

Experimental assessment of nonergodicity in tetracene single crystalsG. B. Parravicini,^{1,2} M. Campione,³ F. Marabelli,¹ M. Moret,⁴ and A. Sassella⁴¹*Dipartimento di Fisica, Università di Pavia, I-27100 Pavia, Italy*²*CNR-IPCF, Piazza A. Moro 7, I-00185 Roma, Italy*³*Dipartimento di Scienze Geologiche e Geotecnologie, Università di Milano Bicocca, I-20126 Milano, Italy*⁴*Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, I-20125 Milano, Italy*

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Dielectric spectroscopy is applied to the study of phase transitions in the range from room temperature down to 12 K in single crystals of tetracene (TEN), a well-known material which, like most organic semiconductors, shows polymorphism. The present analysis, through proper experimental procedures, permits us to identify the wide range ($T > 150$ K) of instabilities and of strong hysteresis effects as clear evidence of a nonergodic state and then also to clarify some open questions, first of all the role of the sample thermal history, including the temperature variation rate and some apparent sample dependence of the results. Furthermore evidence is obtained of two transitions at 144 and 45 K.

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I. INTRODUCTION

Among organic semiconductors, tetracene, pentacene, and, more recently, their derivatives show the highest charge mobilities and are thus recognized as promising materials for applications in organic electronic and optoelectronic devices.^{1–4} Most of these compounds display polymorphism, with several different crystal phases very close in energy.^{5–8} This is why understanding the effect of temperature and of thermal cycles on the specific crystal phase is not easy (nor is the control of the crystal growth conditions to select a specific phase); however it is crucial for the achievement of optimal performances for charge transport as well as for other physical properties.^{1,9,10}

Single crystals of one of these materials, tetracene (TEN), have been investigated by several different experimental techniques, such as x-ray⁷ and neutron³ diffraction, optical spectroscopy (fluorescence, reflection^{11–14}), and Raman spectroscopy,^{15,16} which revealed a rich polymorphism, temperature driven as well as pressure driven.^{8,9,14,17} Besides the main phase transition, commonly accepted, with characteristic temperature in the range 160–200 K (Refs. 7, 12, 15, and 17), it is unclear how many phases are actually formed at low temperature; namely, indications of structure modifications have also been reported for $T = 144$ K (Ref. 15) and near 70 K (Ref. 11). Furthermore, the coexistence of different phases during large T intervals has also been reported⁷ and recently confirmed by Raman spectra in relation with potential energy surface and lattice dynamics calculations;¹⁶ relevant hysteresis effects upon heating have also been recorded by some authors^{7,16} although without any systematic experiments or wide temperature cycles.

In addition, among unclear aspects of TEN behavior, the existence of large T ranges of nonequilibrium states,^{13,17} continuous structural modifications,¹⁵ and dependence on the thermal history⁷ and on the T scan rate¹² have been reported. The dependence of the TEN crystals' behavior on sample preparation and on the mechanical surface coupling of the sample with substrates or contacts has been tentatively invoked by some authors as a possible origin of such features, particularly with regard to the transitions' characteristics (critical T

values and extension of the transitions in temperature). These aspects must be considered and systematically investigated, in particular when thinking about organic systems displaying a similar behavior and referred to as nonergodic (see, for instance, Ref. 18).

The present work is devoted to the detection and study of the temperature-driven phase transitions in TEN single crystals by means of dielectric measurements,^{19,20} performed in the temperature range 12–295 K, definitely wider than those reported up to now in any single paper. Specifically with the aim of investigating the main characteristics assessing a nonergodic behavior, i.e., the thermal history dependence of the physical quantities, their crucial dependence of the temperature scan rate, and the occurrence of the aging phenomenon, several complete cooling/heating cycles were carried out on different samples and with different scan rates. The experimental results are discussed also by comparison with the literature and permit us to clarify some open questions. More specifically, we confirm the existence of two low-temperature transitions of TEN; we study in detail the main transitions above ≈ 150 K, demonstrating the nonergodicity of crystalline TEN in this T range, and therefore are able to draw a complete picture of its thermal behavior from 12 K up to 300 K.

II. EXPERIMENT

Tetracene single crystals were grown with the physical vapor transport method²¹ by using nitrogen as a gas carrier and heating the source at 170 °C; they are thin flakes exposing a wide, clean, molecularly flat (001) surface, a few mm² in size, which does not require cleavage before use. The TEN crystal structure belongs to the triclinic system, with two molecules in the unit cell and parameters $a = 6.06$ Å, $b = 7.84$ Å, $c = 13.01$ Å, $\alpha = 77.13^\circ$, $\beta = 72.12^\circ$, and $\gamma = 85.79^\circ$ (Ref. 22).

The dielectric measurements were carried out by an LCR meter (HP-4284A) applying a 50-mV voltage at a frequency of 500 kHz, within the dielectric spectrum plateau (extending up to 1 MHz) recorded for the real part of the permittivity. The TEN crystal was placed with its (001) face on a crystalline sapphire substrate with a previously deposited aluminum stripe and subsequently another Al stripe perpendicular to the first

one was evaporated on top of the crystal (see the sketch of the sample geometry in the inset of Fig. 1(a)). Such a cross-connected geometry allows the precise evaluation of the area where the electric field is applied; in addition, it permits the connection of the wires at the end of the Al stripes, far from the crystal, minimizing the sample/electrode mechanical strain.

A closed two-stage helium cryostat (Air Products), driven by a controller device, was employed for scanning the temperature in the range 12–295 K, adopting scan rates of about 1 K/min and 5 K/min and maintaining the same heating and cooling rates for several measurement cycles. As a consequence of both a good thermal contact of the sample with the temperature source and of the slow T scan rate, each single measurement integrated over 10 ms occurred under isothermal conditions. A calibrated silicon diode was used for temperature monitoring.

A number of TEN crystals with different thicknesses of a few micrometers, about 1 mm² in surface, were preliminarily measured with the aim of verifying the reproducibility which was demonstrated to be very good, particularly in the critical temperatures. The dielectric response was found to be independent of the sample thickness. This result implies the absence of eventual substrate-coupling effects within the explored T range. Here, the data collected on a 3- μ m-thick TEN crystal, with an effective surface of 0.8 mm², are presented and discussed.

III. BACKGROUND

Under isothermal conditions (as in our measurement conditions), the entropy of a dielectric material subject to an external electric field E can be expressed by the following fully general relation:^{23–25}

$$S(T) = S_0(T) + \frac{E^2 \varepsilon_0}{2} \frac{\partial \varepsilon_s}{\partial T} = S_0(T) + S_E(T), \quad (1)$$

where S_0 is the entropy of the system at zero field, E is the field amplitude, ε_0 is the vacuum permittivity, ε_s is the static dielectric constant (in our case, the real part of the dielectric function in the low frequency limit), and T is the absolute temperature. The last term in Eq. (1) is the entropy change due to the polarization of the dielectric by the field, directly proportional to the derivative $\partial \varepsilon_s / \partial T$. Equation (1) shows how application of an electric field increases the entropy if $\partial \varepsilon_s / \partial T$ is positive, while it decreases entropy if the same quantity is negative. In disordered systems, e.g., in liquids, it is known that an applied field creates order, since it orients the electric dipoles (permanent or field induced) otherwise randomly arranged. As a consequence, entropy being a measure of disorder, the entropy variation induced by the field (Fröhlich entropy) is negative, and then $\partial \varepsilon_s / \partial T$ should be negative. On the contrary, in crystalline solids under an electric field, a fraction of the dipoles undergoes discontinuous quantum transitions between preferred orientations: this gives rise to an increase of the entropy of the system, and then $\partial \varepsilon_s / \partial T$ should be positive. When phase transitions are considered,²³ a solid-solid (order/order) transition manifests itself as a variation of the positive slope of the $\varepsilon_s(T)$ curve, since the entropy contribution supplied by the field is positive both before and after the transition, with values in accordance with

the degree of order of the two phases. In the transition interval, a characteristic two-opposed-peaks lineshape of $\partial \varepsilon_s / \partial T$ is displayed, in correspondence with the positive and negative slope in the related ε_s peak, with the negative part marking a temporary disordered state in the material.

IV. RESULTS AND DISCUSSION

A. Cooling

In Fig. 1(a) the relative dielectric constant ε_r and the ac conductivity σ of a TEN crystal are reported as a function of temperature in the range from 12 to 295 K, as collected while cooling the sample. The values were extracted from capacitance and conductance data taking into account the geometry and size of the sample for ε_r and using, for obtaining the conductivity, the following relation:

$$\sigma(\omega) = \varepsilon_0 \varepsilon_r \omega t g \delta, \quad (2)$$

where ε_0 is the vacuum permittivity, ω the field angular frequency, and $t g \delta$ the loss factor.²⁴ On lowering the temperature the relative dielectric constant first presents a continuous steep decrease to about 220 K, where a small shoulder is evidenced, with a subsequent change of slope. Between 162 and 147 K, the $\varepsilon_r(T)$ curve displays a peak centered at 160 K. Immediately below, a region of irregular behavior appears, extending down

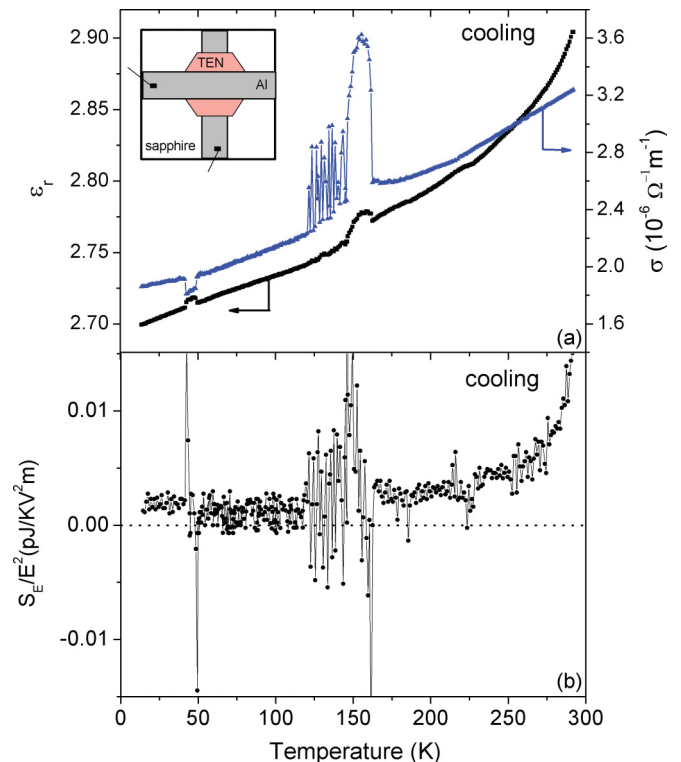


FIG. 1. (Color online) (a) Temperature dependence of the relative dielectric constant ε_r and of the conductivity σ , as obtained from the dielectric measurements during cooling from RT down to 12 K of a 3- μ m-thick TEN single crystal in the plane parallel capacitor configuration sketched in the inset. (b) Temperature dependence of the field-induced entropy S_E (per unit volume, normalized to the square field amplitude) obtained from the derivative of the dielectric constant in panel (a).

to the temperature of about 120 K. At lower temperatures, $\varepsilon_r(T)$ decreases with a most constant slope, smaller with respect to that of the high T region, interrupted by two opposite jumps near 50 K. Finally, at the lowest temperatures, a linear T dependence of ε_r is found again.

The behavior of σ as a function of T shows, after an initial decreasing, a slope change at about 220 K and then the occurrence of a peak in the same T range 162–147 K as the ε_r peak. For $T < 147$ K continuous conduction instabilities in the sample are detected down to about 120 K, again in strict correspondence with the irregularity interval found for the dielectric constant. Below about 120 K, a nearly constant decrease rate of $\sigma(T)$ is observed, interrupted around 50 K by two jumps, matching again the ε_r behavior.

According to the literature (see, e.g., Refs. 26 and 27), a peak in a temperature region, both of the $\varepsilon_r(T)$ and $\sigma(T)$ curve, is related to the occurrence of a phase transition in the sample. In our case the results in Fig. 1 show that TEN, upon cooling, undergoes a phase transition with characteristic temperature $T = 160$ K and about 12 K temperature width. Before the transition, the ε_r shoulder at about 220 K, together with the corresponding slope changes of both curves, suggests that the system undergoes some molecular rearrangements preceding the main phase transition at 160 K.

Below this main transition and down to 120 K, either ε_r or σ do not display the regular behavior typical of a well-defined stable phase. In this respect, it is worth considering Ref. 15, where a second low-temperature transition at 144 K is reported. Under this hypothesis, the proximity of the two characteristic temperatures, only 16 K apart from each other, may establish a coexistence-competition regime of the two corresponding crystal phases. Furthermore Sondermann *et al.*,⁷ on the basis of x-ray diffraction measurements, showed the occurrence, upon cooling, of a phase transition starting near 150 K and completed at 125 K. Specifically, in such a wide T region the progressive disappearance of the higher temperature phase signals and the contemporary onset of the new phase peaks are displayed; such overlapping would have prevented the observation of a second transition near 144 K. A similar behavior is described also in Ref 16, where only the Raman spectrum at 130 K is very similar to the subsequent spectrum at 80 K (so stating a stable condition in this T range, in accordance with our results), while the preceding spectrum collected at 150 K shows characteristics rather close to those of that collected at 230 K.

In Fig. 1(a), a second negative peak of the dielectric constant is displayed in the 40–50 K interval in correspondence with the curve jumps, also confirmed by a peak in the $\sigma(T)$ curve; at the lowest temperatures both $\varepsilon_r(T)$ and $\sigma(T)$ present a regular behavior. This whole behavior in the dielectric properties indicates a further, sharper low- T phase transition in the measured TEN crystals.

In Fig. 1(b) we report the plot of S_E/E^2 , i.e., of the entropy contribution of the applied field to the system per unit volume, normalized to the squared field intensity, with respect to T , as obtained from the derivative $\partial\varepsilon_r/\partial T$ of the experimental permittivity data [see Eq. (1)]. In the range 162–147 K the entropy curve presents the typical feature of a transition between two solid phases (two opposite peaks), plus an instability region down to about 120 K. Below 120 K and above

162 K, different average values of the entropy contribution are found, characteristic of such two phases. These results give full evidence of different order conditions for TEN in those T intervals. Specifically, in the 120–50 K region $\partial\varepsilon_r/\partial T$ appears almost T independent; i.e., the entropy of the crystal remains unvaried in accordance with the hypothesis of a stable crystalline phase of TEN.

At the lowest temperatures, a further structural phase transformation occurs in TEN, as evidenced at ≈ 45 K, where the $S_E(T)$ curve shows again the typical line shape indicating a transition. Coherently, below 45 K the field-induced entropy displays a specific level, higher than that of the preceding 50–120 K phase, constant with T and with a low noise, indicating the formation of a new stable structure in the explored TEN crystals. Such results nicely confirm the findings in Ref. 11, where, on the basis of a completely different experimental analysis, a transformation in TEN below 70 K was deduced.

Looking at the higher T region, the initial large continuous lowering from ambient temperature to ≈ 230 K of the field-induced entropy shows that the system progressively loses stability, without the appearance of any critical phenomena. In the 230–210 K range, a phase transition feature is displayed (involving much lower energy variations with respect to those at 160 and 45 K) that separates different entropy levels. It is noticeable that the critical temperature of such a transition, 218 K, is fully consistent with the T value that marks the observed variation of the conduction process, with the mentioned change of the $\sigma(T)$ slope. In summary, the results just discussed show that, with temperature decreasing, crystalline TEN undergoes a nearly continuous variation of the degree of order down to the transition at 218 K, with discontinuity and finally some further instabilities before the main phase transition at 160 K. This overall behavior is in accordance with previous works in the literature.

Kolendritski *et al.*¹³ inferred the occurrence of a transition at ≈ 160 K from reflection spectra; above this temperature the authors speak about an out-of-equilibrium condition, demonstrated particularly by the observed continuous shift of Davydov splitting with T . On the other hand, Jankowiak *et al.*¹⁵ evidenced in TEN two transitions at 144 and 182 K from a gradual change with T of the Raman spectra, starting from ambient temperature. Finally, also in Ref. 12 a redshift of a characteristic optical absorption peak was found to occur almost continuously from 300 to 170 K, reaching the stability at different temperatures in the range between 170 and 200 K, depending on the sample.

B. Heating

By heating the sample from the lowest temperatures, at the same T scan rate as upon cooling, the dielectric constant, the conductivity, and the related Fröhlich entropy are collected and displayed in Fig. 2. Again, in the T range 40–50 K, permittivity jumps, related to a phase transition, do appear. This transformation manifests itself at the same temperature as upon sample cooling, therefore being reversible and free from appreciable hysteresis effects; in addition, it is also present in the $\sigma(T)$ curve. By further increasing temperature, a well-defined peak of the dielectric permittivity is found

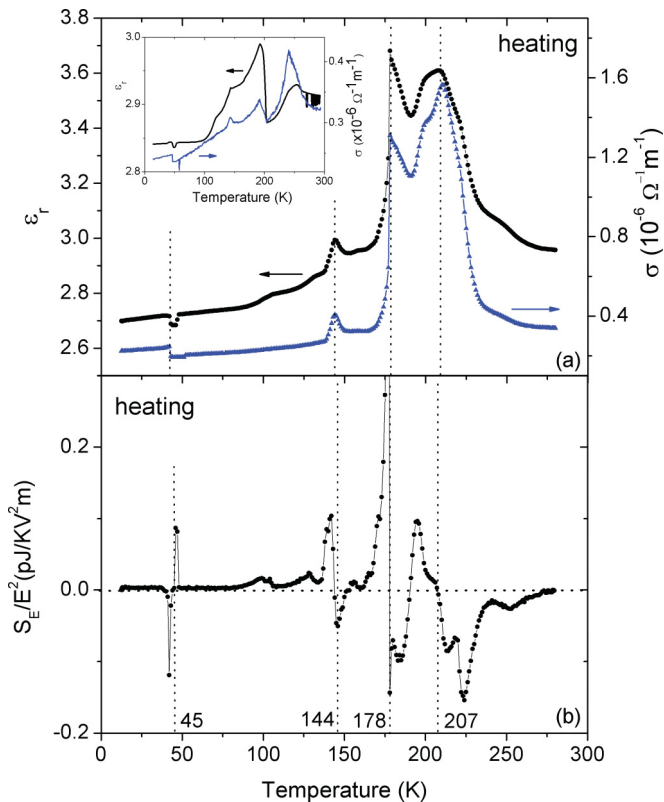


FIG. 2. (Color online) (a) Temperature dependence of the relative dielectric constant ϵ_r and of the conductivity σ , as obtained from the dielectric measurements during heating from 12 K up to RT of the same sample as in Fig. 1 and with the same temperature scan rate. Inset: same as in panel (a), but obtained upon heating the sample at a higher rate. (b) Temperature dependence of the field-induced entropy S_E (per unit volume, normalized to the square field amplitude) obtained from the derivative of the dielectric constant in panel (a). In both panels the vertical dotted lines indicate the critical temperatures 45, 144, 178, and 207 K.

at 144 K. In the same T range, a conductivity peak is also recorded. The entropy plot shows, in the 136–151 K interval, the characteristic two-opposite-peaks feature centered at 144 K [Fig. 2(b)]. It is noticeable that such evidence of a low-temperature transition fully agrees with the findings of Ref. 15. The absence in the 120–147 K range of the chaotic manifestations observed upon cooling validates the above-expressed hypothesis of a coexistence-competition of different structural phases in the crystal when lowering the temperature.

At temperatures >150 K a different overall behavior with respect to that found in the cooling experiments is displayed by the dielectric properties and the consequent induced entropy. Indeed the $\epsilon_r(T)$ curve presents a large and wide structure resulting from at least three main contiguous peaks. Namely, starting from about 170 K a large enhancement of both ϵ_r and σ is displayed, characterized by a very sharp rise at 178 K, typical of a first-order transition. The subsequent decrease is interrupted by the onset of a second large asymmetric structure composed of two close peaks. The highest one, having the maximum at 207 K, is preceded by a lower one at ~ 200 K. Also in this case, the permittivity and conductivity behavior are fully

coherent. Looking at the Fröhlich entropy behavior in Fig. 2(b), a narrow and sharp structure is found, followed by a double-peak configuration extending from 190 K up to RT, which appears to contain further transition features corresponding to the lower ϵ_r peak.

This behavior provides evidence of several distinct subsequent structural transitions, each one with its own characteristic temperature, very close to each other. The achievement of the high-temperature phase appears therefore to occur through a succession of distinct unstable phases. In particular, the first enhancement of the permittivity and of the conductivity at 178 K can be related to the spacing of the (001) planes, which is reported to show a slope inversion at about 180 K (Ref. 7). Furthermore the field-induced entropy remains negative (disordered state) also at room temperature, clearly demonstrating that the transition to the stable high- T phase is not yet complete. Indeed, the initial permittivity value is recovered only after keeping the sample at RT for over 12 h (aging effect); the same behavior is reported in the literature, where the initial RT structure is found after a thermal cycle only by heating the crystal up to 340 K (Ref. 7) or to 400 K (Ref. 16). Here we note that, upon heating, the temperature-dependent dielectric behavior of TEN single crystals in the 180–240 K range agrees with the picture proposed by Sondermann *et al.*,⁷ based on the existence of an asymmetric double minimum potential for the position of the pseudo-face-centered molecule within the unit cell.

With the aim of specifically investigating the transition kinetics, a further set of measurements was accomplished by heating the crystal at a fixed, higher scan rate of 5 K/min. The results, shown in the inset of Fig. 2(a), confirm the occurrence of the two low-temperature transitions at the same T values and show substantially unchanged ϵ_r and σ values, *independently* of the scan rate. On the contrary, at higher temperatures (>150 K) the two main structures in both the permittivity and conductivity curves are observed at different temperatures with respect to the lower scan rate, and a strongly reduced height of the peaks is found together with a change of shape and relative height.

As a whole, the results of the presented investigation give evidence that the transition kinetics in TEN crystals, for the $T > 150$ K range, corresponding to the main structural phase transition, presents a different behavior in the heating process with respect to the cooling one; furthermore, during heating a marked dependence on the temperature scan rate is detected. Namely, depending on the thermal history and on the temperature scan rate, different values of the detected properties are measured, given the thermodynamic state (temperature, pressure, and applied field). Such behavior, besides the recorded spontaneous evolution of the system with time at room temperature and constant pressure, is the signature of a nonergodic system, i.e., a system whose properties depend on the sample thermal history, on temperature variations, and on observation time, and can, therefore, be different under the same thermodynamic conditions.²⁸ Examples exist in the literature of several nonergodic materials, such as polymers,²⁹ perovskites,^{30,31} organic molecular materials,¹⁸ and glasses,²⁸ which have recently awakened a renewed interest. Such a general result also clarifies the experimental findings, where variations in critical temperatures and nonequilibrium states,

as well as large hysteresis and diffused transition phenomena, are observed and also reported by several authors.

V. CONCLUSIONS

In conclusion, the analysis of the temperature dependence of the dielectric behavior of single crystals of TEN permits us to confirm the occurrence of two low-temperature transitions at about 45 and 144 K, already reported in the literature by some authors in some samples, without any systematic study. Then, in the temperature range above about 150 K, where the main transition occurs, a nonergodic behavior is detected through properly designed and repeated cooling/heating experiments. In particular, while cooling the sample down to 12 K, a continuous evolution of the dielectric behavior of the TEN crystal is observed starting from room temperature, with a more evident transition signature at about 160 K. On the contrary, by heating the sample up, starting from 12 K, the main transition is found to be composed by two distinct, yet closely subsequent, transitions through unstable crystal phases; the

characteristics of such transitions are found to vary with the sample thermal history, with the temperature scan rate and also with the time spent by the sample at a fixed temperature.

Finally, information on the dielectric permittivity and on the conductivity of the different TEN phases is obtained over a wide temperature range. Besides, the full reliability of the results and their completeness with respect to other previous studies are obtained by the low cooling and heating rates used, assuring a homogeneous transformation of the whole crystal, and by the careful choice of a massive sample, where the effects of mechanical coupling with the measuring electrodes are minimized.

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