

Anomalous increase in the conductivity of the system α -(BEDT-TTF-d₈)₂I₃ in the region of the metal-insulator phase transition

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The conductivity of the deuterio analog α -(BEDT-TTF)₂I₃ has been found to change sharply along the crystallographic a axis at temperatures above the metal-insulator phase transition. The possible mechanism responsible for this phenomenon is discussed.

The available data on the electric, thermoelectric, and magnetic properties of the organic conductor¹⁻⁴ α -(BEDT-TTF)₂I₃ indicate that a dielectric transition ($T_p = 138$ K) occurs in the system as the temperature is lowered.

In the present letter we report the observation of anomalous conductivity properties of α -(BEDT-TTF-d₈)₂I₃ at temperatures above the phase transition.

The α -(BEDT-TTF-d₈)₂I₃ crystals were obtained by electrochemical oxidation of BEDT-TTF-d₈ using a standard procedure.³ These crystals have nearly an orthorhombic shape with typical dimensions $2 \times 2 \times 0.02$ mm. The parameters of the unit cell of α -(BEDT-TTF-d₈)₂I₃ are in good agreement with those¹ described for α -(BEDT-TTF)₂I₃.

The conductivity of single crystals was measured with a direct current by the four-contact method in the direction of the a and b axes (along the long and short diagonals of the diamond). The notation of the axes is the same as in Ref. 1.

The anisotropy of the conductivity was measured by using a method similar to that used by Montgomery.⁵ Since preparation of a rectangular-shaped sample with the sides coinciding with the a and b axes of the crystal produced cracks in it, we placed the contacts at the center of the sides of the diamond, as shown in the inset of Fig. 2. The sharp corner of the diamond is 82° , and the contacts 1–2, 2–3, 3–4, and 1–4 are spaced roughly the same distance apart (± 0.1 mm). In a single thermal cycle we measured two resistances for different configurations using the four-contact scheme: (a) contacts 1 and 4 are current contacts and contacts 2 and 3 are potential contacts (R_{23}); (b) contacts 1 and 2 are current contacts and contacts 3 and 4 are potential contacts (R_{34}). We then determined their ratio (R_{23}/R_{34}) which is proportional to the ratio of the conductivities of the crystal along the preferred axes, τ_a/τ_b .

The following systematic features can be singled out from the experimental results shown in Figs. 1 and 2. 1) At temperatures between 300 K and 180 K, the conductivity changes in proportion to $\sigma \sim T^{-1/2}$, which is different from the way in which the conductivity changes in ordinary metals ($T^{-1/2}$) and in quasi-one-dimen-

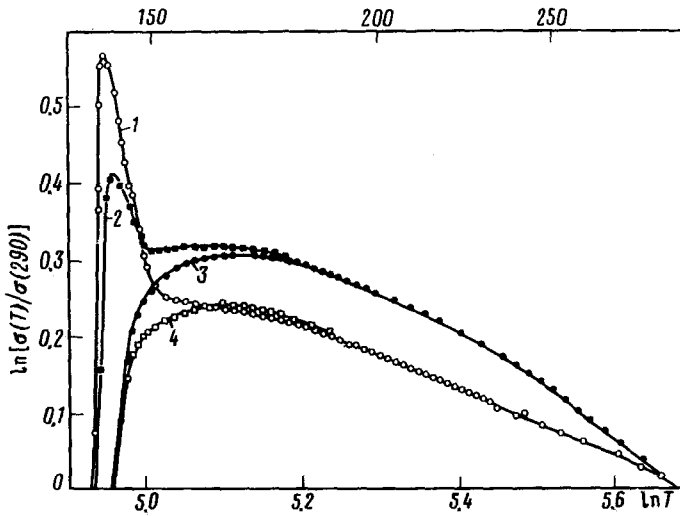


FIG. 1. Temperature dependences of the conductivity along the a axis of four α -(BEDT-TTF- d_8) $_2$ I $_3$ crystals. Curve 2 was plotted after sample 4 was doped in saturated iodine vapor for 15 min at room temperature.

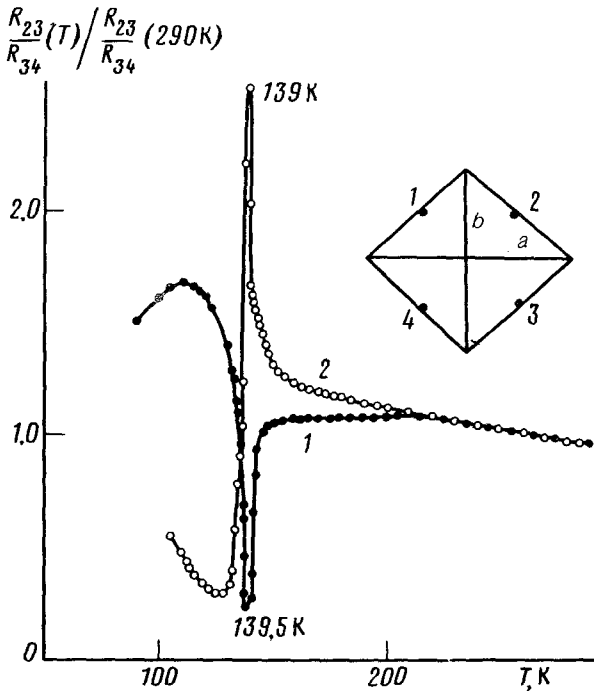


FIG. 2. Temperature dependences of the conductivity anisotropy of the α -(BEDT-TTF- d_8) $_2$ I $_3$ crystals of stoichiometric composition (1) and nonstoichiometric composition (2). Inset—Configuration of the contacts.

sional conductors ($T^{-1/2}$) which have been studied extensively.⁶ 2) At temperatures 180–140 K before the transition, the conductivity σ_a of the crystals belonging to the same group is different: (a) in most crystals, the conductivity peaks at 165 K and then falls off smoothly. This is a standard behavior¹ for α -(BEDT-TTF)₂I₃; (b) in some crystals, the conductivity continues to increase and it exhibits a sharp, anomalous peak in a narrow temperature region 148–140 K immediately preceding the transition. 3) The anomalous increase in the conductivity σ_a at temperatures just before the transition stems from the deviation of the complex from stoichiometric composition during the synthesis or doping. 4) At temperatures preceding the transition, the conductivity along the b axis did not increase in any of the crystals studied. 5) A decrease in σ_b immediately preceding the transition occurs over a narrower temperature region. 6) The metal-insulator transition temperature, determined from the maximum $d \ln \sigma / d(1/T)$ is the same for both σ_a and for σ_b ($T_p = 138 \pm 0.5$ K). 7) The transition temperature does not vary from one sample to the next. 8) The conductivity anisotropy, which varies considerably in the transition region, below the transition ($T \approx 100$ K) approaches a value approximately equal to that obtained at room temperature.

The properties like those of (2)–(5), which are characteristic for quasi-one-dimensional crystals TTF-TCNQ and TTT₂I₃, can be explained in terms of an additional conductivity mechanism involving an incommensurate charge-density wave caused by the Peierls instability.^{6,7} However, the one-dimensional nature of the electronic spectrum, which accounts for the divergence of the function $\chi(q)$ of the linear response of the electron density to the external potential, is clearly responsible for the satisfaction of the Peierls-instability criterion $[1 - \lambda(q) \cdot \chi(q)] < 0$, where $\lambda(q)$ is the electron-phonon coupling constant, and for the detection of the dielectric gap along the entire Fermi surface.

In a two-dimensional system, however, $\chi(q)$ has a faint spectral feature, and the criterion specified above holds only at reasonably large values of λ . This particular situation occurs in layered compounds of transition-metal dichalcogenides in which the Peierls instability manifests itself in the formation of a charge-density wave, but does not lead to the dielectrification of the system.⁸

According to the structural, electrical, and optical data,^{1–3,9} α -(BEDT-TTF)₂I₃ is a quasi-two-dimensional conductor. The assumption that the charge-density wave may contribute to the conductivity and that the transition is of a Peierls nature must therefore be based on a large value of λ .

The following factors are evidence in favor of a large electron-phonon coupling constant of the system: (a) low electrical conductivity of the crystals at room temperature (because of the strong scattering of electrons by phonons) and (b) the large value^{6,8} of T_p [$T_p \approx T_F \exp(-1/\lambda)$, where T_F is the Fermi temperature].

We can therefore assume that these anomalies in the conductivity stem from the Peierls distortion of the lattice along the a axis. The dielectrification of the system immediately after the Peierls transition may be the result of the involvement of other mechanisms such as the anion ordering.

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