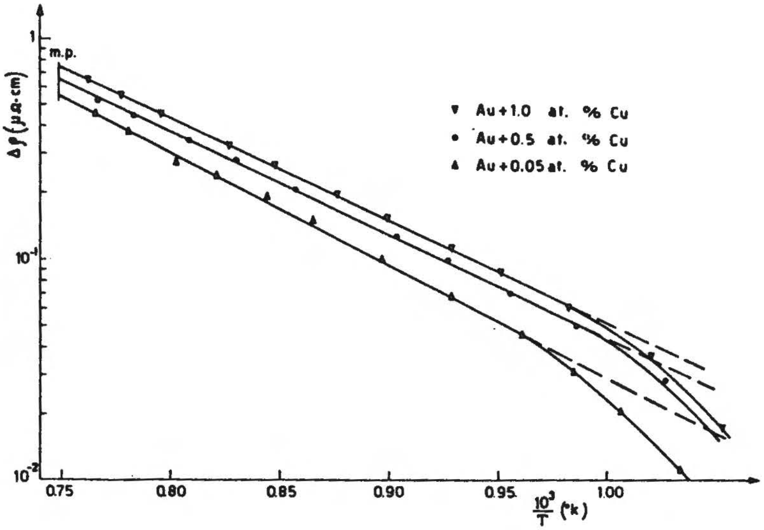


Fig. 15 - (From ref. 37) Arrhenius plot of the extra resistivity Δρ of copper-doped gold wires (37).

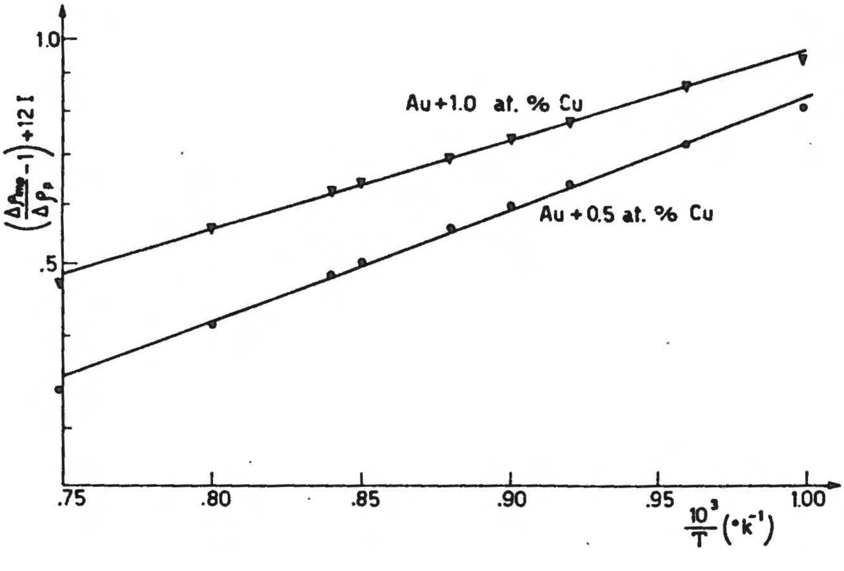


Fig. 16 - (From ref. 37) - The experimental determination of the impurity-vacancy binding energy B in Cu-doped gold: the slope of the straight lines gives B in units of 10^3k (the Boltzmann constant).

professor at the University of Catania) she calculated and experimentally checked the thermoelectric power of Cu_3Au (Fig. 13) as a function of order (32), to gain an insight into the connecting changes in electronic structure of the Fe-Ge binary system, and Ascoli started (with Bollani, Guarini and Kustudic) pressure diffusion experiments to measure the activation volume for the diffusion process (33); while Guarini and Schiavini set up a very sensitive microcalorimeter to detect the heat release of Cu_3Au across the critical temperature transition (34). In the meantime Ascoli started (first with Germangnoli and Guarini, then with Guarini, Bergamini and Queirolo) equilibrium resistivity measurements in pure (35, 36) amd doped (37) noble metals thus measuring the impurity-vacancy binding energy (Figs. 14,15,16).

But we are up well beyond 1960 and we have to stop here.

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RESEARCH IN SOLID STATE PHYSICS AT ISPRA

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The activity of a Solid State section at Ispra was materially founded at the end of 1959, when two small groups of C.N.R.N. (I) moved into newly prepared laboratory space at the reactor site.

By that time, some of our future competences were taking shape, but a precise programme was still under elaboration. the majority of personnel were young graduates, issued from the research on point defects in Pavia. Merlini had just begun to raise a new activity of X-ray diffraction, after returning from the United States early that year.

Merging these elements, into a full-sized Service of the reactor centre required a lot of effort, in order to afford new tasks of applied research and to prepare specific installations for this purpose. Progress in these directions took place in the following years, well beyond 1960. In the spirit of the present Meeting we shall touch briefly on these developments, only to illustrate the aspects of continuity with previous preparation. For many of us, this history goes back to the panorama of Solid State physics in the middle fifties, in Italy or abroad, and particularly in Pavia.

Developments from Pavia

The initial steps for a future Ispra group were taken at the end of 1957 with the constitution of a small task force, temporarily sited at the Istituto di Fisica Superiore of this University. The operation was sponsored by the sicentific management of C.N.R.N., with a local supervision by F. Fumi and L. Giulotto; its purpose was to start the preparation of means and personnel for future service in the nuclear center, which was in advanced construction at that time.

In this context some of us began their personal career with the centre of Ispra. Camagni was recruited first, with fresh experience of self-diffusion and chemical diffusion gained during a previous research fellowship at the University of Leeds (UK). Shortly later he was joined by A. Manara who had spent two years with E. Germagnoli at CISE (Milano) working on defect formation and annealing in noble metals, with the use of resistivity techniques.

Topics related to atomic diffusion and recovery phenomena were then of special concern for our Institution, being emphasized by strong practical reasons. Early before, the graphite accident in the reactor at Windscale (UK) had given to Europeans a dramatic proof of the far-reaching connections between nuclear safety and the physics of defects.

To the intention of C.N.R.N. , the research on diffusion was resumed in Pavia, with an extension to impurity migration in ordered Cu/Zn; some work was also started on microcalorimetry and defect recovery in metals. Around these activities, a number of thesis students and of young graduates were trained in the following period, 1958-60. Some of these people (C. Bassani; M. Boni; S. Pace) were to enter soon as founding members in the Solid State Laboratory of Ispra.

In this phase, however, a good part of our scientific interests was still immersed in the flourishing tradition of Pavia, concerning point defects and colour centres in ionic solids. To this Camagni and Manara had been connected since the times of their thesis work and throughout subsequent developments, led by F. Fumi and G. Chiarotti (II).

In those days, the conceptual picture of point or extended defects was rapidly growing and an exciting climate was surrounding all information related to this subject. Important proofs - mixed of experimental elegance and simplicity - had succeeded in clarifying the nature and the implications of the basic phenomena. One can only mention a few highlights, such as the beautiful observations of dislocation motion and multiplication (Washburn et al., 1953; Gilman and Johnston, 1956); the direct evidence of point defects via their volumetric effects (Simmons and Balluffi, 1956-58); the repeated confirmations of vacancy mechanisms in atomic diffusion, gathered from the Kirkendall effect. In the meantime, detailed information from the most diverse fields was unified under novel and convincing elaborations, which in turn opened the way to further exercise (we all remember the inspiring influence of F. Seits's models and review papers in that period!).

As was remarked at this Meeting, defects were tiny objects with an enormous potential for multi-disciplinary implications. It is instructive for this purpose, to recollect the first enthousiastic steps that were taken, together with Chiarotti, to revisit the old Gyulai-Hartly effect, i.e. the question of excess conductivity in plastically deformed alkali halides. Adding simple refinements to the procedures of earlier work, novel features were quickly discovered. These, however, partly contradicted the starting picture of a reservoir of free vacancies (left behind by deformation). We soon started to develop ideas about clustering and secondary reactions, involving the excess vacancies and to plan new experiments for testing them. The whole matter then revealed complicated links with various aspects of plastic flow: it was necessary, at this point, to reconsider the "genetic" relationships between point defects and moving dislocations and to study more complex experiments, apt to correlate the excess conductivity with the glide process. Later on, this programme was accomplished by Camagni and Manara in Ispra, with their investigations of charge transport and relaxation vs. strain hardening, during steady-state deformation. The main role in conductivity was finally ascribed to stable aggregates of incipient vacancies, whose dissolution is assisted by mechanical work. These entities correspond to dislocation debris, as confirmed independently by the correspondence between the early stages of cross-glide and the yield of excess vacancy centres during irradiation.

Another line of work was in the traditional field of colour centres. After the research on divalent impurity centres, which was coming to completion, we were concerned in that period with the problem of colouration mechanisms. An original study was carried out in 1959/60, in collaboration with Chiarotti, on X-ray induced luminescence and its kinetics, as a means to probe electronic balance and defect production in irradiated alkali halides. Contributions to this phase of activity were given by G. Bonissoni and S. Ceresara as C.N.R.N. stagiaires.

This line was continued initially at Ispra, using radioluminescence to study the formation of molecule-ion complexes. Later the general experience on colour centres was progressively focussed on problems of direct concern for radiation damage (e.g., role of defect structures and secondary reactions in the radiolytic process). This activity continued throughout the sixties, with a series of studies on deformed or impurity-doped alkali halides (P. Camagni, M. Boni; collaboration with E. Sonder at Ispra).

Growth of the X-ray laboratory

In 1958 Merlini, while working in the United States, was contacted by F. Fumi and later, by C. Salvetti (Director of the centre of Ispra) with the offer to join and direct the effort for the constitution of the Solid State laboratories at the reactor site. At the beginning of 1959 he was back to Italy, starting the preparation of an X-ray section, with a diversified programme of structural investigations. A specific competence in this field was a recognized need for our group, in view of future tasks of materials research.

Merlini's experience had been formed in previous years in various laboratories that were leading centres for the development of structural diagnostics in "nearly" perfect crystals. Following a Ph., D. thesis at the University of Illinois, devoted to the annealing textures of copper and brass, he had spent two post-doctoral years with Prof. A. Guinier at C.N.A.M. in Paris. There he took part in the progress of high resolution X-ray topography, applied to the detection of small lattice bendings, or tiltings, due to the presence of dislocation walls. In this context he approached the study of dynamical diffraction, which he continued later at Berkeley, in Dr. Washburn's laboratory of the University of California.

After the middle of the 1950's, the structural characterization of imperfect solids was in full development. Shortly before, a particular landmark had been laid with the beautiful experiment of Washburn, Parker and Bainbridge which gave the first direct proof of the existence of a dislocation wall and of its motion under an applied stress. In the following years, transmission electron microscopy and X-ray topography attained sufficient perfection to make dislocation lines visible. In the meantime, the predictions of dynamical diffraction theories were having their first important demonstrations from the experiments on "anomalous" transmission in Calcite (by Borrmann and co-workers in Berlin) followed by decisive investigations of B.W. Batterman on semiconductor crystals. Progress in these fields was of course intimately linked with that attained by crystal growth technologies.

Previous practice with these developments gave a good background to the preparation of basic structural studies, which were planned for Ispra. The acquisition of complex equipment was pursued in 1959; after a short period of set up in Milano, this equipment was installed in the new laboratory and research started, with the initial collabroation of M.D. Giardina and S. Pace. Later, R. Colella joined this activity as a member of our group, followed in successive years by C. Ghezzi and others as thesis students or stagiaires.

The early phase of research (1961-66) was marked by successful investigations of the so-called Borrmann effect in Zn single crystals of high perfection; anomalous transmission was shown to accompany diffraction from the basal planes (the geometry, for which the dynamical propagation of the X-ray field is least affected by the lattice disorder, due to a favourable orientation of the dislocation lines in the h.c.p. structure). The experiments progressed with the investigations on the temperature dependence of anomalous transmission in Zn and Ge. The results confirmed the critical dependence of diffraction intensities on lattice disorder and thermal disorder, raising the point of a specific use for probing point defects in otherwise perfect crystals. Such indications opened a fruitful way to subsequent studies of radiation damage, in neutron or alpha-irradiated semiconductors.

Installation at Ispra

Throughout 1960 and part of the following year our group was busy with a variety of tasks, imposed by the installation of the laboratories. Reactivation of our past activities and the new committments of applied research required the potentiation of specific infrastructure (equipment for precision mechanical testing; renewal of spectrophotometric apparatus; extension of X-ray techniques for routine diagnostics). Particular efforts were made to raise a workshop for materials preparations, including single-crystal growth, heat treatments, etc. Preliminary planning of irradiation experiments forced us to take acquaintance of nuclear installations and techniques; part of the staff was temporarily converted to radiation dosimetry for the survey of neutron fluxes in reactor channels, that were candidates for future irradiation facilities.

Meanwhile, we had to make a certain reappraisal of our competences, in order to harmonize with the requests of a reactor centre.

Early indicatiosn by C.N.R.N. considered the utilization of a Solid State service in two closely related areas: i) radiation damage studies and ii) applied research on nuclear and structural materials. A nucleus of basic research on point defects and structural properties was to insure the scientific support for these developments. To this end our previous activities in Pavia and the experience of X-ray diagnostics, partly reoriented to the study of irradiation phenomena, offered a sufficient basis. Developments in these fields during the initial phase at Ispra have been mentioned in the preceeding paragraphs and are reviewed in Ref. 2) and 3). Theoretical support in these matters was given by G. Nardelli, associated with our group at that time.

We had in this period the assistance and the encouragement of Dr. S. Billington, Head of the Physics Division of the Oak Ridge National Laboratory (Argonne, Ill., USA) who had been called to advise on a basic programme of reactor-oriented Solid State physics. These contacts were to activate a series of links with O.R.N.L. in successive years (visiting stages of Bassani and Merlini in Argonne; collaboration with F.W. Young and M.S. Wechsler's groups; work of E. Sonder in Ispra). They also prepared the International Summer School on Radiation Damage, which was helk at Ispra in 1960, with the organizing contribution of our staff.

Our activity was conditioned, in the meantime, by other decisive events. In the course of 1959, the Italian government had decided that Ispra would become a Joint Research Centre of the Euratom Community. Nuclear installations were the first to pass under the new authority. The Solid State laboratory, formally a service of Reactor Engineering, remained with C.N.E.N. for a while, but it was destined to be incorporated into J.R.C. by the beginning of 1962. Long before this change took place, we had to make a rethinking of our scientific plans, so as to prepare for Euratom projects. Special concern was devoted to the research on Uranium compound, particularly UC, which were candidate fuels for an organic-cooled, heavy-water moderated power reactor (the ORGEL project). This laid the foundations for a number of stimulating developments. Diffraction studies, which were required at first for crystalline characterization of UC, were later extended to the observation of vibrational properties. Reflectivity techniques, aimed to investigate the metallic properties of this compound and to probe surface oxidation, opened the way to systematic competences in the field of ellipsometry.

Interest for new cladding materials accelerated the efforts to develop irradiation facilities. The engineering of a liquid-nitrogen irradiation loop, to be installed in a channel of the Ispra-I reactor, was begun in this transition period. The construction took a great deal of work in successive years (chiefly by C. Bassani).

By the middle of 1962, after joining Euratom, the activities of the original groups were finally settled on definite lines, which were to continue for many years. About one year later, W. Schule joined the laboratory, contributing to the potentiation of the research on the radiation damage of metals and alloys, which thereupon constituted another pole of activity for our group.

The advent of the new institutional frame brought an initial increase of material resources, which eventually slowed down owing to the overwhelming role assigned to nuclear technologies in the Centre. Our staff also remained fixed for a long time, with isolated exceptions. This imposed a certain bargain with our leading Departments, which were mostly interested in technological work. The situation was changed around 1970, when we merged with other specialized groups in a new Physics Division, with an independent programme of condensed matter physics.

At the time of turnover, our personnel comprised 8 scientists and 2 technicians, many of whom had been raised through University research, often utilizing the intermediate channel of C.N.E.N. postgraduate grants. The withdrawal of the Italian administration interrupted the expansion that was in progress along this line. Collaboration with University groups of Solid State Physics never ceased anyhow (the training of thesis students being a privileged ground). For all of us, it a pleasure to recollect the vivid exchange we had in those years with friends in Pavia and Milano (later on, with the Parma group) who shared with us the enthousiasms and the culture of the origins. In due course of time, these links favoured the permanent association of the Ispra unit with the structure of G.N.S.M.

(I) The Italian Atomic Energy committee of that time (later, C.N.E.N.)

(II) A review of the research in Pavia during the 1950's is given in the communication by G. Chiarotti. Contributions by members of the C.N.R.N. group appear in Ref. 1 of the present paper.

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THE BEGINNING OF NEUTRON DIFFRACTION IN ITALY [a] [b]

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Since the time of James Chadwick, neutrons have been popular among Italian physicists. As Emilio Segre recollects in the *Enrico Fermi - Note e memorie* (collected papers), immediately after the discovery of the neutron, Fermi realized that the research on artificial radioactivity, undertaken by I. Curie and F. Joliot using charged particles as projectiles, could be expanded tremendously by using neutrons instead. In his Nobel speech on 10 December 1938, Fermi states: by neutron bombardment "a systematic investigation of the behaviour of the elements throughout the periodic table was carried out by myself with the help of several collaborators, namely Amaldi, D'Agostino, Pontecorvo, Rasetti and Segre".

In the middle 1940s, as soon as 'intense' neutron fluxes became available at the Argonne pile, Fermi's interests inevitably focused on aspects of the physics of neutrons, and physics by neutrons, which had been assigned low priority in the drive towards wartime objectives.

When in 1955, a year after the death of Fermi, the Italian Government decided to install a CP-5 type research reactor at Ispra, Edoardo Amaldi, the then vice-president of what was then the Comitato Nazionale per le Ricerche Nucleari (CNRN), could not remain indifferent to the beautiful physics which was being developed using reactor neutrons at the Argonne, Oak Ridge, Brookhaven, Harwell and Chalk River laboratories. In 1957, while the Ispra reactor was being constructed, Amaldi decided to form a group with the objective of building a crystal spectrometer to explore the structure and properties of condensed matter.

I cannot refrain here from disclosing a personal recollection. When Amaldi, my Maestro, invited me to contribute to the research programme which he was heartily supporting, I happened to be engaged, both as a CNRN researcher and as a resident research associate with the physics division of the Argonne National Laboratory, in the experimental determination of the half-life of the neutron decay, using a diffusion cloud chamber. At that time, while I was there, I was fascinated by the American way of work and life, to the point at which I had reached the decision to emigrate to the United States: but Amaldi's determination was inflexible!

I sailed back to Italy. Once in Rome, I shared an office in the Institute of Physics of the University, with my friends and colleagues Antonio Paoletti (who has kindly helped me to collect these memoirs) and Francesco Paolo Ricci. Around the end of 1957 the group

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[a] This paper has not been presented to the Meeting. However, it is published for sake of completeness.

[b] This contribution has been first published under the title *'Start-up' in Italy* in "Fifty years of neutron diffraction", G.E. Bacon Editor, Adam Hilger, Bristol (1986)

was strengthened by Marcello Zocchi and Antonio Santoro, two chemical crystallographers, who added their scientific interests to our research programme. Soon we realized that a mechanical engineer was needed to help us to write the specifications for the spectrometer, to design it, and to supervise its construction by Nuova San Giorgio in Genova and its installation and alignment at the Ispra reactor beam. Our need was recognized as sound and Francesco Marsili was promptly employed by the CNRN. His stimuli and his work during the early years of neutron diffraction in Italy proved invaluable. We benefited also from the help of professional electronic physicists, like Umberto Pellegrini and Elio De Agostino.

After September 1957, the group at Rome devoted several months to a systematic scanning of the bibliography, and to a critical analysis of the effect of the collimator widths on the resolution and luminosity of crystal spectrometers. This analysis was originally undertaken both to optimize the performance of the spectrometer, while dreaming of it, and to answer insistent requests by Marsili. Our results were confirmed later by C.G. Shull and B.O. Loopstra, and in the early 1960s they were extended to the case of the three-axis spectrometer. I am told that our work of those years is still being utilized as a basis for the deconvolution of the intrinsic line widths from the measured intensity of the scattered neutrons in experiments of conventional diffraction, elastic diffraction (I) and inelastic scattering.

While the design and construction of the spectrometer and the installation of the Ispra neutron source proceeded, the physicists of the group were offered by the CNRN the privilege of working for periods of the order of one year in the most important North American laboratories.

Paoletti went to Brookhaven, Caglioti to Chalk River and Ricci to the MIT.

At Brookhaven, Paoletti worked with Robert Nathans in the field of magnetism. At the polarized neutron spectrometer Paoletti collaborated initially on the determination of the distribution of the magnetic moments of iron on the different sites of the ordered alloy Fe Al. Subsequently, again with Nathans, he determined the magnetic form-factor of the 3d electrons of cubic cobalt, and discovered an important deviation of the distribution of the magnetic electrons from the spherical symmetry. This work marked the beginning of an intense experimental and theoretical activity on the detailed distribution of the magnetization density in solids.

At Chalk River, Caglioti worked with Bert Brockhouse in the field of the dynamics of atoms in crystals. The experimental work on neutron inelastic scattering in 1959 had just moved from NRX to the more intense NRU reactor, and the 'constant Q' method had just been invented. Brockhouse was a real Cicerone to all the subtleties of reciprocal space-time, for all the researchers converging to his group from Canada and from all over the world. With Brockhouse, Arase, Rao, Sakamoto, Sinclair and Woods we measured the phonon dispersion relations of lead at several temperatures. We thus derived the interplanar force constants and, furthermore, we had access to the intricacies of the electron-phonon interactions responsible for the Kohn anomalies related to the caliper dimensions of the Fermi surface in lead.

At Cambridge, Ricci worked with Shull on theoretical problems and experimental methodologies: unfortunately the MIT reactor was not ready yet; but nevertheless all of us in the group benefited from the experience Ricci gained from Shull at the time.

Meanwhile, back home, the situation was changing, Ispra became a joint research centre of the CEE, and the then Comitato Nazionale per l'Energia Nucleare (formerly CNRN, now ENEA), had decided to build its centre for nuclear research near Rome at Casaccia, and to install in it a Triga Mark II research reactor.

A bifurcation occurred: as originally planned, Caglioti, Ricci, Santoro and Zocchi moved to the CNEN Laboratory of the Euratom Centre of Ispra, while Paoletti and Marsili installed a polarized neutron spectrometer at the Triga source of Casaccia.

In 1960 Italy was a leading country on the international map of neutron spectrometry: the first European three-axis neutron spectrometer for inelastic scattering and the first European polarized neutron spectrometer were operating in Ispra and in Casaccia respectively. Ispra and Casaccia attracted a number of distinguished visitors from abroad. The friends we made at that time have helped our collaborators, directly of indirectly, to preserve the neutron tradition in Italy: like vestals, Franco Rustichelli and Filippo Menzinger are still blowing the fire of neutron research.

In the 1960s, our research programmes were naturally being developed in accordance with the specific competence previously acquired. In Ispra phonon dispersion relations for acoustic and optic modes in zinc at several temperatures were determined, and several studies on crystallographic and liquid systems (bromine, zinc and gallium) were performed using both conventional and elastic diffraction. In Casaccia an ample programme was developed on the distribution of magnetic moments in ordered ferromagnetic alloys (Co-Pt, Fe-Pd, Fe-Si, Mn-Ni). Furthermore other neutron scattering groups were being formed, around other research reactors, namely at the Centro Studi Nucleari Enrico Fermi of the Politecnico di Milano, at the SORIN in Saluggia and later at the CAMEN in Pietrogrado, near Pisa.

Suddenly, during midsummer 1963, a major shock - il caso Ippolito - shook the CNEN. That remains an enigma, for many of us marking the beginning of the end of an unrepeatable and stimulating scientific and human experience.

NOTES

(I) Elastic diffraction, performed for example by a three-axis spectrometer whose analyzing crystal is set at the impinging neutron energy, is conceptually different from conventional (two-axis) diffraction.

In conventional diffraction, contributions are collected from all diffracted neutrons, irrespective of their energies, so that every single neutron takes a sort of instantaneous picture of the system. In elastic diffraction, on the other hand, contributions are taken only from outgoing diffracted neutrons whose energies coincide with that of the incident neutrons within the experimental energy resolution, E, of the (three- axis) spectrometer: every single neutron thus takes a sort of time exposure of the system over a time t of the order of 8h ln 2/ΔE, where h is Planck's constant.

Although conventional and elastic diffraction are basically different (especially when looking at liquids or hydrogeneous solid substances for example), a sloppy semantic superficiality still induces professional researchers to refer to *conventional* diffraction of neutrons or X-rays in terms of *elastic* diffraction. The present occasion is perhaps the last important one for me to fight such a misconception!

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EXPERIMENTS ON LIQUID AND SOLID INERT GASES AND ON SUPERCODUCTIVITY IN GENOA

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When, in 1954, I came back to Italy from the United States, I was faced with the option: either to stay in Rome, under Professor Amaldi, in order to continue my collaboration with Careri and his group, or to go to Genoa, the residence of my family. At the University of Genoa the Physics Institute was very poorly equipped, but Pancini and Borsellino had recently won a chair there and they wanted to transform the place into an active research center. It was a hard dilemma. After a few months spent to make up my mind, I accepted the second choice, since I became convinced that, under the direction of Pancini, I had a good chance to start a new independent research laboratory on my own. You should remember that Pancini was a firmly convinced supporter of the idea that every true experimentalist had to build his own equipment practically from scrap and this was a sort of challenge to me. It must be said that Pancini was setting up an excellent machine shop and a good electronic laboratory.

In the second half of 1954, with little money, I started to set up in Genoa a laboratory in the field of molecular physics. The main goal was to build a mass spectrometer having high sensitivity, in order to study mainly isotope fractionation processes both in nature and in the laboratory. This research program was the continuation of that carried out in Chicago in 1952-53. I should mention that I had a doctor degree in chemistry and that in Rome I had taken a second degree in physics, working on nuclear physics applied to geology.

Every single piece of the spectrometer was designed and built completely inside our Institute, including the basic electronics. Only the deflecting magnet was committed to Ansaldo - San Giorgio and given to us without charge. Three people collaborated with me, namely Sanna, an electronic engineer, Reinharz, an austrian physicist and Vallauri, who became afterward my wife. The technicians in the shop were very helpful and dedicated.

About two years and a half were spent to complete the construction of the mass spectrometer; its performance was finally very good, somewhat better than that of the instruments I had used in Chicago. But this is not the whole story. I told you that I had little money, mostly from INFN, something like five million lira, if I remember correctly. This sum was not sufficient to cover all the expenses. But we found a way to overcome the difficulty. At that time I met Professor Tongiorgi, who was interested in establishing in Pisa a center of nuclear geology. He was very interested in having a mass spectrometer similar to ours for studying paleotemperatures and stable isotope fractionation in nature and he had more money than us. So it was decided to build our mass spectrometer in three identical copies and sell one of them to Tongiorgi's laboratory. The financial problem became thus much less serious.

At the same time my original idea of studying isotope fractionations in nature was given up (or better transformed into a collaboration with Tongiorgi), while our own research program pointed toward measuring isotope fractionation in phase equilibria. It was at this time of my scientific career that my interests became rather exclusively directed to physical problems.

Starting in 1957, experiments were carried out in Genoa in order to measure the single-stage fractionation factor in the vapor-liquid equilibrium of simple systems. Among them were the inert gases argon and neon, for which the simplicity of interatomic forces gave hope for a satisfactory theoretical interpretation. The measurements were carried out in a rather wide temperature range around the boiling point of liquid nitrogen and, for neon, around that of liquid hydrogen. The need of cryogenic liquids introduced us into the field of low temperature physics. Several steps were undertaken: an air liquefier, producing liquid nitrogen by distillation, was bought; a collaboration with the growing low temperature laboratory in Frascati was undertaken (the talk of Careri concerns this facility); and a visit to Leiden was made in order to learn how to handle liquid hydrogen and liquid He and how to build cryostats.

Another important event concerning my future research work should be mentioned. In the summer of 1957 the first Varenna school on solid state physics (promoted by Fumi and Polvani) was held. There I was faced for the first time with the wide problematics of crystalline bodies and I had the fortunate occasion to meet some of the best solid state physicists working in USA and in Europe. There I could hear from the direct voice of the authors the rapid progress in the fascinating field of the structure and collective excitations of different types of solids.

For the above described reasons, the year 1958 became a crucial year not only for my personal scientific interests, but for all future research work in Genoa.

First it was decided to start, in parallel with the isotope work, an experimental study of solidified inert gases. Money and people were needed. They were found with the help of the European Research Office of the U.S. Army, that at that time was carrying out (together with the Navy) a policy of sustaining fundamental research in Universities and government research laboratories, allowing also the payment of research people. Second, it was decided to set up a low temperature laboratory for doing work at liquid He temperatures; such facility was needed for carrying out the thermal conductivity measurements on solid argon, but we had already in mind to extend our interest to other low temperature properties of solids, particularly superconductivity. Financially, we had some support from the "Comitato per la Fisica" of CNR, while INFN was involved by giving us laboratory technicians. I was lucky to have three of them, all very active and helpful.

It may be useful at this point of the talk to have a look at the titles of the doctor degree thesis, in connection with our experimental work. They were two in the course of academic year 1957-58 and six in the course of year 1959-60 (Table I). You surely recognize several of the names of the people involved. From the titles of the thesis completed in the academic year 1959-60, you can see that in 1959 we were fully involved in solid state physics at low temperature.

We learned how to design and build different kinds of cryostats, how to recover the evaporated helium (a complete plant for helium recovery was built with excellent results) and, in particular, how to make good use of the low temperatures in the experiments (e.g. reducing the noise, gas purification, cryogenic pumping, etc.) a policy that remained valid through the following years.

Within 1962, the main work on the isotope fractionation was accomplished and from that time on the laboratory was mostly involved in studying properties of solids at low temperatures.

I did not find records about the budget of our little research group from 1957 to 1959, but I think it was of the order of five to ten million lira per year, and became fifteen million lira in the financial year 1960. The group was made of three to five research people and three technicians. More detailed accounts concerning the period 1960-1963 can be found in "I gruppi di Fisica della Materia INFN-CNR": Suppl. Ricerca Scientifica 34, vol. 3, p. 203 (1964).

I will now give separately short accounts about the three different research lines undertaken in the Genoa laboratory at the end of the fifties namely isotope fractionation in phase equilibria, properties of solid argon, and first experiments in superconductivity.

Isotope fractionation in phase equilibria

I recall to you that the small differences in thermodynamic properties of different isotopic species is a quantum effect (obviously the differences can become larger at low temperatures for light elements like helium and hydrogen). Classically, no difference is expected. As far as isotope effects in phase equilibria are concerned, the experimental method used until the fifties was to measure the properties of enriched or separated isotopes, if available. Around 1950 Professor Urey, a specialist of isotopes and the discoverer of deuterium, became interested in measuring accurately the isotopic fractionation occurring in natural processes. His main interest was to determine a paleotemperature scale by measuring the abundance of oxygen stable isotopes in shells. He established a laboratory in Chicago and supported the construction of a differential mass spectrometer having a sensitivity of about one part per million in the measurement of isotopic abundances (for instance the abundances of O^{16}, O^{17} and O^{18} in oxygen).

I went to Chicago to work in Urey's lab in 1952 and studied various problems, the main work being the determination of abundance of deuterium in meteorites. I had already done some work on natural isotope abundances in Rome, where Careri and I had built the first mass spectrometer made in Italy.

During my staying in Chicago, I realized that, by using a Urey type high sensitivity mass spectrometer, the isotope fractionation in chemical equilibria could be measured with good accuracy without the need of enrichment, provided that one of the isotope was sufficiently abundant (for example N_{15} in nitrogen, A_{36} in argon, etc.). Therefore, when I started my work in Genoa, I thought to build a mass spectrometer having enough sensitivity both to measure isotope variation in nature and to accomplish this kind of experiments.

Once the spectrometer was built, in 1957-1958 the first measurements of the isotopic fractionation in vapor-liquid transition at equilibrium were performed in collaboration with Scoles and Vallauri. The measurements were dealing with A, N_2, and O_2 below the boiling point [1]. The apparatus was made completely out of glass. The fractionation factor was measured with an accuracy of about 2%, better than that obtained by working with enriched isotopes.

Later (1959), in collaboration with Casanova and Vallauri, a more thorough study was made using liquid Ar and Ne: the isotopic fractionation was measured in a wider temperature range, approaching the critical point [2]. The apparatus was more sophisticated, partly made of metals to sustain the higher pressure needed. The apparatus was designed to operate both at liquid nitrogen temperatures (for argon) and at liquid hydrogen temperatures (for neon). The last experiment was carried out in Frascati, using the facilities of the cryogenic laboratory established by INFN. The fractionation occurring between solid argon and its vapor was also measured, starting 1960, using a steady flow method, again with Scoles and Vallauri [3].

These studies were particularly interesting since, using inert gases, a comparison with the theory appeared to be feasible, since the intermolecular forces were well understood. A first theoretical study of the fractionation in solid-vapour equilibrium was made in 1959 with the collaboration of the group of Milan [4], using an anharmonic model devised by Henkel. This work was carried out by Casanova, Fieschi and Terzi.

Just afterward, the general theory of isotope fractionation in phase equilibria was faced. The statistical mechanical basis of the problem was already set down by the work of Wigner, Mayer and others, by using a development of the partition function in power of $(h/2\pi)^2$, which is accurate enough for the small isotope effects observed for argon and neon. An improvement over the old theory was accomplished by Casanova, Levi and myself [5,6,7], with the result of expressing the single stage fractionation factor

$$\alpha = (N_1/N_2)_A/(N_1/N_2)_B$$

in the form

$$\ln \alpha = h^2/(96\pi^2 k^2 T^2)\ (1/m_1 - 1/m_2)\ [<\Delta^2 U_B> / <\Delta^2 U_A>]$$

where the subscript A and B refer to the two phases in equilibrium.

The recognition of the importance of the quantity

$$<\Delta^2 U> = <\delta^2 U/\delta x^2 + \delta^2 U/\delta y^2 + \delta^2 U/\delta z^2>$$

where U is the total potential energy, the average being made over the classical configuration space, was a significant progress in the field. We recall briefly that $<\Delta^2 U>$ is negligible for a dilute gas, while it is proportional to $(\mu_1 - \mu_2)$ for a harmonic solid, where μ is the mean square frequency for the lattice vibrations (a correction must be applied for anharmonic effects), and is equal to

$$4\pi\rho \int_0^\infty g(r)\ (d/dr)\ (r^2\ du/dr)\ dr$$

for a simple liquid g(r) is the radial distribution function, ρ the density, and u the two-body potential).

The expressions given above show that the fractionation factor α for simple liquids and solids in equilibrium with the vapour is related the an averaged force constant, having simple expressions which may be compared with other thermodynamic properties of the condensed phase.

The theory was applied to our experimental data on liquid argon and neon, resulting thus in valuable information for the progress of the theory of liquids.

Properties of solid argon

The experiments on isotope fractionation carried out for neon and argon gave us confidence with the handling of these gases and of their condensates at low temperature. We were in a good position to start measurements on other properties of solidified inert gases. These measurements were seen with favour by theoreticians since the simplicity of intermolecular forces allowed them to perform more straightforward computations and thus compare with more confidence their results to experimental measurements. One of the problems was to check the validity of the theories on transport properties that were developed at that time. In particular the problem of self-diffusion in solids was receiving attention. Fieschi, Nardelli and Repanai in Milan were working in this field [8].

On the other hand we became convinced that the measurement of self-diffusion in solid argon, although very difficult, was feasible. I must point out that, while single crystals of metals or ionic crystals are easily produced (and in fact plenty of diffusion measurements were available at that time for these solids), single crystals of solidified inert gases are much more difficult to grow, because of high vapor pressure, low thermal conductivity and low working temperatures. As a consequence, around 1960, only a few attempts had been done to prepare single crystals out of solids bound by van der Waals forces.

In collaboration with Milan (M.Beltrami) we started to learn how to prepare single crystals of solid argon; it was a very hard task, but the preliminary experiments were encouraging and gave us confidence that we should be able to overcome the difficulties. I already told you that, in order to get money and research people, we were helped by the European Research Office of the U.S. Army. At the beginning of 1960 a contract was signed having the title: "Self diffusion in solid argon". Two people were hired with that money, Dr. De Paz, a chemist, and, later on, Dr. Berne', a physicist from Milan.

The experiment with single crystals of solid argon proved to be much more difficult than we were expecting [9]. Single crystals of argon were eventually obtained by the Bridgman method, but this took from us a lot of patience and endurance. What proved to be really difficult was to keep the surface of the crystals steady during the diffusion of the tracer, which was A_{36}. The story in the following: at the temperature where the diffusion coefficient is sufficiently high to be measured, the vapor pressure of argon is very large, so that it was difficult to prevent, during the long diffusion time, some argon vapour to distill from one place to another of the crystal surface. We were eventually able to obtain significant figures for the diffusion coefficient $D=D_0\exp(-Q/RT)$ and its temperature dependence, but the errors were exceedingly large. In order to overcome this handicap, De Paz devised a different method of measuring D, by making controlled polycrystalline layers of argon of different thicknesses and by carrying out diffusion of A_{36} over them. I will not go into details. We could finally come out with reasonable values of the activation energy Q, while the preexponential factor D_0 was given with a rather poor accuracy.

Similar difficulties arose in the measurements of thermal conductivity in single crystal argon rods. I will not give the details of this experiment. They are all contained in Ref. 9.

In conclusion, although we were somewhat unhappy with the results, the experiments with solid argon made us to learn a lot of physics. The reward for the long time spent for doing these measurements is that nobody succeeded later, as far as I know, to produce data better than those we obtained 25 years ago [10].

Superconductivity

As soon as it was decided, at the end of 1958, to carry out research at liquid He temperatures, we thought that superconductivity should be the field where to start working first. Experimental research in superconductivity was on a big wave, excited by the success of Bardeen, Cooper a Schrieffer theory; a lot of laboratories in the world started to do new experiments in the field and the results coming out were very exciting (as it is again now).

We worked hard in Genoa to set up the first cryostats. We were helped by the people of the cryogenic laboratory in Frascati and we received the liquid He from them. We had also much help from the visits of B.B. Goodman and of E.A. Lynton, which gave several seminars on experimental aspects of superconductivity. Later H. Rosenberg gave a series of lectures on different problems of low temperature physics, which were a great aid to our experimental work.

We were the first in Italy to study superconductivity. The experimental work started in the year 1960 when three students were given doctor degree thesis directed at that purpose. The students were, as already shown in Table I, Gallinaro, Ciani and Rizzuto. The work they did in their thesis was preliminary, but was determinant for us to learn how to deal with the subject and how to proceed alon successful lines of research.

Gallinaro was involved in new methods of studying the transition curve of superconductors in a magnetic field Ciani studied the problem of the effect of impurities on the superconductivity of pure metals, while Rizzuto was given the task of building a He3 cryostat, which was considered to be a "must" for doing competitive research in the field.

From these thesis evolved the subjects which were subsequently the clue of our research in the following years, namely

a) The suppression of superconductivity by magnetic impurities. Lynton and Goodman aroused our interest in the effect of impurities on the superconductivity of pure metals. On the other hand we were in contact with the "Istituto dei Metalli Leggeri" in Novara, where Tiziano Federighi was involved in pure and applied research on aluminum and aluminum alloys; he was ready to furnish us with specimens. Gallinaro and Rizzuto had set up an excellent method for measuring accurately superconducting critical temperatures and transition curves. Finally, owing to the work of Rizzuto, the He_3 cryostat was performing very well, reaching a temperature of 0.3 K.

All these reasons pushed us to carry out an experimental study on the effect of transition metal impurities on the critical temperature of non- transition metals. The problem had been not yet studied in detail. The aim of the experiment was to understand the mechanisms by which superconductivity was suppressed. We worked first with aluminum alloys. It was found that the superconducting transition temperature Tc of Al decreased rapidly as the concentration of Fe, Mn and Cr was raised [11]. This decrease is partly due to smoothing out of the gap anisotropy, but is also due to the formation of localized virtual states [12]. Subsequently, we studied the effect of the same impurities on Zn [13]; it became clear that when localized magnetic moments are present (this is the case for dilute alloys of Mn and Cr in Zn), the decrease in Tc is very strong, amounting to a few hundred degrees kelvin per atom percent.

The experiments were carried out for several other elements and impurities [12] and were concluded in 1963. We were able to clarify the effects of transition metal impurities on the superconductivity of non transition metals. The largest effect is present when localized magnetic moments are formed.

b) The penetration and migration of magnetic flux in type- II superconductors. The experiments were carried out by Gallinaro in superconducting tubes (hollow cylinders) of Pb-Bi alloys, by changing the magnetic field applied parallel to the axis of the tube. Since there is no Meissner effect, but rather a discontinuous movement of flux threads across the wall of the tube, we observed jumps in the magnetic field measured inside the tube. We had hope to detect a minimum value of these flux jumps, which should correspond to a quantized flux line. We did not succeed in this task, but a series of interesting curves, showing the way by which the field enters or leaves the samples, were obtained. These results were presented in 1963 at the SIF meeting, but never published, since a complete study of the phenomenon had appeared in the american literature (Kim et al.).

The single quantized flux threads were detected in Genoa much later (in 1965) by an induction method in thin cylindrical specimens of Pb-Tl, having radius comparable with the penetration depth (a few microns) [14], in close connection with the theoretical work by Bobel and Ratto.

Final remarks

I would like to conclude this talk by making a few general remarks on the work done in the period 1954-1960. These remarks may be common to what has happened in other research laboratories but they are worth to be mentioned.

1) The choices made in the research lines took into consideration the possible evolution of research. In other words experiments were started non only on the basis of the immediate interest of the research worker, but also by taking into consideration the possibility of future evolution of the experimental research field chosen.

2) The technological aspect of the newly opened research lines was given a primary importance. To make two examples: when we decided to enter the field of solid state physics, we thought immediately of making use of low temperature techniques. Similarly, among the different solids which could be studied, we choose solidified inert gases, which were a challenge due the difficulties involved in the preparation of single crystals.

3) Although quite a long time was spent in the effort of establishing new experimental techniques, the use of the criteria reported under 1) and 2) was always rewarding. That is, the experience accumulated in those years was instrumental for the experimental progress made later. I make again an example: our familiarity with low temperature techniques was one important ingredient for planning and carrying out in 1972 atom scattering from surfaces at a level that became immediately competitive on the international scale.

I want finally to emphasize the importance of building up in the laboratory the significant parts of the apparatuses needed for experiments. This attitude is opposite to that of buying most of the instruments from which the apparatus is made. The first philosophy is the winning one, when one tries either to establish a new experimental laboratory or to maintain the high level of the existing one. In this way one is able to maintain a tradition of skill and excellency in the experimental research group.

I believe that the experience acquired in 1954-1960 in building high vacuum equipments, in handling cryogenic fluids, in making cryostats, and in general in constructing a large part of our apparatuses still has some effect in the good level of experimental capabilities at Genoa in the present days.

TABLE I

Titles of the doctor degree thesis in the period 1957-60

GIACINTO SCOLES (laurea in chimica)

Tensione di vapore di alcuni liquidi isotopici semplici (A, O_2, N_2) (1957-58).

GUALTIERO CASANOVA

Dipendenza dal peso atomico di alcune proprietà termodinamiche (Teorema degli stati corrispondenti: sua verifica con gli effetti isotopici) (1957-58).

EMMA ANCONA

Pressione di vapore di liquidi isotopici costituiti da molecole bioatomiche (O_2, N_2, CO). (Tra il punto triplo e il punto critico) (1959-60).

ANGELA MARIA PRIORI

Dipendenza dalla temperatura degli effetti isotopici (1959-60).

GAETANO GALLINARO

Studio della curva di transizione dei superconduttori con metodi in corrente alternata (1959-60).

SERGIO CIANI

Effetto di impurezze controllate sulla temperatura di transizione e sulle proprietà magnetiche dei metalli superconduttori (1959-60).

CARLO RIZZUTO

Un criostato ad He^3 con ampio spazio sperimentale per misure di superconduttività (1959-60).

NICOLA SACCHETTI

Anomalie della resistività dei metalli a basse temperature (1959-60).

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EXPERIMENTS ON IONIC SOLIDS IN MILANO

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The average amount of knowledge on solid state physics when I graduated (1950) was limited to some phenomenological approaches acquired in the physics basic course. The experimental training of an Italian doctor in physics was also negligible, except for the experience eventually gained working on an experimental thesis. The research tradition, in most Universities, was in nuclear physics and cosmic rays; my thesis was a phenomenological model of geomagnetic effects of cosmic radiation. Solid state physics was either unknown or considered as being an application field worthy of little interest and prestige.

In 1952 prof. Piero Caldirola who was open minded and opposed to the "monocultura", encouraged me to work in the field of what is now called "Structure of matter" and suggested that I study under the direction of prof. Fausto Fumi, who had just returned from the U.S.. A small group of theoretical physicists gravitated around Fumi but still in 1955, when I had just come back from the University of Leyden, with a Ph. D. on irreversible thermodynamics, our cultural level was low, we were very busy solving the problems of Kittel I, and were reading our "Bible": the textbook by Mott and Gurney, and our "St.Paul's Letters", the famous review papers by Seitz, perhaps mislead by the apparent simplicity of these works. Still not prepared to fully understand the deeper implications of the field, we were fascinated by the alkali halide crystals as model systems for studying the properties of the lattice imperfections in insulating crystals. I still remember the great impression made upon me by prof. Mott's and prof. Seitz's visits and lectures, and specially their patience and kindness in listening to our early model of some color centers or of some optical conversion. Prof. Fumi was our focal point during these early years, not only when he was actually present in Milan, but also when he sent us his advice and suggestions from abroad.

Around 1958 we started receiving some financial support from the CNR and INFN and were planning to start some experimental activity using the optical absorption technique. Prof. Caldirola gave us his moral and practical support; he was a member of the Physics Committee of the CNR and provided us with the money for the first experimental equipment, a Beckmann DU spectrophotometer. We also started building an equipment for growing alkali halide crystals, using techniques known in the Middle East in the IV Millenia B.C.: we were actually forming and baking clay for the wall of the oven. The first attempt failed, the oven fell apart, but soon we were able to grow reasonable good samples, pure and doped: I still remember how happy we were, when we could extract our first nice single crystals. The qualitative results of the first experiments on the absorption spectra were presented at the annual meeting of the SIF, but we had to wait a year more before being able to complete the first short note - on the conversion induced by X-ray irradiation on the absorption bands of additively colored KCl.

We not only had to obtain financial support (for many years we had to pay for the subscription to some of the most important periodicals ourselves) but we also had to stake out a place for ourselves. The first success was reached when we obtained a 12 square meter room, but there were eight of us, so we had to order very small desks, 110x60 cm^2. One of the theoreticians, a young lady studying molecular states, was in our small office and I remember her incessant and loud chatter; later on she married a silent German physicist and, as far as I know, they are still doing pretty well.

At the beginning, some of the equipment for the growth had to be placed in a dark and damp basement, but later on the situation improved.

At the end of 1960 the available equipment allowed us to work on absorption and emission spectrophotometry, thermoluminescence and ionic conductivity, down to L.N.T., on crystals colored additively or by X-ray irradiation. The first cryostat, made in the workshop of the Institute, was not practical and very heavy, but soon, with the help of projects provided by foreign laboratories, we improved considerably; the vacuum leaks had to be detected by looking at the soap bubbles or at air bubbles from the plunged equipments. Still the budget was limited and the failure of a phototube was an event comparable to a calamity. None of us had had previous experience; the whole experimental work of assembling the equipment was carried on by good and dedicated 20 years old students: Baldini, Dalla Croce, Cappelletti, Oggioni, Bucci, Podini, Segre, Criscuoli, Giudici, Colombo, Giorcelli; a young graduate at Pavia University, Giorgio Spinolo, joined the group in 1961, a chemist, Maria Beltrami and a very skilled technician, Mario Scalvini, in 1960. Some of them now are University professors, others have positions of responsibility in industry.

From some of the early experiments we could obtain mainly qualitative results, interpreted through plausible models, on subjects such as: color center conversion due to X-ray irradiation, electron traps generated by plastic deformation, bleaching of F and Z_1 centers due to photostimulated hole capture.

Sometimes we were able to single out problems of wider interest, but we were not able to handle them efficiently, either because of inexperience or because of a limited experimental set up. One example is the problem of surface states, another one is the radiative exciton decay. The approach to the first one was very naive, to study the thermoluminescence and the EPR of X-irradiated fine powder, in order to maximize the surface-volume ratio and to detect eventual surface traps. The results were confused, probably affected by the formation, at the surface, of unidentified molecular compounds due to absorbed gas (our vacuum equipment was absolutely insufficient) and were never published. In the second case we started from the hypothesis that a fraction of the large amount of electron-hole pairs created by secondary ionization induced by the high energy X photoelectron would bind into an exciton before returning to the ground state. We actually obtained a strong u.v. intrinsic emission, under steady X ray irradiation of single crystals, the same designated by Teegarden and Weeks to the recombination of free electrons and trapped holes, but we were not able to assign it to the decay of the self-trapped exciton. The problem was solved a few years later by Kabler and others.

Now I would like to turn to the research which has given satisfactory results: the photostimulation spectrum of thermoluminescence and the ionic thermo-conductivity. In the first case we obtained an extension of preexisting methods, suitable for studying the mechanism of the thermal glow; in the second one we developed a new technique for studying the thermally activated reorientation of dipolar imperfections. Both methods are relatively simple, from the experimental point of view, but very accurate and suitable for the purpose they were intended to be used for. Nowadays the first of them is no longer of interest, because there are more sophisticated techniques for studying defects in insulators; the second was widely used in many laboratories for many years and is still useful. I shall describe them in some detail:

a - It is known that thermoluminescence (TL) from crystals irradiated with ionizing radiation and then heated, is a difficult phenomenon to interpret; in fact ionizing radiation produces, in principle, many effects, such as: building into the bulk of the sample hole and electron traps, hole and electron emitters, any kind of color centers, and filling all kind of traps with free carriers of both signs. In order to simplify the picture one has to investigate separately the process of trap filling with a given type of carrier, and this can be achieved by means of photostimulation with light whose wavelength is absorbed by a color center of known nature: a sample is X-irradiated at a higher temperature T_A, then cooled in the dark to a temperature T_B and subsequently illuminated by a selected monochromatic beam of wavelength λ. Empty traps, created at T_A by X-rays, are filled at T_B with carriers excited by the light from color centers, either F- or V- type. The TL run is performed in the temperature range T_B-T_A. A difficulty inherent in this type of experiments is the following: some of the color centers have a ionization quantum yield orders of magnitude lower than others, therefore, illumination in the spectral range of absorption bands which are nearly undetectable (for instance the L bands), gives a large number of free carriers, while clearly defined absorption bands could give a negligible contribution. In order to overcome this and other difficulties, we suggested that one should perform a complete stimulation spectrum, which is obtained by means of many subsequent TL run: each time the (low intensity) incident light (Fig. 1) is slightly changed. By comparing the stimulation spectrum - taken into account the proper corrections - with the absorption spectrum and with the photoconductivity spectrum, one can make the proper assignment on the nature of the traps. Fig. 2 shows a nice correspondence between the TL stimulation spectrum and the absorption spectrum for one glow peak, and with the photoconductivity spectrum for a second glow peak. The first kind of trap can be identified as an F' center, and it is shown that it can be filled also by tunneling from the first excited state of the F center. Working along these lines one can also easily study the selective photo-depopulation of traps. Glancing through a recent book on thermoluminescence (S.W.S.McKeever, 1985) I was surprised to find out that this method is still extensively referred to.

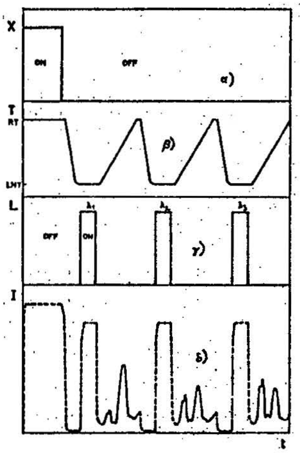

Fig. 1 Schematic diagram of the procedure for obtaining stimulation spectrum: (α) x rays; (β) temperature; (γ) light; (δ) emission.

b - The second technique, ionic thermoconductivity, was proposed by C. Bucci and myself and extensively developed by R. Capelletti. It can be better understood in the framework of the properties of electrets.

Electrets. Dielectric solid materials can undergo physical treatments which induce a quasi-permanent electrical charge. This means that the charged state is not an equilibrium one - as in ferroelectrics - but that it lasts for a relatively long time without appreciable decay, under appropriate conditions. Early findings of this property date back to the pre-history of science, namely from the observations of the attractive electric force exerted by rubbing amber or glass (Thales, VI Century B.C.).

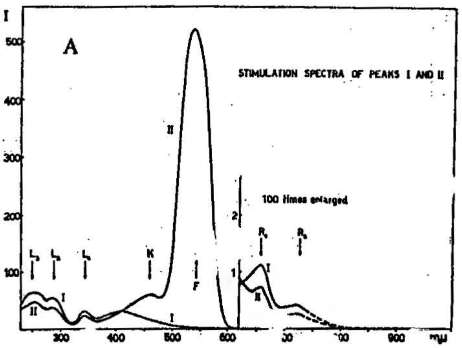

Fig. 2A Stimulation spectra of peaks I and II (the dashed region shows only the rough behaviour of the spectrum). The position of the electronic absorption bands is also shown (I in arbitrary units).

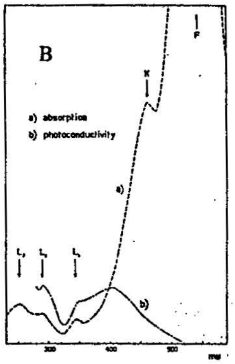

Fig. 2B (a) Absorption spectrum, as reported by Lüty ; (b) photoconductivity (stimulation spectrum) as reported by Wild and Brown.

Nowadays the field is quite extended, due also to the practical interest in application of electrets as transducers, for electrophotography, etc.. . It is recognized that perhaps in every dielectric material, within an appropriate temperature range, one can induce electrical charges by some type of treatment: by rubbing with another dielectric, by cooling in an external electric field, by an electrical discharge, by an electron beam etc.. . Charge storage is a complex phenomenon and can be due to non-equilibrium distribution of electrons or of ions shaped as a surface charge, a space charge or a bulk dipolar polarization. The same can be said of the charge decay. It turned out that the last case is by far the most suitable for careful quantitative studies, although it is not the most important for applications.

The ionic thermoconductivity technique. The wide knowledge of the physical properties of imperfections in alkali halide crystals, and particularly of their conductivity and dielectric behaviour, provided the basis for the development of another technique, suitable for studying dipolar imperfections. This technique, which we called ionic thermoconductivity (ITC), is based on the possibility of inducing a weak thermo-electret state into alkali halide single crystals containing a small concentration of dipoles, and of studying the thermally activated release of the dipolar bulk polarization in great detail. This is possible and easy since the systems under study are much simpler than the standard electrets: model systems, as widely accepted. Working along this line, considerable progress has been made also in the understanding of the physical properties of bulk electrical polarization of simple electrets. Since the introduction of ITC as a specific mean for the study of imperfections in ionic crystals, studies of the charge decay caused by heating an electret at a constant rate were widely and independently developed; electret researchers usually call the technique Thermally Stimulated Discharge (TDS).

Ionic thermoconductivity essentially consists of the measurements of the displacement current which flows in absence of any external electric field when a crystal, previously polarized by cooling from a suitable temperature with an applied field on, is warmed; the current arises from the thermally activated release of the frozen-in polarization, i.e. from reorientation of the partially aligned dipoles dispersed into the lattice (Fig. 3). In the simple case of non-interacting dipoles, with a single relaxation time $\tau(T)$ and at a constant heating rate b, one has a current density band (ITC band), whose form is the same as the first order kinetics thermoluminescence glow peak: the displacement current at any time t is

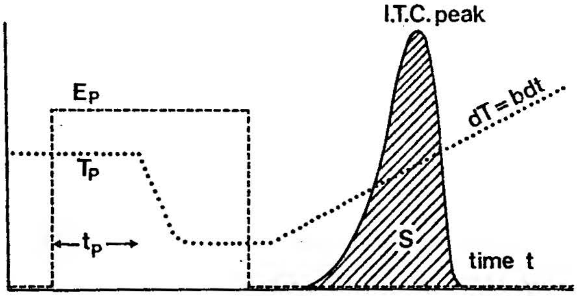

Fig. 3 The process of Ionic Thermoconductivity. Solid line: current; dotted line: temperature; dashed line: electric field.

$$j_i(t) = dP(T_i)/dt = -P(T_i)/\tau(T_i)$$

$$\tau(T) = \tau_0 \exp(W/kT)$$

where $P(T_i)$ is the dipolar polarization of the sample. The area S delimited by the ITC band is proportional to the initial saturation polarization $P_s(T_p)$, hence to the dipole concentration N in the sample

$$P_s(T_p) = N\alpha d^2 E_p/kT$$

where T_p is the polarization effective temperature, N the dipole concentration, α a geometrical factor, d the dipole moment and E_p the polarization field.

The activation energy for the dipole orientation and the frequency factor τ_0^{-1} therefore can be obtained quickly and accurately from a single measurements:

$$\tau(T_i) = -P(T_i)/j_i(T_i) = [1/j_i(T_i)] \int_{T_i}^{\infty} b^{-1}\, j(T)\, dT$$

The method is sensitive, approaching a detection limit of 10^{-7} mole fraction of dipoles, moreover the study of $P_s(T_p)$, as the sample undergoes different treatments, allows one to draw interesting information on any physical process which induces changes of N. This can be done because ITC measurements are performed at much lower temperatures than dielectric losses, therefore the recovery of processes such as aggregation, dissolution and radiation damage annealing are greatly suppressed.

In the above we have considered the simplest case of a single relaxation time. When two or more relaxation times are so close that the corresponding ITC peaks overlap, the technique can be slightly modified in order to resolve them, by polarization at intermediate temperatures and peak cleaning by partial discharge; peaks whose activation energies are spaced as close as 0.01 eV can be resolved, for comparable concentrations.

Applications to alkali halide crystals. The results obtained by means of ITC on the kinetic parameters W and τ_0 in alkali halide crystals doped with divalent cations fit well with those obtained by means of other techniques; moreover the values of the temperature independent pre-exponential factor τ_0 is obtained with a much greater accuracy. The dipoles, in this case, are formed by a divalent cation and by a positive ion vacancy, bound by electrostatic interaction. However, the most original application of this technique is not to be found in this field, although within this framework a great deal of valuable information has been obtained on imperfections of a different kind, for example off center ions, divalent anions and dipolar molecular anions and on ionic crystals other than alkali halides.

Studies of the change induced in the kinetic parameters of some suitable dipolar impurities by excitation with light, of the change in the number of dipoles induced by thermal treatments of the sample, and of the creation or the destruction of dipoles caused by radiation damage (Fig. 4) are by far more interesting.

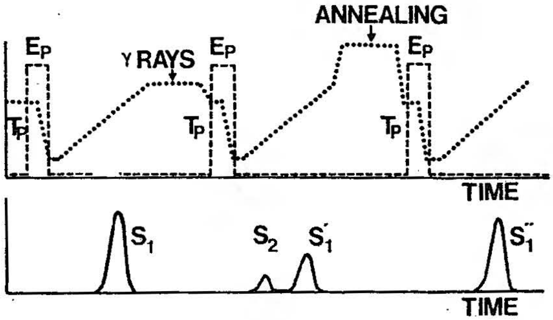

Fig. 4 Radiation damage. The I.V. dipole concentration, proportional to the area S_1, is reduced upon λ-irradiation (S'_1) whereas an additional ITC peak is developed (S_2). Recovery of the I.V. peak (S''_1) is achieved after proper annealing.

In principle the method can be applied to the analysis of the bulk dipolar polarization of dielectrics, where the electronic conductivity is negligible, and yields direct quantitative information in all cases of non-interacting permanent dipoles and related phenomenology. Processes such as carrier injection at the electrodes, electronic space charge, electronic traps etc. are clearly non studied in this way.

The development of ITC, based on the analysis of simple systems, such as alkali halides, has opened the way for the quantitative study of dipolar processes also in electrets. In fact, electret behaviour is a general property of solid dielectrics, like dielectric absorption and dielectric loss, and caused by the same mechanism as these effects, and alkali halide crystals doped with polyvalent metals are weak thermoelectrets with simple electret behaviour. Hence, the electret is not studied for sake, but rather for an understanding on atomic scale of solid state phenomena.

Looking back at those early activity years of our small group in Milano I have come to the conclusion that our most valuable result is not to have published some papers on optical or on electrical properties of alkali halide crystals, but that it lies in our determination to form a group of experimental physicists in the field of solid state. I think we succeeded in spite of the initial difficulties; many of the young fellows who started their career in Milano at the end of the fifties' are now good physicists and have obtained relevant results. Many of them are still my good friends. I think we all should be grateful to Professor Piero Caldirola, for having encouraged us and for his invaluable support.

REMINISCENCE OF A HALF CENTURY OF SOLID STATE SCIENCE WITH ITALIAN LINKS

Frederick Seitz

Rockefeller University, New York

It is a very great pleasure to return to Italy, in particular to Pavia, not least for the privilege of seeing so many old friends. As you can imagine, this experience stirs up old memories and prompts me to speak a bit about the past but it also gives me an opportunity to note changes that go with the evolution of science and technology.

I grew up in California - in San Francisco, one of the most complicated and cosmopolitan cities in United States having a wide ethnic mix ranging from all parts of Europe and Asia. Very few of the fellow students in my classes in elementary school had both parents born in United States.

As you all know, San Francisco, like Rome only more so, has many hills and valleys each of which had, and to some degree still has, its own cultural climate. The mainly residential valley in which I was raised and which is now the most populous region in the city contained the old Spanish Mission Road - the Camino Real which goes down the coast toward Mexico. In fact my father's business was on it and we lived in a large apartment on this main avenue. The side streets perpendicular to the Camino were exclusively residential and tended individually to be ethnically homogeneous. Two of the closest ones, namely Santa Rosa and Norton Streets, were in fact populated by Italian families whereas the next street in the other direction, namely Francis Street, was populated mainly by Irish families. San Francisco was very popular with immigrants from northern Italy which they found compatible because of the climate and geography. Almost all were from the middle class. Moreover, they had easy access to good ships that could sail from ports such as Genoa to various ports in United States.

The largest single group of Italians occupied a region at the north central part of the city called North Beach - just northwest of Chinatown and along the Bay. Needless to say, the main business street in that area was full of Italian shops and was called Columbus Avenue. The italians in my own neighborhood, more to the south, were part of the same turn of the century wave of immigration and they often referred to our own district as Nuova Liguria - a name which was used on many of the shops, along with red, white and green decorations and window pictures of Victor Emmanuel and Garibaldi - and sometimes Enrico Caruso.

The great majority of my childhood playmates lived in the streets populated by Italian families. They tended to be much more joyously friendly and less pugnacious to someone from the main street than were, for example, the corresponding young people from the Irish families on Francis Street.

Very few of these childhood friends went on to college as I did; so I tended to lose track of most of them once my parents moved to the suburbs after retirement. I did, however, stay in very close touch with my closest childhood friend, Silvio Del Vecchio, whose family ran an ethnic food store which included a butcher shop.

Instead of going to the regular university, most of my childhood friends, with one or two exceptions, ended up either in family business or clerking, or as salesmen of insurance or real estate, perhaps undertaking some part-time additional education in night school. This tendency was cultural and economic rather than related to innate ability because matters changed radically when the next generation came along. You now find the third generation descendants of the immigrants strongly represented in the professions and in major business posts all through California not to mention politics. One of the very large exceptions of course was the Giannini family which founded the Bank of Italy that played a very important role in the development of California during the last and first half of this century. The name was eventually changed to the Bank of America when it became a national bank. Unfortunately it passed out of family hands and faces many of the troubles of the large banks in United States as a result of unsound foreign loans made during the oil boom of the 1970's.

With this in my background, the arrival of Fausto Fumi, who had grown up in Genoa, to the Carnegie Institute of Technology in 1948 for graduate study was more than a welcome event since he added an entirely new dimension to the life of our physics department there. We soon learned that the great orchestra conductor, Victor de Sabata, was an uncle. Those were the days when the long-playing record was new and we were soon collecting discs involving de Sabata and La Scala.

Up to that point, almost all of the Italian scientists who entered into the American scene had been associated in one way or another with the arrival of Enrico Fermi in 1936 at the time Premier Mussolini began to work in close cooperation with Hitler. Almost without exception those earlier Italian scientists were involved with high energy particle physics. One must give very special recognition to Fausto for being the adventuresome Columbus of solid state physics and coming essentially alone to United States. Among other things he had to brave the industrial smoke of Pittsburgh since at that time it was truly the iron city and was only beginning to clean up its environment - a process which has since been almost too successful. The city lost some of its prosperity when it cleaned up the smoke, but is regaining it through the promotion of special services.

In 1949 our solid state group, including Fausto, moved from Pittsburgh to the University of Illinois in a community which was far cleaner but much less urban. It was, as the saying goes, centrally isolated but a very good place to work. It was during this period that Fausto met his wonderful wife to be, Lina, who was studying architecture at the University at the time. I am sure that she is with us in spirit today.

In the early 1950's the Italian Physical Society acquired the Villa Monastero in Varenna on Lake Como. On returning to Italy Fausto became involved with the officials of the Society in developing the Villa into a real working place. In 1954, as a result of his activity and kindness, I was invited to the grand opening of the Villa as a study center and was able to give one of the early lectures. Mrs. Seitz and I took advantage of the opportunity to rent a car and spend a full month traveling around Italy from Naples northward, including the length of the Po Valley from Genoa to Ravenna and Venice. Our tour involved visits to Rome, Pisa, Siena and Florence among other places. We had the good fortune to be well ahead of the great tourist typhoon which promises to overwhelm all the antiquities of Europe by the end of the century.

Soon after this, in 1954, Dr. Bassani arrived in Urbana, as a result of encouragement coupled to arrangements fostered by Fausto, in order to take up where Fumi had left off.

He was soon followed by Chiarotti but by that time the Italian solid state family was prepared to go to other places as well as Illinois. This included universities such as Rochester and Iowa where there was a well established Illinois alumnus such as David Dexter or David Lynch, or a close associate such as O.C. Simpson at Argonne National Laboratory. Eventually, however, they went to many other places as the opportunities grew.

Professor Ralph O. Simmons, the former head of the department of physics of the University of Illinois provided me with a list of the names and background of all of the physicists from Italy who spent a period of time in the department along with the background available in the departmental files. These appear in Table I. Not all worked in the field of solid state physics but I believe the list will be of interest in any event. Table II contains names,provided to me by Professor Fumi, of individuals who came to united States or Canada but were not necessarily linked to the department of physics at Illinois. They were either in other departments at Illinois or at other institutions. Today, of course, the flow of scientists back and forth across the Atlantic is fairly routine to the extent that budgets and interests make it possible.

Let me turn to another aspect of the field of solid state physics which I believe deserves attention on this occasion. In the days of Galileo Italy was not only the cultural leader of Europe but also the major commercial and manufacturing center. Genoa was, for example, the banking center of Europe. The tides of international fortune and misfortune brought about major changes for reasons which had nothing to do with the intrinsic capabilities of the people. Instead, political conflicts and lack of the type of national unity which took place in France and Austria led to disruptions. The banking center moved, for example, from Genoa to Augsburg to Amsterdam and then to London in the course of the next two centuries. Today it is in New York but tomorrow it may well be in Tokyo or perhaps it will return to Genoa.

The rise of the Common Market in Europe and the form of commercial unity which is now possible offers all of Europe a most remarkable opportunity. Italy is, in fact, in a particularly favorable position to regain a substantial position of leadership in science and technology as well as in commercial enterprises. There was, in the past, a widespread mood in almost all countries in Europe that rested on the belief that progress in a country begins with the action of a highly centralized and benevolent government which will guide all decisions. While no one today would underestimate the benefits of good leadership in government, we seem almost universally, in the Free World, to realize that the collective actions of many independent individuals and organizations can be even more important for progress than the government, particularly if the government does not arbitrarily impede private action.

What, you may ask, does this have to do with solid state physics? The answer is little or much depending on the opportunities it may open for solid state physics in Italy and the way in which they are received by the community of physicists or, indeed, the larger community of related scientists and engineers. One must grant that this is a matter of personal choice on the part of each individual. Most of us quite appropriately became interested in this field as a result of interests in fundamental science and the desire to become involved in adding to the knowledge of the field. Many may choose to restrict their attention to such interests to the exclusion of others throughout their lives. On the other hand, it may prove possible, without offending the highest standards of science in the least to contribute to the general development of the country and the larger community by putting some aspects of our science to work in practical ways. Individuals such as John Bardeen, Nevill Mott and Heinz Pick can be regarded as prototypical scientists who maintained a deep interest on both sides of the advances in our field. For me one of the reward of being in close association with the field for some fifty-five years has been to see the vast changes in technology which have come about through the application of basic research in our field to technology.

Since I have been reminiscing - a very dangerous matter for an individual my age - I might say a few words about the fifty-five odd years in which I have been associated with solid state physics or, as it sometimes is called in United States, solid state science, or condensed matter physics or materials science.

When I entered the field as a graduate student in the early 1930's the overall field was strongly compartmentalized into three major divisions which had relatively little interaction. I came to know the situation in detail as a result of direct experience in the next ten years. While these divisions still exist, the flow of information between them is now much greater than it was and the research groups in each have many common bonds, mainly because of the applications of solid state physics.

One division was related to work in the field of metallurgy and ceramics. This was then almost exclusively in the hands of individuals with a strong engineering background. On the whole, work in the non-ferrous field was more flexible than that dealing with iron and steel. The basic sciences had made inroads into this work to the extent that fields such as chemical and spectroscopic analysis, optical microscopy, pyrometry, and x-ray diffraction played roles of varying importance, mainly for the purposes of control and standardization. There were some good research centers both in industry and in the universities in Europe but their interests were usually limited. The same was true to a lesser extent in United States.

The second division related to research on materials of interest for electrical engineering and electronics. Included was research on topics such as electrical conductivity, magnetism, thermoionic emission, rectification, photoelectric emission, piezoelectricity and related matters which were important at the time. This research had a much closer tie to fundamental science than that in the first division. Many of the investigators had a strong grounding in physics and chemistry and were sensitive to developments in these fields. In fact, their work in applied areas often posed interesting problems in the basic sciences, such as was the case for field emission of electrons from a cold cathode.

The third division related to the investigations of what might be called the fundamentalist scientists. Their interests, primarily scientific, were born out of the curiosity that motivates basic science. In the search for refinements in their work, they developed methods of synthesizing single crystals of many materials, methods which at least in part have found their way into present day technology. I shall not take your precious time here by attempting to list fields of work which were of fundamental interest at that time but many have had an enduring quality.

Early Applications of Quantum Mechanics

My own interest in solid state science began early in graduate study and was then entirely of a fundamentalist nature. At that time there was a rising development in the field of physics in applications of the mathematical theory of groups, closely coupled with applications of the newly developed equations of quantum mechanics to various systems. All of this caused me to become involved in a reexamination of the properties of the crystalline symmetry groups which had been discovered and developed in the previous century. Moreover, I had the very good fortune to become Eugene Wigner's first American graduate student and with him developed a new method for constructing electronic wave functions in simple but real solids - a development that has advanced greatly in recent years as a result of the work of many talented investigators on an international scale and the evolution of the digital electronic computer. It might be emphasized that up to this point most of the attempted realistic solutions of the Schroedinger equation for electronic systems had focused on free atoms and simple molecules. It now became possible to broaden the base of such theoretical work.

Although Wigner turned his main interest to nuclear physics after the discovery of the neutron, he continued to retain an interest in the properties of solids for many years to come. Moreover, several strong schools of solid state science continued to spring up such as those under J.H. van Vleck, J.C. Slater and N.F. Mott.

Industrial Links

In 1935, as I completed graduate work and accepted a position at the University of Rochester, I was invited to spend the summer at the General Electric Research Laboratories with an assignment to the division involved in basic research on lamps for lighting purposes. This provided a wonderful opportunity to establish first-hand relationships with groups in many fields of applied research including electronics, metallurgy, ceramics and organic chemistry. In retrospect, this experience had a lasting effect on attitudes toward my own research from that time forward. The range of research in such a laboratory was so intriguing that I joined it on a full time basis for two years during the period in which the fluorescent lamp was being developed and had much pleasure in exploring the field of crystal luminescence. I returned to academic work at the University of Pennsylvania in 1939.

Prior Separation of Experiment and Theory

Before World War II there was relatively little coupling between ongoing experimental work and theoretical research in basic solid state science. Good experimenters have always been individualists and in the main followed their own bent in this field, using their own ideas as they wished. Theoretical physicists were entitled to study and use their results but were, so to speak, on their own. Samples of strong experimental groups were that of G.I. Taylor in Cambridge, England who, incidentally, had a very good classical theoretical background of his own and Robert Pohl in Goettingen, Germany who had excellent physical intuition. In returning to academic work in 1939 I decided that an attempt should be made to obtain more coordination between theoretical and experimental work through the development of closely cooperating teams which involved both types of interest. It is difficult to say how far such a program could have evolved in the atmosphere of the 1930's in view of the limitation of resources everywhere in that period, but we did have a modest start at the University of Pennsylvania with some degree of success.

World War II

All conventional planning was soon disrupted greatly by World War II. Most members of the scientific community in United States were enlisted in military oriented research in one way or another. Some fields of science which had been very active were sidetracked completely whereas others, such as microwave science and nuclear physics, received special attention in some selected areas.

Solid state physics attracted attention in United States at that time and received an impetus which not only endured to the present time but, in fact, became closely coupled to international work in the field after the War ended, forming what was, effectively, a worldwide research effort.

My own research was spread out over several areas in the course of the six year duration of the War and brought me and colleagues increasingly into close association with the three divisions of research which were mentioned in the introductory paragraphs of this paper.

Conventional Ordnance

Initially there was much stimulation of conventional ordnance. This provided an opportunity to gain a close insight into the status of research on a broad scale in such topics as ferrous and non ferrous metallurgy and specially ceramics. The best research in these fields was either being done in industry abroad, in academic institutions or in the electronics or nuclear power industries for their own purposes.

It has, incidentally, been very interesting to observe concepts such as those of lattice defects which were initiated by fundamental scientists in the 1920's and 30's as part of the process of gaining understanding of the various properties of real crystals gradually diffuse into the applied areas and become a part of the normal discipline of the metallurgists and electrical engineers.

Silicon-Germanium Research

A problem which had far reaching consequences to the modern world was turned over to the materials research community early in World War II as a result of the development of microwave radar systems. It became necessary to produce nonlinear electronic elements (diodes) that could serve as heterodyne mixers in the reception and amplification of radar signals. This had been achieved in the main with the use of vacuum tubes in the lower radio frequency range but such tubes could not be miniaturized sufficiently to be used in the microwave range. Research on a relatively primitive basis showed that some samples of metallurgical grade silicon, which was highly impure, displayed rectifying properties at microwave frequencies so that a marginally adequate mixer could be prepared from it. A broad group of investigators from both the academic and industrial research groups arose to meet this challenge. By the end of the War we not only had reasonable control of the field but also had what might be called a workable silicon and germanium technology for producing diodes.

Our solid state team at the University of Pennsylvania had the privilege of being among the early innovators in this research. We were greatly helped in our work as a result of cooperation with the research laboratories of the Dupont Company in Wilmington, which was willing to take on the task of producing pure silicon in usable quantities. I believe it is safe to say that the overall wartime work of investigators such as our group provided part of the platform which made the subsequent development of the transistor feasible in the time scale in which it occurred.

It is perhaps worth emphasizing here that this episode represented something in the nature of a major watershed in the history of materials science on an international scale. Henceforth advanced in electronic technology would become increasingly involved with solid state devices even though only a small fraction of those who led this field of technology appreciated the magnitude of the revolution which was at hand.

Nuclear Reactors

Immediately after the research team carrying out nuclear research under A.H. Compton, Enrico Fermi and Eugene Wigner at the University of Chicago constructed a functioning nuclear reactor (1942) an effort started to develop large-scale graphite reactors to produce significant amounts of plutonium.

In the course of work on the large-scale graphite reactors, Wigner observed that by the time a practical scale of operation would be achieved, the neutron flux would be sufficiently large to cause appreciable disruption of the atomic lattice of graphite. This disorder could not only have an influence on the structural integrity of the graphite but could have associated with it the generation of unstable stored energy - represented by the lattice disorder - which might be released as an uncontrolled thermal wave. A research group was set up at Chicago to investigate these effects and to simulate them as well as possible before very large-scale reactors were set in operation.

At the time these studies began, I had moved to the Carnegie Institute of Technology in Pittsburgh and had the opportunity to devote most of the resources of a physics department of modest size to solid state research. An arrangement was made to have our group there cooperate with that in Chichago in attempting to open this new area of study. It is sufficient to say that with use of a combination of available theoretical knowledge and carefully designed experiments, it proved possible to gain fairly accurate knowledge of what one might expect to happen to the various material components of the large-scale reactors and, at least in some cases, plan corrective measures. We found that the changes which occurred in the graphite were as serious as Wigner anticipated that they might be. Moreover, the disordering which occurred in metallic uranium as a result of the bombarding action of fission fragments and the production of rare gases were even more dramatic. All of these issues are now well understood by the reactor technologists in the free world.

Other Areas of Research

A number of other areas of materials research received substantial stimulus during the War. There was, for example, extensive work on new materials for cathode ray screens, on dielectric and magnetic substances for use at microwave frequencies and a renewal of research on piezo-electric crystals.

Post War Period

When contemplating the future fate of the field of solid state physics toward the close of the War, I wondered if it would return to the slow pace that characterized the period before 1939. The opposite proved to be the case and, in fact, it is only now, forty years later, that it appears that resources could become sufficiently limited to slow what might be termed the natural evolution of the field. Not only did support expand, with a great release of constraints,after 1945, but the international community gradually became exceedingly active again as economic conditions improved. The move to the University of Illinois at this period with an opportunity to staff a substantial fraction of a very large department made future opportunities seem very bright for me and colleagues.

Apart from the expanded financial support for basic materials research which became available, there were three other changes which occurred that had a stimulating effect.

First, the field of physics, both experimental and theoretical, became openly popular among science students everywhere, in contrast to the 1930's when it interested only a few individuals.

Second, the interplay between theoretical and experimental work became much closer everywhere. Not only were the new, young experimenters who entered the field more broadly familiar with theoretical physics but they sought close links with theoretical colleagues who were interested in their work whenever possible.

Finally, new types of instrumentation which broadened and accelerated the opportunities for experimental work became available at attainable prices. I recall that one of our graduate students at the University of Illinois was able, in a relatively short time with the use of equipment available at our department, to carry out a research program in the field of color centers in the alkali halides that would have required five to ten times longer in the 1930's.

International Conferences

It must also be recalled that airplane travel became convenient and popular at this time so that international conferences were far easier to convene than ever before. This had the effect of binding the international materials community together on a common base in a way which had not been possible previously. It also permitted many young scientists and students to travel easily, which had not been the case before.

Influence of the Transistor

The invention of the transistor in 1947 not only accelerated a trend which was already gaining momentum but made the engineering community ever more conscious of the need to form close links with physicists and chemists in the exploitation of new ideas. Prior to World War II very few electrical engineers in United States were, for example, familiar with Maxwell's equations. The revolution associated with microwave electronics demonstrated the need for a more basic approach to electromagnetic phenomena. The invention of the transistor had an even more profound effect since those in other branches of engineering such as metallurgy and ceramics also had to become more directly familiar with solid state science and all of the things which go with it, including an understanding of the nature and importance of imperfections and surface phenomena.

The first result of the expanded vitality in the field of solid state science was to make it possible to attack, on many fronts, problems which had been only partly visualized and understood with far greater precision and thoroughness. However, entirely new phases of the field were also about to be opened.

John Bardeen and his colleagues exploited an entirely new avenue of theoretical analysis with the development of the first viable theory of superconductivity (1957) - a topic that had remained essentially a scientific mystery since its discovery in 1911. The analytical techniques needed to achieve this understanding were borrowed in part from those in quantum mechanical field theory and, in a sense, represented the first major theoretical innovation in about twenty-five years, in fact, since the appreciation of the importance of electronic correlation energy by Wigner in 1934. The recent discovery of superconductivity near 100 K in four-component compounds containing copper oxide has clearly expanded horizons in this field.

The Laser

Another landmark of the same period was the development of the crystalline laser which opened a broad new highway for communication between the materials scientist and the optical engineer, who up to this time had been only marginally affected by recent developments in materials science.

Beyond this we now witness the wedding between optics and electronics which promises a revolution of its own.

Integrated Circuit

The invention of the integrated circuit while a product of engineering and applied science rather than of basic science can nevertheless be attributed to the accomplishments of solid state science in the period from 1945 to 1960 since it would have remained a paper concept without all the scientific advances that had taken place. In fact, the evolution of the integrated circuit since its first realization has required continuous scientific inputs at very sophisticated levels. Nor is the end in sight. It remains to be seen what interesting basic problems will arise as one pushes miniaturization below the one micron level.

Computer-based Theoretical Work

The interaction between technology and experimental science has always been close in the sense that the experimenter has frequently been dependent on advances in technology to further his own work. We are now experiencing a broadening of this effects in as much as the modern computer - made possible through discoveries in basic materials science - has opened up vast new opportunities for analyzing theoretical problems which could not have been approached in other than a very peripheral and qualitative way. In fact, the computer is generating an entirely new revolution in the approach to theory, not least in the domain dealing with complex interacting systems. This revolution is still in its infancy.

Need for Large-Scale Equipment

If there is an outstanding need to stimulate further advance in the field of materials science it lies in the supplementation of present types of equipment that are generally available with new large-scale equipment such as synchrotron sources for the ultraviolet and x-ray regions. Small-scale research will still be highly important, however such new sources will make it possible to work with materials and specimens which are currently at the borderline as far as precise investigation is possible. Such equipment, being very expensive, by previous standards, will have to be operated on an appropriate community basis. Fortunately we now have, on an international scale, ample experience in handling the problems of shared use so that access to such new large scale resources provides the main obstacle to this development.

It is said that the great physicist, Wolfgang Pauli, would not take on Hans Bethe as an assistant in the 1920's because the latter had worked on the quantum theory of metals which Pauli termed "dirty physics". The field has come a long way toward gaining respect since then.

TABLE I

ITALIAN CONNECTIONS

STUDENTS, RESEARCH STAFF, TEACHING FACULTY

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Gianni ASCARELLI

Ph.D. (1959) M.I.T.; Dottore (1954) Univ. Roma; B.S. (1954) Univ. Sao Paulo Research Associate (1959-61) University of Illinois

[cyclotron resonance in AgCl, with F.C. Brown]

Group Leader, Italian NRC; Lecturer, Univ. Roma (1961-64)

Associate then Full Professor Physics (1964-) Purdue University

[solid state experiment including semiconductors, electrons in liquids, collective modes in dipolar liquids, polynucleotides]

Department of Physics, Purdue University, West Lafayette, IN 47907 (1986 address)

Massimo ALTARELLI

Dottore (1969) Univ. Roma

Research Associate (1970-71) Univ. Rome; Research Associate (1971-74) Univ. Rochester

Vis. Research Asst. Prof. (1974-75), Assistant Professor (1975-79),

Vis. Associate Professor (1978-80) University of Illinois

[excitons, semiconductor band structure]

Scientist, MPI Stuttgart (1980-)

Max-Planck-Institut fur Festkorperforschung, Heisenbergstr. 1,

Stuttgart 80 7000, West Germany (1985 address)

Alfonso BALDERESCHI

Dottore (1969) Scuola Normale Superiore, Pisa; (1965) Univ. Milano

Research Associate (1969-70) University of Illinois

[Pines, Bardeen ARPA/AFOSR, magneto-optics of semi-conductors, excitons]

Inst. Phys. Appliquée, Ecole Polytechnique Fédérale, PHB Ecublens,

CH 1015 Lausanne, Switzerland (1985 address)

Maria Luisa BARCELLONA

Laurea (1970) Univ. Catania

Assistant (1972-82), Associate Professor (1982-84) Univ. Catania

Visiting Associate Professor (1985, 1987) Univ. of Illinois

[fluorescence of biological materials - E. Gratton]

Department of Biochemistry, University of Catania, Viale Andrea Doria, 6, 95100 Catania (1986 address)

Aldo BELLENI-MORANTE

Docenza (1968) Univ. Firenze; Dottore (1961) Univ. Firenze

Research Associate (1968-69) Univ. Illinois (also NATO Fellow)

[neutron transport theory, with F.T. Adler]

Professor of Theoretical Mechanics, Istituto di Matematica Applicata, Viale Morgangni 44, 50134 Firenze (1983 address)

G. Franco BASSANI

Laurea (1952) Univ. Pavia

Postdoctoral Fellow (1953-54) Milano

Research Associate (1955-56), Univ. Illinois

[impurities, dislocations in NaCl-R. Thomson; alpha & beta bands-N. Inchauspè; OPW energy bands in Si]

Visiting Professor (1979-80) University of Illinois

Asst. Prof. Univ. Palermo (1957), asst. Prof. Univ. Pavia (1958-59);

Assoc. Physicist, Argonne Nat. Lab. (1960-64); Prof. Univ. Messina (1965-66); Prof. Univ. Pisa (1967-70); Prof. Univ. Roma (1970-80?)

Scuola Normale Superiore, Piazza Dei Cavalieri, Pisa 56100 (1985 address)

Gilberto BERNARDINI

Ph. D. (1932) Univ. Firenze; Dottore (1928), Univ. Pisa & Scuola Normale Superiore, Pisa

Asst. Prof. (1932-37) Univ. Firenze; Professor (1939-44) Univ. Bologna;

Professor (1945-49) Univ. Roma; Vis. Prof. (1949-51) Columbia Univ.

Research Professor (1951-57) University of Illinois

[elementary particle physics]

Director of Research, CERN synchro-cyclotron (1957-60), Director S. C

Division (1960-62); Director of Research (1962-65); Director of Scuola Normale Superiore, Pisa (1964-?)

President, Italian Physical Society and director-editor of Il Nuovo Cimento (1962-67),

Accademia Nazionale dei Lincei, Pisa (1980 address)

Renato BOBONE

Ph.D. (1960) Univ. Illinois; (also grad study at Case); Laurea (1944) Politecnico Torino

Assistant (1955-60) University of Illinois

[nuclear beta decay and gamma correlation - H. Frauenfelder]

General Electric Knolls Atomic Power Laboratory (1960-1987) retired 1036 University Place, Schenectady, New York 12308 (1987 address)

Giorgio CARERI

Laurea (1945) Univ. Roma

Assistant Professor (1950-56) Univ. Rome; Professor 1957-60 Univ. Padua; Professor Univ. Rome (1960-); Fairchild Distinguished Visitor, Cal Tech. (1976-77); (first) Scientific Director ENI Monterotonda

Visiting Professor (1977-78) University of Illinois

Istituto di Fisica, Universita' di Roma (1978 address)

Vittorio CELLI

D.Sc. (1958) Univ. Pavia

Research Associate (1959-61) University of Illinois

[theory of dislocations - R. Thomson]

Asst. Prof. (1962-64) U.C. San Diego; Asst. Prof. (1964-66) Univ. Bologna; Assoc. Prof. to Professor (1969-) Univ. Virginia

Department of Physics, University of Virginia, McCormick Rd., Charlottesville, VA 22901 (1986 address)

Gianfranco CHIAROTTI

Dottore (1951) Univ. Pavia

Research Assistant Professor (1955-57) University of Illinois

[diffusion and color centers in alkali halides - AF/R. Maurer]

Istituto di Fisica, Univ. Roma, Piazzale Scienze, 5, 1- 00185, Rome

(1985 address) title is Professor of Physics

Giampaolo CO'

Ph.D. (?) (1984) Rheinische Friedrich Wilhelms Univ. Bonn; Laurea (1979) Univ. Bologna; Diploma (1974) Brescia

Research student (1978-79) CNEN Bologna; (1981-84) KFA Julich

Research Associate (1985-87) University of Illinois,

[nuclear theory - J. Wambach]

Department of Physics, University of Illinois, 1110 West Green St., Urbana, Illinois 61801 (1987 address)

Bruno CRESPI

Laurea (1982) Univ. Trento

National Service in Italy (1983)

Assistant (1984-), Fellow (1985-86) University of Illinois

[Ph.D. candidate - elementary particle theory - L. Jones]

Department of Physics, University of Illinois, 1110 West Green St., Urbana, Illinois 61801 (1987 address)

Giulia DE LORENZI

Dottore (1981) Univ. Trento

Visiting Scientist, CEN Saclay (1979); Scientific Collaborator IRST, Trento (1982)

IBM Postdoctoral Fellow (1983-84), Research Associate (1984-85), University of Illinois

[condensed matter theory - C.P. Flynn]

H-Division, Physics EPT, Lawrence Livermore National Laboratory, Livermore, California 94550 (1985 address)

Adelchi FABROCINI

Dottore (1977), Univ. Pisa; Licea (1969) Campobasso

Assistant Professor (1978-81),Assistant Researcher(1981-) Univ. Pisa

Visiting Scientist and La Riccea Fellow (1985-86), Research Associate (1986-87) University of Illinois

[Ph.D. candidate - nuclear and quantum liquid theory - V. Pandharipande]

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[dislocation damping: AEC - A. Granato]

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[nuclear and quantum liquids theory - V. Pandharipande]

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Libera Docenza (1953) Univ. Padova

Assistant (1948- ?) Univ. Padua

Research Associate (1956-57) University of Illinois

[cosmic rays, mesons, gamma-ray interactions - E.L. Goldwasser]

Associate Physicist (1958- ?) Armour Research Foundation

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Fausto G. FUMI

Dottore Univ. Genova (1948)

Carnegie Inst. Tech. (1948-49)

Special Research Assistant & Postdoctoral Fellow (1949-51) University of Illinois

First Director of departmental Institute of Physical Sciences of the Univ. Genoa in 1969; in 1976 was member of solid state commission IUPAP; chair, Metal Physics Section, Condensed Matter Division, European Physical Society, and member National Physics Committee, Italian Research Council.

Dept. Physics, Univ. Genoa, Via Dodecaneso 33, 16146 Genova (1985 address) - title in 1978 was Professor of Solid State Physics

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[fluorescence spectroscopy of biological substances]

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Franco A. LEVI

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Enrico Bezzi Milano machine production (1941-42); Milani, D.A., Bologna (1942-43); Acting Asst. Prof. (1945-49), Assistant Professor (1949-58?), Professor (19?--), Univ. Perugia

Research Assistant Professor (1958-59) University of Illinois

[ultrasonic studies of solids - J. Koehler]

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Nunzio O. LIPARI

Ph.D. (1970) Lehigh University; Dottore (1967) Univ. Messina

Research Associate (1970-72) University of Illinois

[band structure of insulators; impurities -- A.G. Kunz]

IBM Watson Research Center (1972-)

[nuclear, particle theory -- ONR/NSF D. Jackson]

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[synchrotron radiation for biological fluorescence - E. Gratton]

PULS (Progetto per l'Utilizzazione della Luce di Sincrotrone), Laboratori Nazionali, Frascati CP13, Roma (1981 address)

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Ph.D. (1952) Univ. Milano; E. Eng. (1157) Politecnico Milano

Assistant (1952-55) Univ. Milano

Smith-Mundt & Fulbright Fellow (1956-67), Research Associate (1956-58) University of Illinois

[nuclear detectors, nuclear physics - ONR Frauenfelder]

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FIAT; "fatally devoted to administrative and political work in my senior years"; in 1975 was Advisor of Italian Ministry of Research

Anna Marie SARUIS

Docenza (1971) Univ. Bologna; Laurea (1955) Univ. Cagliari

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Visiting Professor (1984) University of Illinois

[nuclear theory]

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Assistant (1982-) University of Illinois

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Scholarship (1960) INFN (National Institute of Nuclear Physics)

Scholarship (1961) CNR, Professor Incaricato (1961-75?), Univ. Milano

Research Associate (1962-64) University of Illinois

[luminescence of alkali halides - F.C. Brown]

Professor (1975?-) Univ. Milano

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Gherardo STOPPINI

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Assistant (1949-54) Univ. Roma

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[cosmic rays, photomeson production - G. Bernardini]

Professor (1968?-- ?) Univ. Pisa

Istituto di Fisica, Univ. Roma (1983 address)

TABLE II

NAME	INSTITUTION	FACULTY	PRESENT POSITION
Ascoli	Brookhaven		
Baldini	Univ. of Rochester	Dexter	
G. Boato	Univ. of Chicago	Urey	Univ. of Genoa
Bordoni	M.I.T.		Univ. of Rome
Borsa	Univ. of Illinois	Rowland	
Bucci	Univ. of Pennsylvania	Burstein	
Caglioti	Chalk River	Brockhouse	Pol. Inst. Milan
Celli			
Colella	Cornell		
Felcher	Brookhaven		
Frova	Univ. of Illinois		
Merlini	Univ. of Illinois		
U. Palma	M.I.T.	Rossi	Univ. of Palermo
B. Palma Vittorelli	M.I.T.	Rossi	Univ. of Palermo
Paoletti	Brookhaven Nat'l Lab.	Nathans	Univ. of Rome
D. Sette	Catholic University	Herzfeld	Univ. of Rome
Stella	Iowa	Lynch	
Tosi	Argonne		

PROPOSAL FOR ARCHIVES ON THE "HISTORY OF SOLID STATE PHYSICS IN ITALY: 1900-1960"

Fabio Bevilacqua

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Gruppo Nazionale di Storia della Fisica del C.N.R., Unità di Pavia

Today it is widely recognized that science is a prominent part of modern culture. Still, scientific results and technological applications are much better known than the patterns of research and scientific creativity. The implications of this state of affairs are negative both for the active scientist, who tends to lose sight of the historical pattern he is part of, and for the general public, astonished by the ever-changing ultimate scientific "truth". Solid state physics is no exception: its results are now closely related to everyday life (NMR, chips, superconductivity) but with origins that are rather obscure. The success itself of this meeting, with the interest which has arisen for the publication and recording of information so far accessible to only a few, shows that greater efforts have to be made towards a history of modern physics.

History of physics is also a bridge between relevant specialized activities and wider cultural contexts: a documented outline of its own history would be of great benefit for a discipline like solid state physics which is gaining an increasing institutional support in Italy.

A proposal for an archives does not mean a proposal to write an "official history" but to collect and preserve sources for future reference for historians. The aim again is not for "priority" and "nationalistic" claims but for framing successes and difficulties in the national and international context of a now well-established and prosperous community of Italian physicists.

But why do we need new archives? Are the existing ones not sufficient for the purpose?

A look at the main international archives is necessary to put our proposal in context. The most successful archival experience to my knowledge is the collection of the Sources for History of Quantum Physics. As some of you might know John Wheeler, among others, stimulated a joint committee of the American Physical and Philosophical societies to outline a plan. T. Kuhn, J. Heilbron and P. Forman were appointed for three years' work. Between February 1962 and May 1964 95 people were carefully interviewed and a repertory, regarding 280 physicists, of letters, manuscripts, notebooks, personal commentaries, biographies, bibliographies was produced. Among these were four Italians: Amaldi (interviewed), Fermi, Garbasso and Rasetti (int.).

Copies of the archives are now in Berkeley, Philadelphia, Copenaghen, Rome, ... Undoubtedly these archives stand as a model.

J. Heilbron (with B. Wheaton), at the Office for History of Science and Technology (OHST) of the University of California - Berkeley, kept working on archives with "global" plans:

a) An inventory of sources for history of twentieth century physics (ISHTCP) was produced. It consists of a list of 5.500 physicists who between 1896 and 1952 published in the following journals:

Physical Review, Proceedings of the Royal Society, Philosophical Magazine, Annalen der Physik, Physikalische Zeitschrift, Journal de Physique.

The inventory reports information about 750.000 letters exchanged between these physicists. The letters are located in 1.000 libraries in 30 countries.

For our purposes the exclusion of the Nuovo Cimento from the set of journals should be noted.

b) In 1981 the same team produced a massive bibliography of secondary sources on the history of twentieth century physics: 7.000 books and articles, by both historians and physicists have been recorded. There are 138 entries in the section Solid State Physics, only one of which refers to the Italian community (the author is the Italian Zambone and the paper (1911) is about mineralogy).

Among the 725 physicists for whom the bibliography records substantial biographical studies 14 are Italians, namely Amaldi, Corbino, Fermi, Garbasso, Giorgi, Levi Civita, Mayorana, Pacinotti, Perucca, Ricci Curbastro, Ricco, Righi, Ronchi, Volterra.

Together with the bibliography, OSHT produced an inventory of published letters to and from physicists from 1900 to 1950. From 25.000 quotations of letters reproduced in the secondary literature 776 physicists were identified. 21 of these physicists are Italians: Abetti, Amaldi, Caldirola, Carrelli, Corbino, Fermi, Garbasso, Gentile, Giorgi, Levi Civita, Mayorana, Occhialini, Pacinotti, Persico, Piccioni, Picone, Pontecorvo, Rasetti, Righi, Segre, Volterra.

The union of the two sets (725, 776) of physicists gives about 1.000 "distinguished" physicists: that is, about one out of six of the physicists recorded on the Inventory deserved a biographical study, or a quotation of a letter from the historians.

Of this set of distinguished physicists only 25 are Italians.

At OHST work is in progress on a list of 178 nominees for the Nobel prize (1901-1933) two of whom are Italian, and on the 45 Nobel prize winners in physics (1901-1938) two of whom are Italian.

Summarizing the OHST results the following panorama of Italian physicists in the international context emerges.

	General	Italians
Quantum physicists	280	4
Physicists (1896-1952)	5.500	? (list not available)
Biographical studies	725	14
Quotations of letters	776	22
Distinguished physicists	1.000	25
Nominees (1901-1933)	178	2
Nobel Prize Winners (1901-1938)	45	2

These figures are very interesting but might put Italian physics in a wrong perspective. In fact the Nuovo Cimento was not scanned and the production of biographies of recent Italian physicists by the recently established Italian academic community of historians of physics is slight. All that suggests that the image of the Italian community of physicists is not carefully represented.

Thus we have to ask ourselves some preliminary questions: how many physicists were actually working in Italian institutions? How many were publishing in Italian journals? And how many on Solid State Physics?

In 1900 in Italy there were 16 Physics Departments: Bologna, Cagliari, Catania, Genova, Messina, Modena, Napoli, Padova, Palermo, Parma, Pavia, Pisa, Roma, Sassari, Siena, Torino.

The number of physics researchers resulting from the survey of Polvani (1) is 223 for the period (1900-1939). The number of members of the Society of Italian Physicists was 225 at the foundation (1897) 30% of whom were academics. Galdabini and Giuliani (2) give the data reported in table I.

Galdabini and Giuliani (2) give also interesting figures for the number of papers published in Il Nuovo Cimento and for their subject classification (table II).

The percentage of papers on condensed matter is not low: about 18%. Galdabini and Giuliani have also worked out the "Early lines of research in Italy: 1900-1940" (3) in the field of solid state. This work points out that "solid state physics, as a definite field of research, developed in Italy only after the second world war". As this meeting is making evident the subject was carried forward with great enthusiasm and good results at least in Genova, Ispra, Milano (University and C.I.S.E.), Padova, Palermo, Pavia, Pisa, Roma, Torino.

Fast developments led to the foundation of the Gruppo Nazionale di Struttura della Materia of the C.N.R. and more recently of the C.I.S.M. (Centro Interuniversitario di Struttura della Materia)

All this indicates that the OHST figures for Italian activities in Solid State Physics should be modified and made more in keeping with actual historical events.

The Archives for History of Solid State Physics in Italy from 1900 to 1960 could be set up along the following steps.

1- *Scanning the three main Italian journals*:

Nuovo Cimento (about 200 papers on solid state physics from 1900 to 1940)

Rendiconti dell'Accademia dei Lincei

La Ricerca Scientifica

2- *Identification of contributions divided into the following categories* (3):

elastic, thermal, electrical, magnetic properties; galvanomagnetic, thermomagnetic, Volta and photoelectric effects; optical properties of ions in solid solutions or crystals.

3- *Biographies and bibliographies of identified set of physicists.*

Comparison with ISHTCP list (a first contribution was given in Pavia with the publication of the collected works of Luigi Giulotto).

4- *Recorded interviews with living relevant contributors*

(a first set was realized by L. Belloni, S. Galdabini and G. Giuliani).

5- *Search and collection (or microfilm) of manuscripts, letters, notebooks, personal commentaries.*

6- *Preservation and restoration of relevant experimental devices in a Museum/exhibition.*

This proposal is made to everybody willing to contribute, but is specifically addressed to the historians of G.N.S.F. and to the physicists of G.N.S.M. and C.I.S.M.

If the proposal is accepted and adequately funded we will have a first contribution for large scale archives for History of Modern Italian Physics. This will be relevant not only for Italian physicists and historians of physics, but also for the international community of historians.

TABLE I * +

NUMBER OF PHYSICISTS

ACADEMIC YEAR	1871-72	1899-900	1914-15	1926-27	1939-40
a) Professors	17 (2)	25 (3)	22 (6)	24 (8)	29 (4)
b) Professori Incaricati	4	1 (1)	5 (1)	26	13 (4)
c) Assistants	17	31+2	45+1	48+3	60+4
d) Liberi Docenti	==	12	23	25	20
r) Researchers (a+b+c+d)	38	71	96	126	126
t) Technicians	23	23	30	35	36
Researchers per technician	1.7	3.1	3.2	3.6	3.5

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* Adapted from reference (2)

+ Under the denomination of "Professors" we have grouped the professors with a chair without distinguishing between "ordinari" (stable) and "straordinari" (to be confirmed in the position). "Professori Incaricati" were professors without a chair appointed every year. Under the denomination of "assistants" we have grouped without distinction the "assistenti" and the "aiuti" (assistants of higher degree). In this table we have included also the physicists from private universities. We have not taken into account the mathematical physicists. However, their numbers have been reported in brackets. The number of assistants has been given as a sum in order to report the number of voluntary assistants, given by the second term of the sum. The voluntary assistants were unpaid but with obligations similar to those of assistants. The meaning of "Libero Docente" changed slightly over the period taken into consideration. Generally speaking, to become a "Libero Docente" one had to pass an examination based on discussion of his scientific work and a lecture; a "Libero Docente" was then in charge of giving an unpaid course without any other obligation. Usually a "Libero Docente" had a job outside the university: it is therefore difficult to establish how much of his time was devoted to research. However, generally speaking, a "Libero Docente" did publish scientific papers and had more or less close links with the university. We have included under the entry "technicians" people involved only in workshop or laboratory activities. Sources: "Annuario del Ministero della Pubblica Istruzione" 1871-72; 1899-900; 1914-15; 1926-27; 1939-40.

TABLE II * +

CLASSIFICATION OF PAPERS PUBLISHED IN "IL NUOVO CIMENTO"

NUMBER	NAME	CONTENTS
I	Classical Physics	Mechanics, Optics, Acoustic, Thermodynamics, Electromagnetism
II	Properties of condensed matter	Properties of solids and liquids
III	Atoms and molecules	Properties of atoms and molecules
IV	Nuclear Physics	Radioactivity, nuclei, cosmic rays, elementary particles
V	Relativity	Special and general relativity
VI	Quantum and statistical Mechanics	Quantum and statistical mechanics, quantum electrodynamics
VII	Applied Physics	Scientific instrumentation, "true" applied physics
VIII	Others	Papers not attributable to anyone of the preceding seven groups

PERIOD	NUMBER OF PAPERS PUBLISHED
1900-1904	262
1905-1909	255
1910-1914	278
1915-1919	161
1920-1924	148
1925-1939	189
1930-1934	195
1935-1939	155

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* Adapted from reference (2)

+ The survey of the papers published in "Il Nuovo Cimento" between 1900 and 1939 has been carried out on the basis of 23 groups. Though this subdivision may be useful for following the time evolution of some particular research field, it is too detailed for our purposes. Therefore, the data are discussed in the paper on the basis of the above eight groups. The group "others" was initially intended for those papers not attributable to anyone of our original 22 groups. The group VIII of this table contains, besides miscellaneous ones, papers on astronomy, geophysics, various rays (including X-rays), rarefied gases, didactics and history of physics. It also contains papers on spectroscopy not expressly intended for the study of atoms or molecules. We have taken into account only papers by Italian physicists or by foreign physicists working in Italy. We have not counted the review papers written on invitation by the editors.

REFERENCES

(1) G. Polvani, "Il contributo italiano al progresso della fisica negli ultimi cento anni", in "Un secolo di progresso scientifico italiano: 1839-1939", Roma, 1939

(2) S. Galdabini, G. Giuliani, "Physics in Italy between 1900 and 1940: the universities, physicists, funds and research". To be published in "Historical Studies in Physical and Biological Sciences"

(3) See these Proceedings

DEVELOPMENT OF SOLID STATE PHYSICS IN ENGLAND AND GERMANY

Nevill Mott

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The organizers of this conference asked me to speak on the development of solid state physics in England. This was so closely linked with the development of the subject on the continent of Europe, in the prewar period - particularly in Germany - that I felt as a good European that I must extend my terms of reference. Also I cannot even begin my talk without referring to the very great influence of Frederick Seitz on all of us, and perhaps particularly on Italy, both through his book, his research programme and his willingness to accept students from overseas. Two of my earliest memories of Fred are discussing with him, I think in 1938, the Landau concept of self-trapping of an electron in an ionic lattice - what we now call a polaron. And I remember too, at the International Conference on theoretical physics in Japan in 1953 - the first of its kind since the war - Fred giving two lengthy lectures on F-centres to a packed hall of Japanese students taking down every word. Fred certainly spread the gospel of F-centres as a worth-while subject for research in many countries, not least in Italy. I am sure that Fumi, Tosi, Bassani, Chiarotti among others would acknowledge their debt to him.

But it is about Europe that I want to talk. I do not think that with us the expression "solid state physics" came into use untill after the war of 1939-45, but of course many of the concepts, particularly the quantum mechanical framework, belong to the period 1927-39. Even before that we knew quite a lot. In Cambridge University I remember as a student attending a lecture on "Electron Theory of Metals". As early as 1900 Drude (1) had published his paper "Zur Electronentheorie der Metalle" and indeed in the same year J.J. Thomson (2) had proposed that in metals the current was carried by electrons, his newly discovered particles. From this assumption, by 1926 the Wiedemann-Franz ratio and the value of the Hall coefficient were deduced. We did not understand why in metals electrons were free to move and in insulators they were not. I remember asking my lecturer whether there was an explanation, and he said he did not know of one. This experience was, perhaps, the origin of my life-long interest in metal-insulator transitions. Max Born's work, even before the first world war, had given us an understanding of cohesive forces in one kind of solid, the alkali halides. Moreover, before the appearance of the new quantum mechanics, the old quantum theory of oscillating systems had been applied to solids in various ways by Einstein and Debye; we understood why the specific heat froze out at low temperatures; but we did not understand why the electrons in metals did not give a significant contribution.

Looking back on the few year after the appearance of the first papers on quantum mechanics, it strikes me as extraordinary how quickly some of the puzzles were resolved. The understanding of antisymmetrical wave functions (Heisenberg), leading to Fermi-Dirac statistics, Sommerfeld's application of these statistics to electrons in metals in a way which neglected both the interaction of electrons with the lattice and with each other, Pauli's theory of paramagnetism in metals, Bloch's treatment of electrons moving in a periodic lattice which showed why the mean free paths in metals were so large, and Wilson's realization that the Bloch wave functions, together with the exclusion principle explained my old problem, the difference between metals and insulators, all followed within five years, that is by 1931. In 1933 there appeared the monumental and comprehensive article by Sommerfeld and Bethe in the Handbuch der Physik. This calculated almost everything that could be calculated, if the interaction between electrons was neglected.

What strikes me now was the confidence with which that generation of physicists went ahead with models which neglected this interaction. It was not a small effect. Of course in early models of atomic structure this was done, the effect of other electrons being simply to screen the field of the nucleus. Nevertheless, the optimism with which simple models were used was a feature of the period. Until 1933, apart from A.H. Wilson who was rather a solitary worker, I do not think that there was much interest in the U.K. in these developments - Cambridge was dominated by Rutherford and nuclear physics; I started research there and in Copenhagen and devoted myself to collision processes and their applications to nuclear problems. I do remember R.H. Fowler, Rutherford's son-in-low, talking to us about Wilson's work and its application to semiconductors; personally I had never heard of such things, and I don't think it aroused much interest. Rutherford - the legend goes - divided science into physics and stamp-collecting, and I guess he would have classed solid state physics as stamp collecting. And Niels Bohr - the most wonderful teacher and friend who taught me what a career in theoretical physics should be - colud never come down from the heights to such a subject. Once - I think shortly after the war - he asked me to tell him what was happening in solid state, but after a few minutes he said "very interesting" in a tone which meant that he was not listening ...

But in 1933 I moved from Cambridge to a chair in Bristol, and turned over to solid state because of the work going on there. Lindemann, later Lord Cherwell and Churchill's advisor and already an influential man, was worried at the small attention given in our country to the new theories of electrons in metals, because of their potential importance for industry, and had persuaded a government agency to offer a grant to Lennard-Jones, professor of theoretical physics there, to look into this matter. Lennard-Jones used the grant to hire a young theorist, Harry Jones, but shortly afterwards he was tempted away to a chair of theoretical chemistry in Cambridge, and I succeeded him in Bristol. Here I found that Jones had applied quantum mechanics to give an explanation of the crystal structures of the so-called Hume-Rothery alloys. I was greatly attracted to using quantum mechanics for problems that could be of interest to industry - so I set to work to read Sommerfeld and Bethe, and three years later published a book with Jones, "Theory of the Properties of Metals and Alloys" with the object of extending the results of their article to alloys. The other influence at Bristol which turned me to solid state physics was some experimental work under Herbert Skinner on the soft X-ray emission band from light metals, lithium, magnesium and so on. These showed - as predicted by theory - that the conduction electrons occupied a band several electron volts wide, with a sharp upper limit. But the theory was one that neglected the interaction energy between the electrons, and it was not immediately clear why this very large effect should not greatly broaden this upper limit. In 1934 Jones, Skinner and I published a paper in the Physical Review (3) which explained why this should be so. In 1956 Landau (4) used an argument, essentially similar, to show that the Fermi surface in K-space was a real concept, and not just a mathematical fiction. One might perhaps have guessed this, as soon as Keesom and Kok (5) showed that the specific heat of a metal at low temperatures was linear in the temperature, corresponding to a fraction kT above the Fermi limit. This was, indeed, in 1934, the same year as our paper.

Apart from our work in Bristol, the main centre in the U.K. for the application of quantum mechanics to metals was the school of E.C. Stoner in Leeds, who applied the "collective electron model" to describe the magnetic properties of metals.

In Bristol, after we had published "Mott and Jones", I was joined by Ronald Gurney, and with him we turned our attention to non-metals, particularly to semiconductors. In those days it was not realized that silicon and germanium were semiconductors; they were thought by many to be "poor metals" - as in fact are if heavily doped. It was only during the war that, in the United States, sufficiently pure crystals of these materials were produced, Dr. Seitz being involved in the direction of this work. In the book which Gurney and I wrote (Electronic Processes in Ionic Crystals, Oxford 1940) silicon and germanium are not mentioned, though there is a chapter on semiconductors. Copper oxide was our semiconductor, but the title of the book, and the most important chapters, shows how much it was inspired by the work of Robert Pohl at Gottingen on colour centres, (F-centres) in alkali halides. Pohl - it seems to me - is the true father of that most important branch of solid state physics which deals with non-metals and with the enormous effects on their properties of traces of impurity. Every few weeks there came from Gottingen a reprint from the Gottingen Nachrichten, describing with admirable clarity the effects on the electrical and optical properties of these centres. Pohl, as his reminiscences (6) make clear, had little use for theory; "Papierphysik", he called it. "Theories change, but facts remain" - he said. But Gurney and I wanted to know what these centres were. At first we thought they were self-trapped electrons, that is Landau's polarons. But when we realized that they were electrons trapped by an anion vacancy, we had a model with which we could make calculations, and a theme that could be the foundation of a book. The calculation, with the help of our librarian M.J. Littleton (7) and carried out with a Bruswiga machine, set the pattern for much work in the future with modern computers, such as that at Harwell under Dr. A.M. Stoneham. But the war intervened, and these theories did not give rise to experimental work in this area in our country.

What lead Robert Pohl to this work? He recounts (6) that, coming to the chair at Göttingen after the war of 1914-18, no liquid air was available and instead of working on photo-emission, as he intended, he was driven to investigate photoconductivity which did not entail a high vacuum or a clean surface. He gives the impression that - because his work did not relate to Bohr's atomic theory - it was not held in high regard by his colleagues James Frank and Max Born, and he was gratified when Seitz and I considered it of importance, although we were theorists. It is rather ironic that it was considered to have no relation to Bohr's theory. Bohr's theory of the hydrogen atom could be used to describe the state of the electron in a donor in silicon or germanium, the electron being in a conduction band with appropriate effective mass. The electron in a F-centre is similar, but with a large core correction. But Pohl did not think in terms of band theory. He once stated that he had not read the paper of A.H. Wilson which made the distinction between metals and insulators, though he was aware of it.

I would now like to turn to the post war period, and to two subjects in which the contribution of the U.K. has been considerable, namely that of dislocations in crystals, and the electrical properties of non-crystalline materials. Speculation about the former began before the war, with the three papers that came out in 1934 by G.I. Taylor (8), E. Orowan (9) and G. Polanyi (10). Taylor's paper showed in particular that internal strains could be responsible for the resistance to the motion of dislocations. Taylor produced a theory of work-hardening in which the density of dislocations increased during plastic flow and the strains which hindered the motion of a given dislocation were caused by all the others. But Taylor's model was one-dimensional, treated only edge dislocations and - as he once told me - he had no model to explain how the dislocations were formed. None the less it produced a theory which accounted quantitatively for some experimental work by his co-workers on the work-hardening of single crystals. Nabarro and I (11) took hold of the idea that hardness was caused by internal strains and produced a theory of age hardening of alloys.

After the war Charles Frank joined my Bristol Laboratory and I suggested to him that he should look into the theory of crystal growth. He soon realized that, if new islands had to be nucleated on a crystal surface, there would have to be a high degree of super saturation in the gas or solution. This would *not* be the case if a screw dislocation terminated on the surface; Frank learned about these from published work of J.N. Burgers. Thus he was lead to his theory of spiral growth, for which much experimental evidence was obtained, and from it, simultaneously with W.T. Read in the U.S.A., to the model of the Frank-Read source as the agent for the formation of dislocations in a crystal undergoing plastic deformation.

Also in Bristol were the first experiments on making a dislocation visible by "decorating" it. J.W. Mitchell was working on silver bromide and the precipitation of silver under illumination, stimulated by the theory of the photographic latent image which Ronald Gurney and I had produced just before the war (12). He found (13) that silver was precipitated along a network of lines, visible under the optical microscope, which could be identified with dislocations. At the same time Alan Cottrell (14) was explaining the yield point of iron by the tendency of carbon to segregate on dislocations, thus locking them into position.

It is perhaps curious how late in the development of science came any attempt to explain the most useful property of metals, their ductility. The theory, when it came, did not involve quantum mechanics, or for its experimental test, advanced instrumentation. But it was not until we had the electron microscope that we could see dislocations without "decoration", or observe them in motion. I very well remember the day when some of Peter Hirsch's young men came into my room at the Cavendish Laboratory and said "Prof - come and see a moving dislocation".

Finally, I would like to say something about the electrical properties of non-crystalline solids. Interest in these originated in Eastern Europe, in Romania under Radu Grigorivici and Prague under Jan Tauc, in which countries the first international conferences were held in 1965 and '67, and in Leningrad under Boris Kolomiets. The group under Kolomiets studied the chalcogenide glasses, and their most striking result was that these materials could not be doped (15), while the crystals can. Thus the conductivity rises dramatically when a glass, not quite stoichiometric, crystallizes. The present author (16) gave an explanation of this property in 1969, the "eight minus N rule". Other early work in this area was John Ziman's (17) theory of the resistivity of liquid metals, written while he was a lecturer in the Cavendish Laboratory, and in America P.W. Anderson's paper (18) of 1958, "Absence of Diffusion in Certain Random Lattices". This paper showed that a metal, that is to say a material in which a condensed electron gas is present, could be an insulator at zero temperature even though the density of state N(E) was finite at the Fermi energy. In the early days there was a great deal of controversy about that (19).

The present author was the first to point out (in 1967) that, in the conduction band of a non-crystalline material, a sharp* energy E_c (later called the mobility edge) must separate localized from non-localized states, so that charged carriers in non-crystalline semiconductors have energies near E_c. Much of the experimental work on non-crystalline silicon and germanium is interpreted on this model, though it remains controversial. The leading experimental group in the United Kingdom is that of Walter Spear in Dundee. His techniques for measuring drift mobilities, used originally for observing polarons in sulphur and other materials, have been applied to amorphous silicon, and seem to show the existence of the mobility edge. His most important conclusions, obtained rather more than ten years ago, are:

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* The energy is sharp in a rigid lattice. In reality it is slightly broadened in the conduction band of semiconductors, the interaction with phonons leading to a finite life-time. But in metals at zero temperature it should be sharp.

(a) In evaporated or sputtered layers, a high concentration of dangling bonds leads to a short lifetime of photoexcited electrons. For films produced from a glow discharge in silane (a-SiH), most of these bonds are passivated by hydrogen, incorporated in the silicon to the extent of 5% or more; these show strong photoconductivity.

(b) These materials, unlike the glasses, can be doped by incorporating PH_3 or B_2H_4 in the glow discharge, so that p-n junctions in sheets covering large areas can be prepared. (20)

This has lead to a new industry, photovoltaics using silicon solar cells, for pocket calculators, watches and increasingly for more large-scale production of electricity of these cells (round 10% at present), to increase their stability and reduce their cost. Whether we shall see them installed in sunny areas as a major source of electricity, only the future can tell - but as fossil fuels become scarce and the dangers of nuclear reactors more apparent, it is difficult to see what else we shall have. If so, our children and grandchildren may depend on solid state physics, even more than we do at present.

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THE DEVELOPMENT OF SOLID STATE PHYSICS IN FRANCE AFTER 1945

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The precise topics of this colloquium is the development of Solid State Physics in Italy. So the role of the foreigners who have been kindly invited here is to bring information about the events in their own countries which may have had an influence in Italy. If I shall restrict myself to what happened in France, that should not be considered as a chauvinistic view of science. I shall not describe in detail what has been made especially in french laboratoires, but rather describe the conditions of the development of Solid State Physics in France after 1945.

First of all, let us give a rapid view of the state of physics in France in 1940, i.e. at the end of the period between World Wars I and II. That has been remarkably studied by D. Pestre[1]: his conclusions seem rather severe, but they are undoubtedly founded upon correct data. The main features are the following:

i) the small number of searchers; all of them belong to Universities, but only part of the Professors and Assistants do effectively research.

ii) the level of the budgets of research is incredibly low by our present standards: the public, and thus the politicians, have a weak interest in Science, in particular because the unavoidable links between science and industry are not clearly understood.

iii) in addition, some features are specific to France: there has been considerable losses of brilliant young scientists during the 14-18 war (in comparison, the Germans have much better preserved their elite); theoretical physics was certainly underdeveloped: good experiments, the collection of very sure data were preferred to theoretical speculation, regarded as woolly-minded.

That reflected a philosophical attitude, inherited from the positivism of A. Comte, and a profound mistrust for ideas not directly deduced from the observation. Of course there has been some brilliant exceptions, Louis de Broglie, Leon Brillouin, for instance. But let us point out that both worked isolated, almost without students; they did not care to build a school around them. So those who have studied physics in France in the thirties had a very vague idea of Quantum Mechanics and they had not been trained to use it.

A major difference with the present situation was the lack of regular communications with the foreign laboratories, and even between the french laboratories. A remarkable event has been the first international conference of magnetism, held in Strasbourg in July 1939.

These views are valid for Physics in general: what about the special domain we are interested in ? In France, as everywhere in the other developed countries, the concept of a special chapter of Physics devoted to solid state did not exist. In fact, the name itself was adopted after the appearance of the famous book of F. Seitz in 1940. There were laboratories working on special properties of a solid or a kind of solids; but these properties were not regarded as consequences of general theories of the behaviour of atoms and electrons in crystals.

Let us quote some of the french laboratories which were the more active in these fields, just before the war:

- the laboratory of magnetism, founded in Strasbourg by P. Weiss: L. Néel began his career in Strasbourg. Another group worked in Bellevue (near Paris) with the largest electro-magnet built in France (Aime Cotton).

- optical properties of crystals were studied in Bellevue and in Paris.

- the crystallographers were originally members of mineralogy departments: there were some equipments for X-ray diffraction used for structure determinations (mainly inorganic crystals and natural minerals, Ch. Maugin, J. Wyart). But already since 1936, some typical problems of Solid State Physics had been approached: the temperature diffuse scattering (J. Laval), microheterogeneities in metallic solid solutions by small angle X-ray scattering (A. Guinier).

- the Physics of Metals, which was, in fact, the study of the mechanical properties of metals, was developed mainly outside the Physics Departments of the Universities, but rather in technical or chemical laboratories, because metallurgy was then considered as a branch of chemistry. Some research groups had a good international reputation (Portevin, Chevenard).

To sum up, there were in 1940 in France a few individuals, prepared to launch themselves in Solid State Physics. But much too few were aware of the importance of the new Quantum Physics.

Then came the dark days of the war and of the occupation: of course, the scientific activity was considerably reduced. We have suffered severe losses, but they were not on the same scale than the catastrophic hecatomb of World War I.

A few years after the end of the war, the situation of science in France had considerably improved, the change being very rapid. During the fifties the gap between the scientific level of France and of the anglo-saxon countries was progressively reduced. It happened that this scientific "Renaissance" of France coincided with the very rapid development of the new Solid State Physics in the world. So many of those who were at that time attracted by Science chose Solid State Physics, which looked as a domain of very large possibilities.

We are going to try to analyze the process of modification of the scientific climate, in order to understand why such advances in Solid State Physics could be realized during the postwar period.

Some conditions were not peculiar to France, as, in the first place, the change of the public opinion about science. The belligerent nations had learned the role of science in the fate of a country (radar, atombomb, ...). Although France has played no role in these developments, every-body was there nevertheless convinced that now a nation could not hope to be a great power without having its share in the scientific progresses. So the ridiculous research budgets of the prewar period were soon only a bad remembrance (of course, as it is the rule, scientists were not fully satisfied with their budgets).

Still more important was the sudden arrival in the laboratories of many young gifted students who, some years before, would have chosen other careers, in teaching, industry or administration.

In France, two specific features have, in my opinion, played the major role to promote the new Solid State Physics.

i) We had been during four years completely cut from the outside world where science had progressed; and, as already told, in the old generation, there were rare individuals familiar enough with the most modern domains of physics to be able to lead groups of young people in good directions: especially the lack of theoreticists was very serious. That is why many of our best students spent some years in reputed laboratories outside France, mainly in U.K. or U.S.A. to acquire the formation which was indispensable to begin rapidly valuable researches: afterwards they became leaders in the fifties and sixties. So, A. Abragam made his thesis at Oxford, J. Friedel in Bristol with Sir Nevill Mott, etc... They came back to France, the problem of brain-drain being negligible. The friendly help we have received from the scientific community has been a decisive factor for the start of progresses in France. The international relations remained satisfactory. In particular, our links with the Italian colleagues have been always strong, thanks especially to the Summer Schools (Les Houches, Varenna).

ii) A second important feature has been an administrative structure: the rapid creation after the war of several powerful agencies, which have been more efficient than the existing Universities or the CNRS, still at its beginning. The Universities were faced with the problems due to the considerable increase of the number of students; the laboratories which had to be created were out of proportion with the existing ones. On the other hand, the statutes of the Universities were too rigid to accomodate a sudden flow of young searchers and, finally, the conditions for an indispensable links with industry were not adequate.

The first agency was CEA (Commissariat à l'Energie Atomique). It is certain that the main idea of its founder, C. de Gaulle, was, at the first place, to give France an access to the "Nuclear Power". But, since the beginning, the Directors of CEA, especially F. Joliot-Curie, have very wisely set up groups of fundamental researches besides the numerous various technical departments. The part of the total budget of CEA devoted to research was rather small, but, in absolute value, much larger than the budget of any University. The researches in CEA have not been limited to nuclear physics, but covered many domains, in particular, theoretical physics and solid state physics. In a few years, CEA had a very strong groups of solid state physics, mainly because CEA succeeded in hiring scientists of very high quality.

Another Agency, created in 1946, was ONERA (Office National d'Etudes et de Recherches Aéronautiques (now aerospatiales)). The domain of ONERA is clearly defined by its name: here also, a part of the activity was reserved to fundamental researches: the role of ONERA in Materials Sciences has been very important.

IRSID (Institut de Recherches Sidérurgiques) has been also founded a few years after the war. It is an industrial laboratory, financed by the whole steel industry. Today, it is mainly technical but, at the beginning, IRSID played an important role in the physics of metals.

A little later, the CNRS (Centre National de la Recherche Scientifique) was progressively but considerably developed. CNRS had started in 1936 on a very modest scale.

The originality of CNRS lies in its dual role: it has its own laboratories and it is a very important source of money and personnel for the best laboratories of the Universities. So the full time searchers of CNRS are mixed with members of Universities having their teaching duties.

Experience has shown that this formula was good. One of the advantages of CNRS is its system of evaluation of the activity of the personnel and the laboratories by the "Comité National".

The phase of the modernization of the Universities came later, roughly from 1955 to 1970. Now, all the science faculties in operation in any french city have been built during that period. It was obviously fully justified because the old ones were completely unadapted as well to the number of students as to the needs for good researches. In any University town, new buildings were erected, and new jobs created. The chairs, called "general physics" were diversified: the first chair of solid state physics was created in Paris in 1958. Many groups specialized in this discipline were started: it was relatively easy because the necessary basic equipment was not too heavy.

If the initial impulse for the researches in solid state physics came partly from outside the universities, an equilibrium had been reached between universitary and not-universitary research centers. It is important to point out that, in general, the relations between the two kinds of laboratories have been good: frequent exchanges took place and part of the research in university laboratories has been subsidized by CEA or ONERA, through contracts. The existence of a good spirit of collaboration between the individuals has been fortunate, because, as it is well known, that is more efficient than the best administrative structures.

THE FORMATION OF SOLID STATE PHYSICS GROUPS IN FRANCE IN THE PERIOD 45-60

I would like now to analyze the origins of some important groups of research and their evolution in the general environment, which has just been described. Of course the division into separate groups is somewhat arbitrary because there are always links between them. We are not trying to be complete, but rather to show what have been the various processes of formation of these groups. In any case, the order we have adopted relies by no means on a judgment upon the importance or the quality of the group.

The Orsay group

The "Laboratoire de Physique des Solides d'Orsay" started in 1960: its origin was the desire of J. Friedel, A. Guinier and R. Castaing to unite their research groups in a common laboratory. All of them were Professors at the Paris University, but they worked in various places (Ecole des Mines, Conservatoire des Arts et Metiers, ONERA), because the overcrowded University had never been able to offer them any space. The building of the new campus at Orsay gave them the first opportunity to work in a laboratory within the University they belonged to. The initial group grew continuously: other Professors or CNRS searchers joined it (P.G. de Gennes, G. Toulouse, etc...). The first building, shared with other laboratories, became rapidly too small: a new building was finished in 1970. Now the laboratory has reached a stable size (100 searchers).

J. Friedel began his works on the theories of solid state with Prof. Sir Nevill Mott: he has been always interested by the two aspects which are generally separated: the atomic structures of solids (dislocations, mechanical properties) and the behaviour of electrons in crystals (electrical, magnetic,... properties). So he was for a great part responsible of the development in France of all the various branches of solid state physics. Practically, every physicist of that discipline has been directly, or indirectly, student of J. Friedel.

The works of A. Guinier on X-ray diffraction had begun before the war: it was then showed that, thanks to an improvement of the diffraction techniques (monochromatization of the primary beam), it was possible to register, not only the Bragg reflections, but also the scattered radiation outside the reflections in the whole reciprocal space. One could then detect and study the defects of periodicity of the crystals: that gives essential data to the solid state physicist. Before its installation at Orsay, his laboratory lived thanks to the help of ONERA, but its situation was much better in Orsay, mainly because interactions with the other groups, experimentalists and theoreticians, became very easy.

R. Castaing began his career at ONERA; there, he had at his disposal in 1948 one of the first electron microscope in use in France. He developed various techniques for the preparation of samples: remember that, at that time, the instrument itself was already very good but its utility in solid state physics had not yet been proved because one did not know how to prepare "good" samples, which should be very thin and nevertheless representative of the bulk of the matter. Then R. Castaing built the first electron microprobe; later on, he developed other methods of point analysis, in particular with G. Slodzian (ionic microprobe). The example of the work of R. Castaing is typical: around 1950, it was quite impossible to realize a big instrument as a microprobe, within an universitary laboratory. That has been possible in ONERA, which received in that case an important help of another laboratory, IRSID.

The Orsay Laboratory gives a good image of the development of many research groups in France: just a few nuclei after 1945, a rapid growth supported by various sources, from 45 to 60, and then, a normalization thanks to CNRS and the University.

The Ecole Normale Supérieure Group.

A large, and very modern, physics laboratory had been finished just before the war (such a construction was exceptional). In 1945, it was yet far from being completely full. It had a very important advantage, namely, the remarkable source of young talents, the students of ENS. The Director, Y. Rocard, was free to choose future orientations for his laboratory: he had the remarkable intuition of the great possibilities of a domain quite recently opened, the semi-conductors. During a visit to the USA, he met a young marine officer which was making a stage in F. Seitz's laboratory, P. Aigrain.

Y. Rocard persuaded him to abandon the Marine for a scientific career and offered him to lead a group ad ENS. That was the beginning of the semi-conductors laboratory, which acquired rapidly a good international reputation. The group after so many years is still flourishing (J. Bok); many of those who founded new groups in various Universities were coming from the ENS group. An interesting popularity of the ENS group has been its strong links with industrial laboratories(CSF, Thomson, for instance); that was not usual in France and the success of these relations was a good example for others laboratories.

The Grenoble Group.

It is well known that Grenoble is now, outside Paris, the more active french city for science and technology. Its astonishing development began just at the end of the war and one can say that its origin is the action of a single man, Louis Néel. L. Néel had to leave Strasbourg at the beginning of the war, the whole faculty of science being transferred to Clermont-Ferrand. L. Néel, looking for the best suitable place for his work, chose the Grenoble University: it was then a small place with a staff of only a few people and very little equipment. Practically alone, L. Néel set up a laboratory for magnetism. Progressively high quality scientists came to Grenoble, because they were attracted by the strong personality of L. Néel. The growing laboratory was no more confined to magnetism as formerly in Strasbourg, but opened to different techniques (that was the effect of the concept of Solid State Physics which was then prevailing): crystallography (E.F. Bertaut), low temperatures (L. Weil); dielectrics (N. Felici), etc... Much later, a group of theoreticists was formed (Ph. Nozières and M. Cyrot). Grenoble gave many examples of the benefits of interdomains collaboration: the discovery of Garnet by the crystallographers of the Bertaut group is a suite of the preoccupations of the magnetism group.

When CEA decided the creation of a research center outside Paris, Grenoble has been chosen, partly because of the quality and the activity of the team gathered around Néel. Conversely, this creation provoked a considerable increase of the scientific city. L. Néel has been at the same time Director of the CNRS lab and of CENG. Besides CENG, with the new big instruments, like neutrons reactors and accelerators, CNRS developed its own laboratories and a new University was built.

On account of its successes, Grenoble became the site of several international research Institutes, which again were a new factor of development (Laue Langevin High Flux Reactor, Intense Magnetic Fields, and soon Synchrotron Radiation Sources). It is noteworthy to remark that in spite of the diversification of the activities of Grenoble, the pole certainly remains Solid State Physics.

The CEA Group.

Almost every techniques of Solid State Physics have been developed in one of the laboratories of CEA. But we would like to insist on one of them only, which is specifically based upon the use of the facilities of CEA: the study of phonons in crystals. In 1940, J. Laval had established a theory of the diffraction of waves by phonons; the experiments, carried out with X-rays, proved the possibility of determining the dispersion curve of phonons; but these experiments were very difficult, in particular for the crystals with more than on atom by unit cell. After the discovery of neutron diffraction by Shull it appeared that the inelastic scattering of neutrons was a much more powerful tool, because it was possible to measure directly the frequency of the phonon.

It happened that some of the students of J. Laval, well aware of the theory of lattice vibrations, entered the CEA. So, as soon as the Saclay reactor was in operation. J. Herpin, P. Meriel, D. Cribier and B. Jacrot developed successfully the inelastic techniques for phonons and also magnons. This kind of research remained during years a strong point of the program of CEA, not only in Saclay, but also in Grenoble, and especially ILL. The same group studied also neutron diffraction for the determination of atomic and magnetic structures in relation with the magnetism group (ferromagnetism, helimagnetism etc...).

CONCLUSION

In 1940, the level of science in France was undoubtedly too low. It is a fact that France had not succeeded to follow the powerful scientific movement which took place from 1920 to 1940 in other countries, in Europe or in the States. 20 years afterwards, the situation had substantially changed: on the average, the scientific activity in France was comparable to that of neighboring nations. Of course, given the size of France, the different special disciplines are not all at the top level; but such fluctuations are normal, and without inconvenients, on account of the multiple communications through the borders. On the contrary, it is preferable that different countries be well in advance in a few narrow domains.

The scientific Renaissance in France has been especially beneficial to the Solid State Physics, which was then rapidly growing to become one of the more important domains of Physics. However, I would not like to appear too optimistic: it remains certainly some negative points, which have not been overcome during the glorious period 45-60.

The connections between fundamental research and their applications are still insufficient. Perhaps the character of the average french scientist is more responsible of this defect than some inadequacy of the administrative structures. For the majority of scientists a success in fundamental research, especially in abstract theory, has a greater intellectual value than the realization of a new useful instrument or the preparation of a series of solids, one of which will perhaps have remarkable properties. The French has not the continuous obsession of a possible fruitful application. We had recently a typical example: the first "miracle" superconductor had been prepared in a french laboratory; its electrical conductivity had been measured carefully up to -100 C. But no one of the team had the systematic reflex to check the new product for an eventual superconductivity, even if one knows that a success is highly improbable. Another significative example is the story of the Castaing microprobe. A very good laboratory prototype had been built in ONERA. In 1953, no other apparatus in the world had similar performances, and it was obvious that it was wanted by many metallurgical and mineralogical laboratories. But the study and the realization of a commercial apparatus by a french company has been very slow: the first one was operating 10 years after the initial paper of Castaing. So a valuable technical advance which should have been beneficial for the french instrumentation industry has been partly lost.

The growth rate of CNRS and of the Universities has been anomalously high, chiefly around 1960: at that time, it was relatively easy to get money to extend a laboratory or to buy new equipments. But that happy time could not go on indefinitely: stabilization began around 1970. Unfortunately at the same time the economic situation became more difficult. Money became rare for scientists, not only for new projects but simply for the maintenance and the correct functioning of the existing equipment. It is a fact that now some groups have difficulties to avoid a real decay of their working possibilities. One must be conscious that the activity which we have known around 1960 is higher than in a long term equilibrium state.

During the period of explosion of scientific research, the immediate need for searchers and University teachers were considerable. Many new jobs were created and the recruitment of the personnel has been very rapid. We feel today that perhaps, in some cases, it has been too rapid, and that the quality has not ever been maintained at the desirable level. When the period of stabilization came, the number of opportunities for young searchers dropped suddenly. The body of scientists in the whole is almost frozen since a few years, deprived from the necessary renewal by young people, whereas the majority of the older is still far from the retirement age. That constitutes a very serious problem for which, as far as I know, no perfect solution has been proposed. One can fear that, in the latest years, we have lost many young talents who could not be used in scientific researches. To sum up, Solid State Physics started in France from a low level, almost nothing, in 1945. Then it grew up rapidly, reaching its maximum in the sixties. Since 1970, scientists have had many difficulties to maintain their level of activity: insufficient budgets, too few young searchers, and perhaps, the older ones have a little lost the enthusiasm they had during the triumphant youth of Solid State Physics.

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MAGNETISM IN FRANCE THROUGH THE HISTORY OF THE MOLECULAR FIELD FROM 1895 TO 1948

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1-Modern magnetism in France was essentially the task of four physicists: Pierre Curie, Paul Langevin, Pierre Weiss and Louis Néel. In this scope, Curie and Langevin worked alone; on the contrary, Weiss and Néel worked with several collaborators.

There are many aspects in magnetism of matter; so I have to limit my talk to a few selected points. I chose to speak about the introduction of the *molecular field* and about the main steps of its evolution. This choice will allow us to put together some parts of these four physicists' works from 1895 to 1948.

2-Before beginning, just a recall about general aspects of the problem of magnetization:

-In order to describe the magnetic properties of materials, one must have a quantitative measure of magnetization. Such a measure is the *intensity of magnetization* or the *magnetic moment per unit volume*. We represent it by the symbol I.

-When a piece of unmagnetized iron is subject to an external magnetic field, the magnetization induced in the iron by the field is described by a magnetization curve obtained by plotting I against the field strength H. Figure 1 shows a typical curve where the two main characteristic features are shown: the saturation magnetization I_0 and the hysteresis loop. Materials which have magnetic properties similar to iron are *ferromagnetic*.

-Another class of materials is characterized by a magnetization proportional to the applied field. The *susceptibility* χ of a material of this type is defined as the increase in magnetic moment caused by the application of a field: $\chi = I/H$. χ is a positive coefficient, independent of the field strength and dependent on the temperature. The materials of this class are paramagnetic. In order to describe the properties of paramagnetic materials χ is plotted against the temperature T.

3-Pierre Curie published a paper in 1895 (1) about the magnetic properties of materials at various temperatures. His measurements led him to formulate the first experimental law in the history of magnetism. Let's give a short review of his conclusions:

- Above a certain temperature, a ferromagnetic material behaves like a paramagnetic one. The higher the temperature, the better χ versus T obeys the law: $\chi = C/T$.

- Among the paramagnetic materials that he studied, the variation law $\chi = C/T$ could be considered like a rather good approximate law.

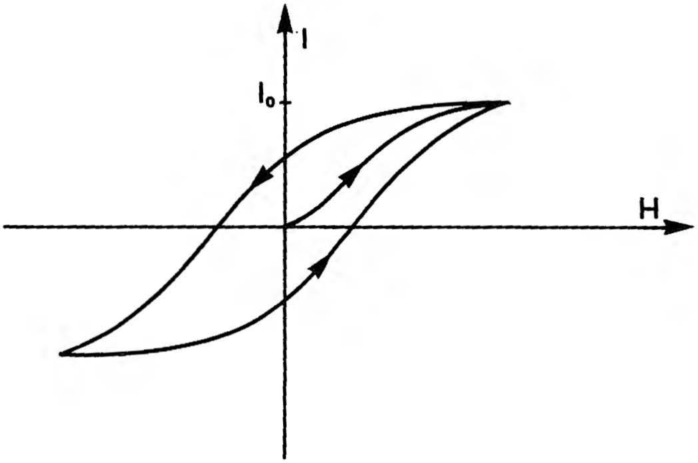

Fig. 1

Curie did not find this law by chance. In 1865, Wiedemann, a German physicist, had proposed the law : $\chi = \chi_o (1 - \alpha t)$ for several paramagnetic salts. Moreover, he thought that α could be measured by the same number as the gas expansion coefficient $1/T$, the same for all salts. Later, in 1890, five years before Curie's work, Plessner, another German physicist, confirmed this particular type of variation. In Wiedemann's expression, χ_o was the susceptibility at the melting-point of ice. Curie wondered whether such results were a pure coincidence or the expression of a natural law. If it was a natural law, the fact should remain true even after choosing another reference point for the temperature. Hence: $(1/\chi)(d\chi/dT) = -(1/T)$ from which the result $\chi = C/T$ followed immediately. That was why Curie calculated the product of χ by T. He concluded that Wiedemann's results, Plessner's results and his own measurements wouldn't allow to confirm the guess of his two predecessors about paramagnetic salts. As to the law $\chi = C/T$, named today Curie's law, it could only be, in his mind, either a limit law for ferromagnetic materials or an approximate law for paramagnetic materials. In other words, Wiedemann's guess influenced Plesser and inspired an idea in Curie.

Curie did not forget to stress the exceptions to his rule. That is why he only said: "*The law of variation has a hyperbolic shape and c varies inversely with absolute temperature as often as it does not*" (2). At that time, exceptions were rare enough for Curie's formulation being accepted as a law. Later, the number of exceptions grew and grew but, meanwhile, Curie's law had received a theoretical support thanks to Langevin.

4-Langevin's theory of paramagnetism is well known. His paper (3) was published in 1905, before the appearance of the first quantum theory. Langevin justified the possibility for an atom or a molecule to have a magnetic moment μ with the classical knowledge of that time. Then, he transposed the kinetic theory of an ideal gas in a gravitational field to the case of a population of independent elementary magnetic moments interacting with a magnetic field H.

As a result of his calculation, he obtained the formula:

$$I = I_O (\coth a - 1/a)$$

where $a = \mu H/kT$ and $I_0 = N\mu$ (N is the number of magnetic moments per unit volume).

The two interesting features of this result are:

- the saturation magnetization I_0, when a is very large;

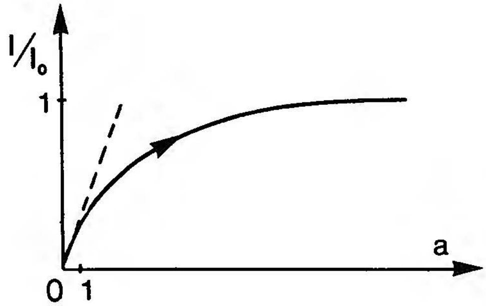

Fig. 2

- a linear dependence of I on H/T when a<<1, given by the approximate expression:

$$I = I_0\, a/3 = N\, \mu^2\, H/3\, k\, T = C\, H/T \qquad \textit{(Equation 1)}$$

In the latter expression, we recognize Curie's law. Now, the constant C allows the calculation of the value of a microscopic quantity, the elementary magnetic moment μ. Besides, the shape of the curve of the function I(a) (figure 2) looks like the curve of magnetization of iron (figure 1). Then, it could be reasonable to assume the existence of a saturation magnetization for paramagnetic materials too. In order to justify the fact that such a saturation magnetization had not been observed yet, Langevin used Curie's measurements to calculate the magnetic field strength needed to observe the beginning of saturation in oxygen (a paramagnetic gas) and found that it was beyond the reach of experiment.

Such an unverifiable possibility could however open up a way toward an explanation of the ferromagnetic phenomenon. As he had, so far, left aside mutual actions between magnetic moments in his theory, Langevin wondered whether such actions might act like an intense field and make possible the saturation in a ferromagnetic. The idea of a molecular interaction whose effects would be comparable with those of a magnetizing field had just been launched.

5-At this stage, it is interesting to mention that magnetism, all along its history, has been taken up with two different viewpoints. One viewpoint is directed at the isolated element: atom, molecule or magnetic moment; the other embraces a piece of matter. The former intends to deduce the ferromagnetic properties of matter from the knowledge of its constituents; the latter gives up the ambition of elucidating the details and intends to give an account of the effects.

Langevin's theory could satisfy both approaches. On one hand, it offered the hope to improve the knowledge of the microscopic constitution of matter by calculating the value of magnetic moment with the aid of the expression $C = N\mu^2/3\kappa$ which exempted from reaching experimentally the saturation magnetization I_0. On the other hand, it invited to develop the idea of an internal magnetizing field in order to describe the ferromagnetic property.

Weiss will successively adopt both of these viewpoints. In 1907 his comprehensive view will lead him to formulate his famous molecular field hypothesis. Later, when he focuses his attention on the isolated magnetic moment, he will misguide himself in the fruitless research of the experimental magneton. It is a pity that he gave up his first fruitful approach. It resulted in a waste of time till Néel resumed, twenty years later, this approach which led him to the theory of antiferromagnetism.

6-Two steps led Weiss to the formulation of the molecular field hypothesis. Before 1905 he was interested in magnetism in crystals. He especially made a lot of investigations about pyrrhotite crystals (4). Such a crystal is strongly anisotropic. Weiss reported that it is quite difficult to magnetize the sample in the direction perpendicular to the cleavage plane. In the cleavage plane, he defined an axis where the magnetization was easy and another one, orthogonal to the former, where it was more difficult. He managed to give an account of his observations and measurements in this plane by imagining the action of a demagnetizing field in the direction of difficult magnetization. He wrote: *"Everything happens as if a demagnetizing field, due to the substance structure, canceled a component of the field proportional to the component of the magnetization vector in the difficult magnetization direction. As a result, the remaining applied field component would be parallel to the magnetization vector"* (5).

In other words (figure 3), the demagnetizing field is $H_d = -NI \sin \varphi$ and $(\underline{H}_{applied} + \underline{H}_d)$ is a vector parallel to the magnetization $\underline{I}$. From that, it follows immediately:

$$H\, I \sin(\alpha - \varphi) = N\, I^2 \sin\varphi \cos\varphi \quad (\textit{Equation } 2).$$

Weiss named this demagnetizing field the "*structural field*". In his mind, it was a uniform field due to the structure of a material observed at a macroscopic scale.

At this point of his investigations, Weiss assumed that, in a ferromagnetic substance (pyrrhotite was classified at that time in the ferromagnetic category), something opposes the magnetization in the difficult magnetization direction. Hence, we may suppose that a substance would be easily magnetized if something, caused by its structure, wouldn't oppose its natural bent. In other words, a ferromagnetic material misses an attribute whereas a paramagnetic one has got it.

In 1907, Weiss's opinion is radically different(6). Now, a ferromagnetic material has an attribute and a paramagnetic one has not got it. This attribute is brought by the interactions between magnetic moments which promote the magnetization in an applied field. That is (¶4) Langevin's hint, that we mentioned above, about a magnetizing field. Weiss had made use of it: it resulted in the "*molecular field hypothesis*".

7-As Weiss was interested in understanding the pyrrhotite properties, we will briefly show how he introduced his new idea in the former description of the pyrrhotite crystal.

Weiss considered that the crystalline edifice possessed three orthogonal planes of symmetry and that each of the three components of the molecular field was proportional to the corresponding component of the magnetization vector with a different positive coefficient for each of the three axes.

Let N_1, N_2 and N_3 be these coefficients. The three components of the molecular field h are: $h_x = N_1 I_x$, $h_y = N_2 I_y$ and $h_z = N_3 I_z$. In the magnetic plane of the pyrrhotite crystal, Weiss only needed the first two components. In order to restore the parallelism of the magnetization vector and the effective magnetic field that he had assumed previously (fig. 3), this time he had to add, to the applied field, the components h_x and h_y with fit values for N_1 and N_2 (fig. 4).

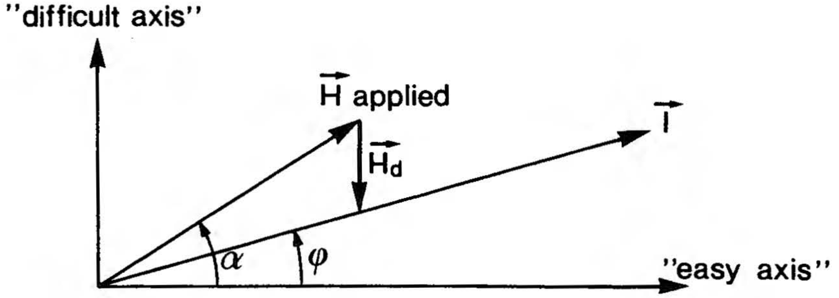

Fig. 3

In that way, he obtained the relation:

$$H I \sin(\alpha - \varphi) - (N_1 - N_2) I^2 \sin\varphi \cos\varphi = 0$$

This approach is fundamentally different from the first one, in 1905. In spite of this unquestionable fact, Weiss endeavoured to conciliate them. He used the formal similarity between the latter equation and equation 2 and concluded that N in equation 2 might be identified with N_1-N_2 in the new equation. He wanted to see the structural field as somewhat of a resultant molecular field. The larger increase of the field in the x-direction than in the y-direction could be interpreted as a decrease of the magnetic field in the y-direction. In another statement, Weiss will write later (7): *"The structural field is not a demagnetizing field but a molecular field deficit"* (his italics).

The formulation of the molecular field hypothesis is a break in the history of magnetism. Moreover it inaugurates the theories of collective phenomena. The beginning of a new era doesn't cancel, however, what occurred before. That is particularly true in the protagonist's mind. In Weiss mind, the molecular field kept up the original characteristic he assigned to the structural field: being uniform at a macroscopic scale. This previous notion at the back of his mind will prevent him from making a larger use of his hypothesis.

As he succeeded in explaining the magnetism in the pyrrhotite crystal with the help of the molecular field, Weiss thought he had got a proof of the efficiency of his new concept. In fact, Weiss never elucidated the behaviour of pyrrhotite. Its properties can only be explained with the notions of phases and modes that Néel (8) introduced in the study of the magnetic domains in 1944.

The right hypothesis which founded the theory of ferromagnetism had actually got its origin in the wrong understanding of magnetic properties observed in a substance which

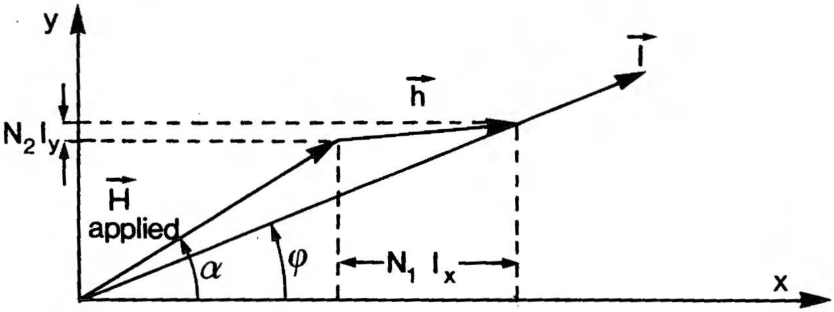

Fig. 4

was not so much a true ferromagnetic one. In fact, pyrrhotite is rather somewhat of a ferrimagnetic substance (9).

8-The concept of molecular field turned out really fruitful when applied to isotropic materials. Weiss (10) extended the Lagevin's theory to ferromagnetism by adding the molecular field to the applied magnetic field. In an isotropic substance the molecular field expression is simply: $h = N I$; hence, the coefficient a (¶4) is: $\alpha = \mu(H + NI)/kT$ and the formula $I = I_0(\coth a - 1/a)$ is unchanged.

This formula is very important in the theory of ferromagnetism because it purports that, at zero applied field ($H = 0$), a ferromagnetic substance is spontaneously magnetized as long as the temperature remains below a certain temperature T_c. The problems linked to the spontaneous magnetization go beyond the limits of our investigation. So, we don't expatiate any more on this disturbing result. As we are concerned with the concept of molecular field, we will turn our attention to another aspect of this formula.

We saw that (¶4) the magnetization I is linearly dependent on a when a<<1. By the introduction of the molecular field, the expression (1) in ¶-4 is now written:

$$I = C(H + NI)/T \quad \text{or } I = CH/(T-T_c) \quad \text{where } T_c = N\,C$$

This law is not exactly Curie's law. Weiss noticed, however, that iron, just above the transition temperature, as reported by Curie, obeys this law. Thus, Weiss (11) distinguished the *spontaneous ferromagnetism* below T_C from what he called the *incited ferromagnetism by the applied field,* above T_C. In other words, just above T_C, the interactions between magnetic moments are not yet negligible. At higher temperature, they are quite inoperative and the substance then obeys the Curie law as an ideal paramagnetic one.

The latter law $I = CH/(T-T_C)$ turned out to be useful for paramagnetic materials too. Curie had noticed that some substances had a susceptibility which did not obey the simple hyperbolic law $I = CH/T$: the χ versus $1/T$ curve had a steeper slope. Weiss showed that, in those cases, a law like $I = CH/(T-\theta)$ was obeyed. In this expression, θ is no more a transition temperature since only paramagnetic materials are concerned here. This phenomenon could be described as somewhat of a *paramagnetism magnified by the molecular field.* This law, obeyed by many substances, is known as the Curie-Weiss law.

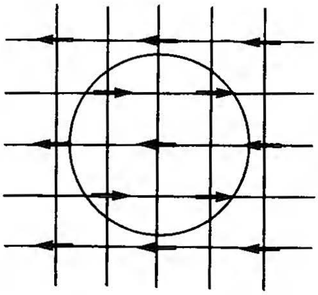

Fig. 5

In conclusion, the concept of molecular field had been helpful in ferromagnetic as well as in paramagnetic materials. In both cases it enhanced the magnetic character of a substance and could be evaluated with the relation: θ (or T_C) = N C.

9-Weiss took another step (12), in 1911, to extend the use of this law. He noticed that iron had, in its γ-phase, a susceptibility which decreased more slowly than expected according to the simple hyperbolic law $\chi = C/T$. The experimental curve was represented by the equation $\chi = C/(T-\theta)$ where θ was, this time, a negative coefficient. Such a result could be explained with the help of a negative molecular field coefficient N. The molecular field was no more magnetizing; it opposed the magnetization. Weiss concluded: "*It is the first time that we are led to give this sign to the field produced on a molecule by the other molecules enclosed in its sphere of molecular action, but it doesn't seem there is any objection to raise*" (13).

At this stage, Weiss had to make up his mind about the size of the sphere of molecular action. Did it enclose a large number of magnetic moments or, on the contrary, few of them?

Weiss hesitated between the two answers. On one hand, he knew that the interactions should decrease with the sixth power of the reciprocal distance. He had got this result by comparing his observations with Maurain's observations on magnetic thin films (14). If this result was true the sphere around a magnetic moment should enclose only the nearest neighbours and the reduced number of them should imply a sensible effect due to their fluctuations. On the other hand, the stability of the magnetization let believe that the fluctuations were without any effect and that, consequently, the number of magnetic moments involved in the molecular field was large.

Weiss inclined to the second hypothesis. As we already mentioned, the structural field was linked to demagnetizing effects without variation on a range of several microns and Weiss inclined to attribute to the molecular field the features he had first given to the structural field.

On the contrary, if he had chosen to reduce the size of the sphere of molecular action till it enclosed only the first neighbours, he could have explained the negative molecular field as a negative interaction between two neighbours. Fig. 5 shows such an interaction in a special configuration.

In 1911, Weiss was already engaged in the research of the magneton. We have to wait until 1928 before a continuation may be given to the story of the molecular field.

10-Néel started with the curve representing the inverse of the susceptibility $1/\chi$ as a function of the temperature for various alloys of iron. It was known that this curve is linear at high temperature, obeying the law $1/\chi = C/(T-\theta)$ but is bended at lower temperature (fig. 6). It is therefore convenient to define a paramagnetic Curie point θ_p given by the linear law and a ferromagnetic Curie point at which ferromagnetism appears. The theory of Weiss doesn't distinguish between these two temperatures. Since the latter describes a ferromagnetic material as a paramagnetic one endowed with a uniform molecular field, Néel decided to evaluate the effect that a non-uniform molecular field would have. He based his work on the fact that the interactions between magnetic moments should be of short range. Néel was aware of Heisenberg's theory of short range exchange interaction but it doesn't seem that this paper was decisive for him; anyway he would have begun in the same way since, as he says,: "If Weiss had thought out properly the consequences of an interaction of the type $1/d^6$, he would have realized that the molecular field could not be uniform" (15). But, as we mentioned, Weiss was more interested in the origin of the molecular field through the understanding of the constitution of the atom. Nèel took the question at another level: "*I am not making any hypothesis about the origin of the potential energy between two carriers (of magnetic moments); I shall simply assume that it exists*" (16). The non-uniformity of the molecular field is taken into account by separating the environment of a carrier into two zones. The first zone encloses the nearest neighbours. They give a very strong contribution and, because of their small number, their fluctuations have a large effect. The second zone contains the more distant carriers. Each one has a weak contribution but, because of their large number, their combined effect is not negligible. On the contrary their fluctuations are not important. That is why Néel described the contribution of the carriers inside the second zone by Weiss' molecular field.

As a result of a statistical calculation, Néel explained the behaviour of ferromagnetics over a range of one hundred degrees around the transition point. He showed in particular that the fluctuations of the molecular field due to the nearest neighbours could account for the two Curie temperatures (fig. 7).

This outcome assured him that the right approach was in defining a local molecular field, not necessarily the same in all points of the substance, since it had to depend on the immediate environment around each point. The Weiss molecular field had not, however, to be dropped, but used as an average value of the local molecular field.

Such an idea could be extended to substances containing several kind of atoms. Néel thus introduced a binary alloy, constituted of atoms A and B, with three molecular field coefficients representing interactions between A and A, B and B, A and B. The action of the atoms which are neighbours to A is described by a local field h_A, equal to the sum of terms proportional to the contributions J_A of atoms A and J_B of atoms B to the total magnetization. Thus:

$$h_A = a\,J_A + b\,J_B$$

(*equations 3*) (17)

$$h_B = b\,J_A + c\,J_B$$

This model gave him results nearer to experiment for these alloys.

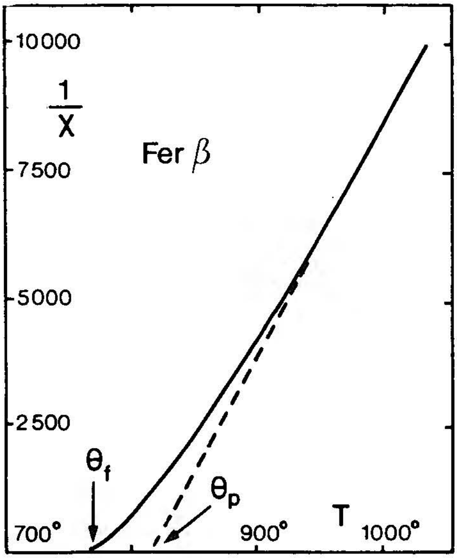

Fig. 6

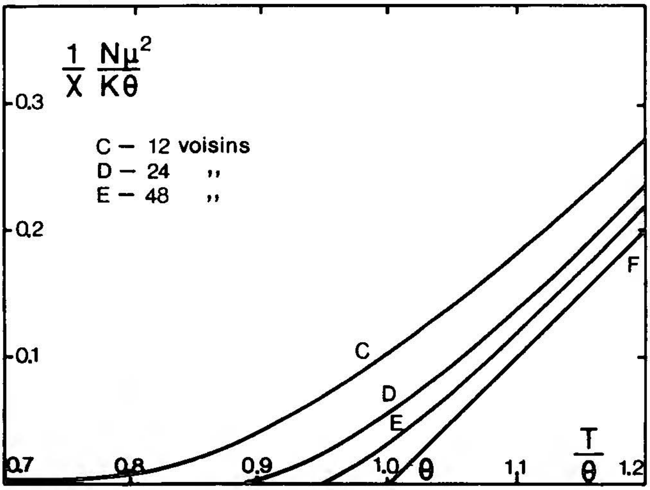

Fig. 7

$$h_A = a\,J_A + b\,J_B$$

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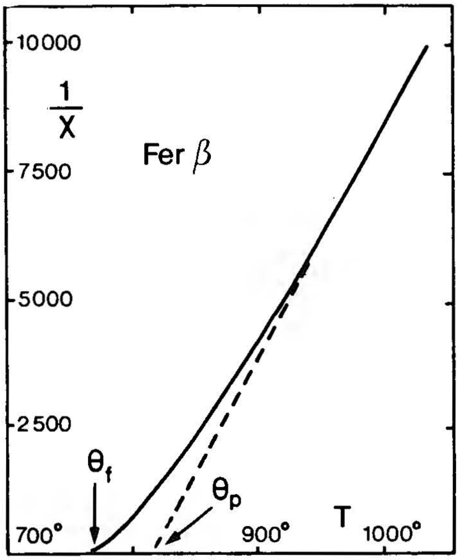

Fig. 6

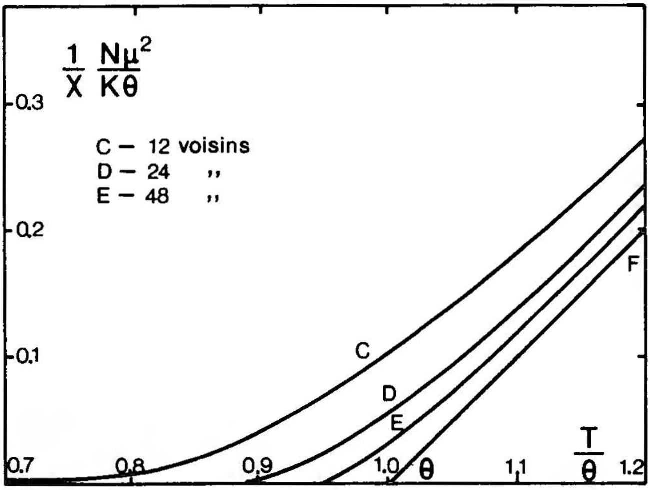

Fig. 7

Moreover, this coupling between neighbours can be imagined so that the moments, instead of being aligned in the same sense, are in the opposite sense. Néel proposed an example: in a body- centered cubic crystal, the negative interactions of this kind would align the moments at the corners of a cube in one direction and those at the center in the other. This lattice would comprise the superposition of two simple cubic lattices, each one with saturation magnetization in opposite senses, so that it would appear not magnetized. Néel showed that this regular arrangement, whether it could exist, should loose its order above a certain temperature. The phenomenon would be analogous to the transition in a ferromagnet (18). Néel had just described what is called "*antiferromagnetism*", which would be observed only two years later (19) (fig. 5).

The good use of the molecular field had consequently allowed Néel to predict the existence of the antiferromagnetic state before such materials had been observed. On the other hand, other magnetic materials, amply studied experimentally, continued to intrigue physicists. These were the ferrites. Up to a certain point, the explanation of their behaviour was enclosed inside the two equations (equations 3) already written. In 1948, Néel (20) showed that the properties of the ferrites came from their lattice which could be separated in two sub-lattices like an antiferromagnetic could. The difference was that, in the case of the ferrites, the two saturation magnetizations didn't cancel: this is now called the *ferrimagnetic state.*

11-It is thus proved that the concept of molecular field has been very helpful in the history of magnetism.

In contrast with its power of clarification is the fragility of its premises. This is worth a few words.

We mentioned that Curie (¶3) could formulate his experimental law because of the few number of substances which were far from obeying it. Later, this number grew. So we may wonder what would have happened in 1895 if Curie had been aware of so many exceptions. We can guess that the χ' law wouldn't have been set forth.

Thereby, Langevin's theory would have lost its credibility (¶4) which was based on Curie's experimental work.

As to the hypothesis of the molecular field, in spite of the fact that it repeats up to a certain point a suggestion made by Langevin about a magnetizing field, it may be considered as being independent. But we must keep in mind (¶8) that it is only after being combined with Langevin's theory that the molecular field opened the way to the theory of ferromagnetism.

So, in 1907, the theory of ferromagnetism was caught in a chain, the first link of which could have, after all, never been discovered.

These comments are not made by sheer caprice. In 1910, Kotaro Honda (21), a Japanese physicist, challenged the Curie law. He wrote: "*When we use my experimental results, we find, instead of the two Curie laws, the following law: a raise of temperature has on the magnetization coefficient of an element the same effect as the raise of the atomic weight of this element*". The fact that the susceptibility of many elements doesn't obey the Curie law explains why Honda remained so incredulous with respect to the theory of ferromagnetism according to Weiss. For him, the first link of our chain missed.

If we remember the uncertain way Weiss used to define the molecular field, we see that two precariousnesses have led to a sound theory.

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THE CONCEPT OF THE COLOR CENTER TILL 1940

Jürgen Teichmann

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There are several reasons why ionic crystal point defects in general and alkali halide color centers in particular occupy an important place in the history of solid state physics. To some degree their significance is a reflection of a larger issue-the role crystal imperfections played in determining the properties of real materials. A number of these properties, some of fundamental technological importance such as the electronic conductivity of semiconductors or mechanical properties of metals, are indeed controlled by minute additives of foreign atoms or irregularities in crystalline structure, such as grain boundaries and dislocations. Of all crystal imperfections, point defects are the simplest. Localized positions of atomic dimensions with an anomalous occupation in the ideal crystal, such as atomic vacancies, foreign atoms in normal lattice places, interstitial atoms, and color centers are termed point defects. Despite small concentrations, they can have a strong effect on many macroscopic crystal phenomena as local defects in the extensively undisturbed lattice, for example on optical properties, electrical conduction and diffusion. As free gas atoms or ions in diluted solutions, they do not reciprocally influence each other in the first approximation. These were relatively easy to examine experimentally and to handle theoretically. Thus the systematic study of real crystals began with point defects.

No exact starting date can be set, since many nineteenth century observation proved relevant to subsequent studies of imperfect crystals. Before the physics of imperfect crystals emerged as an established research speciality towards the end of the 1930's, it had developed along three main lines. For the sake of simplicity, they will be called the thermodynamical-chemical, empirical-physical, and the last line of development, building on the second, the quantum physics approach. The first grew out of the interest in ionic conductivity and diffusion in ionic crystals. Stimulated by the concept of interstitial ions suggested by Joffe in 1916, this led to the development of a general thermodynamic treatment of point defects by Frenkel, Jost, Wagner and Schottky about a decade later. The underlying concepts were the realization that even in a very pure real crystal a certain number of intrinsic structural defects are always present for thermodynamic reasons, and the identification of four types of simple defects a priori possible in ionic crystals (combinations of vacancies and/or interstitial ions). Similar processes played an important role in this research on the technically important semi-conductor (Cu_2O)-discovered in 1926.

Simultaneously optical and electrical studies of insulating crystals were begun around 1920 by several research centers, most notably Robert Wichard Pohl's school in Göttingen. Although the Göttingen school did not restrict itself to alkali halides, the latter proved the most suitable model materials for the study of dispersion, absorption, luminescence, ionic and electronic conductivity, diffusion and thermoelectric effects. Unlike metals and semiconductors, pure, perfect alkali halides do not conduct electricity and are transparent

within a wide spectral range, However their electrical and optical properties are extremely sensitive to imperfections, thus enabling the use of well developed, precise measurement techniques for the study of point defects. Alkali halide color centers, a class of imperfections essentially consisting of current carriers trapped at simple structural defects, were the first lattice imperfections to be studied in considerable detail. There were reasons for using alkali halides as model materials for the study of lattice defects. From a purely pragmatic point of view, they were easily available, were inexpensive, and artificial crystals with controlled impurity content could be grown with relative ease.

The third major line of development, which merged with the thermodynamic and empirical approaches to form the speciality of color center physics at the end of the thirties, was a series of attempts to apply quantum mechanics to imperfect crystals, especially to the results of the Pohl school. The contribution of Nevill Mott's Bristol school was particularly significant in this area.

We now will concentrate on the development of Pohl's school in Göttingen. About the importance of this work, F. Seitz wrote in his famous review "Color Centers in Alkali Halide Crystals" 1946:

> "In the field of solids, the properties of the alkali halides have an enduring interest, since the crystals have continuously yielded to persistent investigation and have provided us with a better and better understanding of some of the most interesting properties of all solids . The entire subject remained of passing interest until Pohl and his coworkers subjected the discoloration to an extensive series of experiments over a ten years period. It is a rather remarkable characteristic of this work that, although the investigators have never had a very deep interest in the fundamental interpretation of the properties of the discolored alkali halides in terms of modern atomic theory, the experiments they have carried out have been exactly those that are needed to furnish the basis for such an interpretation. This fact indicates that they possess a very deep intuitive sense concerning the physically important quantities which enter into their problem!".

R.W. Pohl, since 1918 professor in Göttingen, was influenced by research in rock salt coloration (specially Joffe and Röntgen, published 1921) by research in luminescence (specially Lenard) and by research in electrical conduction (specially photoeffect measurements). We may say that starting at the end of the first world war, a research program devoted almost exclusively to experimental crystal physics was pursued at the first Physical Institute at the University of Göttingen under the direction of Robert Wichard Pohl. This program, the first of its kind, become more and more comprehensive with time while being virtually ignored by the rest of the world. The Pohl institute can be designated as the first great school of solid state physics.

Pohl began investigating the internal photoeffect in insulator crystals like zincsulfide and diamond - the first publication came in March, 1920. He distinguished here between primary and secondary current. This was really a first attempt to obtain a consistent theory of photoconduction in crystals, even if from a modern viewpoint this distinction was only temporarily useful in mastering the complex relationships through measurement. Pohl probably realized this himself. He is supposed to have jestingly defined the secondary current in conversation as everything which was not understood.

From 1921 (Röntgen's work was stimulus and specially from 1924 Pohl focused his research on alkali halides. In 1925 his institute succeeded to produce synthetic single crystals from the melt - in usable and well defined purities. This was very helpful for precision-experiments to clear up the non colloidal absorption, Röntgen had found. Here the concept of atomic centers (the "Farbzentren" - F - so called since 1930) and excited centers (the "F'- zentren" from the thirties) started soon after 1925.

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The third major line of development, which merged with the thermodynamic and empirical approaches to form the speciality of color center physics at the end of the thirties, was a series of attempts to apply quantum mechanics to imperfect crystals, especially to the results of the Pohl school. The contribution of Nevill Mott's Bristol school was particularly significant in this area.

We now will concentrate on the development of Pohl's school in Göttingen. About the importance of this work, F. Seitz wrote in his famous review "Color Centers in Alkali Halide Crystals" 1946:

"In the field of solids, the properties of the alkali halides have an enduring interest, since the crystals have continuously yielded to persistent investigation and have provided us with a better and better understanding of some of the most interesting properties of all solids . The entire subject remained of passing interest until Pohl and his coworkers subjected the discoloration to an extensive series of experiments over a ten years period. It is a rather remarkable characteristic of this work that, although the investigators have never had a very deep interest in the fundamental interpretation of the properties of the discolored alkali halides in terms of modern atomic theory, the experiments they have carried out have been exactly those that are needed to furnish the basis for such an interpretation. This fact indicates that they possess a very deep intuitive sense concerning the physically important quantities which enter into their problem!".

R.W. Pohl, since 1918 professor in Göttingen, was influenced by research in rock salt coloration (specially Joffe and Röntgen, published 1921) by research in luminescence (specially Lenard) and by research in electrical conduction (specially photoeffect measurements). We may say that starting at the end of the first world war, a research program devoted almost exclusively to experimental crystal physics was pursued at the first Physical Institute at the University of Göttingen under the direction of Robert Wichard Pohl. This program, the first of its kind, become more and more comprehensive with time while being virtually ignored by the rest of the world. The Pohl institute can be designated as the first great school of solid state physics.

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Pohl himself grew more and more into the role of spiritus rector and organizer of the institute, disseminating the results and caring for the further placement of his people. Rudolf Hilsch took over the leading role in the intensive experimental work after the departure of Bernhard Gudden in 1925. Absorption experiments in the ultraviolet range under 250 nm date from 1926. Initially thin crystal plates (down to a few tenths of a millimeter) were still used. Following the example of atomic physics, all wavelength regions were searched for laws. Among others, the main reason for this search was the significance of sylvine and rock salt for spectral apparatus optics as well as for crystal luminescent base material.

By 1927 the number of "centers" involved in discoloration had been calculated from measurements of anomalous dispersion and of different absorption variables. Most important here were the half-width value and the maximum absorption constant. Alkali halide luminescent materials and rocksalt irradiated by x-rays yielded values on the order of 10^{15} color centers per cm^3. Photochemical interest now pushed the quantitative side of the "discoloration of the first kind," as it was called in Göttingen, once again into the foreground-especially for the determination of the quantum yield. In 1930 Smakula published a formula for calculating the number of "discoloration centers" (as he still called them) similar to that from 1927, which was subsequently named after him.

In 1931 Erich Mollwo, since 1930 a doctoral candidate at the institute and after Hilsch Pohl's most important collaborator, succeeded in finding a surprisingly simple relation between the frequency of the absorption maximum and the lattice constant d of the respective crystal at room temperature: vd^2 = constant. This relation still bears his name.

A second discovery by Mollwo at this time was of direct importance for experimental research. Since the frequency of the absorption maximum decreased with rising temperature while the lattice constant had to increase, exact measurement of the temperature dependence of this frequency were of interest. However ìthe color of the irradiated crystal was unstable at high temperatures. Stability could be achieved by the additive coloration method, i.e. heating the crystals in alkali vapor. In certain temperature regions a colloidal coagulation can occur, but Mollwo was able to prevent this by quenching the crystals, suddenly taking them from high to low temperatures.

Thus additive coloration became a general tool of color center research for the first time. It also led to Mollwo's third discovery of this year-though neither explicitly stated nor clearly enough investigated-the proportionality between the vapor pressure and the number of color centers in the crystal.

This relation - finally published in 1937 - would soon lend more weight to the "vacancies" thesis for the interpretation of color centers.

Mollwo was also the one in the position to state conclusively in 1933 that color centers had to be intrinsic atomic defects in the crystal.

At the same time there were other developments in Göttingen which made color center physics interesting for the broader aspects of solid state physics and technology, greatly influencing the interpretations of the F-centers. In 1932 Ostap Stasiw found that the blue color centers in a KCL crystal discolored by the additive method at 1000 volts current and 400 C temperature wandered to the anode and left the crystal colorless in the direction of the cathode. The rear border of the center distribution was sharply outlined while the forefront remained unclear. If he reversed the polarity, a blue residual band wandered black along the same path to the former cathode.

This experiment was varied in subsequent publications and demonstrations. In particular the "blue cloud" was produced directly by applying an electric field to a pointed cathode in a previously clear crystal and made to wander to the flat anode.

This visible electron migration - electrons were jokingly designated as blue in the institute - was a triumph for Pohl and his procedure of combining electrical and optical experimental methods as much as possible. Color centers were now interpreted as loose combinations of cations and electrons which could be separated by heat.

The "Stasiw-cloud" certainly made an impression on the world interested in science- as impressive as solid state physics could be at that time. This effect was reproduced in many institutes, sometimes only as a demonstration, which Pohl masterfully conducted everywhere he went. Hypotheses about the phenomena were exchanged. In particular, semiconductor scientists such as Schottky and Wagner suddenly became interested in alkali conductivity with an "additive" excess of a component in semiconductor crystals such as cuprous oxide, unfortunately not optically accessible. Moreover with its one pointed electrode the Stasiw crystal possessed a different forward and backward resistance, analogous to semiconductor rectifiers. Pohl immediately called attention to the possible technical future.A further important result at this time was the discovery of bands in the ultraviolet region by Mollwo in 1935, caused by heating alkali salts in halide vapor instead of alkali vapor. Seitz later called these V-bands.

However research on the dependence of the product of the quantum yield times Schubweg (mean range) in a unit field of color center temperature and concentration, if F-centre were transformed into F'-centre, became far more important then the V-bands. Among other things Glaser and Lehfeldt found an astonishing reduction of the above mentioned product for the lowest temperature, for NaCl about one thousandth below -150C. This product-at the same temperature- was further inversely proportional to the color center concentration.

1937 H. Pick found a maximum value of two for the yield of the transformation from F-centers to F'-centers. Even before the exact quantitative explanation of the inverse reaction of F'-centers into F-centers, first published in 1940, all of the experimental jigsaw pieces could be put together to form a clear picture. Naturally only one color center per light quantum could be destroyed by light absorption in the color centers. The liberated electron-in Pohl's words "...leaves in its place a positive alkali ion. The electron then diffuses in the electric field, and at the end of a finite range is captured by a positive ion in the neighbourhood of another Farbzentrum. Thus it forms a new alkali atom. Both the neighboring alkali atoms (which are in a region of superfluous negative charge) have an absorption spectrum somewhat different from that of two single Farbzentren, and appear optically in the form of two F'-centres."

This means that one light quantum destroys two color centres. The model of a color center as an electron in a halide ion vacancy, coming from the discussion at the famous international meeting in Bristol in 1937, made it still clearer. An electron coming from a halide ion vacancy would be captured by a second vacancy already containing an electron. This vacancy, now with two electrons, was a F'-center. The number of color centers, now effective as electron traps, naturally limited the mean free path of the electrons. This explained the inversely proportional connection between the product of the quantum yield times the Schubweg and the color center concentration.

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Since 1932 Pohl was well informed on the concept of vacancies (which had been started from Joffe and Frenkel) through a continuing discussion with Schottky - but he did not accept it. Schottky soon became the most important mediator between technology and physics in the area of point defects. Schottky's and Wagner's large general work already 1930 on the "theory of ordered compound phases" now examined different types of "lattice defects" systematically; interstitial atoms, vacancies, and substitution of one component of the compound crystal by the other.

This publication followed important experimental examinations of the conductivity of Cu_2O in order to clarify its barrier layer effect. In 1932 Wagner and Dünwald found that rising oxygen pressure on Cu_2O caused the conductivity to rise. Transport measurements showed that copper ions-only a small fraction in comparison to the hole current-wandered. Further it was clear to them that increased conductivity meant an increased number of defects. Therefore they concluded that instead of excess oxygen ions, the oxygen-rich lattice had to have excess copper ion vacancies. The vacancy thesis was applied by Schottky in 1933 to the alkali halides (in a publication mainly on Cu_2O).

His famous 1935 publication, which introduced "Schottky's disorder" (named by Jost), owed its existence to alkali halide research as well, or more exactly, to the problem of ionic conduction in alkali halides. Schottky took his reflections on vacancies in these crystals as an opportunity to discuss possible disorders again, this time specifically in ionic crystals of the NaCl type. He cited Frenkel and especially Jost in this regard. What was new here, as opposed to his work 1930, was the assumption that equally many positive and negative (anion and cation) vacancies actually exist in the NaCl type. He proved this through energy calculations. As an aside, Schottky put forth the thesis of anion vacancies in the proximity of cation-electrons in order to explain color centers.

The Dutch scientist J. Hendrik de Boer, employed in the Philips research laboratory in Eindhoven, look over Schottky's F-center model in his 1937 book and into the discussion in Bristol, July 13-16th. For the Bristol conference - which goes back to Mott's initiative. Gurney and Mott jointly presented a paper on the atomic structure of the color center, which again was based on the ideal crystal lattice. It referred to Landau, Frenkel and A. von Hippel and developed the model of an "electron trapped by digging its own potential hole". The corresponding positive charge was not taken into consideration.

The comprehensive talk by Pohl (see above) was seen as most important in Bristol. During the discussion, de Boer first of all considered the Göttingen research as very important for other solid phenomena. He considered a discussion of color center theses opportune for exactly this reason, in opposition to Pohl's suggestion to wait for experimental decisions in this area. On the basis of Schottky's disorder, the model of an electron "trapped in the neighborhood of a point where a negative ion is missing" was accepted. One reason was the proportionality of the number of color centers to the alkali ìvapor pressure. This spoke against the Landau model. Furthermore, different results from Pohl could be easily explained in this way, such as the transmutation of U-into F-centres. The vacancy as the point of lowest energy and the extension of the wave function of the electron to the six neighboring ions were finally accepted. The F'-center model as two electrons in the potential well of a vacancy was developed from additional oral information by Pohl as well.

All this was given depth by subsequent publications out of Bristol. These provided an improvement of the Schottky (Jost) energy calculations from 1935 on a quantum mechanical basis. As an end product, the classic of ion crystal research "Electronic processes in ionic crystals" appeared in 1940 from Mott and Gurney, which definitively put the "theoretical clothes" on Pohl's work and showed "that the phenomena observed in alkali-halides shed a great deal of light on the more complex behavior of substances of greater technical importance, such as semiconductors, photographic emulsions and luminescent materials".

For further reading look at J. Teichmann, K. Szymborski: Point defects and ionic crystals - the color centers as most influential line of development. In: L. Hoddeson, E. Braun, J. Teichmann, Sp. Weart (eds): History of Solid State Physics. In print at Oxford University Press.

CONJECTURE AND CONFIRMATION

The History of the Dislocation

Ernst Braun

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Early Theories of Plastic Deformation

The beginning of modern physical understanding of the mechanical behaviour of metals can be dated to the period following the first world war. Progress was made mainly through the application of new scientific experimental techniques, particularly the use of X-rays for the study of crystal structure and the growing of single crystals of metals. These two techniques, together with the extensive use of optical metallography and stress-strain measuring equipment, formed the basic armoury for an attack of physics on mechanical properties of metals.

In the years between 1918 and 1934, a tremendous amount of experimental work on the plastic deformation of single crystals of a variety of substances was carried out. Gradually a detailed description of the behaviour of crystals under stress was obtained, but no plausible theoretical explanation was apparent. Although a variety of theoretical explanations existed, the first truly satisfactory hypothesis, which was to provide a common basic explanation for all the known phenomena, was not put forward till 1934, when dislocation theory was proposed as one of many conjectures.

Three features of plastic deformation of metal crystals appeared especially puzzling and thus provided avenues for further investigation. The first is the fact that crystals deform and fracture under stresses which are many orders of magnitude smaller than those predicted for the strength of ideal crystals from the theory of cohesive forces. The second is the fact that a plastically deformed crystal shows increased resistance to further deformation, a phenomenon known as work hardening. Finally, it was hard to understand why slip should occur on many planes simultaneously, forming systems of slip bands, instead of leading to fracture in the plane in which slip was initiated.

Prior to 1934, two main explanations for all or some of the phenomena observed were put forward and variously developed. The first theory, proposed mainly by Beilby (1921), postulated localized melting of the crystal in the glide plane. According to this theory, glide between crystal planes occurs in a locally liquid region, which allows limited movement and then solidifies into a glassy phase. This hard amorphous layer locks adjacent ìplanes together and gives rise to work hardening.

> According to this theory, hardening results from the formation at all the internal surfaces of slip or shear of mobile layers similar to those produced on the outer surface by polishing. These layers only retain their mobility for a very brief pe-

> riod and then solidify in a vitreous state, thus forming a cementing material at all surfaces of slip or shear throughout the mass (Beilby, 1921, p.123).

One of the counter-arguments against this theory was that the molten region could be expected to lead to slip in an arbitrary direction, preferably closer to the direction of stress, rather than permit slip in the glide planes only, as observed in experiments. Nevertheless, Beilby's theory was extremely influential and it was quite generally believed that plastic flow occurred in temporarily liquid regions of the crystal. It was equally widely held that the actual strength of work-hardened, alloyed, or polycrystalline materials was determined by the amorphous layers lying between regions of crystalline perfection.

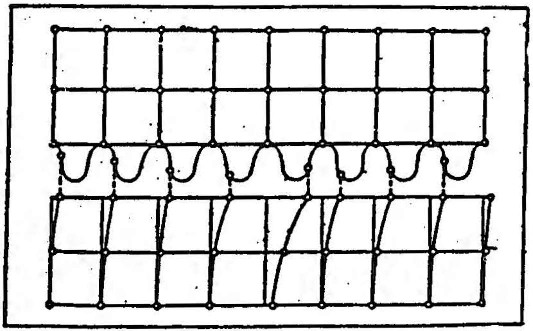
> By 1920 the average metallurgical student was as fully convinced of the existence of amorphous metal as his modern equivalent is of the existence of dislocations, and one of the main objects of metallurgical research was to determine separately the properties of the crystals, and the properties of the boundaries (Allen, 1953, p.102).

Right from the beginning, virtually all theories of plastic deformation assumed some sort of defective lattice structure. Thus as early as 1920 the principle of lattice defects was vaguely enunciated. While Beilby suggested temporary liquefaction and amorphous solidification, Griffith (1920) suggested that crystals contained very fine cracks and calculated the strength of materials by equating the loss in elastic energy caused by the extension of a crack to the gain in its surface energy. These calculations show that realistically small forces can lead to the propagation of a crack and thus to plastic deformation. Griffith's theory of crack propagation as a mode of plastic deformation was one of the direct predecessors of dislocation theory. A personal factor, which perhaps eased the transition from crack theory to dislocation theory, was that Taylor, one of the fathers of dislocation theory, worked with Griffith at Farnborough during the early part of World War One and was therefore thoroughly acquainted with the theory of cracks (G.I.Taylor, 1965).

Zwicky (1929) suggested that mosaic blocks were formed in crystals by contraction during solidification, rather on the pattern of cracks forming in drying mud. The misfit between mosaic blocks eases their movement when the crystal is stressed and thus explains the ease of plastic deformation. Mosaic structure was a common component of several theories of plastic deformation and of work hardening; indeed the mosaic block ìsurvived and later became part and parcel of dislocation theory. It was plausible to think that building blocks which did not fit together perfectly would yield to applied stresses more readily than a perfect lattice. The mosaic block theory could also explain work hardening if the blocks piled up against each other and locked together, thus making further movement more difficult.

The theoretical explanations of the phenomena associated with plastic deformation of crystals fell well short of being satisfactory and hence the field remained open to new hypotheses. Taylor showed that both the crack theory and the mosaic block theory suffered from inconsistencies. It was clear that the major obstacle to the plausibility of any of these theories was the fact that, particularly in cubic crystals with an abundance of possible slip planes, the amount of hardening obtainable by any of the postulated mechanisms was insufficient to account for observations. Taylor used the argument particularly against the mosaic block theory and preferred the crack theory, though, as is clear with hindsight, only as a stepping stone toward dislocations (Taylor, 1928).

The two people who came perhaps closest to the concept of dislocations, yet without formulating it in a generally useful and acceptable way, were Prandtl and Dehlinger. They both assumed, as did many others, that a crystal consisted of a mosaic of small blocks, separated by some kind of sub-boundaries. Prandtl (1928), in a paper describing a model rather than a real crystal, explained work hardening and slip by assuming that sheets of



Eine Verhakung

Fig. 1 - From U. Dehlinger, *Annalen der Physik* 2 (1929) p. 768.

atoms would jump irreversibly from one position of equilibrium to another. Such jumps would leave behind defective structures. Dehlinger (1929) came even closer to the concept of the dislocation in postulating an imperfection which he called "Verhakung". In this concept an imperfection is confined to a small region of a surface of misfit, while further away from this region the atoms are in near perfect alignment. Thus he combines the postulate of mosaic structure, i.e., a surface of misfit, with a localized defect consisting of atoms displaced from their normal lattice positions. The effect of such non-uniform displacement of atoms is the setting up of internal strains and such strains were assumed to be the cause of work-hardening.

In his Habilitationsschrift[1] in Stuttgart, Dehlinger refers to Prandtl as the originator of his own concept of "Verhakung", though there really is only a loose similarity of the "Verhakung" with Prandl's model and a very close similarity with the later concept of the dislocation (see Figure 1). The common and independent assumption of the two models is a periodic field of forces acting on a row of atoms in a crystal lattice.

Dehlinger's attention was mainly focussed on recrystallization. He saw the"Verhakung" as the link between regions of the crystal with different orientations, i.e., within a mosaic sub-structure resulting from plastic deformation. The word "Verhakung", derived from "Haken" (hook), was introduced at a time when German physicists did not yet look over their shoulders toward their Anglo-Saxon colleagues and has no English translation. Although the "Verhakung" looks very similar to a dislocation, its function is merely to take up lattice distortions and not to ease glide.

Dehlinger assumes that plastic deformation starts at points of easy glide (Gleitlockerstellen); some kind of defect, consisting of a loose region, which predisposes the crystal towards slip. During deformation those defects are eliminated and the new defect, the "Verhakung", is formed. The mechanism of formation is described as follows:

> When two rows of atoms are pulled past each other, some atoms may, because of irregularities in the glide plane, be left behind the others and eventually be caught by the attractive force of an atom in the opposite plane other than in correspondence with its normal position (Dehlinger, 1929, p.763-4).

The word "dislocation" was introduced into the theory of mechanical properties of solids by A.E.H. Love in an appendix to chapters VIII and IX, apparently added in the third edition (published in 1920), of his famous "Treatise on the Mathematical Theory of Elasticity". Love translates as "dislocation" the Italian word "distorsione", used by Volterra and others to describe a many-valued displacement in an elastic medium. The term was thus originally introduced for a displacement in a continuum, not in a crystal.

First Introduction of the Modern Idea of Dislocations: 1934 - 1947

The year 1934 was the annum mirabilis of dislocation theory. Three papers were published in that year which can all be seen as originators of the modern idea of a linear crystal defect - the dislocation - which is the prime cause of all phenomena related to the plastic deformation of crystalline solids. The most extensive and most influential of the three papers was that by G.I. Taylor, a Royal Society Professor in Cambridge and a most eminent figure in British Science. Taylor's paper begins with a critical review of experimental observations and possible theories of work hardening. The first mechanism he mentions is that of the formation of blocks during deformation and the locking of blocks, holding up slip. He argues against this mechanism for all those crystals which possess more than one direction of easy glide. In the second mechanism blocks are not formed by deformation, but the mosaic structure is inherent in the crystal. The argument against the effective operation of a locking mechanism is much the same as in the first case.

In these theories the crystal is inherently weak and mosaic imperfections increasingly strengthen it. Taylor does not mention the various speculations why a crystal should be weak, such as the theory of weak points (Lockerstellen), discussed previously. The third theory, which is in better accord with calculations of inherent strength, assumes the perfect crystal to be able to withstand very large stresses and the observed weakness of crystals is attributed to stress concentrations by internal cracks. He refers to his own paper of 1928 to argue that increasing deformation leads to an increasing number of cracks. He then considers the mechanism of slip in detail and comes up against the difficulty of accounting for unique directions of slip without requiring whole faces to slip simultaneously. This would need very large forces, and would make it difficult to account for work hardening. Taylor therefore suggests - and this is the crux of his argument from which everything else follows - that slip might not occur "simultaneously over all atoms in the slip plane but over a limited region, which is propagated from side to side of the crystal in a finite time" . He then suggests that the stresses near the edge of the region which has already slipped make "the propagation of slip ... readily understandable and ... analogous to the propagation of a crack".

The actual definition of a dislocation is given in the text describing a figure in Taylor's paper.From a detailed discussion of the atomic mechanisms involved, Taylor reaches the following conclusions as first approximations:

> (1) Above a certain critical temperature T_D any stress, however small, will cause dislocations to travel,
>
> (2) "At temperatures below T_D the centres will not move till the shear stess attains some finite value".

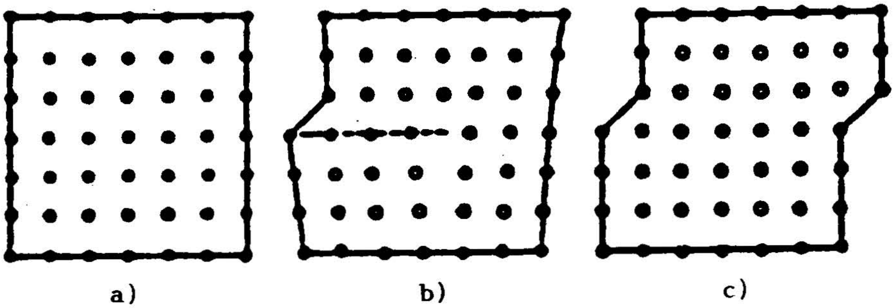


Fig. 2 - Positive Dislocation. In the diagram *(a)* represents the atoms in the lattice of a crystal block; *(b)* the condition of this block when a slip of one atomic spacing has been propagated from the left to right into the middle; and *(c)* the block after the unit slip or "dislocation" as we may call it, has passed through from left to right. (From G.I. Taylor, *Proc. Royal Society* A145 (1934) text p. 368, drawing p. 369).

Thus the weakness of real crystals can be explained if slip occurs by a dislocation mechanism.

Taylor assumes that crystals do not a priori contain dislocations, but that these are either formed at surfaces or by thermal fluctuations. Taylor certainly thought that dislocations would form quite readily as a result of thermal activation and could then move easily under the influence of even small stresses. As plastic deformation progresses, more and more dislocations would form and the stress field associated with them would make further movement more difficult. Work hardening is thus the results of the stress fields set up by an increasing density of dislocations. Taylor supports his qualitative arguments by approximate calculations and obtains the correct orders of magnitude.

> "If the crystal is initially perfect, the first few dislocations migrate through it under the action of a shear stress which may be regarded as infinitesimally small. As the distortion proceeds, however, the number of dislocations will increase and the average value of d will decrease so that the resistance to shear will increase with the amount of distortion" (Taylor,1934, p.383).
>
> (He assumes a temperature above the critical temperature T_D. d is the spacing of dislocations in a regular row).

The second extensive paper introducing the concept of dislocations was based on work done by Egon Orowan under the direction of R. Becker at the Technical University of Berlin. Unhappily, the work was interrupted by the political events of 1933, when Orowan had to return to his native Hungary as a first stage of his flight from Nazi persecution. The first two parts of Orowan's paper (1934) deal with temperature dependence and dynamics of plastic deformation and only the third part deals with the mechanism of glide (pp. 634-659). Orowan realizes that the dislocations (Versetzungen) he suggests are identical with those suggested by Polanyi. Interestingly, Orowan assumes some form of cracks or notches (Kerben) as the cause of weakness of crystals and sees dislocations only as a mechanism of glide.

> We may say that the weakening effect of notches present in the crystal spreads by dislocations through the glide plane".... "The transition between the part of the plane which has slipped and that which has not slipped yet, which has here been characterized by added stress is, from the point of view of the lattice geometry, identical with the dislocations described by Polanyi (Orowan, 1934, p.640).

Polanyi's paper (1934) is the shortest of the three, but in some ways the one that proved most acceptable in its arguments. He finds cracks unconvincing and argues that whatever defect causes the weakness of crystals, it ought to be of a "crystallographic" nature. Polanyi refers to Prandtl and Dehlinger as forerunners of his own dislocation (Gitterversetzung), in which "10 atoms on one side are opposed by 11 atoms on the other side of the line". Polanyi admits that he has no explanation for work hardening and realizes that continuous creation of dislocations is necessary for extended deformation. He has no clear mechanism of formation, but thinks that "dislocations ought to form preferentially at the crystal surface".

Although the three papers were all published in the same "miraculous" year, and all three contained virtually identical descriptions of what we now call an edge dislocation, the papers had very different origins and their authors imagined different mechanisms of plastic deformation.

G.I. Taylor, at that time the most established and most eminent of the three, had close acquaintance with Griffith's theory, which was the theory of plasticity with the best mathematical foundation current at the time. This work was associated with the "British school" around Carpenter and Elam, whereas Orowan and Polanyi belonged to the German school around Polanyi, Schmid, Mark, Boas and others. The results of much careful experimentation in both schools are summarized in two major monographs of 1935, by Elam and by Schmid and Boas.

The year 1934 was distinguished by yet another event of significance to solid state physics. An International Conference on Physics was held in London, which contained a substantial section on "The Solid State of Matter". At this conference two further schools of some significance in the field of plastic deformation were represented: the Netherlands school with an important paper by W.G. Burgers (1935) and the Soviet school, represented by A. Joff (1935).

Burger's paper deals mainly with recrystallization, but one or two of his remarks may shed light on the immediate reception of dislocation theory. He refers to the different recent theories and suggests that they all share the common view that the macroscopic glide process consists of a combination

> of "local glide steps", the occurrence of which is closely related to the presence, even in the undeformed crystal, of some kind of deviations from the "ideal" lattice structure. Although the various theories differ apparently regarding the exact nature of these deviations ("Lockerstellen" (Smekal), "dislocations" (Taylor), "Versetzungen" or "Verhakungen" (Polanyi; Orowan; Dehlinger)) and so to the way in which they initiate slip (as a consequence of local stress concentration or of special conditions of potential energy), their conceptions agree in so far that local glide steps occur under the influence of shear forces, which,

> while being originally small compared to that expected for an "ideal" lattice, increase with the number of deviations (Burgers, 1935, p.140).

From the early days of research on the strength and plasticity of solids, much speculation centred on the surface. After all, the surface is an unavoidable defect in the crystalline structure and its role was speculatively that of a source of dislocations, or, experimentally, a determinant of strength. Some of the experiments were reported by A. Joff and discussed by A. Smekal at the 1934 London conference.

> In the case of rock-salt, two experiments were performed by Levitskaya and myself to demonstrate the importance of surface conditions. Dissolving the surface by hot water during the loading experiment, we found strengths exceeding the usual value by a factor of twenty or even more (Joff, 1935, p.75).

Joff is well aware of the many attacks upon his conclusions, but has arguments against all his detractors. He makes no mention of dislocations and regards "surface crevices" as the cause of weakness of crystals. "The practical weakness is sufficiently explained by the Griffith crack theory" (Joff, 1935, p.80).

It should not be imagined that dislocation theory, as soon as it had been enunciated, swept all before it. Metallurgists largely ignored dislocations and indeed hardly believed in them until a much later period, when they had been experimentally observed and their existence proven with as much certainty as anything can be be proved in science. Physicists accepted the mechanism as a plausible and possible one, but it was no more than yet another hypothetical explanation in a field which had been experimentally reasonably well documented but in which plausible explanations abounded and yet none fully convinced. Dislocation theory gradually gained acceptance as it proved the most plausible, most fruitful and, eventually, experimentally best verified theory. This was not a scientific revolution, no heroic change of paradigm, but a gradual emergence from confusion and multiplicity of explanations of complex and varied phenomena. Neither was it a rejection of older theories by falsification, but rather an eventual preponderance of one theory and atrophy of others.

A number of physicists made further contributions to dislocation theory in the years between 1934 and the end of the Second World War. Particularly the brothers W.G. and J.M. Burgers published ireview articles on Viscosity and Plasticity in which they pointed out that dislocations could pile up against obstacles and thus exert a back-stress which could cancel the applied stress, thus explaining work hardening (Burgers & Burgers, 1938).

It was the fluid mechanics expert J.M. Burgers, who went back to the mathematical theories of dislocations in elastic media and came to describe the dislocation in terms of a vector, now generally known as the Burgers vector. This mathematical description also led to the screw dislocation, first presented at the 1939 Bristol conference on Internal Strains in Solids and published in the Netherlands in the same year and in England in 1940 (Burgers, 1939 and 1940).

Alas, the work by J.M. Burgers came too shortly before the war to make much of an impact until many years later. During the war British physicists either did not work on mechanical problems or, if they worked on strength of materials, were concerned with the cold drawing of shell cases or with the resistance of armour plate to projectiles. Similarly, German physicists had to worry about very much more mundane things than dislocations. Apart from munition and armour, they had to produce substitute alloys for materials unavailable in besieged Germany.

Although it is always emphasized that war enhances the progress of science, this is true only in selected fields. As the more abstruse parts of the theory of strength of materials, such as dislocation theory, certainly showed no immediate promise of helping to win the war, they were cast aside. Dislocation theory did not receive the dubious benefit of enhancement by war, nor can one think of any indirect benefits which the war effort might have bestowed upon it.

Although the foundations to dislocation theory had been laid and some details worked out by 1940 or so, they remained an obscure hypothetical part of physics and were mostly disregarded during the war. In the balmy days of post-war enthusiasm, when all the pent-up desire for pure research was given free rein in a world which believed in progress through science, dislocations rapidly established themselves as a fruitful and valid sub-field of solid state physics.

One of the means of establishing an international community in a field is to organize conferences. These are useful to report progress, to establish consensus and, above all, to make contacts and exchange views in informal discussion. Another important feature of the international physics community are summer schools. At these young scientists have a chance to meet the "grand old men" of the field and to learn the latest state-of- the-art. Of possibly even greater importance is the fact that the up-and-coming young scientists meet each other and establish links of friendship and collaboration. The best of all possible worlds was had at Bristol in 1947, when a conference on the Strength of Solids was held at the conclusion of a summer school on the same topic.

The first session of the conference dealt with creep and plastic flow, and the first paper was given by Mott and Nabarro. Dislocations had come a long way by then.

> In most modern theories of slip, it is assumed that slip begins at one end of the crystal and travels across it, thus avoiding the concept of simultaneous slip (Mott and Nabarro, 1948, p.1).

Mott and Nabarro may have been the first to describe a dislocation as a "line discontinuity" and thus opened the way to treating it as a geometrical entity with certain properties. This further step toward abstraction, treating the dislocation as a line rather than going back in each consideration to the atomic arrangement of the crystal, proved of major importance.

At the very same conference, several more pioneering papers were presented. Cottrell's paper on the effect of solute atoms on the behaviour of dislocations was the first of a line of work on hardening by solute atoms and therefore on yield in real materials, such as steel. As Cottrell said in an interview in 1983: "The big prize was to understand yield in steel". The idea was jointly developed in an interesting exchange between Cottrell and Nabarro. The latter had written a paper on pinning of dislocations by solute atoms (Nabarro, 1946) and Cottrell added to it by considering that solute atoms were mobile and could be precipitated on dislocations. Nabarro picked up Cottrell's idea during a colloquium in Bristol and developed it further (Nabarro, 1948). Cottrell's further contribution was presented at the Bristol conference and is best expressed in his own abstract:

> It is shown that solute atoms differing in size from those of the solvent can relieve hydrostatic stresses in a crystal and will thus migrate to the regions where they can relieve the most stress. As a result they will cluster round dislocations forming "atmospheres" similar to the ionic atmospheres of the Debye-Hckel theory of electrolytes. The conditions of formation and properties of these atmospheres are examined and the theory is applied to problems of precipitation, creep and the yield point (Cottrell, 1948, p.30).

Charles Frank's contribution to the 1947 Bristol conference perhaps best illustrates the speculative stage of dislocation theory at that time. His paper is imaginative, plausible and fascinating, but largely speculative. Indeed, dislocations and all that is connected with them, were still pure conjecture. Frank assumes that dislocations reach velocities of the order of the velocity of sound. If so, they can be reflected at free boundaries and thus traverse the crystal many times, increasing the slip. Glide will cease in a plane when it becomes too heavily laced with dislocations.

It may be justified to pause at this point and draw up an ìintermediate balance-sheet, to the end of 1947, with a few brief statements:

(i) A small band of a new breed of solid state or metal physicists had emerged to whom it was obvious that dislocations played a role in the plastic deformation of crystals.

(ii) There was little preoccupation with the old question of cracks and weak regions; it was simply assumed that dislocations were there and could easily be generated and provided both the cause of easy glide and its mechanism.

(iii) Dislocations were now viewed as lines with elastic properties and with forces acting on them and between them.

(iv) Dispersion hardening as well as solute hardening were ascribed to dislocations and work hardening was explained by locking, piling up and interaction of dislocations.

(v) Grain boundaries and sub-boundaries were beginning to be viewed as arrays of dislocations.

(vi) Partial dislocations, screw dislocations and stacking faults had been considered.

(vii) Precipitation on dislocations had been predicted but not observed.

(viii) Finally, it must be re-emphasized that dislocations remained an hypothesis without direct proof.

The Direct Observation of Dislocations

The postulate of dislocations was related to several physical phenomena. The first, described here in some detail and the prime cause for the postulate of dislocations, is the behaviour of real crystals during plastic deformation. The second, mentioned briefly, is the mosaic structure of real solids. This has been postulated in various forms either to explain the mechanical behaviour of solids or the intensities of x-ray diffraction patterns from real solids. The postulated mosaic patterns can best be explained in terms of dislocations. The third body of evidence relates to the rate of growth of crystals. The real crystal grows from a slightly supersaturated vapour many orders of magnitude faster than an ideal crystal theoretically should, and this discrepancy was, as we shall see, explained with the aid of dislocations.

The story of crystal growth and dislocations is inseparable from the name of Charles Frank at Bristol. Mott asked Frank to do some lectures on crystal growth and he used as his source the book by Max Volmer (Kinetik der Phasenbildung), which was in his possession from his post-doctoral days with Debye in Berlin. Volmer described the growth of iodine crystals from the vapour at 1% supersaturation. Burton, another Bristol man, calculated that in a perfect crystal the supersaturation required for the observed rate of growth would have to be 50%. The difficulty about crystal growth from the vapour is that if an atom attaches itself to a perfect surface, it is much more likely to leave the surface again than to be joined by a second atom on the same site. If, however, one atom attaches itself to a surface step, it is held there by cohesive forces in two dimensions and forms a stable nucleation centre for the next atom to attach itself. Thus a surface step is a precondition for crystal growth at reasonable rates at low supersaturation. A screw dislocation emerging at a surface can provide just such a step and the crystal can grow in a spiral, which perpetuates the required step while it grows.

In the autumn of 1949, another summer school cum conference was held in Bristol, and Frank mentioned his new idea on screw dislocations at this conference. This aroused the interest of a young researcher from Tolansky's laboratory, J. Griffin, who had examined surfaces of beryl crystals in phase contrast microscopy and observed spirals which looked precisely as those Frank had conjectured. In the first flush of enthusiasm nobody noticed that the observed features were much larger than of atomic dimensions. The pictures were shown to all and aroused great excitement. It was the first visible experimental triumph for the theory of dislocations and a fine example in which two theories, those of nucleation and of dislocations, came together to produce an experimentally verifiable prediction.

Later, it was somewhat sobering to discover that the steps seen on the pictures were too large to be single growth steps and were, in fact, the result of impurity adsorption and etching. When John Forty, then Frank's research student, found similar spirals on magnesium and silver crystals, it became clear that monatomic steps were indeed essential for rapid growth of crystals from the vapour, but the spirals were made visible by chemical attack or deposition on them (Forty and Frank, 1953).

As Frank pointed out at the above conference, in reply to a question, the reverse of the growth process should also occur, so that dislocations emerging at surfaces should be the sites of preferential etching. "Dissolution .... should proceed in a manner closely equivalent to growth .... by unbuilding at molecular terrace lines ending on screw dislocations...." (Frank, 1949, p.72).

Horn was the first to show that preferential etching indeed occurred at the site of the emergence of a screw dislocation (Horn, 1952). This first observation was followed by a large ìnumber of others and indeed etch pits became an important technique in the semiconductor industry. They also became an important step on the road to general acceptance of dislocation theory. By the mid-fifties, so many unmistakable traces left by dislocations had been observed that practically nobody doubted their existence any longer and the understanding of processes of plastic deformation had improved greatly.

Growth steps and etch pits are manifestations of dislocations emerging at crystal surfaces and, perhaps unsurprisingly, these provided the first visual evidence for the reality of dislocations. The decoration of dislocations in the interior of crystals was to follow very soon.

Jack Mitchell, another post-war arrival in Bristol, picked up Mott's old interest in the theory of the photographic process. When he found hundreds of optically flat glass discs from some war-time optical work lying around in the laboratory, he used these to grow thin single crystal sheets of silver bromide to conduct experiments on photographic sensitivity. Fascinating as the story of the photographic latent image is, it is peripheral to our main interest. It deserved mention, though, because the occupation with the latent image and his interaction with Frank and others at Bristol pushed Mitchell toward the discovery of decorated dislocations in the interior of crystals.

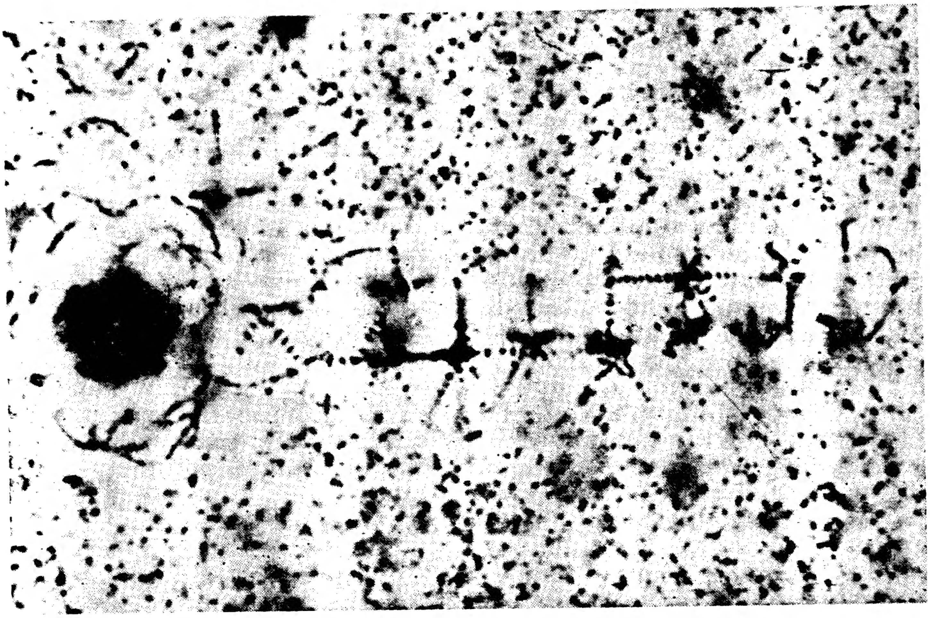


Fig. 3 - Prismatic dislocations produced by a Hysil glass sphere. Systems of similar dislocations on a much smaller scale, with axes along ‹100› directions, surround the larger decorating silver particles. x2400. (From A.S. Parasnis and J.W. Mitchell, (1959)).

Fig. 4 - Edge dislocations on slip planes in a crystal of potassium bromide made visible by decorating with gold. (From D.J. Barber, K.B. Harvey and J.W. Mitchell, (1957)).

Discoveries do not happen by accident, but those who seek sometimes accidentally find what they had not sought, provided that their knowledge and existing theory make them receptive to what they see. This is the true nature of much-praised serendipity.

Mitchell set out to discover the mechanism of latent image formation and discovered the visible world of dislocations in the interior of crystals; "they were simply there". In fact the first systems of sub-boundaries, consisting of rows of dislocations, were made visible under the optical microscope by photolytic silver depositions along these boundaries in crystals of silver bromide and silver chloride exposed to light (Hedges and Mitchell, 1953). These observations were continued for several years by a succession of research students and much work was done on crystals of silver- and alkali-halides which were heat treated, deformed, sensitized and decorated in different ways. A very brief review of the state-of-the-art to about 1960 was given by Mitchell (1962).

Fig. 3. shows a beautiful example of a system of dislocations caused by the inclusion of a tiny glass sphere in a crystal of silver chloride, while Fig. 4. shows slip planes in a crystal of potassium bromide.

Another aspect of the internal decoration of dislocations was discovered by Dash (1956). He worked on silicon, which cannot be plastically deformed at room temperature, and studied high temperature plastic deformation processes by the decoration of dislocations with copper diffused into the crystal. The copper can be seen in an infrared transmission microscope and the interior dislocations can be matched with their points of emergence, the latter being shown by etch pits.

We shall now shift our attention to the final step in establishing dislocations as a fact by making them visible in the electron microscope and focus on the Cambridge school, which descended from Bragg and centred on Hirsch. Hirsch too went to the famous 1947 Bristol conference and heard a paper by ìHeidenreich and Shockley concerning the theory of partial dislocations. His interest was aroused by the fact that Heidenreich had used an electron diffraction facility in an electron microscope, to look at misorientations in cold worked metals. Some time later, when Heidenreich reported his electron microscope observations of small subgrains in cold worked aluminium, Hirsch was struck by the fact that Heidenreich could obtain pictures in seconds, while his own x-ray microbeam diffraction patterns took many hours. Hirsch went to see another research student, who worked with a Metropolitan Vickers EM3 electron microscope. Using this, spotty electron diffraction rings were quickly obtained from cold worked (beaten) thin foils of gold. Electron micrographs were also taken, but their complex structure was to be described and analyzed in a further paper. The paper was never published, because Hirsch thought that beaten foils were too complex to analyze and wanted to introduce the technique of electrolytic thinning, previously used by Heidenreich, instead.

By 1954 Hirsch had became convinced that it should be possible to observe dislocations in an electron microscope and set a new research student, M.J. Whelan, to work on this task. In the meantime, a new electron microscope, the Siemens Elmiskop I, had been delivered to Coslett's electron microscopy group and this instrument gave far superior resolution. Whelan, together with R.W. Horne, started in October 1955 taking micrographs and diffraction patterns of cold worked aluminium and gold. The sub- boundaries in the aluminium foils

> were found to consist of individual dots or short lines, which we thought were probably dislocations, since their spacing agreed well with the prediction of Frank's formula, from the measured values of misorientation across the boundaries. However, we could not be sure, since it was possible that the dots or short lines could be due to Moir effects from two overlapping crystals. On 3 May 1956 Horne used the microscope in the "high resolution mode" with the double

> condenser system. He also pulled out the condenser aperture to increase the beam intensity. The lines were observed to move parallel to traces of (111) planes. This left us in no doubt that the lines were indeed images of individual dislocations, and that their glide was observed in the experiments (Hirsch, 1968, p.162).

These experiments were widely reported and the cin film of moving dislocations, which demonstrated almost everything that theory had predicted, presented irresistible proof of the true existence of dislocations and the essential correctness of the theory describing their behaviour. Nevill Mott and G.I. Taylor were among the first to be shown the experiments and were, of course, delighted. Even metallurgists were forced to believe in dislocations now.

Hirsch, Whelan and Horne were not, however the only discoverers ìof the visible dislocation. Walter Bollman worked at the Batelle Laboratory in Geneva on electron microscopy and when he was examining thinned electropolished specimens of stainless steel, one day, in June 1956, he observed what to him were obviously dislocations.

Bollman attended a conference in Reading on 24 - 26 July, 1956, at which Whelan first disclosed the Cambridge findings. He contacted the Cambridge group, and showed them his own pictures of dislocations. They all agreed that Bollman and Hirsch et al. had made the same discovery independently and nearly simultaneously. One result of the discussion between Hirsch, Whelan and Bollman was a joint study, which established that dissociation of dislocations and the formation of stacking faults by the movement of partial dislocations could be observed directly in stainless steel (Whelan et al, 1957).

The Practical Impact of Dislocation Theory

Metallurgists resisted dislocations to the last but could resist no longer when they had been so spectacularly substantiated in studies on surface spirals, decoration and, as a final triumph, by direct observation in the electron microscope. Though how important dislocation theory is to the practical metallurgist is hard to tell. Frank, one of the leaders of research on dislocations, has few illusions in this matter, at least as far as "normal" engineering is concerned.

> Dislocations may be important to people who make turbine blade alloys. I hope that dislocation theory has been a useful guide to people doing that sort of job.
>
> A man shapes a piece of malleable metal by hitting it with a hammer and the manner in which he hits it is scarcely modified by any consciousness that he is causing dislocations to move in the crystals (Frank in an interview with E.Braun).

Undoubtedly the understanding of the behaviour of metals has been greatly enhanced and this improved understanding has probably helped in the solution of some advanced practical metallurgical problems, as in special alloys for aircraft, materials for nuclear reactors and other extreme applications. Thus the practical utility of the knowledge of dislocations may not be overwhelming in the field which gave birth to it, but is useful in what is now termed "high technology". Dislocations proved very important in materials for the semiconductor industry, an industry which makes notoriously high demands on everything it uses. It turns out that dislocations affect the electrical properties of semiconductor materials, such as silicon, and methods for growing virtually dislocation free material had to be developed.

With the extremely small feature sizes of modern integrated icircuits, any distortions caused by dislocations are intolerable and silicon crystals with extremely low densities of dislocations are used for modern device fabrication. In non-critical regions of the material dislocations can be used deliberately to "getter" unwanted impurities and so-called "backside damage" is often employed. Modern devices require such incredible accuracy that the motion of a few dislocations can suffice for significant mechanical distortion. The presence or absence of dislocations needs to be most carefully manipulated and thus, fifty years after their discovery, dislocations play their greatest role in materials and in ways which in the thirties had not been thought of. The highly science-based semiconductor industry requires all available scientific insights for the manufacture of its materials, and thus the science of dislocations has made its practical contribution, albeit in an unexpected field (Queisser, 1983).

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CONCLUSIONS

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I would hate to take up too much time with some so-called conclusions. At the end of a meeting the audience can be supposed to have had a sufficient share of words, so it may be unwelcome to add my platitudes to these worthy proceedings. Therefore, I shall limit myself to a few sketchy remarks.

First, I would like to affirm that the meeting has been a successful one, and at the same time an enjoyable one. The origins of modern solid state physics research in Italy, and to some lesser extent also in other countries, have been recalled and competently illustrated, with the benefit in many cases of the contributions of the very people who started, or were connected with those beginnings. This has made the meeting lively, and provided the basis for the enjoyable part. But there has been also a highly creditable "technical" part, that is, the description of early stages of specific scientific endeavours, of the motivations of their inception, of the development of the research work until significant results were reached or at least perceived.

It is clear that such information is an indispensable part of the material with which history of science is built. Only a part, obviously, since the information contributed by the protagonists, in case they have not become professional historians, my be somewhat personal and passionate rather than detached and comprehensive; but an indispensable part nonetheless, because it supplies insight and knowledge otherwise bound to be lost.

Recording views and details available only to the protagonists of past enterprises seem all the more necessary today that the habit of entertaining significant scientific correspondence between research workers is being supplanted by ephemeral telephonic communications. Historians of the future will miss the cherished tool of perusing collections of letters!

It is then to be appreciated that throughout this meeting videotaping was available, thus allowing to record not only every word said, but even the facial expressions of the speakers pronouncing those words.

Gathering and preserving documents - whatever their form: written, spoken or visual - is naturally the first step of the building of historical accounts.

At such stage one need not be preoccupied with choosing which documents deserve to be kept. All available documents should be collected in archives, with adequate provision for their recovery. Then the historian will have plenty of material to work on, choosing, interpreting, summarizing, and to some extent surmising. Is his trouble worthwhile? The answer to this question may be not straightforward in the case of history of science, since the study of this subject is complicated by the need to combine historical scholarship with scientific understanding, and it is controversial which requirement should be favoured. But I would not let my answer depend on philosophical convictions in regard of the "right" way of interpreting history of science.

Having been trained as a physicist I subscribe to the opinion (of Schrödinger, as reported by W.T. Scott in his book "Erwin Schrödinger", MIT Press, 1967, p. 101) that science "can only develop by unfolding out of its own history", implying that the study of the scientific past is more important for the present day research worker than the reconstruction of bygone political and sociological circumstances. In keeping with my promise, I shall not dwell further on the matter.

I am pleased, however, to feel entitled to say that this meeting has contributed indeed something, in a specific field of interest, to the preservation of the memory of the scientific past.

Now, to conclude, I would like to thank all the speakers, all those who contributed to the discussions, all the participants and all the persons that with their dedicated work made this meeting a success.

And to top the list of people deserving our gratidude, let me thank on behalf of everybody prof. Giuseppe Giuliani, who proposed this meeting to begin with, and devoted so much competence, time, and energy to make it a reality.

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