Normal-pressure superconductivity in an organic metal $(BEDT\text{-}TTF)_2I_3$ [bis (ethylene dithiolo) tetrathiofulvalene triiodide]

É. B. Yagubskiĭ, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich,
M. V. Karatsovnik, A. V. Zvarykina, and L. I. Buravov
Institute of Chemical Physics, Academy of Sciences of the USSR

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A new organic metal, $(BEDT\text{-}TTF)_2I_3$, which does not have a dielectric instability and which goes over to the superconducting state at normal pressure with $T_c = 1.4 - 1.5$ K, has been synthesized. In very pure specimens, a change in the temperature behavior of the resistance, which is seen as a sharp increase in the rate at which the resistance drops with decreasing temperature, occurs at $T = 4$ K. This change in the temperature behavior of the resistance has not been observed in other organic superconductors.

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Until 1978, it was unclear whether attempts to synthesize organic superconductors would be successful. All organic metals known up to that time became dielectrics sooner or later with decreasing temperature for reasons related in some way to the quasi-one-dimensional nature of their structure. To stabilize the low-temperature me-

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tallic state in these compounds, it was therefore necessary to decrease the degree of their one-dimensionality, using both synthetic methods and hydrostatic pressure.

The existence of a stable metallic phase in the limit $T \to 0$ was first observed in 1978 in tetraselenotetracene chloride (TSeT) with the composition $(TSeT)_2Cl$, in which the metal–semimetal transition disappears under pressures exceeding 5 kbar.[1] Some time later, suppression of the dielectric transition under pressures greater than 10 kbar was observed in the compounds tetramethyltetraselenofulvalene (TMTSF) with dimethyltetracyanoquinodimethane DMTCN with the composition (TMTSF)–DMTCNQ.[2]

Although the high-pressure metallic phases turned out to be nonsuperconducting in both cases, the stability of these phases in the limit $T \to 0$ clearly indicated the possibility of creating organic superconductors.

In 1980, Bechgaard[3] synthesized an entire series of compounds based on TMTSF with the composition $(TMTSF)_2X$, where $X = PF_6, AsF_6, SbF_6, NO_3$, in which the met-

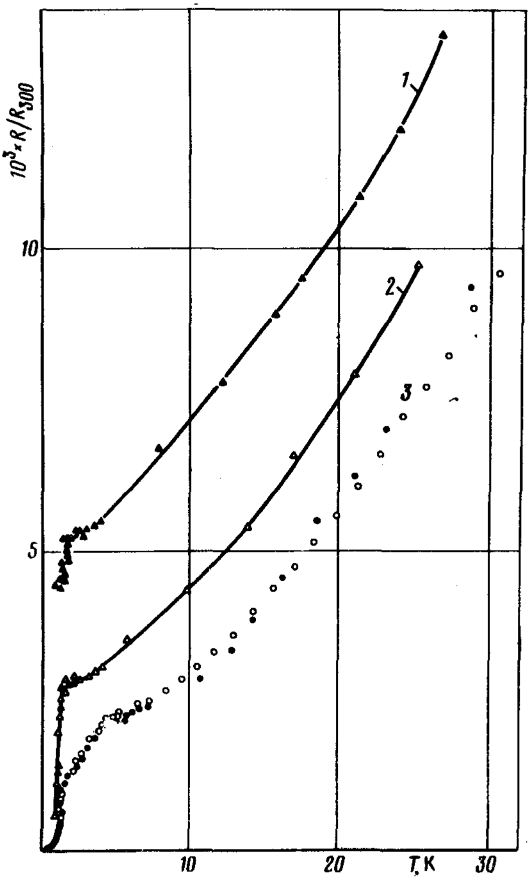

FIG. 1. Temperature dependence of the resistance of $(BEDT\text{–}TTF)_2I_3$: △, ▲ plates; ○, ● two needle-shaped single crystals.

al–insulator transition is suppressed under pressures above 9–10 kbar, and in some compounds of this type, superconducting transitions were observed in the high-pressure metallic phase.[4] An important step forward was taken in 1981, when it was reported[5] that one of the Bechgaard compounds $(TMTSF)_2ClO_4$ goes over into the superconducting state under normal pressure with T_c in the vicinity of 1 K.

In this paper we are reporting a second organic metal which goes superconducting under normal pressure, bis(ethylene dithiolo) tetrathiofulvalene triiodide with the composition $(BEDT–TTF)_2I_3$.

The BEDT–TTF molecule was synthesized in 1978.[6] Several compounds with Bechgaard anions were recently obtained on the basis of this molecule.[7,8]: ClO_4, ReO_4, and PF_6. One of these compounds with the composition $(BEDT-TTF)_4(ReO_4)_2$ does not exhibit a dielectric instability under pressures higher than 6 kbar and goes over to the superconducting state near 1.5 K.[8]

Crystals of $(BEDT–TTF)_2I_3$ were obtained by an electrochemical method.[9] During synthesis, two types of crystals grow: crystalline plates with a thickness of 20–30

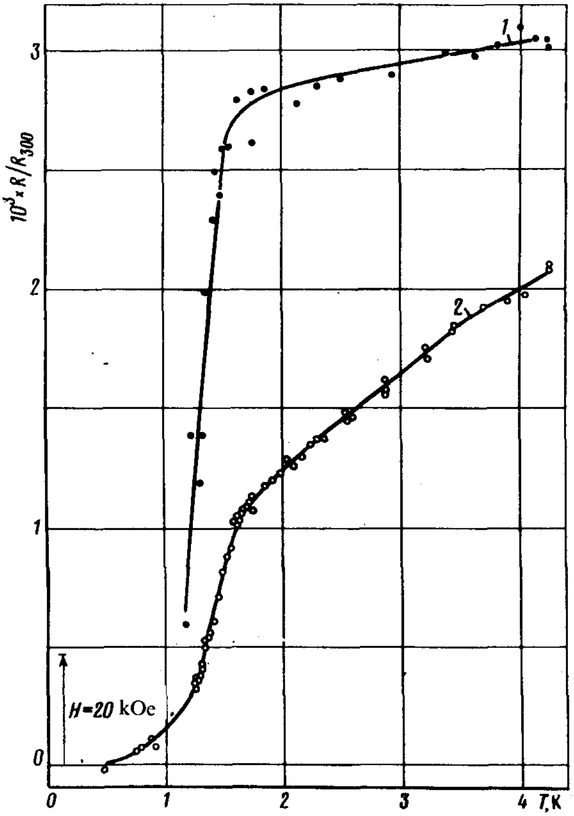

FIG. 2. Typical curves of the superconducting transition. 1) Plates; 2) needles. The arrow indicates the resistance in a transverse field $H = 20$ kOe at $T = 0.15$ K.

μm and an area up to 3×3 mm and needles with characteristic dimensions $0.01 \times 0.05 \times 2$ mm. At room temperature, the conductivity measured along the long axis of the needles and in an arbitrary direction in the plane of the plates has the same order of magnitude, $30\ \Omega^{-1}$ and $30\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Figure 1 shows the behavior of the resistance of two plates and two needles in the temperature range below 30 K. The measurements were performed using a four-contact method with dc current. The typical resistance of the contacts was $10\ \Omega$. Temperatures below 1.2 K were obtained by adiabatic demagnetization of potassium chrome alum. A semiconducting thermometer was used to measure the temperature.[10]

It is evident from Fig. 1 that the crystalline plates are less perfect than the needle crystals. For the plates, the ratio $R_{300}/R_{4.2}$ varies considerably from specimen to specimen and, for the three crystals investigated, lies in the range from 170 to 300. At the same time, the resistance of two sequential needles exhibited nearly the same temperature dependence with the ratio $R_{300}/R_{4,2} \cong 5 \times 10^2$. We note that the drop in the resistance of all specimens accompanying cooling below 4 K does not stop down to the onset of the superconducting transition. For plates, this drop is not large and it could be assumed to be a byproduct of the ordinary temperature dependence of the resistance; for needles, however, this explanation is clearly inadequate because in this case, the rate of drop of the resistance below 4 K is appreciably higher than the rate of drop of the resistance at temperatures slightly above 4 K.

Figure 2 shows the low-temperature parts of the resistance curves for two specimens. It is evident that the superconducting transition begins at $T = 1.6$–1.7 K, and if the critical temperature is estimated from the center of these curves, we obtain $T_c = 1.4$–1.5 K.

Figure 3 shows the curve of the breakdown of the superconducting state by a magnetic field. The measurements were performed on a needle at $T = 0.15$ K in a low-frequency alternating current. The magnetic field was oriented approximately along the b axis[9] perpendicular to the measuring current flowing along the needle (a axis[9]).

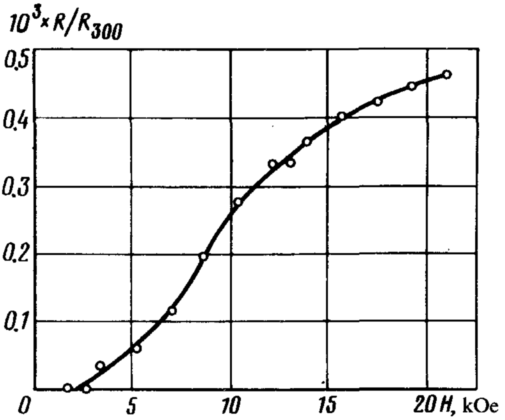

FIG. 3. Curve for the breakdown of the superconducting state in a magnetic field $H \perp I$ at $T = 0.15$ K.

Traces of resistance appear in fields 2–2.5 kOe. The resistance of the specimen in a field of 20 kOe at $T = 0.15$ K is indicated in Fig. 2 by the arrow. It is evident that this resistance is approximately one-half the resistance immediately before the superconducting transition.

Thus, it follows from these data that at $T_c = 1.4 - 1.5$ K $(\mathrm{BEDT{-}TTF})_2I_3$ is a superconductor under normal pressure. The change in the behavior of the resistance as a function of temperature observed in pure specimens at 4 K, i.e., long before the superconducting transition point, has not been observed in other organic superconductors. The explanation of this behavior requires a special investigation.

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We also discovered another crystalline modification in the system $(\mathrm{BEDT{-}TTF})_x I_y$ with an orthorhombic lattice, which becomes superconducting at $T_c = 2.5$ K under normal pressure

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