

Tetraselenotetracene chloride—an organic metal without a metal-dielectric transition

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(Submitted April 14, 1977)

Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 10, 480-484 (20 May 1977)

We report the crystal structure and the main properties of a new organic quasi-one-dimensional metal $(TSeT)_2Cl$. The room-temperature conductivity of the complex is $(2.1 \pm 0.2) \times 10^3 \Omega^{-1} \text{cm}^{-1}$. The complex undergoes a phase transition at 25 K but remains metallic down to infralow temperatures.

PACS numbers: 61.65.+d, 72.15.Eb, 75.30.Cr, 64.70.Kb

1. All the known organic compounds of the quasi-one-dimensional type, which are metallic at high temperatures, sooner or later become dielectrics at low temperatures. The only exception is the complex of TCNQ with HMTSeF, which becomes semimetallic at low temperatures.^[1] We describe in this paper the structure and the main properties of a new compound,^[2] tetraselenotetracene chloride¹⁾ with composition $(TSeT)_2Cl$, which remains in the metallic state down to infralow temperatures.

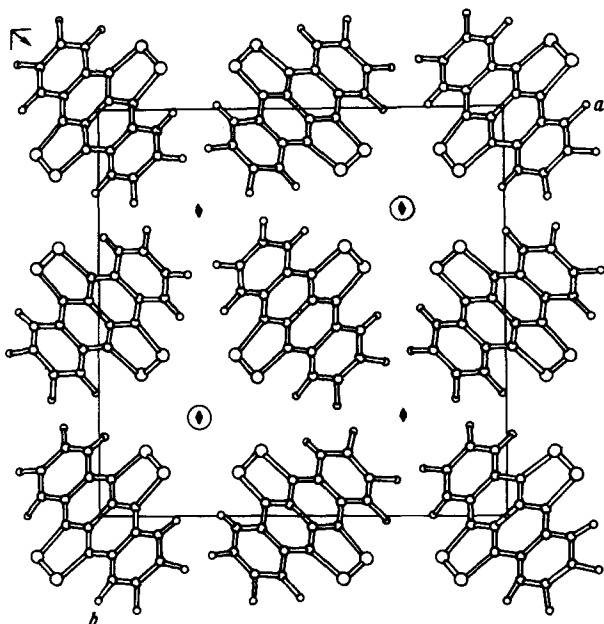


FIG. 1. Projection of the structure of the complex on the ab plane.

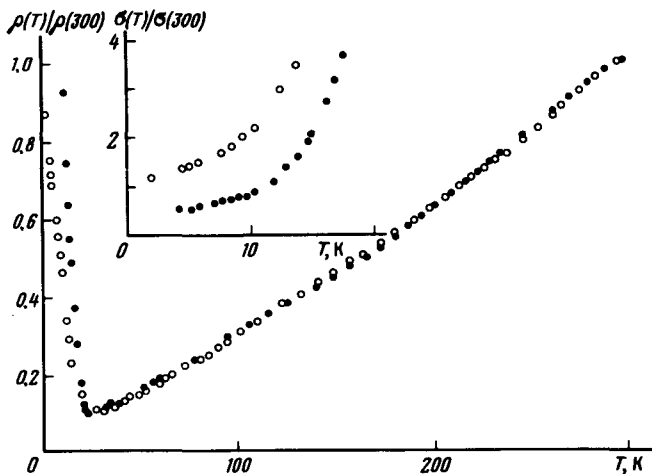


FIG. 2. Temperature dependence of the resistivity along the c axis. The insert shows the behavior of the conductivity of the complex at low temperature.

2. The $(\text{TSeT})_2\text{Cl}$ crystals in the form of black needles up to 3 mm long and up to 30 μm thick were obtained by slowly cooling ($1\text{--}2^\circ\text{C}$ per hour) from 100°C to room temperature a solution of TSeT and the oxidizer FeCl_3 or $\text{N}(\text{CH}_3)_4\text{FeCl}_4$ in dimethylformamide. All the initial substances were carefully purified beforehand.

Figure 1 shows the projection of the crystal structure of the complex on the ab plane. The principal crystallographic data are $a=b=17.444/3/\text{\AA}$, $c=5.118/1/\text{\AA}$, $\gamma=90\pm 0.05^\circ$, $Z=2$, and space group P^2/n . The arrangement of the TSeT molecules corresponds to the space group $P4_2/n$. Introduction of Cl^- ions into the lattice transforms the tetragonal group into monoclinic, with the Cl^- ions situated on twofold axes, while the TSeT I and TSeT II molecules are at the symmetry centers $[100]$ and $[\frac{1}{2}0\frac{1}{2}]$, respectively.

The TSeT—TSeT interplanar distance in the stack is 3.37\AA . The planes of the molecules TSeT I and TSeT II make an angle 41° with the direction of c , and are approximately parallel (angle 9°) to the planes $(22\bar{1})$ and $(2\bar{2}1)$, respectively. The distance between the Cl^- ion and the four Se atoms from the stack surrounding it are shortened and are equal to the sum of the Cl^- ion radius and the covalent radius of Se ($1.85+1.17=3.02 \text{\AA}$).

3. At room temperature, the conductivity of the complex, measured with direct current along the c axis, is $(2.1\pm 0.2)\times 10^3 \Omega^{-1}\text{cm}^{-1}$, and is the highest of the presently known conductivities of organic compounds. Its temperature dependence is shown in Fig. 2. At temperatures above 30 K, the resistivity depends practically linearly on the temperature ($\rho \propto T^{1.06}$) and the difference between the behaviors of different single crystals is small. At 26 K, the conductivity reaches a maximum, increasing by one order of magnitude from room temperature. In the interval 25—10 K, the conductivity decreases abruptly, but its value, as seen from the insert of Fig. 2, tends as $T \rightarrow 0$ to a finite value on the order of the room-temperature value. Measurements performed on a pellet down to 0.1 K have shown that its conductivity ceases to vary below 0.5 K.

$\chi_{\text{para}} \cdot 10^{-4}, \text{cm}^3/\text{mole} (\chi_{\text{para}} - \chi_{\text{imp}}) \cdot 10^{-4}, \text{cm}^3/\text{mole}$

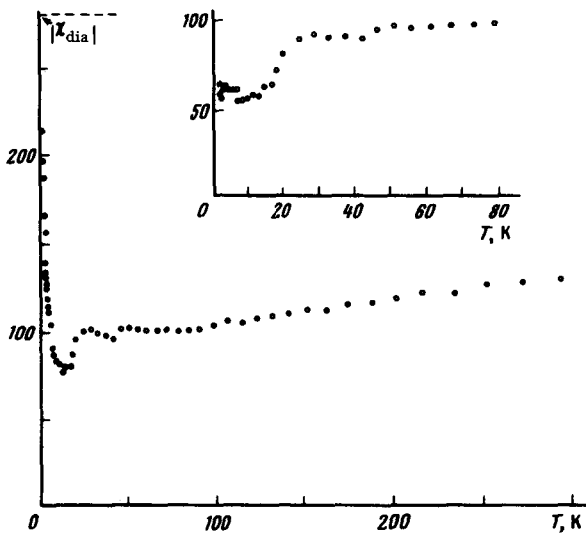


FIG. 3. Temperature dependence of the paramagnetic part of the susceptibility. The insert shows the behavior of the susceptibility obtained after subtracting the impurity Curie contribution. The molar susceptibility is calculated per mole of composition $\text{TSeT} \cdot \text{Cl}_{0.5}$.

4. The temperature dependence of the paramagnetic part of the susceptibility of the complex is shown in Fig. 3. The diamagnetic contribution of the core was calculated in accordance with Pascal's rules. The susceptibility changes little in the interval between 300 and 25 K. Below this temperature, a decrease of the susceptibility sets in, but is broken by a low-temperature tail which is due to the presence of paramagnetic impurities in the sample.

Below 10 K, the variation of the susceptibility is well described by the function C/T , with a constant C corresponding to a content of 7×10^{-4} free spins per molecule. The inside of Fig. 3 shows the behavior of the susceptibility of the complex, obtained after subtracting the Curie contribution. It is seen that the susceptibility remains practically constant above 25 and below 15 K, decreasing in this interval from 10^{-4} to $6 \times 10^{-5} \text{ cm}^3/\text{mole}$. We note that the start of the abrupt decrease of the susceptibility coincides with the temperature of the maximum of the conductivity.

5. The character of the crystal structure of the complex is typically one-dimensional, and in first-order approximation we have a set of equivalent stacks of TSeT molecules, the one-dimensional conduction band of which is 3/4 filled. The presence of shortened contacts between the stacks via the Cl-bridges can lead to a certain bending of the flat Fermi surface, but it can hardly change significantly the one-dimensional character of the electron motion. Assuming the band to be one-dimensional and cosinusoidal, we can use the high-temperature value $\chi = 10^{-4} \text{ cm}^3/\text{mole}$ to estimate the Fermi velocity $v_F = 2\mu_B^2\nu/\pi\hbar\chi$ and the band width $\Delta E = 2\hbar v_F/c \sin k_{FC}$; here μ_B is the Bohr magneton, ν is

the number of filaments per cm^2 , and c is the period along the chain. This yields $v_F = 1.7 \times 10^7$ cm/sec and $\Delta E = 0.6$ eV.

The experimental data indicate that in the region of 25 K the complex undergoes a phase transition from one metallic state to another. One can attempt to understand the character of this transition by noting that the presence of two pairs of nonequivalent stacks of TSeT in the unit cell should lead to a splitting of the initial fourfold degenerate conduction band into two subbands which are slightly shifted in energy and are therefore filled slightly differently. In this situation, the Peierls distortion of the lattice, which leads to formation of a gap at the Fermi momentum of the lower subband, is energywise favored. The upper subband will remain partially filled, and the state of the complex will be metallic, but the number of conducting filaments is decreased by one half. This decreases the susceptibility by an amount that should differ from a factor of two which increasing difference between the carrier densities on the Fermi levels in the initial and final conduction bands.

At the present time it is quite difficult to interpret even qualitatively the kinetic properties of one-dimensional metals. The existence in the interval 25–300 K of a monotonic temperature dependence of the conductivity, and its good reproducibility for different crystals, indicate that in this interval the predominant mechanism that limits the conductivity is due to electron-phonon interaction. This mechanism, however, can hardly reduce to the simple electron-phonon scattering of the usual kinetic theory, since the mean free path $l = \pi \hbar \sigma / 2e^2 \nu$ calculated under this assumption turns out to be unreasonably small (10 \AA at 300 K). The function of the phonons, which should have a sufficiently low frequency to "survive" to 25 K, is more readily to produce a random potential that causes localization of the electrons (cf. [3]).

The phase transition in the region of 25 K changes not only the electron spectrum, but also the phonon spectrum, and this leads apparently to an appreciable change in the mechanism of the electron resistivity. As low temperatures, the behavior of different crystals begins to differ noticeably (see Fig. 3), and this shows that the influence of the impurities becomes substantial.

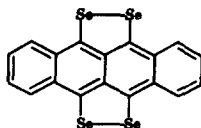
In the strictly one-dimensional case, in the presence of impurities, we have $\sigma \rightarrow 0$ as $T \rightarrow 0$. [4] However, a weak three-dimensionality, which is weaker the fewer the impurities, can apparently make this result incorrect.

We note in conclusion that analogous properties is possessed by the complex $(\text{TSeT})_2\text{Br}$, [2] which is isostructural to the complex $(\text{TSeT})_2\text{Cl}$.

We are grateful to L. P. Gor'kov and A. I. Larkin for useful discussions, and to Yu. S. Karimov and V. A. Merzhanov for help with the measurements.

1)

chemical formula:



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