The effect of an incommensurate superstructure on the electrical resistance anisotropy and superconducting transition temperature of the organic superconductor β-(ET)$_2$I$_3$

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(Submitted 21 February 1990)
Zh. Eksp. Teor. Fiz. **98**, 627–633 (August 1990)

In this paper we discuss the temperature dependence of the resistance of the quasi-two-dimensional organic superconductor β-(ET)$_2$I$_3$ along the high-conductivity crystallographic axis **a** and in the direction perpendicular to the conducting plane *ab* (the **c*** axis), both for the β_L phase ($T_c \approx 1.5$ K) and for the β_H phase ($T_c \approx 8$ K). We obtain results that indicate the possible occurrence of a phase transition of crossover type from $2D$ to $3D$ at $T \approx 23$ K. We discuss possible reasons why the transition temperatures T_c are different for the β_L and β_H phases.

Recently a large number of papers have appeared devoted to the study of quasi-two-dimensional organic superconductors belonging to the family of compounds (ET)$_2$X, where ET represents bis(ethylenedithio)tetrathiofulvalene and X = I$_3$, IBr$_2$, AuI$_2$, Cu(NCS)$_2$, etc., all of which are superconducting at atmospheric pressure. Nevertheless, there remain some unresolved questions about the mechanism for superconductivity in these compounds. A particularly important question to resolve is why there should be a fivefold difference between the superconducting transition temperatures for the β_L and β_H phases of the organic metal β-(ET)$_2$I$_3$, for which $T_c = 1.5$ K (see Ref. 1) and 8 K (see Ref. 2), respectively. The β_H phase can be obtained at atmospheric pressure by cooling a sample under a pressure of $P > 300$ bars down to a temperature $T < 125$ K, and then reducing the pressure.[3]

According to the results of measurements of the magnetic susceptibility,[4–6] the electronic densities of states of the β_L and β_H phases differ by no more than 15 to 20%. The neutron diffraction and x-ray diffraction investigations of Refs. 7–9 show that one difference between these two phases is the presence in the β_L phase and absence in the β_H phase of an incommensurate superstructure associated with the way the ring-like ethylene CH$_2$ groups are positioned in the ET molecule relative to the plane of this molecule. Let us note first that these CH$_2$ groups are entirely disordered for $T > 180$ K. This state of the sample we will call the β_D-phase. In Ref. 3 it was shown that the superstructure has a strong influence on the residual resistivity, indicating that the β_L phase has a great deal of disorder compared to the β_H phase. This superstructure is apparently an important factor in explaining the difference in the temperature T_c for the β_L and β_H phases; however, the mechanism by which it affects the superconducting transition temperature is not yet clearly understood.

In this work we will investigate the temperature dependence of the resistivities both along the high-conductivity crystallographic axis **a**, $\rho_a(T)$, and along the low-conductivity axis **c***, $\rho_c(T)$, as well as the temperature dependence of the resistance anisotropy ρ_c/ρ_a both for the β_L and β_H phases. The results we obtain suggest that both phases may exhibit yet another phase transition at $T \approx 23$ K. We will also discuss possible reasons for the existence of a difference in T_c for the β_L and β_H phases.

METHODOLOGY AND RESULTS OF EXPERIMENTS

Our investigations were carried out on single crystals of β-(ET)$_2$I$_3$. For measurements along the **c*** axis, the sample characteristic dimensions were $1.0 \times 0.2 \times 0.1$ mm^3; these dimensions were $2.0 \times 0.2 \times 0.05$ mm^3 for measurements along the **a** axis. The resistances were measured by the usual four-probe method for an AC current of $\leqslant 100\ \mu$A at a frequency ≈ 370 Hz. As in Refs. 3 and 10, we used low-noise pressure contacts. In order to measure ρ_c and ρ_a for the crystals we deposited gold strips in the pattern shown in Fig. 1. A pressure of $P \approx 400$ bar was created using gaseous helium in a high pressure bomb. Figure 1 shows typical $\rho_i(T)$ dependences ($i = a,c$) normalized by the value $\rho_i(300\text{ K})$ for the various phases (β_D,β_L,β_H) at atmospheric pressure. We note that the phase transitions $\beta_D \rightleftarrows \beta_H$ and $\beta_H \to \beta_L$ affect the function $\rho_c(T)$, as well as $\rho_a(T)$ (Refs. 3, 10), through jumps in the derivatives of the resistivities and in the resistivities themselves, respectively, at temperatures ≈ 180 K and 125 K. In this case, the jumps in the derivatives of the resistivities are roughly the same for both cases; however, the jump in the resistivity ρ_c, as in Ref. 11, is substantially larger than that of ρ_a, amounting to $\approx 30\%$ (for ρ_a, 5%).

In Fig. 2 we plot the low-temperature part of the functions $\rho_c(T)$ and $\rho_a(T)$ for the β_L and β_H phases in the coordinates ρ and T^2. It is clear that these functions are well approximated by the straight lines

$$\rho_i(T) = \rho_i(0) + A_i T^2,$$

which have kinks at $T \approx 23$ K for both phases. It is a characteristic of the β_L phase that the observed value of the residual resistance $\rho_i^L(0)$ is considerably larger than $\rho_i^H(0)$ for the β_H phase ($\rho_i^L(0)/\rho_i^H(0) \approx 10$ to 20), and that the curvature A_i,

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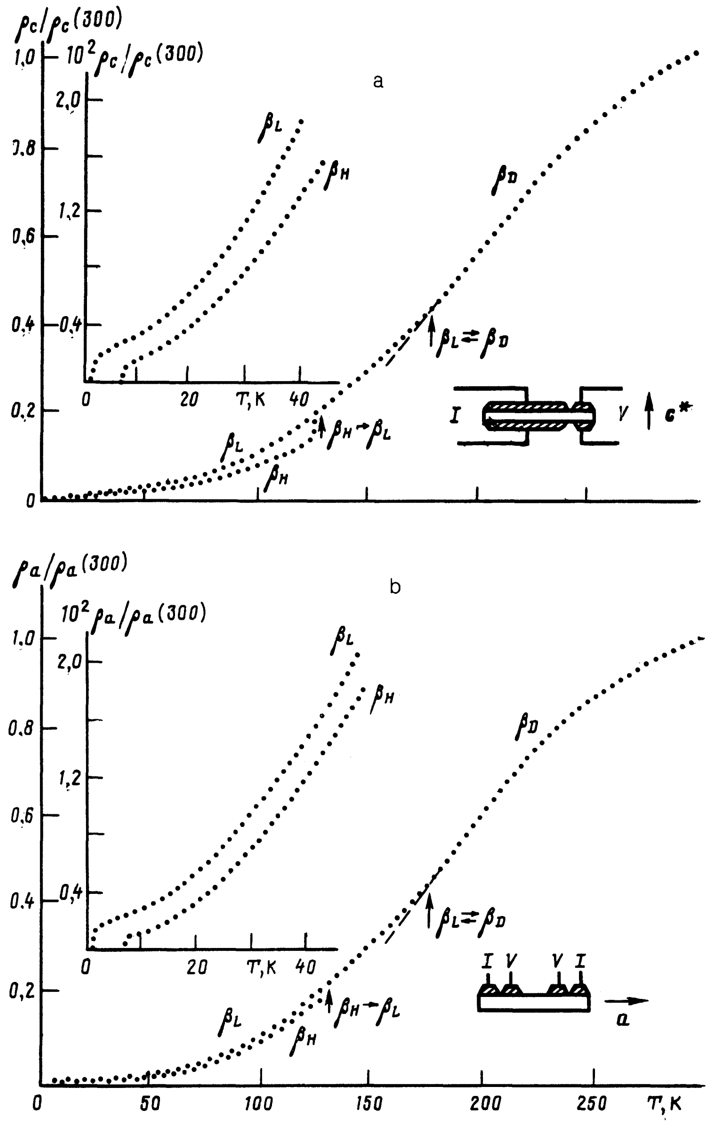

FIG. 1. Typical temperature dependence of the normalized resistance of single crystals of β-$(ET)_2I_3$ along the crystallographic **c*** axes (a) and (b) for the various phases $(\beta_D, \beta_L, \beta_H)$ at atmospheric pressure. The insets show the low-temperature parts of the corresponding functions and the pattern for the contacts in each case.

defined by

$$A_i=\frac{d^2\rho_i}{dT^2},$$

is larger by $\approx 20\%$ for the temperature dependence $\rho_i^L(T)$ compared to $\rho_i^H(T)$ in the region of temperatures $T<23$ K. We emphasize that these changes are roughly the same for both ρ_c and ρ_a at the transition from the β_H to the β_L phase.

Above 23 K a quadratic dependence is observed until $T\approx 70$ to 80 K. In this case, whereas the functions $\rho_i^L(T)$ and $\rho_i^H(T)$ are practically parallel, the difference $\rho_i^L(T)-\rho_i^H(T)$ grows with increasing temperature, leading, as we have already noted, to a sizable jump in the resistivity for the phase transition $\beta_H\to\beta_L$ at $T\approx 125$ K (see Fig. 1).

The temperature dependence of the resistance anisotropy ρ_c/ρ_a is shown in Fig. 3. We note first that the anisotropy value we measure, i.e., the ratio of the transverse resistivity to the longitudinal resistivity for the various samples, is in good agreement with the results of Ref. 12, where the anisotropy was determined for a single sample by the Montgomery method. It is clear from Fig. 3 that the second-order transition involving the superstructure $\beta_D\rightleftarrows\beta_L$ (for $T\approx 180$ K) is practically undetectable in the behavior of the anisotropy, while for the first-order phase transition $\beta_H\to\beta_L$ a discontinuous increase by ≈ 25 to 30% is observed in the anisotropy. Around a temperature ≈ 25 K the magnitudes of the anisotropy in the β_L and β_H phases are comparable, and as the temperature is decreased further they remain roughly the same (≈ 500 K) down to the superconducting temperature. The acceleration observed in the fall-off of the anisotropy in the β_L phase for $T<8$ K is associated with a certain anticipation of the falloff of ρ_c compared with ρ_a. This effect could be due to inclusions of the β_H phase with $T_c\approx 8$ K, which partially shunt the transverse resistivity.[12]

DISCUSSION OF RESULTS

1. It was reported earlier in Ref. 13 that the quasi-two-dimensional organic metals β-$(ET)_2I_3$, β-$(ET)_2IBr_2$, and β-$(ET)_2AuI_2$ are characterized by a quadratic temperature dependence of the resistivity in the high-conductivity plane *ab* at least for temperatures below 20 K. This can be explained by attributing the dominant role to the electron–electron scattering mechanism, according to which $1/\tau\sim T^2$ (here τ is the elastic relaxation time of the current carriers).

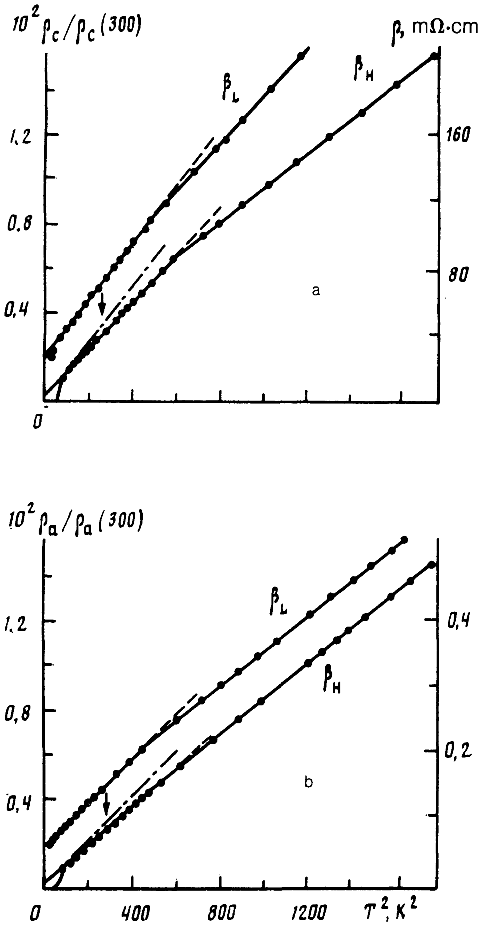

FIG. 2. Temperature dependence of the resistance anisotropy ρ_c/ρ_a of single crystals of β-$(ET)_2I_3$ in the phase states β_D, β_L, and β_H.

In this paper it was shown that for both the β_L and β_H phase of β-$(ET)_2I_3$ this behavior of the function $\rho_i(T)$ is observed both along the **a** axis and along the **c*** axis up to ≈ 70 to 80 K. In this case, as is clear from Fig. 2, kinks are observed in the function $\rho_i(T^2)$ for $T \approx 23$ K, suggesting that a phase transition may be occurring at this temperature. In favor of this assertion are structural features[14] in the thermoelectric power,[15,16] in the magnetoresistance,[17] and in the Hall constant,[18] all observed near $T = 23$ K.

At present the nature of the transition at $T \approx 23$ K remains unclear and requires some detailed study. Not to be ruled out is the possibility that, as a result of this transition, the motion of electrons in the transverse direction (along the **c*** axis) becomes coherent below 23 K, i.e., a $2D$ to $3D$ crossover is being observed of the sort that was reported in Refs. 16 and 17. In favor of this assertion are also data on the magnetoresistance of the β_H phase of β-$(ET)_2I_3$ (see Ref. 17), according to which the Kohler law, which is valid in the approximation of an isotropic relaxation time, is followed only in the region $T < 22$ K. Agreeing very well with this latter fact are our observations of the effect of the superstructure on the function $\rho_i(T)$ below and above 23 K. As we noted above, the change in the curvature A_i and the residual resistivity $\rho_i(0)$ at the transition from the β_H to the β_L phase below 23 K are the same for $\rho_a(T^2)$ and for $\rho_c(T^2)$, i.e., they are isotropic, while above this temperature they are anisotropic. Therefore, in order to describe the conductivity in both the β_L and β_H phase for $T < 23$ K, we can use the well-known formula

$$\sigma_i = 2e^2 N(E_F) v_{Fi}^2 \tau.$$

In this case the relaxation time τ is the same for both axes and the anisotropy of the conductivity is determined by the anisotropy of the Fermi velocity v_{Fi} of the carriers.

2. Clearly, since the phase transition that we predict at $T \approx 23$ K occurs in both the β_L and β_H phases, it cannot be the cause of the fivefold decrease of T_c in the β_L phase compared to the β_H phase.

Turning to the question of what effect the superstructure has on T_c, let us note first that the transition from the β_H to the β_L phase leads to a significant—more than an order of magnitude—increase in the residual resistivity $\rho_i(0)$. As suggested in Ref. 3, this is apparently associated with the large disordering of the β_L phase because of the superstructure-related incommensurate distortion of the lattice and the related appearance of additional scattering by the resulting random potential. At the same time, the change in the temperature-dependent part of the resistivity both along the **a** axis and along the **c*** axis is insignificant. All of this clearly indicates that such characteristics of the electron spectrum as the density of states $N(E_F)$ and the Fermi velocity v_F most likely do not undergo any significant alteration with the appearance of the superstructure.

This conclusion is confirmed by the data of Ref. 19 on the measurement of the relaxation rated of NMR signals from protons in β-$(ET)_2I_3$, according to which $N(E_F)$ in the β_L phase is always only $\approx 15\%$ smaller than in the β_H

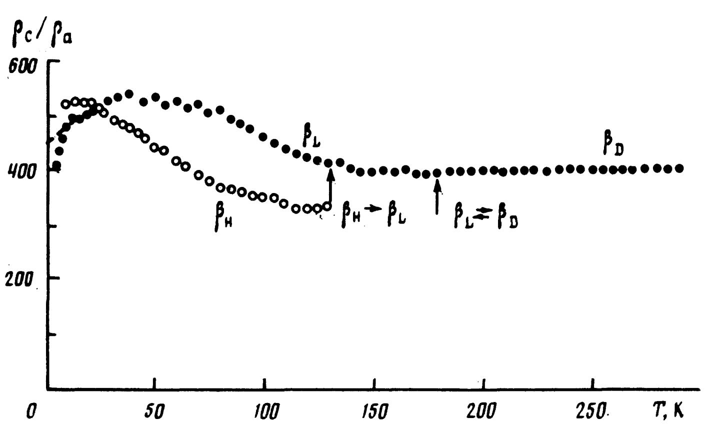

FIG. 3. Typical temperature dependence of the normalized resistance of single crystals of β-$(ET)_2I_3$ along the crystallographic **c*** axes (a) and (b) in the coordinates ρ-T^2 for the β_L and β_H phases.

phase.[20] If this variation of the density of states is used to estimate T_c according to the BCS formula with a Debye temperature $T_D \approx 50$ K (see Ref. 21), assuming the electron-phonon interaction is unchanged, the resulting total decrease in T_c is only by a factor of 1.5, not by a factor of 5. In principle, the observed decrease (by a factor of 3) in the critical temperature as the density of states changes by roughly 15% can be obtained from the BCS formula if we assume[22] that the pairing of electrons is mediated by an optical phonon with energy $\approx 10^3$ K. However, the results of Refs. 23 and 24 on microcontact spectroscopy of the β_L-$(\mathrm{ET})_2\mathrm{I}_3$ material apparently suggest that the primary contribution to the electron–phonon interaction constant comes from a low-frequency (acoustic) phonon. Thus, based on the estimates we made above, a difference in the electron density of states of 15% for the β_L and β_H phases cannot fully explain this strong suppression of the superconductivity when the superstructure appears.

3. We have not yet taken into account the effect on the superconductivity of the random scattering potential which arises in the β_H phase because of the incommensurate superstructural distortion of the lattice. In a number of papers it was shown[25,26] that inorganic metals such as $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, β-$(\mathrm{ET})_2\mathrm{I}_3$, and β-$(\mathrm{ET})_2\mathrm{IBr}_2$, the superconductivity is very sensitive to defects even if they are nonmagnetic. The influence of nonmagnetic defects on singlet superconductivity in metals with low electrical conductivity was discussed in Refs. 27–29, where it was shown that as the degree of disorder increases and the relaxation time for the carriers decreases the superconductivity of these systems is strongly suppressed because of enhancement of the Coulomb repulsion. The results of numerical calculations of the dependence of T_c on $1/\tau$, which take into account this effect for the β_H phases of β-$(\mathrm{ET})_2\mathrm{I}_3$ (see Ref. 30), show that increasing $1/\tau$ by a factor of 2–3 is sufficient to decrease T_c by more than factor of 4–5. As is clear from Fig. 1, in the β_L phase the resistance of $\rho_i(T^2)$ $(i = a,c)$ near T_c is 2.5 to 3 times larger than the corresponding resistance in the β_H phase. Since

$$\rho \propto \frac{1}{N(E_F)\tau},$$

while the densities of states of the β_L and β_H phase differ by $\approx 15\%$, the value of $1/\tau$ in the β_L phase must be 2–3 times larger in the β_H phase, which corresponds, as we have pointed out above, to decreasing T_c in the β_H phase by more than a factor of 4–5, i.e., $T_c \approx 1.5$ K in the β_L phase. From this we see that the significant difference in the superconducting transition temperatures of the β_L and β_H phases can be explained by suppression of the superconductivity by a random scattering potential which arises in the β_L phase because of the incommensurate superstructure-induced lattice distortion. In this case the β_L phase is considered to be a system with singlet superconductivity having a rather low electrical conductivity $(\sigma_{1,2} \approx 1.5 \cdot 10^4\ (\Omega \cdot \mathrm{cm})^{-1})$.

In conclusion, we express our gratitude to E. E. Laukhina and E. B. Yakubskii for sample preparation and to I. F. Shchegolev for useful discussions.

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Translated by Frank J. Crowne