Effect of nonstoichiometry and of pressure on the metal–insulator transition in tetrathiotetracen iodide

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We investigate the effect of pressure and of the iodine content on the metal–insultaor transition temperature (T_p) in the organic metal $TTT_2I_{3+\delta}$. A jumplike change of T_p is observed at appropriate values of δ and of the pressure. This is accompanied by an abrupt change in the conductivity of the metal phase. These effects are interpreted as the result of a transition from the case of commensurate filling of the band to incommensurate and back when the iodine concentration and the external pressure are changed.

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1. INTRODUCTION

Tetrathiotetracene iodide TTT with composition $TTT_2I_{3+\delta}$ is a quasi-one-dimensional organic metal with room-temperature conductivity $10^3\ \Omega^{-1}cm^{-1}$ and exists at iodine concentrations corresponding to δ in the range $0 \leqslant \delta \leqslant 0.1$.[1] The crystal structure of this compound was investigated by several workers.[2-5] $TTT_2I_{3+\delta}$ crystals are made up of positively charged metallized stacks of TTT molecules and chains of I_3^- ions. Both are elongated in the direction of the c crystal axis and form two sublattices whose periods in this direction can be either commensurate or slightly incommensurate. In the case of stoichiometric composition ($\delta = 0$), $c_I = 2c_{TTT}$. With increasing δ, the period of the iodine sublattice c_I decreases, and the period c_{TTT} of the TTT sublattice increase slightly. This attests to the presence of a noticeable force interaction between the two sublattices.

The unit cell of $TTT_2I_{3+\delta}$ contains four TTT molecules belonging to four different stacks. An important feature of the structure is that it contains in the b-axis direction, distances S–S between TTT molecules from different stacks that are shorter than the van der Waals distances. One could therefore expect three-dimensional effects to exert a noticeable influence on the energy spectrum of the carriers and to split the initially fourfold degenerate one-dimensional conduction band as well as to bend the initially flat Fermi surfaces. All this, however, does not eliminate the instability with respect to the metal–insulator transition.

It was established in experiment[1] that when the temperature is lowered the $TTT_2I_{3+\delta}$ undergoes a transition from a metallic to an insulating state. This transition is revealed by the vanishing of the conductivity and of the parametric part of the susceptibility. The temperature T_p of this transition turned out to decrease noticeably with increasing iodine content in the sample, i.e., with increasing δ. The exact values of δ for the different synthesized complexes were unknown, however, and the $T_p(\delta)$ dependence was not investigated qualitatively.

We report here the results of an experimental study of this dependence. In addition, we have investigated in detail the effect of a hydrostatic pressure P on the metal–insulator transition in $TTT_2I_{3+\delta}$. These results were published in part in Ref. 6. The obtained data show that the $T_p(\delta)$ and $T_p(P)$ dependences are jumplike. It was also observed that at the same values of δ and P at which an abrupt change of the transition temperature takes place, the conductivity of the complex in the temperature region near T_p also changes jumpwise. All these jumplike changes are interpreted as a result of a transition from the case of commensurate to an incommensurate filling of the band and back with change in the iodine concentration and in the pressure.

2. EXPERIMENTAL RESULTS

To measure the conductivity we used $TTT_2I_{3+\delta}$ crystals of four compositions with $\delta = 0.01$, 0.06, and 0.08, and 0.10. The value of δ was determined from the ratio of the periods of the TTT and iodine sublattices in the direction of the c axis, measured on x-ray patterns of five or six single crystals of each composition. In all cases the obtained δ was accurate to ±0.01, as determined from the scatter of the data. Typical crystals measured 0.02 × 0.04 × 2 mm. The conductivity was measured with direct current by the four-

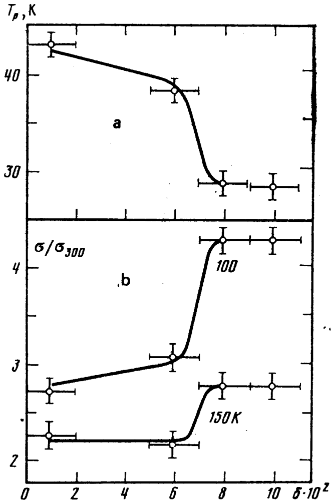

FIG. 1. a) Dependence of the transition temperature of $TTT_2I_{3+\delta}$ on δ; b) dependence of the conductivity of the metallic phase on δ at various temperature.

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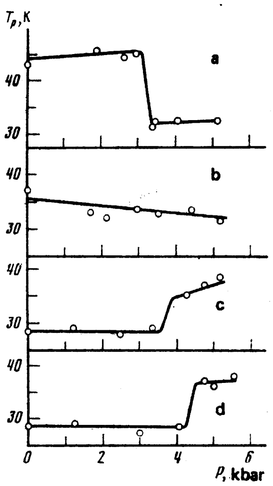

FIG. 2. Dependence of the transition temperature on the pressure for $TTT_2I_{3+\delta}$ crystals of varying stoichiometry: a) $\delta = 0.02 \pm 0.01$; b) $\delta = 0.06 \pm 0.02$; c) $\delta = 0.08 \pm 0.01$; d) $\delta = 0.1 \pm 0.01$.

contact method. The hydrostatic pressure was produced in a chamber of the "piston–cylinder" type whose construction and procedure of producing and measuring the pressure are described in Ref. 7. The metal insulator transition temperature was determined in all cases from the maximum of the logarithmic derivative of the resistance $d \ln R/d(1/T)$. It was shown earlier that the value of T_p determined in this manner agrees well with the temperature at which the paramagnetic part of the susceptibility vanishes.

Figure 1 shows plots of the transition temperature and of the conductivity of the complexes vs δ. An interesting feature of these plots are the jumplike changes of T_p and of the conductivity of the metallic phase at one and the same value $\delta = 0.06$.

The pressure dependence of T_p for complexes of different composition is shown in Fig. 2. For the nonstoichiometric compound with $\delta = 0.06$ (Fig. 2b), T_p has a smooth and slightly drooping pressure dependence. The remaining compositions (Figs. 2a,c,d) show a jumplike change of the transition temperature at the corresponding pressure. For the stoichiometric composition (Fig. 2a), T_p decreases and approaches its value for the most nonstoichiometric compositions at $P = 0$, while the transition temperature of the latter increases somewhat (Figs. 2c,d).

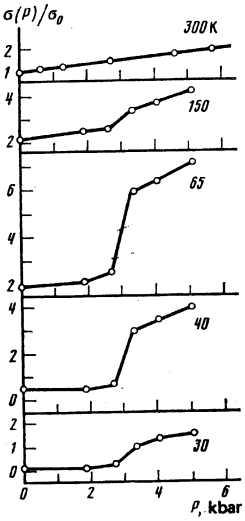

FIG. 3. Pressure dependence of conductivity of $TTT_2I_{3.01}$ crystals at various temperatures.

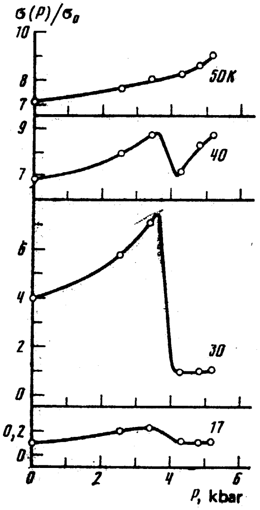

FIG. 4. Pressure dependence of the conductivity for $TTT_2I_{3.08}$ crystals at various temperatures.

Figures 3, 4, and 5 show plots of the conductivity vs pressure for $TTT_2I_{3+\delta}$ complexes with different δ at different temperatures. It is seen from these figures that at the same pressures at which an abrupt change takes place in the transition temperature (see Fig. 2) there is also a jumplike change of the conductivity of the complexes (Figs. 3 and 4). These conductivity jumps are largest near the metal–insulator transition. For a stoichiometric complex with δ close to zero, for which the transition temperature decreases at a pressure ~3 kbar (Fig. 2a), the conductivity increases (Fig. 3). For the nonstoichiometric complex with $\delta = 0.08$, for which the transition temperature increases in the 4-kbar region (Fig. 2c) the conductivity decreases (Fig. 4). The conductivity of the most nonstoichiometric complex with $\delta = 0.1$ behaves similarly. On the other hand, the conductivity undergoes no jumps (Fig. 5) for the complex with $\delta = 0.06$, for which the transition temperature has a smooth pressure dependence (Fig. 3b).

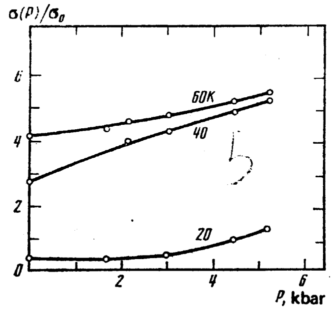

FIG. 5. Pressure dependence of the conductivity for $TTT_2I_{3.06}$ crystals at various temperatures.

3. DISCUSSION

The main peculiarity of the behavior of $TTT_2I_{3+\delta}$, as seen from the foregoing, is that the metal–dielectric transition temperature changes jumpwise both when the iodine concentration changes and when the pressure increases. This leads in turn to a jumplike change of the conductivity of the metallic phase in the corresponding region of concentrations and pressures. We start with a discussion of the concentration dependence of T_p.

A change in the iodine concentration produces, first, a change in the degree of filling of the bands of the conducting TTT chains and, second, a disorder[1] due to the loss of correlation in the arrangement of the iodine chains along the *c* axis. Low-temperature structure investigations[5] show, however, that this disorder vanishes quite rapidly when the temperature is lowered. It can hardly cause the change in the transition temperature. It is all the more difficult to imagine how an increase of the disorder can lead to a jumplike increase of this temperature.

The most natural assumption is that the cause of the observed effect is the transition, with increasing δ, from a commensurate to an incommensurate value of $2k_F$. It is known that,[8] other conditions being equal, the transition temperature is higher for a commensurate filling of the band, this increase of T_p is particularly appreciable in the case of a half-filled band. If a total transfer of the electrons from the TTT chains to the iodine chains is assumed, than at $\delta = 0$ the conduction bands of $TTT_2I_{3+\delta}$ are 3/4 filled. We have noted in the Introduction, however, that at $\delta = 0$ the period of the iodine chains is $c_I = 2c_{TTT}$, and the presence of this doubled period can lead to effects that are typical of a half-filled band even without a radical change in the character of the energy spectrum in the region of the Fermi energy.

So long as the deviations from commensurability are small and the associate change of the fermi energy $\Delta E_F \ll T_p$, the transition temperature will not change noticeably. At larger δ, however, it should drop jumpwise to its value that is characteristic for an incommensurate filling of the band. Taking $T_p \sim 50$ K and $E_F \approx 5 \times 10^3$ K,[1)] we obtain for the critical value of ΔE_F the estimate $\Delta E_F / E_F \sim 10^{-2}$. Since $\Delta E_F / E_F \approx \Delta k_F / k_F = \delta/3$, this yields a critical concentration $\delta \sim 3 \times 10^{-2}$, precisely within the range of δ with which we are dealing.

The jumplike change of the conductivity of the metallic phase, which take place at the same values of δ, can be explained in the proposed picture by the fact that on going from a commensurate to an incommensurate filling of the band the contribution to the resistance by the electron-electron scattering mechanism decreases. Operating in the same direction might be also the recently popular depinning of the charge-density wave. It is hardly likely that its contribution to the conductivity can manifest itself so far from the transition point.

We turn now to the dependence of the transition temperature and of the conductivity on the pressure. The behavior of $TTT_3I_{3+\delta}$ complexes of varying stoichiometry can be qualitatively understood by assuming that an increase in pressure leads to a decrease of the effective value of $2k_F$, i.e., acts in a direction opposite to the increase of δ. Then, when the pressure is increased, the band filling in a complex of stoichiometric composition becomes incommensurate, the transition temperature is lowered (Fig. 2a) while the conductivity increases (Fig. 3). In complexes with larger nonstoichiometry, conversely, a commensurate band filling sets in when the pressure is increased, the transition temperature is increased (Figs. 2c,d) and the conductivity decreases (Fig. 4). On the other hand, the behavior of the complex with $\delta = 0.06$, for which both the transition temperature and the conductivity experience no jumps (Figs. 2b and 5), can then be attributed to the fact that this complex is somewhere on the right-hand boundary of the commensurability region, and the pressures employed are insufficient to take it out of this region. Figure 6 explains the foregoing schematically.

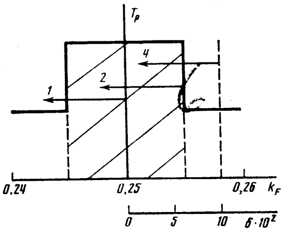

FIG. 6. Schematic dependence of T_p on δ. The region of commensurate values of $2k_F$ is shaded. Raising the pressure shifts the stoichiometric crystal 1 into the incommensurability region and the nonstoichiometric crystal *4* with $\delta = 0.1$ into the commensurability region, but leaves the crystal *2* with δ 0.06 in the commensurate region.

Several mechanisms whereby $2k_F$ changes with pressure are conceivable. One can be realized when the single level of the I_3^- ion spreads out into a band whose upper edge lies above the Fermi level. Then the electron transfer from the TTT chains to the iodine chains is incomplete, and its degree will vary with changing pressure. Another mechanism can be connected with the influence of temperature effects, which can change the effective value of $2k_F$. It is at present not quite clear which of these, if any, is realized. This questions calls therefore for further research.

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[1)] This estimate of E_F can be obtained by assuming that the paramagnetic susceptibility $\chi_p \sim 2 \times 10^{-4}$ cm^3/mol of the complex[1] is the Pauli susceptibility connected with the one-dimensional metallic TTT chains.

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