

# Effect of pressure on the metal-dielectric phase transition in tetrathiotetracene iodide complexes $TTT_2I_{3+\delta}$

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The effect of pressure up to 7.5 kbar on the metal-dielectric-type phase transition in the  $TTT_2I_{3+\delta}$  complexes with different iodine contents was investigated. It is shown that the transition temperature decreases spasmodically in the complex of a stoichiometric composition and spasmodically increases in the complexes with a large iodine content. The possible causes of such behavior are examined.

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Tetrathiotetracene iodides of the composition  $TTT_2I_{3+\delta}$  with  $0 < \delta < 0.1$  are quasi-one-dimensional compounds whose synthesis and structure were described in Refs. 1-3. The specific conductivity of single crystals, which is  $\sim 1000 \Omega^{-1} \cdot \text{cm}^{-1}$  at room temperature, increases proportionally to the iodine content with decreasing temperature: by a factor of 2-2.5 at  $T_{\text{max}} \approx 103 \text{ K}$  for complexes with  $\delta = 0.01 \pm 0.01$  and by a

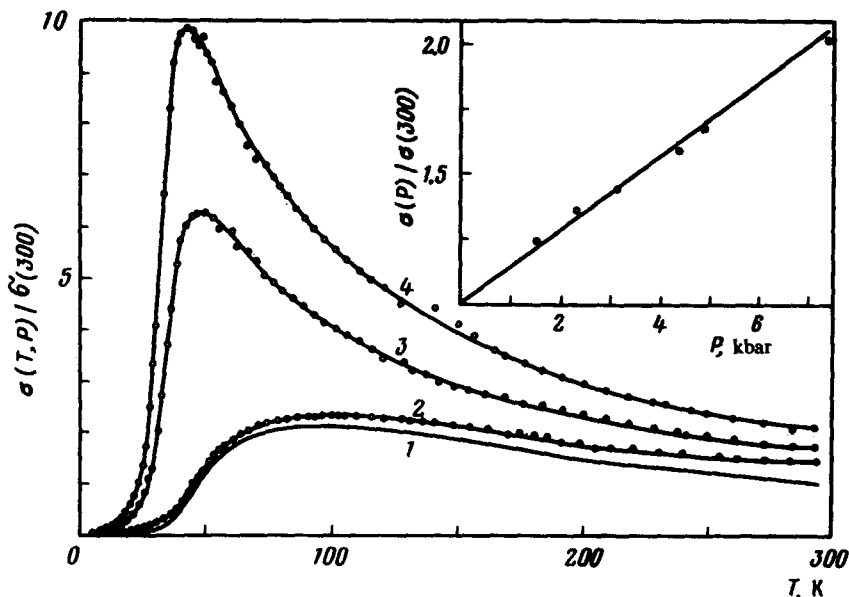


FIG. 1. Temperature dependences of the conductivity of  $\text{TTT}_2\text{I}_{3+\delta}$  complex with  $\delta = 0.01 \pm 0.01$  under a pressure: 1, 1 bar<sup>4</sup>; 2, 2.9 kbar; 3, 4.6 kbar; 4, 7.3 kbar. The indicated pressures were recorded at room temperature.

factor of 10 for complexes with  $\delta = 0.1 \pm 0.01$  at  $T_{\text{max}} \approx 34$  K. Analysis of the conductivity and magnetic susceptibility showed that a metal-dielectric-type phase transition occurs in these complexes,<sup>4,5</sup> whose temperature decreases from  $T_p \approx 45$  K ( $\delta = 0.01 \pm 0.01$ ) to  $T_p \approx 27.5$  K ( $\delta = 0.1 \pm 0.01$ ) with increasing iodine content.

In this study we investigate the effect of uniform compression on the phase transition in the  $\text{TTT}_2\text{I}_{3+\delta}$  complexes with different iodine content. With that end in view, we studied the temperature dependence of the conductivity of  $\text{TTT}_2\text{I}_{3+\delta}$  single crystals of four compositions with  $\delta = 0.01$ (I), 0.06(II), 0.08(III), and  $0.1 \pm 0.01$ (IV) at different hydrostatic pressures. The conductivity was measured with a direct current using a four-contact method. The pressure was produced in a "piston-cylinder" type chamber whose design and method of measuring the pressure and temperature were described elsewhere.<sup>6</sup> Note that the pressure produced in the chamber at room temperature during its cooling to 4.2 K decreases by  $\sim 30\%$ .

Figures 1 and 2 show a family of curves for the temperature dependence of the conductivity of the complexes I and IV at different pressures. It should be noted that the temperature dependence of the conductivity of the complex II under pressure is analogous to that depicted in Fig. 1 and for the complex III is analogous to that in Fig. 2.

The conductivity of all the investigated compounds increases linearly with increasing pressure at room temperature (see insets in Figs. 1 and 2) and much more rapidly at helium temperatures. Moreover, the increase of conductivity is larger in the samples with smaller iodine content. Thus, at  $T = 4.2$  K and  $P \approx 5$  kbar the conductiv-

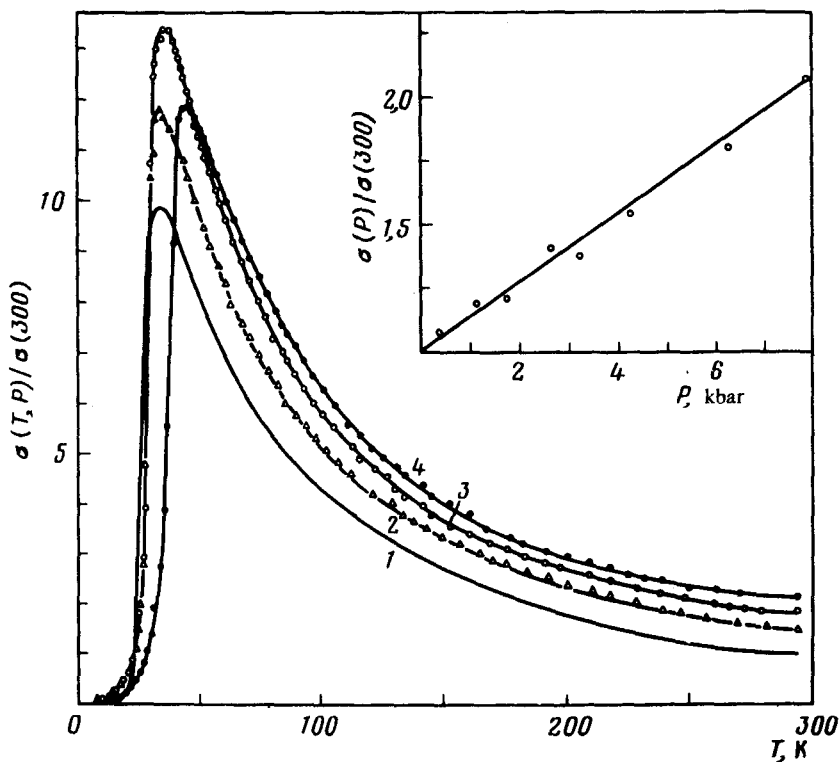


FIG. 2. Temperature dependences of the conductivity of  $\text{TTT}_2\text{I}_{3+\delta}$  complex with  $\delta = 0.1 \pm 0.01$  under a pressure: 1, 1 bar<sup>4</sup>; 2, 4.2 kbar; 3, 5.7 kbar; 4, 7.8 kbar. The indicated pressures were determined at room temperature.

ity is 80 to 100 times higher for the complexes I and 10 to 20 times higher for the complex IV, as compared with that at the same temperature and atmospheric pressure.

Application of pressure also shifts the maximum temperature of the conductivity. For the complexes I and II,  $T_{\text{max}}$  is shifted in the direction of low temperatures from  $\sim 103$  and  $63$  K, respectively, to  $\sim 45$  K. For the complexes III and IV,  $T_{\text{max}}$  decreases slightly at  $P < 5$  kbar and increases at  $P > 5$  kbar. These variations do not exceed  $\pm 10$  degrees.

Analysis of the obtained results enabled us to construct phase diagrams of the four investigated  $\text{TTT}_2\text{I}_{3+\delta}$  complexes (Fig. 3). The temperature of the metal-dielectric-type transition was determined from the maximum of the logarithmic derivative of the conductivity taken over the reciprocal temperature.

We can see from the phase diagrams that the transition temperature varies jump wise, while the magnitude of the discontinuity and its "sign" depend on the iodine content in the  $\text{TTT}_2\text{I}_{3+\delta}$  complexes. At low iodine concentrations the transition temperature changes abruptly in the direction of low temperatures (Fig. 3a). As the iodine

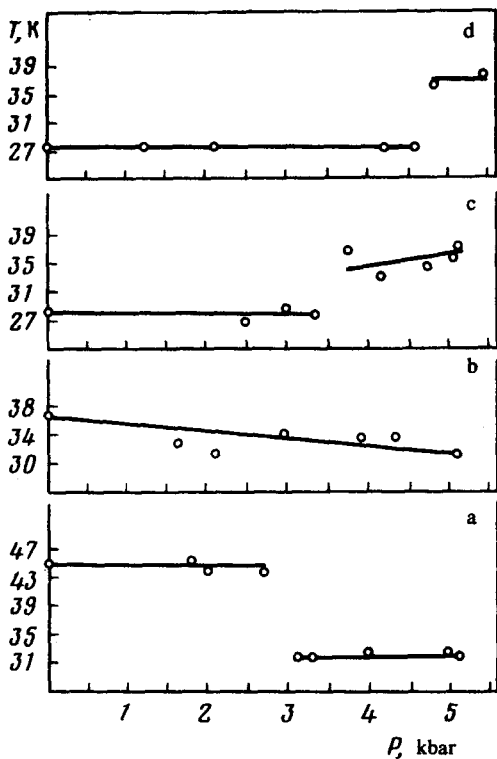


FIG. 3. Temperature of the metal-dielectric phase transition as a function of pressure for complexes with different iodine contents: (a)  $\delta = 0.01 \pm 0.01$ ; (b)  $\delta = 0.06 \pm 0.01$ ; (c)  $\delta = 0.08 \pm 0.01$ ; (d)  $\delta = 0.1 \pm 0.01$ . The indicated pressures were obtained at low temperatures.

content increases, the magnitude of the jump apparently decreases and for the complex with  $\delta = 0.06 \pm 0.01$  there is no evidence of it, but the transition temperature decreases monotonically with increasing pressure (Fig. 3b). With further increase of the iodine content,  $T_p$  begins to increase jumpwise while the magnitude of the discontinuity is proportional to the amount of iodine in the complex (Figs. 3c and 3d). The pressure at which the transition temperature changes abruptly increases from  $\sim 2.8$  kbar for the complex I to  $\sim 4.7$  kbar for the complex IV.

As seen in the phase diagrams, the transition temperature varies jumpwise in the complexes I, III, and IV. One of the reasons for such behavior of the transition temperature as a function of pressure might be a variation of the commensurability of the constants of the incipient Peierls distortion and of the crystal lattice. If there is a decrease in the degree of filling of the conduction band and of the Fermi momentum with pressure, then the discontinuous increase of the transition temperature of the complexes III and IV in the pressure region of 3.5 and 4.7 kbar, respectively, can be related to a transition from the incommensurable constants of the Peierls distortion and of the crystal lattice to the commensurable. However, a discontinuous decrease of the transition temperature of the complex I in the 2.8-kbar region can be related to the

transition from a commensurable case to an incommensurable one, since  $T_p$ , as is well known, decreases as a result of such transition.<sup>7</sup>

An increase of jumpwise variations of the transition temperature with pressure in the complex II can possibly be attributed to the fact that in the investigated pressure range the constants of the Peierls transition and of the lattice are in the state of approximate commensurability.

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<sup>1</sup>L. I. Buravov *et al.*, ICS Chem. Comm. 720, 1976.

<sup>2</sup>R. P. Shibaeva and V. F. Kaminskiĭ, *Kristallografiya (Crystallography)* **23**, 499 (1978).

<sup>3</sup>D. L. Smith and H. R. Luss, *Acta Cryst.* **B33**, 1744 (1977).

<sup>4</sup>V. F. Kaminskiĭ *et al.*, *Phys. Stat. Sol. (a)* **44**, 77 (1977).

<sup>5</sup>L. C. Isett, *Phys. Rev.* **B18**, 439 (1978).

<sup>6</sup>V. N. Laukhin and I. F. Schegolev, *Zh. Eksp. Teor. Fiz.* **78**, 2332 (1980) [*Sov. Phys. JETP* **52** (1980) (in press)].

<sup>7</sup>L. N. Bulaevskii, *Usp. Fiz. Nauk* **115**, 263 (1975) [*Sov. Phys. Usp.* **18**, 131 (1975)].