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The origin of semiconductor physics in Italy: 1945–1965 (*)

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Riassunto. Le attività svolte nell'ambito della Fisica dei semiconduttori dai fisici italiani tra il 1945 e la fondazione del Gruppo Nazionale di Struttura della Materia (GNSM, 1965) sono analizzate e discusse nel loro contesto storico. Prima degli anni '50, la Ricerca italiana risultò solo marginalmente coinvolta nelle tematiche inerenti la Fisica dello stato solido. A partire dagli anni '50 cominciò a svilupparsi nella comunità degli ingegneri elettronici un significativo interesse per gli aspetti più applicativi dei dispositivi a semiconduttore introdotti in quel periodo. Negli anni successivi, la nascita di alcuni gruppi sia sperimentali che teorici guidati da scienziati di valore (alcuni di essi con esperienze internazionali) permise di affrontare i principali temi relativi alla fisica della materia condensata e dei semiconduttori. I lavori svolti da questi "pionieri", discussi nel presente articolo, rappresentarono dal punto di vista storico un contributo di valore inestimabile per le successive generazioni di fisici operanti in quest'area di ricerca.

Abstract. The activities carried out by Italian physicists in the field of semiconductor physics during the period spanning from 1945 to the foundation of the National Group of Structure of the Matter (GNSM, 1965) are reviewed within their historical context. Until the fifties, the Italian research was only marginally involved, if at all, in the main streams of advancement in solid state physics. Starting from the early fifties, an interest for technical applications of the newly introduced semiconductor devices began to grow in the electronic engineering community. In the following years, the birth of a few experimental and theoretical groups lead by highly motivated scientists (some of them with international experience) allowed to deal with the main topics related to condensed matter and semiconductor phenomena. The work developed by these "pioneers", discussed in this paper, represented an invaluable contribution for the new generations of physicists in this research field.

1. Introduction

The development of physics in Italy in the twentieth century has drawn the attention of historians only rather recently. After the pioneering work by Gerald Holton on Fermi's group [1], several studies have dealt with institutional backgrounds [2–6],

(*) This work has been carried out within the research project on the birth of the physics of matter in Italy: `http://fisicavolta.unipv.it/percorsi/hip.asp`.

diffusion of relativity and quanta [7–11], cosmic rays and nuclear physics [12–15]. The attention has been mainly focused on the researches by and around Fermi's group, while topics concerning what is now called the physics of matter (atoms, molecules, liquids and solids) have been investigated mainly (if not only) by Giuliani and his coworkers [16]. The same is true for the post-war years.

The picture that emerges from these studies is now rather well established. Before the Second World War, the Italian physical community was small and scattered over the country: at the end of the thirties the number of academic physicists was around 140 and the research units counted only few people. The smallness of the research groups made it difficult to follow the main streams of development of the discipline and/or master, at least, some of its up-to-date topics. The experimental tradition inherited from the nineteenth century, in the absence of theoretical activity favored a negative reaction to relativity and quanta; the reaction with respect to quanta, in turn, hampered the entrance into new fields of experimental research such as atomic and molecular spectroscopy. The physics courses maintained well into the thirties the structure and the contents inherited from the nineteenth century with only two novelties: the introduction, around 1920, of a course entitled *Fisica Superiore* (in which, but not everywhere, some relativity and quanta topics were taught); and the introduction of a course of Theoretical Physics (*Fisica Teorica*) in the academic year 1936–1937 ([1]). Since then, we must wait till 1961 in order to see a new adaptation of the physics course to the advancements of the discipline with the introduction, in particular, of a course entitled *Struttura della Materia* (Structure of Matter).

Since the thirties, physical research in Italy is known because of the activities of Enrico Fermi and Bruno Rossi in the fields of nuclear and cosmic-rays physics, respectively. But, as concerns the condensed matter, the scene was dim. During the first four decades of the century, experimental research has been done in fields that later will be recognized as pertaining to solid state physics. The topics studied have been: 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. However, the application of quantum mechanics to the physics of crystalline solids (which started in the late twenties) has been completely neglected in Italy ([2]). Therefore, Italian physicists working in these fields approached the end of the thirties with a cultural background typical of a pre-quantum era.

The scenario Italy had to face after the Second World War has been described by Giuliani [18]: "After the Second World War, the international context of scientific research appears profoundly changed: the defeat of nazism and fascism and the war damages have favored the passage of the economic and scientific leadership on the

([1]) But, in that year, good courses of Quantum Mechanics were held only in four or five Universities [17].

([2]) With some isolated exception: in the late thirties, Giovanni Gentile jr. dealt with some problems concerning ferromagnetic properties.

other side of the Atlantic; the huge effort by the United States in the production of the fission bomb has shown how efficient can be a research based on a planned mixing of basic, applied research and technology; the shock provoked by the nuclear bombing of Hiroshima and Nagasaki has again emphasized the necessity of a reflection about the aims of Science and its applications. The start of the cold war and the consequent search of new weapons has dramatically increased the interest of governments in the military and peaceful applications of the new technologies and has spurred the development of research programs of unprecedented economic and organizational commitments, often affordable only through international cooperation. The problems that Italy had to face in order to achieve the scientific and technological background necessary for the country's development were complex and difficult: the war damages and the overall weakness of scientific institutions made the task even more arduous".

Also the task of those researchers who, for personal choice and/or local influences began to work on the physics of condensed matter, was arduous. They have inherited a cultural background in which the physics of condensed matter was still that of the twenties; the university courses they have followed scarcely contained quantum mechanics; even less, its application to condensed matter topics. They had to face a knowledge gap of about twenty-five years.

Condensed matter research developed in Italy as a polycentric process in which small local groups began to work with more contacts with foreign groups than among themselves [19]. In this context, particularly interesting has been the birth of semiconductor physics. Marazzini and the author of this paper have recently published a book on this subject [20]. This paper aims at making available to a wider audience the most significant results of that research.

2. The background

In his opening lecture at the "Solid State Physics School" held in Varenna in 1957, Fausto Fumi defined solid state physics as "...the study of the physical properties of solids and of the particular properties exhibited by atoms and molecules as a consequence of their reciprocal interactions and their regular distribution within the lattice" [21]. Actually, the two main subjects dealt with were the quantum theory of solids and the lattice defects, whereas topics regarding semiconductors were considered as a "product" deriving from these more general studies.

The delay of Italian research in solid state physics is well documented by the program of the meeting of the Italian Physical Society (SIF) held in Como in 1947: it was the first SIF meeting in the post-war period. Antonio Carrelli's talk, *Modern aspects of physics research*, was about the same subject dealt with in Como twenty years before: the application of Fermi statistics to the theory of metals by Sommerfeld. Twenty-five years later, Luigi Giulotto stressed that the only significant studies performed by Italian physicists in solid state physics until the 1950s have been the studies (in the thirties) on the Raman effect by Carrelli in Naples and by Rasetti, Amaldi and Segrè in Rome (modestly ignoring his own contributions in Pavia) [22].

In order to shed some light on the main bottlenecks that have hampered the development of solid state research, it is worth discussing in some detail: i) the prevailing role of nuclear physics; ii) the connection between academic institutions and industry; iii) the distribution of funds; iv) the small number of research groups and the lack of coordination among them.

i) From the thirties to the end of the Second World War, a significant progress has been made in the understanding of semiconductors properties. The post-war years have been characterized by an increasing interest in the field, especially after the invention of the transistor in 1947. However, in Italy, the situation was rather different.

Antonio Rostagni opened the SIF meeting in 1948 with a lecture entitled *Recent discoveries and new instruments in Physics research*, that was almost entirely dedicated to nuclear physics and instruments such as synchrotrons and photomultipliers [23]. In particular, no mention of the invention of the transistor was made.

At the SIF meeting in 1961, Giampiero Puppi (engaged in particle physics research) acknowledged that the funds devoted to elementary particles physics were far greater than the ones allocated to other physics fields [24]. According to Puppi, this situation has been caused by the exceptional development of Fermi and Rossi schools during the 1930s. However, instead of asking for a more equilibrated allocation of funds, Puppi held that the way towards a better equilibrium would have been to stimulate the choices of young physicists towards less developed fields.

Six years later, Luigi Giulotto underlined the lasting of this unequal distribution of funds in a well-documented paper published in the bulletin of the National Group of Structure of Matter (GNSM) [25].

ii) Industries and academic institutions have been (almost) completely separated till the sixties. This is particularly true for semiconductor physics. As Gianfranco Chiarotti put it at the SIF meeting in 1962 "...the Italian research in the field of semiconductors is practically missing [while] the main interest ... seems to deal with the study of lattice defects...". According to Chiarotti, the main causes were "...the lack of a robust scientific tradition [in this area], the absence of a good education system in the field of solid state physics and the almost complete lack of interest of Italian industry in scientific research" [26].

In the late 1950s the first Italian semiconductors firms have been founded: SGS (Società Generale Semiconduttori) in Milan and ATES (Aziende Tecniche Elettroniche del Sud) in Catania. The activities of these two companies were focused on the production of electronic devices. The cooperation between industries and universities was limited to the evaluation of some physical parameters and to the collaboration with few students working on their thesis.

In 1963 a very small percentage (9%) of physics graduates were employed in industry, whereas most of them worked in academic research (78%) or in other sectors

TABLE I. – *Occupational distribution of physics graduates (ref.* [28]*).*

Category of employment	Number	%
Research institutions	494	64.5
Industry	70	9.2
Commercial sector	16	2.1
Teaching	103	13.5
Others	8	1.0
Waiting military service	25	3.3
Unemployed	49	6.4
Total	**765**	**100.0**

(13%) [27]. This trend has been confirmed by Guido Tagliaferri in 1964: see table I [28]. See also Giulotto's comments on Tagliaferri's data [25] (3).

iii) At the SIF meeting in 1962, the Minister of Public Education (Pubblica Istruzione), Giovanni Medici, stated that the budget for scientific research was about 50 billion lire per year, equivalent to 0.2% of the gross domestic product, whereas in other countries the total research investment was ten times greater [30]. Medici also acknowledged that the funds were often distributed without considering the actual needs of the different lines of research.

A detailed analysis of the financial support of solid state physics in the late 1960s was published by Chiarotti in 1982 [31]. Chiarotti recalled that in the years 1965, 1966 and 1967 the yearly investment of CNR (Consiglio Nazionale delle Ricerche) was greater than 20 billion Italian lire, but less than 4% of this amount was allocated to solid state physics research.

iv) The problems arising from the small number of solid state research groups have been highlighted by Giulotto at the solid state physics school held in Varenna in 1954. Giulotto stressed that the main purpose of the school was to give the small solid state community the possibility of discussing the most relevant topics of their discipline and their own results with a few international specialists [32]. In order to better grasp the real meaning of the word "small" used by Giulotto, it is worth recalling that at the SIF meeting held in the same year only one talk (presented by Fausto Fumi) was on solid state physics.

During the SIF meeting held in Bari in 1963, a group of researchers founded a voluntary association called "Gruppi Italiani di Struttura della Materia" (GISM)

(3) As recalled by Giuliani, "Starting from the sixties, Giulotto began a long lasting activity aiming at an equilibrated development of physical researches: the Physics of the Matter, whose technological outcome was of strategic relevance, was badly underdeveloped. However, Giulotto commitment, though based on a correct analysis and sustained by an ambitious goal —to obtain what will be later called INFM (National Institute for the Physics of Matter)— has been hampered by tactical errors and resentful polemics. The path has been difficult and perilous: as a matter of fact, the INFM was founded only in 1994" [29].

whose main purpose was to promote the research in the field of atomic, molecular and solid state physics. This organization was formally recognized by CNR in 1965 as the "Gruppo Nazionale di Struttura della Materia del CNR" (GNSM): eleven years later, the GNSM counted 24 research groups. In the same year the first issue of the already quoted GNSM bulletin was published. Its goal was the sharing of "...information and comments about the progress in an area of Physics that has been characterized by a dramatic development, that is Condensed Matter Physics: atoms, molecules, solid and liquid state of matter". In a recent recollection of those years, Chiarotti stressed how "...in the 1960s the GNSM was a group of people driven by the same motivations [...] The intellectual commitment was extremely high and there was also the strong feeling that the researches [in that field] would have had high relevance for the Italian research and for the country" [33].

3. Engineers before physicists

In Italy, semiconductors topics have been firstly addressed to by the electronic-engineering community. The first Italian reference to transistors appeared in a short note published in the magazine *Poste e Telecomunicazioni* in 1949 [34]. This note described the structure of the point contact transistor, the polarization details, the amplification properties and the equivalent circuit.

In 1950, the same magazine published other papers focused on the new semiconductor device, written by Piero Schiaffino [35] and Lamberto Albanese [36]. Other papers appeared in magazines such as *Alta Frequenza* and *L'Elettrotecnica* and again in *Poste e Telecomunicazioni* ([4]). These papers dealt with the technological and circuital aspects of semiconductor devices. Among other contributions, it is worth recalling the experimental studies by Manfrino [37–39], Sette and Della Pergola [40,41] working at the Istituto Superiore di Poste e Tecomunicazioni, with the support of the Fondazione Bordoni. These papers, as well as the one by Della Pergola and Sette published in *Il Nuovo Cimento* in 1956 [42], were the first focused on the physical properties of semiconductor devices.

4. The first developments

The late 1950s showed a growing interest in semiconductor physics:

a) in 1956, Franco Bassani began to publish several works on band structure calculations; b) in 1957, the school of solid state physics in Varenna included a special section on semiconductors; c) in 1957, the already mentioned SGS (Società Generale Semiconduttori) began to produce semiconductor devices under Fairchild patents.

([4]) A complete review of these publications can be found in ref. [20].

TABLE II. – *Number of Italian papers on semiconductors in the period 1956–1966 published in the magazines listed in the text (ref.* [20]*).*

Year	Theoretical	Experimental
1956	1	3
1957	2	2
1958	0	1
1959	4	1
1960	0	0
1961	4	4
1962	4	3
1963	4	5
1964	0	10
1965	1	6
1966	3	11
Total	**23**	**46**

TABLE III. – *Italian communications at the SIF meetings on semiconductors in the period 1956–1966 and their percentage with respect to the total number of communications (ref.* [20]*).*

Year	Number	%
1956	1	2.8
1957	–	–
1958	3	3.0
1959	1	1.6
1960	0	1.3
1961	2	2.0
1962	1	5.3
1963	3	5.8
1964	5	5.1
1965	7	5.8
1966	5	4.3
Total	**28**	**4.0**

A quantitative description of the growing interest in semiconductor physics is given in table II: the numbers refer to papers published by Italian physicists in the following magazines:

- *Alta Frequenza*,
- *Il Nuovo Cimento*,
- *Journal of Applied Physics*,
- *Journal of Physics and Chemistry of Solids*,
- *Philosophical Magazine*,
- *Physical Review*,
- *Physics Letters*,
- *Physics Review Letters*.

The data reported in table II can be compared with those of table III concerning the communications presented by Italian scientists at the SIF meetings in the same period.

In 1965 Sette published a *Quaderno* on the free electron theory in metals, the energy bands theory and semiconductor properties [43]. In the same year, Giampaolo Bolognesi published the volume *Tecnologia dei semiconduttori*: after a short introduction on semiconductor theory, the book dealt with semiconductor technological processes [44]. The rich bibliography of this volume did not quote any Italian contribution.

5. Experimental researches

5.1. In Rome

The first Italian experimental researches on semiconductor properties have been carried out at the Istituto Ugo Bordoni. This institution was founded within the Istituto Superiore delle Poste e delle Telecomunicazioni in 1952.

Ten laboratories were supported by the Istituto Ugo Bordoni and their activities dealt with several topics, such as: microwaves, semiconductors, wave propagation, electroacoustics, electronic microscopy, transistor-based circuits and radio communications. The semiconductor laboratory was directed by Daniele Sette [45]: it represented the main Italian activity in that research area in the 1950s. The scientists working with Sette were Renato Manfrino, Giancarlo Della Pergola and Venanzio Andresciani.

In 1954, Sette spent a short period in the USA and France in order to gather information about the most recent lines of research in the field of semiconductors. In the USA, he visited several institutes and attended the *Conference of the American Acoustic Society* and the *Conference of the Institute Radio Engineers*, both on semiconductor topics. He then visited the French laboratories of the Centre National d'Etudes des Telecommunications (CNET).

This journey allowed Sette to get in touch with experimentalists and theorists working in fundamental semiconductor research. He also established a communication network providing information about research in progress and available postdoc positions. Sette identified a list of the main techniques used to study semiconductor properties. This list became the agenda on which he decided to concentrate the activity of his laboratory ([5]). Various experimental setups were developed and used in galvano-magnetic measurements (Hall effect and magneto-resistance) and in photoconductivity experiments. Among these studies: a work on chemical attacks on germanium crystals [42]; a study on the ratio between the longitudinal and transversal effective masses in germanium [46]; a paper on the experimental verification of the

([5]) Daniele Sette, private communication.

theoretical hypothesis concerning the energy band structure in germanium and silicon [47] ([6]); and, finally, the study on the mean lifetime of charge carriers [49]. In this work, the mean lifetime was ultimately obtained by using the theory developed by Shockley [50] and Rittner [51].

A detailed discussion of the research activities carried out by Sette and coworkers can be found in [20].

5.2. In Cagliari and Bologna

Semiconductor studies in Cagliari have been promoted by Giuseppe Frangia. In 1959, he offered to Pierino Manca (graduated in chemistry) a research position for the study of semiconductor properties. At that time, Frangia's staff was composed by Carlo Muntoni, Francesco Aramu and other young students. The first activity of this group concerned the preparation of CdS single-crystals samples using the vapor phase growth technique ([7]).

Manca and his coworkers studied the semiconducting properties of iron telluride [52] and the photocurrent decay processes in polycrystalline CdS [53].

Manca worked on sulfide compounds until 1965. In that year, together with Aramu, he studied the crystallographic structure as well as the electrical, magnetic and optical behavior of these compounds. The know-how acquired during the experimental studies on tellurides allowed Manca and Massazza to prove that the properties of $AgFeTe_2$ could be related to the existence of an equimolecular mixing between Ag_2Te and Fe_2Te_3 [54, 55].

Another line of research concerned the optical properties of semiconductors. These studies started in 1962, when Frangia assigned a thesis on the luminescence of CdS to Francesco Raga. The first work appeared in 1963 [56]: it concerned the absorption band edge in wurtzite-type CdS before and after the structure transition CdS_Z (cadmium sulfide with zinc-blende structure) $\rightarrow$ CdS_W (cadmium sulfide with wurzite structure) and its shift as a function of temperature.

The studies about the preparation of solid compounds CdS_xSe_{1-x} $(0 \leq x \leq 1)$ yielded single crystals that were used in optical studies. The luminescence spectra of these materials were analyzed and the results compared with the ones obtained by thermoluminescence techniques. The data obtained confirmed the correlation between the change of the energy gap and the shift of the upper limit of the valence band, while the lower limit of the conduction band remained unchanged. Moreover, the authors were able to shed light on the observed change in the exciton luminescence spectral line. In the following period Raga kept working on these luminescence phenomena in collaboration with Nikitine and others [57–60].

([6]) In this work, the available information (obtained by cyclotrons resonances measurements) on the band structure of germanium was completed by measuring the Hall coefficient of n and p Ge as a function of the applied magnetic field. The results obtained were in agreement with the ones published in the same period by Goldberg and Davies [48].

([7]) Frangia's group introduced it in Italy.

In 1964, Manca, Muntoni and Raga published a paper on the behavior of exciton states under thermal gradient [61]. This subject was extensively investigated by Raga and Nikitine in the following years [57–60].

In the late 1960s, other experimental groups investigated metal and semiconductor properties using different techniques. In the field of electron microscopy, we must recall the activity carried out in Bologna. In the 1950s, the Physics Institute was directed by Ugo Valdré, who introduced the electron microscopy technique in Italy. In the early 1960s, Valdré invited to Bologna Primo Gondi, a young researcher with a good know-how on structural properties of metals. The main topic investigated, by electron microscopy technique, concerned dislocations in germanium crystals and their correlation with plastic deformation, crystal hardening and thermal treatments [62, 63].

5.3. In Pavia and...

As already mentioned, the international growth of solid state physics was exceptional during the 1950s and the 1960s. The flourishing of solid state physics, and more specifically of semiconductor studies, was also stimulated by the possible transfer of basic research into commercial and military products, such as semiconductor devices. The production of these devices presented various problems mainly related to minority carrier currents in diodes, the excessive noise, the surface recombination of minority carriers and the different semiconducting characteristics of several alloys. These problems stimulated a series of experimental and theoretical researches on surface states in semiconductors.

In Italy, the experimental side of this field was deeply investigated by a group of researchers at the University of Pavia supervised by Chiarotti [64]. Chiarotti's team was composed by Adalberto Balzarotti, G. Del Signore, Andrea Frova, Giorgio Samoggia and Angiolino Stella: it began his activity in 1960.

In that year Chiarotti and his co-workers presented a communication at the SIF meeting entitled *Surface conductivity measurements in germanium* [65]. The Hall coefficient, the conductivity and the mobility of surface carriers were measured in a semiconductor whose surface has been exposed to the so-called Bardeen-Brattain cycle [66]. One year later, Frova and Stella published a paper on Tamm theory of surface states [67]. This paper dealt with the details of surface states theory; it emphasized the existing contrast between theoretical predictions and experimental results regarding the change of surface potential produced by an electric field applied perpendicularly to the surface of the sample. On the basis of these considerations, Frova and Stella underlined the hypothesis of a strong correlation between surface level structure and chemical or mechanical treatments.

The low density of surface states made it very difficult to detect optical transitions from occupied valence band states to unoccupied surface states (or from occupied surface states to unoccupied conduction band states). In 1962, Harrick published a paper in which he described the field effect modulated optical absorption technique [68]: the use of a sinusoidally varying electric field made it possible to detect, by looking at the modulated absorption, the optical transitions to or from low-density electronic states. In the same year, Chiarotti's group began to use this technique for studying semiconductor surface properties. The first paper appeared in 1962 and dealt with the effects on germaniun surface produced by oxigen [69]. The dependence of fast surface states on surface contamination was further examined by Chiarotti, Frova and Balzarotti [70] by exposing a sample of germanium to different environmental conditions. Some technical improvements apart, the experimental method used by Chiarotti and his coworkers was quite similar to the one discussed by Bardeen *et al.* in a work published in 1956 [71] (8).

In 1962 Chiarotti obtained a permanent position at the University of Messina, where he moved in the same year together with Balzarotti, Frova, Umberto Grassano, Andrea Levialdi and Gianfranco Nardelli. However, Chiarotti did not stop his collaboration with the rest of the original group in Pavia: a paper focused on the optical detection of surface states using the modulated field effect technique was published in 1966 [72]. The main result was the detection of energy levels correlated to a particular transition from surface states to the conduction band.

In 1963, Frova accepted a Research Associate position at the Semiconductor Research Laboratory in Urbana (Illinois), directed at that time by John Bardeen. This position has been offered by Paul Handler, working at the same lab as vice-director. After joining Handler's group, Frova began to apply the electromodulation spectroscopic techniques used in Pavia to *p-n* junctions in germanium, silicon and gallium arsenide. As a matter of fact, this experimental setup had been previously used by Chiarotti in Pavia in the study of the Franz-Keldysh effect [73] in semiconductor surfaces. In 1965, Frova and Handler carried out an experimental study of the Franz-Keldysh effect in a *p-n* germanium junction [74].

Using the same technique, Frova and Penchina measured the energy gap in germanium obtaining values in good agreement with the ones obtained by the more expensive and complex methods based on photoconductivity and magneto-absorption processes [75]. Frova, Handler and coworkers, studied also the variation of the optical absorption coefficient in silicon and germanium [76]. This paper dealt with a detailed study of the direct and indirect (phonon-assisted) intraband transitions in both elements.

In the same period other investigation methods were developed by various researchers based on electroreflectance and wavelength modulation. In the following years, all these experimental procedures, referred to as *modulation spectroscopy techniques*, allowed to obtain a great deal of information on vibrational and electronic properties in solids.

Another member of Chiarotti's former group was Angiolino Stella. He spent a few years at the Iowa University (from 1961 to 1964) to carry out studies on semiconductor compounds. Stella published several papers in collaboration with D. W. Lynch on

(8) The technique was based on the measurement of the conductivity as a function of the surface potential modulated by an electric field applied perpendicularly to the surface.

this subject ([9]). We recall here the first one concerning the semiconductor compounds Mg_2Si and Mg_2Ge [77]: significant physical parameters, such as the energy gap and the mean lifetime of charge carriers, were determined. These kind of studies, focused on II-IV compounds, represented the core of the activity carried out by Lynch and Stella until the late 1960s.

Finally, it should be mentioned the paper on the pressure coefficient of the band gap in Mg_2Si, Mg_2Ge and Mg_2Sn [78]: the experimental results yielded information about the structure of band edges, despite the low quality of the samples and the low pressures used.

5.4. Researches in non-academic institutions

We shall briefly discuss the activities developed at the Olivetti laboratories located in the Milan area. The first communications by the Olivetti group appeared at the SIF meeting in 1963. Franco Forlani and Nicola Minnaja, focused their attention on the investigation of semiconductor structures related to planar microelectronic devices.

In 1964 Forlani and Minnaja published a paper, *Conduction Phenomena in Si–SiO*$_2$*–Al Structures*, on the properties of the electrical conduction in semiconductor-dielectric-metal structures [79]. For a closer look at the research activity of both authors one can see the proceedings of the SIF meetings of those years ([10]).

Other institutions contributed to semiconductor research in those years. Here, we simply enumerate their fields of research:
- CISE: studies on silicon detectors.
- EURATOM (Ispra): studies on the so-called forbidden reflection in silicon and germanium.
- Istituto Galileo Ferraris (Torino): studies on piezoresistance effects in n-type semiconductors.
- Istituto Superiore di Sanità: studies on germanium with special reference to the complex dielectric constant in intrinsic germanium in the microwave region.

From 1961 to 1966, several groups working in different institutions developed experimental researches on radiation effects in semiconductors. The first work on this subject was presented at the SIF meeting in 1959 by G. Airoldi, Z. Fuhrman, and E. Germagnoli and published in *Il Nuovo Cimento* in the same year [80] (conduction properties and Hall effect in electron-irradiated germanium). As concerns neutron radiation effects in semiconductors, Mario Bertolotti and Sette published the first Italian paper on these subjects in 1961 [81]. In their study, the mean lifetime of minority carriers in irradiated germanium was analyzed in order to verify some hypotheses proposed by Crawford [82] and Gossick [83]. The activity of Sette's group on neutron-irradiated semiconductors was very lively in the first half of the sixties as shown in [84, 85].

([9]) Lynch has been in Pavia in 1959, working with Chiarotti on color centers in KCl.
([10]) A stimulating recollection by Forlani about the events of those years can be found in ref. [20].

Radiation effects with alpha particles (Colella and Merlini at EURATOM) and ionized $O_2{}^+$ molecules (Bacchilega, Gondi and Missiroli in Bologna) were extensively analyzed during the period 1964–1965.

Another research topic was about positrons produced by gamma rays in semiconductors. The first experimental results have been described in two papers published in 1963 and 1964 by P. Colombino, B. Fiscella and L. Trossi [86,87]. The first paper presented the detailed description of the linear slits and the point slits methods ([11]). The second paper concerned instead the angular distribution of annihilation quanta emerging from Si, Ge and Al crystals. The positron decay process in silicon was also studied at CISE laboratories. These studies aimed at determining what kind of electrons (valence or conduction) was involved in the annihilation process. Later, the positron mean lifetime in different semiconductors, such as gallium, silicon, boron and silicon carbide has been studied.

From a more technical viewpoint, the two areas of main interest were the crystal growth and the improvement of measurement techniques. The production of semiconductor samples constituted a vital issue. This is evident if one considers that the germanium samples used in the laboratories of the Istituto Ugo Bordoni came from the USA until the late 1950s. Furthermore, in the early 1960s a great number of Italian researches have been carried out thanks to samples donated by S.G.S., the Italian semiconductor manufacturer founded in 1957. Several papers on semiconductors sample preparation have been published in the magazine *Alta Frequenza* by Manfrino, Sette, Della Pergola and Venanzio Andresciani in the late fifties [89–91]. In ref. [91], Sette and Andresciani discussed the main characteristics of a furnace (Czochralski type) used to prepare germanium crystals of very high quality.

In the field of electronic microscopy, the review by Gondi in 1965 [62] should be mentioned. It shows the enduring interest in the application of this technique to the study of dislocations and lattice defects in semiconductors.

An apparatus for differential spectroscopy has been developed by Guido Bonfiglioli and Pietro Brovetto (both working at the Istituto Galileo Ferraris in Turin) [92,93]. This instrument, of wide application, has been used also in semiconductor research.

6. Theoretical researches

With the exception of two reviews published by Antonio Carrelli in 1946 and in 1949 on the Hall coefficient in Bi–Sb and Bi–Te [94,95], the Italian contribution to the theoretical research on semiconductors was completely absent until the mid-fifties.

In the early fifties the interest for the theoretical aspects of solid state physics began to grow in the Italian community, mainly thanks to the efforts of Piero Caldirola [96] (then director of the Physics Institute in Milan) who put in contact some students coming from Pavia University (Franco Bassani, Roberto Fieschi and

([11]) This technique was originally developed by S. De Benedetti and L. G. Lang in order to study amorphous polycrystalline substances [88].

Mario Tosi) with Fausto Fumi [97], a young theorist who had spent some time in the USA working with Frederick Seitz at the University of Illinois.

The role played by Fumi in the birth of solid state physics in Italy (not only in theoretical research), is underlined by Chiarotti in a recent recollection: "In the summer of 1951 I was doing my thesis under L. Giulotto [...] I attended an informal seminar by Fausto Fumi [...] Fumi was talking of defects showing, to our surprise, that many properties of solids depend more on defects than of the regularity of the lattice. The subject of seminar was the color centers, a thing we had never heard about: Fumi discussed the models proposed for the various centers, models that 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 Institute. [...] So he asked me to work part-time on the problems Fumi had suggested..." [98].

The experimental and theoretical study of defects in solids represented a fundamental step in the development of Italian solid state physics. As Chiarotti put it at the SIF meeting in 1963 "...the Italian interest seems to be focused on the properties related to the presence of lattice defects (52% of the total production in Italy and 15.1% in other countries)...". A summary of the Italian works on lattice defects and color centers can be found in ref. [20]. In the following the discussion will, of course, be concentrated on the studies carried out by Italian physicists in research areas more strictly related to semiconductors.

In his communication at the SIF meeting in 1963, Franco Bassani [99] pointed out that "...the number of Italian physicists studying condensed matter is rather small and an analysis of their contributions cannot give us a complete idea of the importance of this field [...] nevertheless in the last two years the Italian contributions have been so important and significative..." [100]. Bassani listed the main three subjects studied by Italian theorists: i) interatomic forces, thermodynamic functions in ionic crystals and in rare gases; ii) lattice defects; iii) electronic levels in metals and insulators. In the following section we shall focus on the latter subject.

6.1. Electronic levels of solids

A review of the development of the band theory of solids can be found in ref. [101], where the most important calculation techniques of electronic levels are discussed in their historical background. In 1937, during his sabbatical semester at the Princeton Institute for Advanced Study, Slater developed the so-called Augmented Plane Wave (APW) method employing a "muffin-tin" potential. Two years later, Herring, a postdoctoral fellow at MIT, elaborated what became known as the Orthogonalized Plane Wave (OPW) method, where the wave function is a linear combination of low-lying atomic orbitals and plane waves. By the mid-1950s, solid state theorists had several methods at their disposal that could be used to solve the Schrödinger wave equation in a periodic potential. However, until the late fifties the band structure of solids was considered too difficult to be calculated. Nevertheless, a few rough computational works had been performed in the forties in the USA using electromechanical computers.

At the *International Conference on Semiconductors* in Rochester in 1958, the only two communications on energy band topics have been presented by J. C. Phillips and G. F. Bassani but, as the Italian scientist recalls, those sessions were attended only by few participants ([12]). At that time, Franco Bassani was working at University of Illinois in Urbana (1954–1957).

Bassani recalled that during his stay in Urbana "...Fred Seitz had given a course on group theory; the book adopted was a photostatic copy of Wigner's book *Gruppentheorie und Wellenmechanik* [...] 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" [102].

The studies carried out by Bassani in the late fifties concerned mostly pseudo-crystals, *i.e.* ideal crystals composed by atoms which are known to crystallize in some other lattice. This area of research was suggested by Seitz as a useful tool for studying the influence of lattice symmetry and atomic potential on band structure.

In 1957 Bassani published an OPW calculation of the energy band of silicon [103] without using any *ad hoc* parameters. Bassani showed that the energy band structures are mainly determined by the lattice symmetry properties. At the SIF meeting in 1958, Bassani presented two papers on this subject. In the first communication, Bassani and Celli analyzed the energy band structure of lithium atoms in the diamond lattice, and after comparing their results with those obtained by Herman [104] they observed that "...the order of the energy bands is mainly determined by the lattice symmetry...". In the second contribution, Bassani and Ignazio Fidone described the energy band structure of 2-dimensional graphite by using the tight-binding method. They concluded that "...graphite is a borderline case between metal and semiconductor as the occupied and the empty states are very close...".

The theoretical works developed by Bassani and Celli on pseudo-crystals deserve to be analyzed in more detail as they introduced a powerful and simple perturbation approach, based on the OPW method. They considered the crystal potential as a small perturbation on an empty lattice whose states were classified on the basis of the crystal symmetry. From a technical point of view, the fact that this method could give a reliable picture can be justified by the "cancellation effect" due to the orthogonality condition between the electronic wave functions and the core states. This effect can be physically described as a repulsive term that partially cancels the crystal potential. Such a formulation allows to consider a total effective potential referred to as "pseudo-potential".

The same theoretical approach was used for studying the energy band structure of lithium [105]. Bassani and Celli pointed out that "...the approach leaves uncertain

([12]) Franco Bassani, private communication.

some of the detailed features of the energy bands such as the curvatures, but we have preferred not to use any interpolation, since we are mainly interested in the sequence of the energy bands and in their qualitative features".

The energy band structures in pseudo-crystals were further investigated by Bassani [106]: he studied the most important factors determining the energy band structure of a pseudo-crystal made of sodium atoms in a diamond lattice by using the OPW method. The lattice parameter of the pseudo-crystal was chosen in such a way as to give the same electron density as in metallic sodium. Bassani stressed that "...it seems possible to conclude that the sequence of the energy bands is mainly determined by the lattice symmetry and their separation by the electron density".

In 1961, Bassani and Celli wrote a lengthy paper on the pseudo-potential technique [107]. They stressed the role of the perturbation approach and applied the technique to some crystals with the diamond structure. For germanium and gallium arsenide the results obtained were in good agreement with the experimental data of Kleinman and Phillips [108]. The authors pointed out that, on the basis of the applied method, an increase of the lattice constant entails a contraction of the energy scale of the empty lattice eigenvalues making the separation between the final energy levels smaller. This prediction was in agreement with the experimental observation that the energy gap and the valence band width decreases in going from diamond to silicon and to germanium. On this basis, Bassani and Celli explained qualitatively the effect of pressure on the energy gap: an increase in pressure caused a decrease in the lattice constant and then an increase in the energy gap, as experimentally observed. Finally, Bassani and Celli underlined that "...this approach [...] does not rule out the necessity for more precise calculations, but it is justified in view of the present uncertainty related to such calculations. Its main advantage is that of exhibiting explicitly the role of the lattice symmetry, core states and lattice parameter on the energy band structure of different compounds...". Discussing the validity of such a simple approach, they observed that "...the critical role played by the few lowest Fourier coefficients of the potential with the corresponding terms from the core states explains the good results obtained in spite of the poor knowledge of the crystal potential".

The main problem presented by the perturbative approach introduced by Bassani and Celli was that the Fourier coefficients of the crystal potential were greater than the separations of the electronic levels in the empty lattice: for this reason a perturbative method could not be applied. This point has been discussed by Bassani in a private communication [20]: "...we noticed that the orthogonality condition of the inner states introduced a correction in the potential that canceled its contribution near the nucleus: this fact justified the use of the perturbation theory. J. C. Phillips and L. Kleinmann suggested that the two terms should be considered as a pseudo-potential and that its Fourier coefficients could be considered as available parameters. [In the work published in 1961] we were able to prove the existence of some degrees of freedom in defining the pseudo-potential, due to the fact that the system formed by plane waves and inner states was overcompleted. Thus, a general form of the pseudo-potential could be developed with many practical benefits. Among the works that used the pseudo-potential approach, I believe that those were the most important and pioneering contributions. We showed it was possible to neglect the Fourier coefficients of the pseudo-potential corresponding to high values of K of the reciprocal lattice because at short distances the repulsive terms due to the inner states and the crystal potential mutually cancel themselves almost exactly. In such a way we calculated the energy bands of Ge and GaAs by choosing the values of three parameters and using an average potential $V(0)$ adjusted to the value of the energy gap. The accuracy of these calculations turned out to be outstanding and the method based on pseudo-potential is still now used for semiconductors...".

The OPW method, in the perturbation approximation introduced by Bassani and Celli, was used by Bassani himself and Knox for computing lowest conduction states in fcc solid argon at the symmetry points [109]. The valence and conduction states were treated by two different approaches. For the valence states they used the tight-binding approximation and for the conduction band they applied the second-order perturbation approximation developed by Bassani himself and Celli. This calculation was performed in the one-electron approximation.

The many-body extension of the OPW method was analyzed by Bassani and coworkers in 1962 (the correlation term was introduced as a screen effect of the exchange term) and these improvements allowed the calculation of the band structures of rare gases and alkali halides [110]. In the following years Bassani published other contributions on band structure calculation. Among them, a paper (by Bassani, Phillips and Brust) on the band structure of germanium [111], where the reflectivity data of Ge and GaAs are analyzed by using the pseudo-potential technique. A similar approach was used in the study of the effect of alloying and pressure on the band structure of silicon and germanium [112].

Bassani and Yoshmine applied the OPW method to the zinc-blende lattice [113]. The calculation of valence and conduction eigenvalues and eigenfunctions was carried out for a few IV-group elements and III-V compounds. The results obtained by adopting suitable approximations for the core states and exchange potential, showed that all the investigated materials were semiconductors or insulators.

In 1963 Bassani and Liu calculated the electronic energy band structure including spin-orbit coupling effects for semiconducting gray tin [114]. The effect of pressure on the energy band structure was also investigated. In this case, too, the calculated energy gap turned out to be in agreement with the experimental data. The correlation effects were taken into account also in the calculation of the energy band structure in AgCl and AgBr carried out by Bassani, Knox and Fowler in 1965 [115]. This calculation demonstrated that in these cases the maximum of the valence band was positioned at point L in the Brillouin zone and the minimum of the conduction band was at point $K = 0$. The consequent production of an indirect absorption in the visible spectrum and a long lifetime for electrons and holes provided a first explanation of the photographic properties of these crystals [116].

The research on the energy band structure in AgCl and AgBr was presented also at the SIF meeting in 1964, together with another work written by Bassani and Pastori on the symmetry properties of electronic levels in layer compounds like GaS. The final paper on the band structure calculation in the layer compounds was published by

Bassani and Pastori Parravicini in 1967 [117]. The band structure, calculated using a tight-binding semiempirical approach, was related to the basic properties of these compounds, and a few features of the optical excitation spectrum were discussed. The method used in this work represented a pioneering application of the so-called "semiempirical tight-binding technique" that is still now used to study complex systems and nano-structures. The results concerning the electronic structure of graphite explained also the electron energy loss spectrum, as described in the work published in 1970 by Bassani and Tosatti [118].

Bassani dealt also with the electric field effects on optical transitions [119,120] and the magnetic-field effects on energy band structure. The latter topic was discussed in a paper published in 1967 with A. Baldereschi [121], where the existence of Landau levels in all critical points was demonstrated.

Among the works carried out by Bassani in the 1960s one should not forget the results concerning the correlation between band structure and impurity states. In a paper by Bassani, Iadonisi and Preziosi, the existence of a few resonant states in the optical absorbtion region due to secondary minima of the conduction band was investigated [122]. Such a kind of resonances, described for the first time by the Italian physicists, was experimentally confirmed in the following years.

The researches carried out by Bassani strongly contributed to form the first generation of Italian theorists in solid state physics. The great number of studies carried out by Bassani, such as the ones on the pseudo-potential developed with Celli and the collaborations with several foreign scientists, brought his name to the attention of the international community. Besides, the studies published by Bassani stimulated the interest in semiconductor physics in Italy during the sixties.

6.2. Other theoretical researches on semiconductors

In the decade 1955–1965 Italian theorists in the field of condensed matter focused their attention on the following topics: i) calculation of the electronic level in solids; ii) study of crystal potentials; iii) analysis of theoretical aspects related to semiconductor devices. Here, we shall deal only with researches on semiconductors. For the other topics, the interested reader could see [20].

In 1964, Manca and Aramu developed a model that allowed them to explain the semiconducting phase of Fe_2Te_3 compound. That work was first presented at the SIF meeting and then published in *Il Nuovo Cimento* [52].

As previously underlined, the invention of the transistor represented the spark that ignited a huge research on the technical aspects of semiconductor physics. In Italy during the early 1960s, such researches were mainly developed by Forlani and Minnaja working at Olivetti (see the previous section). The activity of these two scientists has been already discussed; we recall here the already cited paper published in 1964 on the conduction mechanism in Si–SiO_2–Al structures [79]. The existence of charge states predicted by this theoretical framework was confirmed by J. Lindmajer a few years later [123].

TABLE IV. – *Italian authors quotations in "Semiconductors and Semimetals" (SaS) and "Solid State Physics" (SSP).*

Author	***SaS***	***SSP***
Airoldi	–	2
Asdente	–	1
Bassani	19	3
Bertolotti	–	1
Bonfiglioli	5	2
Brovetto	5	2
Busca	1	1
Celli	3	–
Chiarotti	2	1
Della Pergola	–	1
Del Signore	1	–
Fieschi	–	3
Forlani	–	1
Frova	16	2
Fuhrman	–	1
Fumi	–	5
Germagnoli	–	2
Grassano	1	–
Grasso	–	1
Levialdi	1	1
Manca	1	–
Minnaja	–	1
Nucciotti	–	1
Palmieri	1	1
Papa	–	1
Rosei	1	–
Samoggia	1	1
Sette	–	2
Tosi	–	1
Vitali	–	1
Wanke	1	1
Total	59	40

7. Conclusions

As shown in the introduction, Italian researchers who, in the fifties, began to work on condensed matter physics, or more specifically, on semiconductors, had to overcome a knowledge gap of about twenty-five years. In the mid of the sixties they had done their job. The number of researchers in the field of solid state physics was still low, if compared with that of the leading countries. However, the cultural heritage left to the new generations by the pioneers we have talked about, allowed this new generations of scientists to build their work on solid basis. The pioneers had accomplished their *historical* task. In front of this accomplishment, the evaluation of their work on the basis of international standards belongs to a background scene. Anyway, for completeness, we have reported in table IV the number of citations of Italian scientists found in the series *Semiconductors and Semimetals* edited by R. K. Willardson and A. C. Beer and the series *Solid State Physics* edited by F. Seitz, D. Turnbull and H. Ehrenreich. The total numbers of works quoted are about 5000 in *Semiconductors and Semimetals* and about 2800 in *Solid State Physics*. We leave to the reader the task of commenting the table and of finding agreements or discrepancies with the feelings suggested by the present paper. However, we cannot refrain from the warning that the citation game is often ruled by criteria that are independent of the scientific value of the quoted or unquoted papers.

* * *

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