Thermoelectric and magnetic properties of the α- and β-modifications of $(BEDT\text{-}TTF)_2I_3$

V. A. Merzhanov, E. É. Kostyuchenko, O. E. Faber, I. F. Shchegolev, and É. B. Yagubskiĭ

Institute of Chemical Physics, Academy of Sciences of the USSR

(Submitted 7 February 1985)
Zh. Eksp. Teor. Fiz. **89**, 292–297 (July 1985)

The α- and β-modifications of $(BEDT\text{-}TTF)_2I_3$ are quasi-two-dimensional organic metals. Measurements of the paramagnetic susceptibility imply that the density of states is relatively high, 8.7 and 6.8 $eV^{-1} \cdot spin^{-1}$ per molecule at $T = 300$ K, respectively. The α-phase becomes a nonmagnetic insulator below 137 K. The sign of the thermal emf changes when the β-phase is cooled, which indicates that the band structure is complex.

INTRODUCTION

The bis-(ethylenedithiol)-tetrathiafulvalene (BEDT-TTF) compounds which contain inorganic anions constitute a new class of organic metals with many interesting properties.[1–6] The characteristic quasi-two-dimensional electron structure of BEDT-TTF conductors[7,8] tends to stabilize the metallic state at low temperatures, and a few of these materials become superconducting at critical temperatures T_c which are the highest yet reported for organic compounds.[2–6]

Iodine reacts with BEDT-TTF to form a wide variety of conducting compounds that differ in composition and structure.[8] Crystals of composition $(BEDT\text{-}TTF)_2I_3$ were found in Refs. 9 and 10 to exist in two polymorphic modifications (α and β), each of which is a quasi-one-dimensional metal at room temperature.[10] Conductivity measurements show that the α-phase undergoes a metal-insulator transition at $T = 137$ K (Refs. 5,11), whereas the β-phase remains metallic down to liquid helium temperatures and becomes superconducting at $T_c = 1.5$ K (Ref. 3).

Most of the work in this area has been concerned with studying the crystal structure and superconducting properties of BEDT-TTF compounds. In this paper we analyze the behavior of the magnetic susceptibility and thermal emf of α- and β-$(BEDT\text{-}TTF)_2I_3$ for a wide range of temperatures.

EXPERIMENT

The electrochemical technique for synthesizing $(BEDT\text{-}TTF)_2I_3$ was described previously in Refs. 9,12 and yields a mixture of α- and β-crystals. We have found a method for synthesizing the α and β phases separately. The α-crystals were grown by oxidizing BEDT-TTF electrochemically in a benzene nitrile solution ($c = 10^{-3}$ mole/liter) at $T = 20$°C (platinum anode, dc current $I = 20\ \mu A/cm^2$, Bu_4NI_3 electrolyte of concentration $c = 8 \cdot 10^{-3}$ mole/liter). The β-crystals were synthesized by chemical oxidation of BEDT-TTF in *N,N,N*-triiodotetrabutylamine (Bu_4NI_3), which was dissolved in trichloroethane or chlorobenzene; the BEDT-TTF:Bu_4NI_3 molar ratio was equal to 1:10.

The magnetic susceptibility was measured by the Faraday method for $T = 1.5$–400 K and $H = 2.8$–9.0 kOe. The samples consisted of a collection of randomly oriented single crystals which were placed in a quartz cup. The total mass of the samples ranged from 15 to 120 μg in the various experiments. The samples were stored for 2–3 days in a vacuum chamber at 10^{-5} torr prior to the measurements in order to remove the adsorbed oxygen.

The thermal emf of the single crystals was measured for $T = 4.2$–350 K by the standard technique. The temperature drop across the samples was less than 0.5 K. The α-phase single crystal plates measured $2 \times 2 \times 0.02\ mm^3$, and the thermal emf S was measured along the a and b crystallographic axes lying in the plane of the crystal. The β-phase crystals were needles of typical dimensions $2 \times 0.2 \times 0.02\ mm^3$, with the long dimension along the a axis. We studied two groups of β-crystals which differed in structural quality and for which the ratio $\rho(300)/\rho(4.2)$ was equal to 150–200 and 500–600, respectively. The measured values were corrected for the absolute thermal emf of the gold electrodes, which was measured using a *Pb* reference electrode.

RESULTS

Several factors contributed to the measured magnetic susceptibility χ. First, the small contribution from ferromagnetic impurities was found by the Honda-Owen rule from the dependences $\chi(H)$ at room and liquid helium temperatures. The results indicated an impurity concentration equivalent to 35 and 25 ppm of Fe for the α- and β-phases, respectively. Second, the contribution from paramagnetic impurities was deduced from the slight low-temperature increase in χ (Curie law) which is generally observed for organic conductors. Their concentration was found to be 0.08 and 0.05 molec.% for the α- and β-phases, respectively. Finally, we used Pascal's rules to find the diamagnetic contribution of the ionic core, which was the same for the α- and β-phases and equal to $5.14 \cdot 10^{-4}\ cm^3/mole$.

The paramagnetic contribution χ_S from the conduction electrons shown in Figs. 1,2 was found by subtracting the above three contributions from the measured susceptibility. The figures show that for the α-phase χ_S is constant at high temperatures but drops abruptly at $T \approx 140$ K and quickly falls to zero, indicating the onset of a metal-insulator phase

0038-5646/85/070165-03$04.00

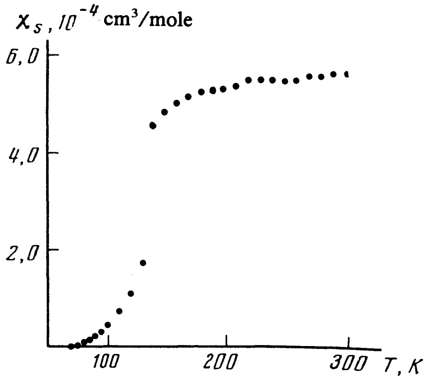

FIG. 1. Temperature dependence of the paramagnetic susceptibility of α-(BEDT-TTF)$_2$I$_3$.

transition. The susceptibility of the β-phase remains nonzero for all T; it is constant for T below 20 K, rises smoothly by 20% for $T = 20$–250 K, and then becomes constant again for $T = 250$–400 K.

Figure 3 shows the temperature dependence $S(T)$ of the absolute thermal emf for α-phase single crystals; at room temperature S was equal to 30 μV/K along both the a and the b crystallographic axes. S decreases as T drops and becomes negative; there is an abrupt increase in $|S|$ at $T = 137$ K, and S reaches $-400\ \mu$V/K at 100 K. The effective activation energy of the thermal emf is equal to 700 K for $T < 120$ K. In terms of S, the metal-insulator transition is very abrupt (<1 K). We did not detect any hysteresis in the transition region.

The dependence $S(T)$ for the β-phase is more complicated (Fig. 4). The thermal emf is positive for high temperatures and is proportional to T for $T > 250$ K. As T decreases, $S(T)$ becomes nonlinear, vanishes at 170 K, and then continues to decrease through negative values; finally, it increases linearly to zero for T below 20 K. The behavior of $S(T)$ for $20 \leqslant T \leqslant 50$ K differs for the two groups of β-phase single crystals—S has a plateau for the less perfect cyrstals, while there is a distinct minimum at $T = 20$ K for crystals with fewer structural defects.

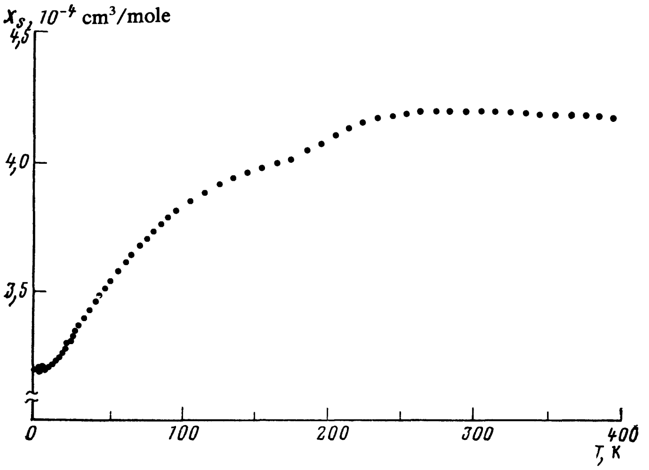

FIG. 2. Temperature dependence of the paramagnetic susceptibility of β-(BEDT-TTF)$_2$I$_3$.

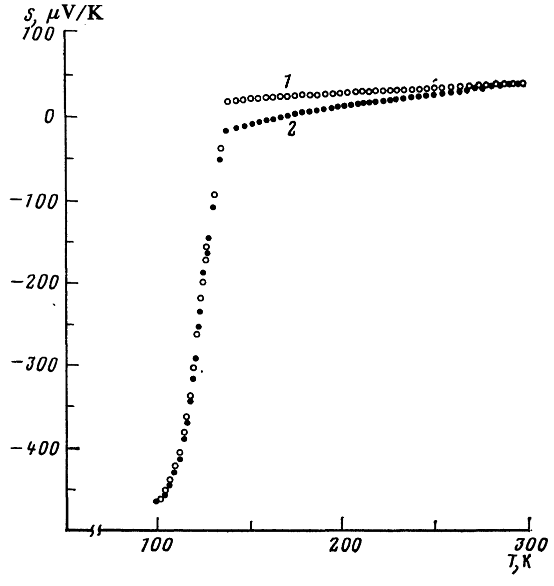

FIG. 3. Temperature dependence of the thermal emf S of α-(BEDT-TTF)$_2$I$_3$ single crystals: 1) along the a axis; 2) along the b axis.

DISCUSSION

Together with data from conductivity measurements, our results indicate that the metallic α-phase of (BEDT-TTF)$_2$I$_3$ becomes a nonmagnetic insulator as T decreases. The high-temperature thermal emf data show that the conducting plane is slightly anisotropic. Structural irregularities in the conducting layer of BEDT-TTF molecules have previously been noted in the α-phase.[10] Although it is plausible that a change in the structure of the conducting layer might be responsible for the metal-insulator transition, the nature of the transition remains in doubt due to the lack of x-ray structure data at low temperatures.

Metallic conduction persists throughout the experimental range of temperatures for the β-phase of (BEDT-

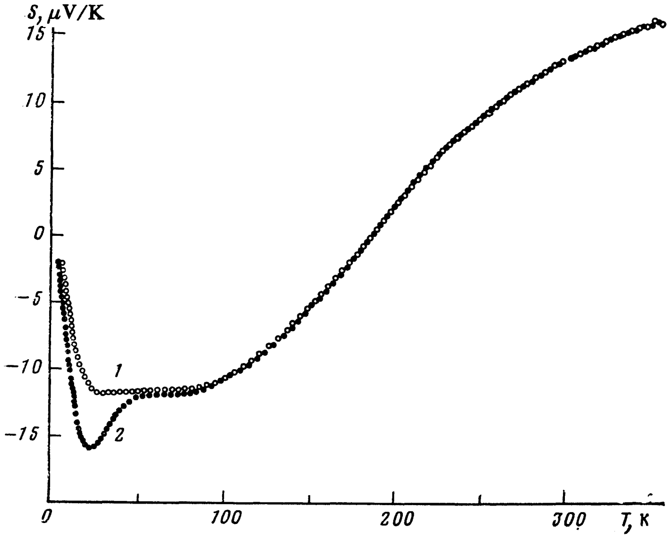

FIG. 4. Temperature dependence of the thermal emf S of β-(BEDT-TTF)$_2$I$_3$ single crystals with $\rho(300)/\rho(4.2) = 150$–200 (1) and 500–600 (2).

TTF)$_2$I$_3$ as is clear from the behavior of the Pauli paramagnetic susceptibility, which is almost independent of T. If we use the expression

$$\chi_s=2N_A\mu_B^2N(E_F)\,[1-{}^1/_3(m/m^*)^2]$$

and neglect the Landau-Peierls diamagnetism (the second term in the square brackets), we can calculate the density of states $N(E_F) = 5.6\,\mathrm{eV}^{-1}$ (per formulat unit for a single spin direction) from the low-temperature values χ_S. In the two-dimensional model of quasi-free electrons, this density yields the estimates $T_F = 1000$ K and $m^* = 4.7m$ for the Fermi temperature and effective mass, which justifies our neglect of the Landau-Peierls diamagnetism. The values of $N(E_F)$ for α- and β-(BEDT-TTF)$_2$I$_3$ are appreciably higher than for most quasi-one-dimensional organic metals.[14] This indicates that the wave functions of adjacent BEDT-TTF molecules overlap less extensively than in quasi-one-dimensional cation-radical compounds with selenium-containing donors. This explains the relatively poor conductivity of the BEDT-TTF compounds.

The temperature dependence of the thermal emf for the β-phase is quite unexpected. Indeed, $S(T)$ is generally linear for metals, yet the experimental dependence has two linear segments ($T = 4.2$–20, $T = 250$–400 K) whose slopes differ in sign. The smooth transition from a linear low-temperature electronic to a linear high-temperature hole-dominated thermal emf occurs for $T = 20$–250 K, i.e., in the same range of T for which the Pauli paramagnetic susceptibility increases. It is significant that the specific resistance of the β-phase,[3] which behaves as $\rho \sim T^2$ for $20 \leqslant T \leqslant 250$ K, becomes linear for T above 250 K. This correlation in the experimental results suggests that as T decreases, there is a smooth transformation in the energy spectrum of β-(BEDT-TTF)$_2$I$_3$ which is accompanied by generation of negatively charged carriers of low mass. Additional evidence for this is provided by Ref. 12, where x-ray diffraction patterns recorded at 125 K revealed additional satellite reflections indicating the formation of a superstructure in the β-phase as T decreased. We also note that the high-temperature thermal emf is an order of magnitude less than would be expected from the state density $N(E)$ deduced from the magnetic susceptibility. This indicates that even at high temperature, there must be at least two types of carriers whose contributions to S tend to cancel. The behavior of $S(T)$ could also be attributed to the different temperature dependences of the electron and hole mobilities for constant electron and hole concentrations; however, this would make it more difficult to explain the change in the magnetic susceptibility.

The difference between the curves $S(T)$ for β-phase single crystals of different structural quality is apparently due to the familiar phonon drag effect, which produces a peak in S at $T = (0.1$–$0.2)\Theta_D$. We can use this to get the estimate $\Theta_D \approx 100$–200 K for the Debye temperature for the phonons that contribute significantly to the resistance. Phonon drag will of course be less important for the dirtier crystals.

Comparison of our results with other data thus implies that the polymorphic modification of (BEDT-TTF)$_2$I$_3$ are both quasi-two-dimensional metals with relatively high state densities at high temperatures. As T drops, the α-phase undergoes a transition to a diamagnetic insulator at $T = 137$ K. The metallic state in the β-phase persists down to the very lowest temperatures; moreover, the charge of the carriers changes sign as T decreases, which indicates that the electron energy spectrum is complicated.

[1] G. Saito, T. Enoki, K. Toriumi, *et al.*, Sol. St. Comm. **42**, 557 (1982).

[2] S. S. P. Parkin, E. M. Engler, R. R. Schumaker, *et al.*, Phys. Rev. Lett. **50**, 270 (1983).

[3] É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].

[4] É. B. Yagubskiĭ, I. F. Shchegolev, S. I. Pesotskiĭ, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 275 (1984) [JETP Lett. **39**, 328 (1984)].

[5] É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 387 (1984) [JETP Lett. 1201 (1984)].

[6] É. B. Yagubskiĭ, V. N. Topnikov, *et al.*, Zh. Eksp. Teor. Fiz. **88**, 244 (1985) [Sov. Phys. JETP **61**, 142 (1985)].

[7] H. Kobayashi, R. Kato, T. Mori, *et al.*, Mol. Cryst. Liq. Cryst. **107**, 33 (1984).

[8] R. P. Shibaeva, Mol. Cryst. Liq. Cryst. **119**, 361 (1985).

[9] V. F. Kaminskiĭ, T. G. Prokhorova, R. P. Shibaeva, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 15 (1984) [JETP Lett. **39**, 17 (1984)].

[10] V. F. Kaminskiĭ, V. N. Laukhin, V. A. Merzhanov, *et al.*, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12 (1985).

[11] K. Bender, K. Dietz, H. Endres, *et al.*, Mol. Cryst. Liq. Cryst. **107**, 45 (1984).

[12] J. M. Williams, T. J. Emge, H. H. Wang, *et al.*, J. Chem. **23**, 2558 (1984).

[13] E. É. Kostyuchenko, É. B. Yagubskiĭ, O. Ya. Neĭland, *et al.*, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2834 (1984).

[14] M. Miljak, J. R. Cooper, and K. Bechgaard, J. de Phys. Coll. C3, **44**, 893 (1983).

Translated by A. Mason