Singularities of the phase states and of the metal-insulator phase transition in the α-(BEDT-TTF)$_2$I$_3$ system

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The temperature dependences of the conductivity along different crystallographic axes (σ_a, σ_b, and σ_c), of the Hall constant (R_H) and of the transverse magnetoresistance of α-(BEDT-TTF)$_2$I$_3$ were investigated. It was observed that notwithstanding the two-dimensional character of the conductivity in the system ($\sigma_a/\sigma_b < 2$, $\sigma_a/\sigma_c = 1900$ at $T = 295$ K) the singularities of the transition to the insulating state ($T_{MI} = 138$ K) (steep pre-transition growth of the conductivity, its dependence on stoichiometry changes) are similar to those of the metal-insulator transition of quasi-one-dimensional conductors. The possible mechanism of the transition is discussed. In the insulator phase (in which the conductivity anisotropy is substantially lower, $\sigma_a/\sigma_c \approx 60$), there are observed at $T \approx 100$–110 K a double reversal of the sign of R_H, a change of the conductivity activation energy, and a return of σ_a/σ_b to the room-temperature value. At temperatures higher than T_{MI}, there occur an unusual temperature dependence of the conductivity ($\sigma_a \sim T^{-1/2}$) and a somewhat lower value of R_H (compared with the value that should correspond to a carrier density in a metal with an energy transport 0.5e per BEDT-TTF molecule). The singularities observed in α-(BEDT-TTF)$_2$I$_3$ are compared with the singular properties of β-(BEDT-TTF)$_2$I$_3$.

The synthesis of a number of highly conducting and superconducting materials—the polyiodides bis(ethylenedithio) tetrathiofulvalene (BEDT-TTF or ET) (Refs. 1–3)— was the obvious breakthrough of a recently developed approach[4] aimed at increasing the dimensionality of a conducting system. Thus, the aggregate of the available data identify β-ET$_2$I$_3$, which undergoes a superconducting transition with a temperature T_c that reaches a record high 7.5–8 K for organic materials, as a two-dimensional metal.[1,2,7–10]

Another polymorphic modification of the triiodide ET-α-ET$_2$I$_3$, which is also a quasi-two-dimensional conductor, is transformed, on the other hand into an insulator ($T_{MI} = 138$ K).[11–14] The low-temperature loss of conductivity, as well as the recently observed features of the pre-transition phenomena observed in the α phase (anisotropic growth of the conductivity, the influence of deviation from stoichiometry on this growth),[15] point to similar properties of the new two-dimensional conductor in quasi-one-dimensional compounds of type TTF-TCNQ[16] or TTT$_2$I$_3$.[17]

Additional experimental material is needed to shed light on the causes of such a rather unexpected similarity (especially of the structure of the conducting ET molecule layer in α-ET$_2$I$_3$, which lead to arbitrary separation, within the layers, of the stacks traditional of one-dimensional systems, along the axis of which the best overlap of molecular orbital takes place), as well as the causes of such a striking difference between the properties of α- and β-ET$_2$I$_3$. We report here the distinctive features of the phase transition and of the phase states of α-ET$_2$I$_3$, which appear in the temperature dependences of the conductivity, of its anisotropy, of the Hall constant, and of magnetoresistance.

EXPERIMENT

We investigated α-ET$_2$I$_3$ crystals obtained by electrochemical oxidation of ET by the standard procedure.[10] Some of the crystals were nearly rhombic in shape (with typical dimensions $3 \times 3 \times 0.02$ mm), but most had the form of a hexagon elongated as a rule along the a axis (sometimes along b) (crystal length 3–4 mm, width 1 mm, thickness 0.02–0.05 mm). We designate the axes as in Ref. 2. Chemical analysis has shown that the crystals are on the average slightly iodine-enriched (with composition ET$_2$I$_{3+\delta}$, where $\delta = 0.04 \pm 0.04$).

Besides the crystals which underwent no treatment after growth, we investigated crystals soaked 15 minutes in saturated iodine vapor at room temperature.

The conductivity was measured by a dc four-probe method. The electrodes were platinum wires of 30 μm diameter, secured to the sample with a graphite-base conducting paste. The contact resistance did not exceed several ohms in the entire investigated temperature range.

The conductivity anisotropy in a direction perpendicular to the ab plane of the plate was measured by the Montgomery method.[18] The anisotropy of the conductivity in the ab plane was measured by a method essentially similar to Montgomery's. Since attempts to produce a rectangular sample with sides coinciding with the a and b axes caused the crystal to crack, we investigated samples with natural faceting. The contacts were located at the midpoints of the sides of the rhomb, as shown in the inset of Fig. 3, and the contact distances 1–2, 2–3, 3–4, and 1–4 were equal to within ± 0.1 mm. In one heating cycle, the 4-probe method was used to measure the sample resistance in two configurations: a) current contacts 1 and 4, potential contacts 2 and 3 (R_{23}); b) current contacts 1 and 2, potential contacts 3 and 4 (R_{34}). We determined next the resistance ratio R_{23}/R_{34}, which served as a measure of the anisotropy. Obviously, the ratio R_{23}/R_{34} is unique related with the ratio σ_a/σ_b, but the functional form of the dependence on the experimental geometry is unknown for this case. We have therefore investigated the temperature dependences of the relative changes of the anisotropy. This dependence gives an idea of the relative

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changes of σ_a and σ_b in a sample having a specific composition.

We investigated the conductivity and its anisotropy of samples of α-ET_2I_3 and its deuterium-substituted analog, and observed no difference whatever between the usual and deuterated crystals. The lattices of α-ET_2I_3 and α-$(ET\text{-}d_8)_2I_3$ are identical and agree well with the published ones.[11,13] The magnetoresistance was measured in an EPR spectrometer magnet, in which B could be varied in the range 0 to 1 T.

The Hall-effect was measured by a standard dc 5-probe scheme in the anticryostat of a superconducting solenoid (0–5 T). The temperature was stabilized accurate to $\pm$ 0.05 K. The field reversal was performed by rotating the sample on a turnable insert.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependences of the conductivity of α-ET_2I_3 crystals along the axes a, b, and c at temperatures above the transition point. (The conductivity at room temperature is 20–60 $\Omega^{-1}\cdot cm^{-1}$.) The conductivity ratio is $\sigma_a/\sigma_c = (1.9 \pm 0.2)\cdot 10^3$. The conductivity along the c axis increases slowly with temperature, reaches a maximum at 180–190 K, and then drops smoothly to $T_{MI} = 138$ K. When the temperature is lowered to 100 K the value of σ_a/σ_b decreases approximately to 60.

The temperature dependence of the conductivity along the a axis varies greatly from sample to sample. Two temperature regions can be indicated for all the samples.

1. $T > 180$ K. In this range there is a broad section with $\sigma_a \sim T^{-1/2}$. In samples, the transition to the $\sigma \sim T^{-1/2}$ dependence is observed below room temperature.

2. Temperature range 140–180 K. In this range different samples behave differently.

a) The conductivity of most crystals reaches a maximum at 160–165 K, and then drops smoothly.

b) In some crystals ($\sim$30% of the 30 investigated) the conductivity continues to increase and has a sharp maximum in a narrow temperature region directly preceding the transition. This maximum can be duplicated for samples of group a) by purposefully changing the stoichiometry (Fig. 1, curve 2—temperature dependence of the conductivity of crystal 4 after soaking it in iodine vapor).

We shall refer to samples whose conductivity has a temperature dependence of type a) as stoichiometric, and those of type b) as nonstoichiometric.

Note that the indicated growth of σ_a in the narrow pretransition temperature region can hardly be attributed to inclusions of the β phase in the crystal. In the temperature interval 150–140 K, a feature of β-ET_2I_3 is a conductivity increase of about 30%, less than the largest of the observed σ_a anomalies.

The conductivity along the b axis, which was measured directly (for two samples) showed no increase in the temperature region preceding the transition (Fig. 1, curve 5). Estimates of σ_b from measurements of the conductivity anisotropy, for crystals with and without pre-transition anisotropy, show that in the pre-transition region σ_b hardly varies from sample to sample, and the anisotropy changes (see Fig. 3 below) are due to changes of σ_a.

Figure 2a shows the temperature dependences of the conductivities σ_a, σ_b, and σ_c in the temperature range 170–100 K. The transition temperature determined from the maximum of the derivative $d \ln \sigma/d(1/T)$, which is the same for all the directions a, b, and c and is equal to 138 $\pm$ 0.5 K. It can be seen from Fig. 2a that the pretransition drop of the conductivity σ_b begins in the immediate vicinity of the transition (at 140–145 K), and the plot of σ_b has in the region of T_{MI} a larger slope than the plot of σ_a.

The temperature dependence of σ_a at temperatures below T_{MI} also has a number of characteristic properties.

1. The change of σ_a in the transition region 140–135 K is most abrupt in nonstoichiometric samples, and least abrupt in stoichiometric ones. The slope of the curve, determined in the transition region, corresponds to an activation energy 5000 K in stoichiometric samples and 16 000 K in nonstoichiometric ones.

2. The temperature dependence of the conductivity below the transition cannot be described by an exponential with a single activation energy (Fig. 2b).

3. The behavior of the samples in the dielectric region correlates with that at $T > T_{MI}$. Stoichiometric samples have

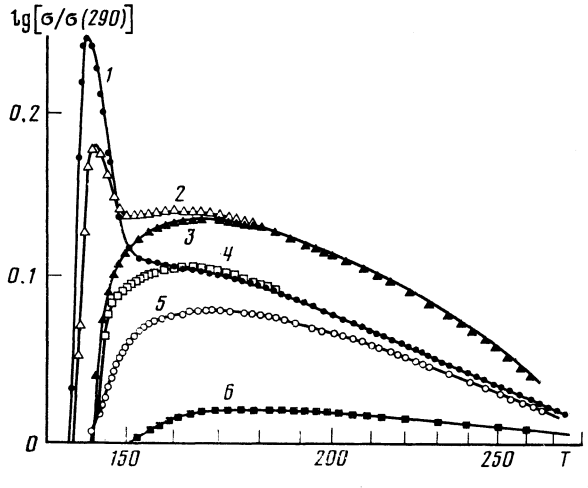

FIG. 1. Temperature dependences of the conductivity of α-ET_2I_3 crystals along different crystallographic directions at temperatures higher than T_{MI}. The quantities are normalized to the conductivity at room temperatures: 1–4—conductivity along the a axis, 5—along the b axis, 6—along the c axis. Curve 2 was obtained for crystal 4 soaked in iodine vapor for 15 min at room temperature.

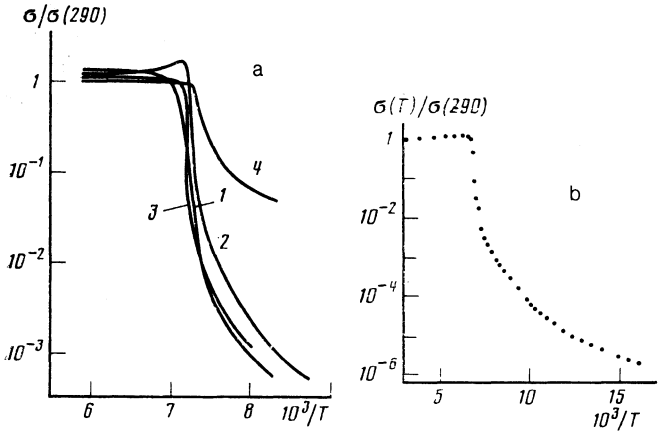

FIG. 2. Temperature dependences of the conductivity of α-ET_2I_3 plotted in coordinates $\log\sigma$ and $10^3/T$ (a) in the phase transition region: 1, 2—along the a axis, 3—along the b axis, 4—along the c axis; (b) general form of the temperature dependence.

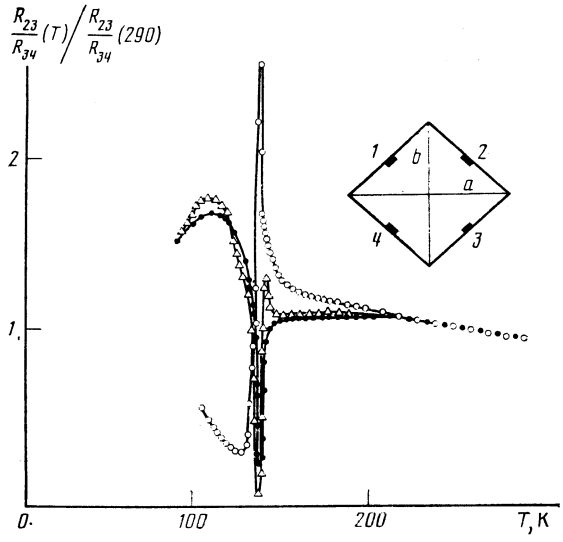

FIG. 3. Temperature dependence of the conductivity anisotropy in the *ab* plane of the crystal for three different samples: (○) with clearly pronounced pre-transition anomaly of the temperature dependence of the conductivity; (●) without a pre-transition anomaly; (△) with weakly pronounced pre-transition anomaly. Inset—schematic diagram of crystal with the contacts.

the lowest conductivity below 110 K, where the nonstoichiometric ones have the highest.

In general outline, such dependences of the conductivity above and below the metal-insulator transition on the stoichiometry of the crystal is reminiscent of the behavior of the one-dimensional system $TTT_2I_{3+\delta}$ (Ref. 17).

The anisotropy of the conductivity in the *ab* plane in the insulator region is also different in stoichiometric and nonstoichiometric crystals (Fig. 3). The differences are due to the different behavior of σ_a, while the bahavior of σ_b is approximately the same in both cases. A feature of the anisotropy change in the *ab* plane is an inflection at 100–110 K. The temperature region $T < 100$ K is characterized by a return of the anisotropy to its room-temperature value.

Investigation of the transverse magnetoresistance (the current was made to flow along the *a* axis, and the magnetic-induction vector B was normal to the *ab* plane and amounted to 1 T) in the temperature region $T_{MI} < T < 300$ K has shown that $\Delta\rho(H)/\rho$ does not vary with temperature and does not exceed $2\cdot10^{-4}$.

Figure 4 shows the temperature dependence of the Hall constant R_H. It can be seen that R_H is positive at high temperatures, reverses sign at 138 K, and increases rapidly in magnitude. At $\approx$100 K, R_H again becomes positive. The

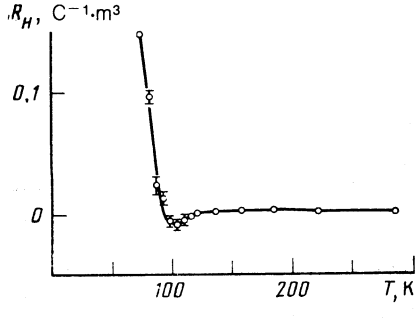

FIG. 4. Temperature dependence of the Hall constant, measured in a 5 T magnetic field.

carrier density, determined from the ratio $n = 1/(eR_H)$ at 295 K, is $(6 \pm 3)\cdot10^{21}$ cm^{-3}. In view of the imperfect geometry of the sample, which tends to lower R_H, and hence tends to increase n and the uncertainty of the Hall-factor (assumed equal to unity), this ratio can be assumed to be in satisfactory agreement with the value determined by the stoichiometry of the crystal ($1.2\cdot10^{21}$ cm^{-3}) (Ref. 13).

DISCUSSION

The experiments reported reveal a number of properties of α-ET_2I_3.

a) Region of metallic variation of the conductivity

In this region we have $\sigma \sim T^{-1/2}$, which is unusual for both classical methods ($\sigma \sim T^{-1}$) and for organic quasi-one-dimensional conductors ($\sigma \sim T^{-2}$).[16] It was shown with TTF-TCNQ as the example[19] that the deviation of the temperature dependence of the resistance (at constant pressure) from linearity is due to thermal compression of the crystal. If it is assumed that in our case the decrease of the sample volume on cooling increases the conductivity like $\sigma \sim T^{-1}$, we find for the α-ET_2I_3 conductivity at constant volume that $\sigma \sim T^{1/2}$. This form of the dependence can attest to an activation character of the conductivity and to the presence of a gap on the Fermi surface even at room temperature. The possible existence of a gap in the electron spectrum at $T > T_{MI}$ indicates also that the sign of the thermoelectric power along the *b* axis is reversed at 170 K (Ref. 10), and also that the value of this conductivity is more readily typical of semiconductors than of metals. The presence in the system of two types of carrier at $T > T_{MI}$ may be the cause of the already mentioned decrease of R_H compared with the determined stoichiometric value.

On the other had had, a metallic character of the conductivity of α-ET_2I_3 in the region $T > T_{MI}$ is indicated by the values, typical of metals, of the magnetoresistance, of the thermoelectric power,[10] and of the Hall constant (Fig. 4) in the entire temperature interval above the transition.

b) The insulator region

A property of the conducting properties of α-ET_2I_3 crystals in the insulator region is the absence of the constant E_a and a noticeable change of a number of properties in the interval 90–110 K. Starting with 110 K, the conductivity anisotropy in the *ab* plane tends to its value at room temperature (Fig. 3), a second reversal of the sign of the Hall constant takes place in the same region (Fig. 4). According to the data of Ref. 13, at $T \lesssim 100$ K dielectrization ceases in iodine-doped α-ET_2I_3 crystals, and a conductivity increase sets in until superconductivity sets in. In the same temperature region, the sign of the thermoelectric power is reversed again and the microwave superconductivity saturates.

These properties, which set in at 100 K, can be explained by assuming that at $T < T_{MI}$ α-ET_2I_3 is a semiconductor with impurity conductivity at low temperature, and that $T \approx 100$ K is the temperature of the depletion of the impurity, probably nonstoichiometric iodine. At $T < 100$ K the majority carriers are holes supplied by thermal ionization of the defects (the excess iodine in α-ET_2I_3 is apparently an acceptor impurity, since it can increase the degree of oxidation of the ET molecules, some of which in the stoichiometry are neutral[13]). The conductivity should change then no-

ticeably from crystal to crystal and correlates with the impurity density. The limiting case of strong doping (this is probably the one described in Ref. 13) can lead to degeneracy and to metallic conductivity or even to superconductivity in the impurity band.

On the other hand, in the analysis of the properties typical of α-ET_2I_3 in the semiconducting phase at $T \approx 100$ K, one cannot fail to point out the following fact. The interval near $T \approx 100$ K is particularly full of anomalies in the properties of other ET iodides, e.g., β-ET_2I_3 and γ-$ET_2(I_3)_{2.5}$, which are in the ground state superconductors (and not semiconductors as the α phase). Thus in the γ phase at $T \approx 100$ K there is observed a maximum of the "humps" and a return to a metallic temperature dependence of the conductivity.[3] In the most thoroughly investigated β phase, 100 K is the temperature at which a commensurate superstructure is formed (with threefold increase of the unit-cell volume).[20] At the same temperature, noticeable changes of the magnetic susceptibility[10] and of the thermoelectric power[10,21] take place in the β phase.

In view of the substantial differences between the structures of the above three compounds (and these differences are due mainly to the different construction of the ET-molecule layers[2]) it can be assumed that this common feature—the appearance of anomalies precisely at $T \approx 100$ K, is a consequence the common character of the changes that occur in the iodine sublattice—the layer of the I_3^- anions.

c) Phase transition region

A number of features in the region of the phase transitions should also be pointed out.

1. A substantially different pre-transition behavior of the crystal along the *a* and *b* axes of the crystal, notwithstanding the practically equal conductivities.

2. The dependence of the conductivity along the *a* axis on the stoichiometry of the crystal in the pre-transition and transition regions.

3. Nonmonotonic variation of the spin susceptibility.[22]

The abrupt growth of the longitudinal conductivity in the pre-transition region and the subsequent dielectrization in the quasi-one-dimensional crystals TTF-TCNQ and TTT_2I_3 can be naturally attributed to development of Peierls-type instability accompanied by formation of an incommensurate charge density wave (CDW).

According to this model, the increased conductivity at $T > T_{MI}$ is explained by the contribution of the fluctuating motion of an incommensurate CDW. Advanced Peierls instablity in quasi-one-dimensional crystals with nearly plane Fermi surfaces produces a gap on the entire surface, and the consequence is dielectrization.

The properties 1 and 2 above of α-ET_2I_3 crystals can also be explained within the framework of a model of the Peierls-transition type if it is assumed that the CDW vector is directed along the *a* axis. Insignificant changes of the stoichiometry of the crystal alter the degree of charge transfer and can lead to a transition from a commensurate to an incommensurate CDW that contributes to the conductivity in the pre-transition region. The explanation of the dielectric transition itself, however, encounters considerable difficulties.

According to structural, electric, and optical data,[10,11,14] α-ET_2I_3 crystals at room temperature are quasi-two-dimensional conductors and, as shown in Fig. 3, the change of the conductivity anisotropy with decrease of temperature is insignificant. In a two-dimensional conductor, application of a periodic potential along one of the directions, say along the *a* axis, should not lead to dielectrization of the system.

Formation of an incommensurate structure was observed in the related compound β-ET_2I_3 at $T = 200$ K (Ref. 23). A detailed investigation[24] has shown that an important role is played in this process by the interaction of the ET molecules with the I_3^- anions.

It can be assumed by analogy that the dielectrization of the α-ET_2I_3 system is a consequence of interaction of the distortions in the ET layer with the anion subsystem. That the anions play a decisive role in the transition is indicated by the following experimental fact. The conductivity along the *c* axis is apparently due to tunneling between the ET layers through the I_3^- anion layer. The minimum barrier-width change that can occur when the configuration of the anions is changed should lead to a change of the conductivity. Indeed, the maximum of the temperature dependence of the conductivity along the *c* axis is observed earlier (at 180–190 K) than in the *ab* plane.

A known mechanism through which the anion subsystem influences the conductivity of organic crystals is anion ordering, which leads to dielectric transition with high activation energies.[25] The available x-ray structure data, however, indicate that the anions are ordered already at room temperature.[26]

An attempt can be made to explain the general course of the temperature dependence of the conductivity, with allowance for the calculated band structure of compounds with two-dimensional molecule arrangement, viz., BMDT-TTF_2PF_6 and BMDT-TTF_2ClO_4.[27] Using in the calculations the transport integrals in two directions in the layer plane, the authors reached the conclusion that these compounds should be either metals or semimetals, and to explain the dependence of the conductivity on the activation temperature it is essential to assume that the site potentials of the nonequivalent molecules in the unit cell differ from one another by ≈ 0.5 eV. The difference indicated is due either to a difference in the arrangement of the nonequivalent molecules relative to the anion, or to strong electron-electron interaction.

If it is assumed that the differences in the potentials of molecules of type I, II, and III (Ref. 11) are insufficient to open a gap in the system, α-ET_2I_3 at room temperature can be a metal or a semimetal. Insignificant changes of the positions of the I_3^- ions on cooling can lead to the required increase of the difference between the site potentials of the nonequivalent molecules, and as a consequence to dielectrization of the system. Such a process can be avalanche-like, since changes in the anion arrangement can enhance the electron localization, which in turn increases the distortions of the anion sublattice. In this case, however, the lattice structure will not be radically altered (there will be no manifestation of a superstructure).

A final evaluation of the nature of the transition can be obtained only by a detailed x-ray structure investigation at low temperature.

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