Lattice disorder effects in the quasi-one-dimensional organic metal $(TSeT)_4Hg_4I_9$

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The thermopower and magnetic susceptibility of the quasi-one-dimensional conductor $(TSeT)_4Hg_4I_9$ are measured. The results show that the weak decrease in conductivity at $T < 100$ K is not due to a Peierls transition but to Anderson localization and transition to the state of a disordered metal. The suppression of the Peierls transition and localization of the electron states at low temperatures are due to a random potential caused by the internal structural disorder in the anion sublattice.

INTRODUCTION

The organic metal iodomercuric tetraselenotetracene $[(TSeT)_4Hg_4I_9]$ is one of the few quasi-one-dimensional organic materials which maintain a high conductivity at low temperatures.[1,2] Together with the tetraselenotetracene halides $(TSeT)_2X$, where X = Cl, Br, I, it makes up a family of quasi-one-dimensional metals having interesting properties.[3,4]

The crystalline structure[2] of $(TSeT)_4Hg_4I_9$, as of many other cation-radical salts of TTT and TSeT, has a markedly one-dimensional character. The cation sublattice consists of regular stacks of the TSeT molecule ordered along the crystalline *c*-axis. There are two types of cation stacks in the structure, distinguished from each other by interplanar TSeT–TSeT distance and by the angle between the plane of the molecule and the stack direction.

An interesting feature of the $(TSeT)_4Hg_4I_9$ structure, not previously found in this class of compounds, is the unusual composition of the anion sublattice. It consists of infinite polymeric chains of $Hg_4I_9^-$ anions distributed between the cation stacks. According to x-ray structure data[1,2] the electronic density peaks corresponding to the mercury and iodine atoms have a diminished intensity which indicates the presence of a certain degree of disorder in the anion sublattice.

Besides the strongly contracted Se–Se distances in the cation stacks the sequence of Se–I–Se interatomic separations is also substantially shortened—the iodine atoms, protruding from the central framework of the anionic array, link each pair of TSeT molecules from neighboring cation chains. Thus, some degree of transverse interaction along the *b*-direction is to be expected.

The conductivity[1,2] of $(TSeT)_4Hg_4I_9$ at high temperatures has a metallic character and is equal to 1000 ohm^{-1} cm^{-1} at $T = 300$ K. As the temperature is lowered it increases, reaching a maximum in the region of 100 K, and then slowly decreases, remaining finite (of the order of room-temperature magnitude) at liquid-helium temperatures. A similar behavior of the conductivity in the $(TSeT)_2X$ salts is connected with a Peierls-type metal-semimetal phase transition, leading to partial insulating behavior of the Fermi surface.

The nature of the low-temperature decrease in the conductivity of $(TSeT)_4Hg_4I_9$ is of theoretical interest, since it has been supposed[2] that the rigid polymeric anion array $(Hg_4I_9^-)_n$ entering into the structure of the complex should inhibit the Peierls transition usually occurring in quasi-one-dimensional materials.

In the present work it is demonstrated by measurement of the thermopower and the magnetic susceptibility that the weak decrease in the conductivity of $(TSeT)_4Hg_4I_9$ for $T < 100$ K is not related to a Peierls transition, but is caused by Anderson localization and the transition to a disordered metallic state.

EXPERIMENTAL RESULTS

Magnetic susceptibility was measured in the 1.5–400 K temperature interval by the Faraday method. Sample mass was 30–50 mg. A small ferromagnetic contribution due to impurities was subtracted from the measured susceptibility; this was determined by the $\chi(1/H)$ dependence for several temperatures and corresponds to a concentration in the sample of 50 ppm iron. A diamagnetic contribution from the closed electronic shells, determined by the Pascal laws and equal to -4.26×10^{-4} $cm^3 . mol^{-1}$, was also taken out (all values are expressed per mole of $TSeTHgI_{2.25}$). The behavior of the paramagnetic part of the susceptibility remaining after subtraction of these contributions is shown in Figure 1. At high temperatures the susceptibility is constant, in keep-

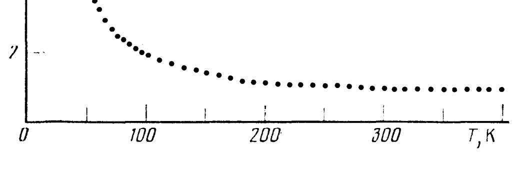

FIG. 1. Temperature dependence of the paramagnetic susceptibility (per mole of $TSeTHgI_{2.25}$).

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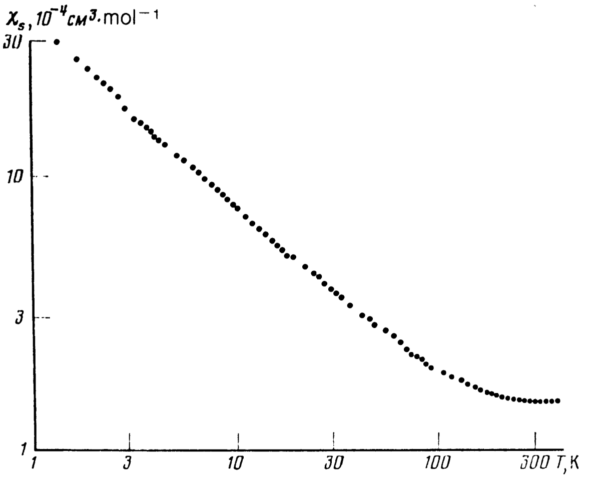

FIG. 2. The data of Fig. 1 in log-log coordinates. For $T < 100$ K the dependence is $\chi_s \propto T^{-\alpha}$, $\alpha = 0.65 \pm 0.01$.

ing with the metallic state of the complex. Below 200 K the susceptibility starts to grow monotonically. This increase is quite reproducible from sample to sample and therefore cannot be explained by the presence of paramagnetic impurities. In Figure 2 the temperature dependence of the susceptibility is shown in log-log coordinates. As is evident from the figure, the low-temperature growth of the susceptibility for $T < 100$ K is described by a straight line in these coordinates, which signifies $\chi_s \propto T^{-\alpha}$, $\alpha = 0.65 \pm 0.01$.

The thermopower was measured on single-crystal specimens of approximately $0.05 \times 0.05 \times 1.5$ mm^3 in the temperature interval from 4.2–350 K. In the temperature dependence of the thermopower (Figure 3) there are three distinct regions. For $T > 200$ K the thermopower depends linearly on temperature, reaching a value of $+27\,\mu$V/K for $T = 300$ K. With a decrease in temperature the linear relation smoothly changes to a $S \propto T^{1/2}$ dependence, which, as seen in Figure 3, holds well in the range of 25–170 K. Below 20 K the thermopower is almost independent of temperature and small. In this region a small variation in the behavior of different samples is seen (in Figure 3 the behavior of one typical sample is shown).

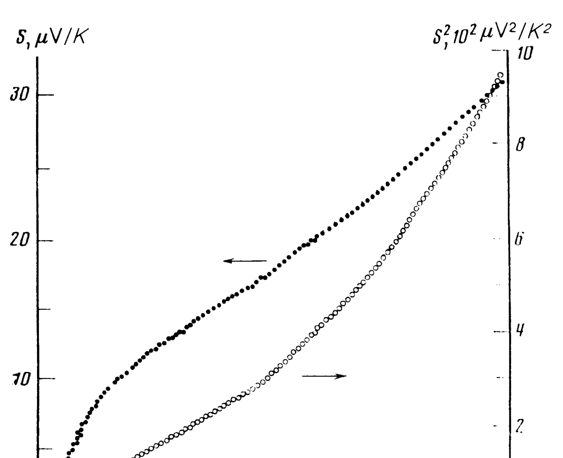

FIG. 3. Temperature dependence of the absolute thermopower. The $S^2(T)$ curve illustrates the square-root dependence of the thermopower on temperature in the interval 25–170 K.

DISCUSSION

The results shown first of all confirm that for high temperatures $(\mathrm{TSeT})_4\mathrm{Hg}_4\mathrm{I}_9$ is in the metallic state. The temperature-independent Pauli paramagnetism of the conduction electrons and the linear temperature dependence of the thermopower are in accordance with the large metallic-type conductivity.

When the temperature is reduced the conductivity of $(\mathrm{TSeT})_4\mathrm{Hg}_4\mathrm{I}_9$ goes through a maximum. A similar conductivity maximum is often observed in quasi-one-dimensional organic conductors and is connected usually with a metal-insulator phase transition, with formation of a charge-density wave (Peierls transition), as, for example, in TTF–TCNQ and similar compounds,[5] or with formation of a spin-density wave, as in the Bechgaard salts[5] $(\mathrm{TMTSF})_2\chi$. In the $(\mathrm{TSeT})_2\chi$ family it is tied to a Peierls-type metal-semimetal transition.[3] In the majority of cases the drop in conductivity below the temperature of the maximum is brought on by the formation of a gap in the spectrum of one-electron excitations and is accompanied by a sharp drop in the magnetic susceptibility and by the onset of an activated increase in the thermopower.

In $(\mathrm{TSeT})_4\mathrm{Hg}_4\mathrm{I}_9$ the susceptibility in the region of the conductivity maximum does not undergo a drop, which indicates the absence of a metal-insulator or metal-semimetal transition. The behavior of the thermopower of $(\mathrm{TSeT})_4\mathrm{Hg}_4\mathrm{I}_9$ in this interval and for lower temperatures is described by a square-root law. Such a temperature dependence for the thermopower is evidence of a finite density of states at the Fermi level and is typical for a disordered material with a conductivity mechanism involving variable-range hopping among localized states.[6] This conclusion is confirmed by the temperature dependence of the conductivity, which is shown in Figure 4 as ln σ versus $T^{-1/4}$ (data of Reference 1). In these coordinates the temperature dependence of the conductivity has a linear portion in the 20–70 K interval. This corresponds to a dependence of the form

$$\sigma=\sigma_0 \exp[-(T_0/T)^{1/4}], \qquad (1)$$

found by Mott for variable-range hopping.[6]

The low-temperature growth in the susceptibility ac-

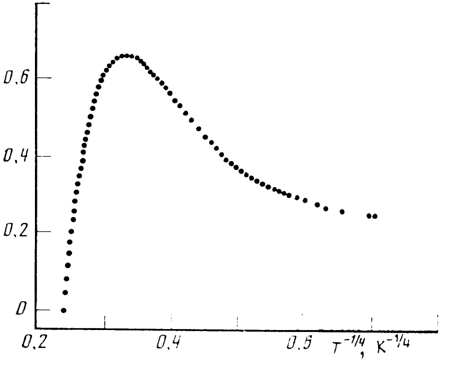

FIG. 4. Temperature dependence of the conductivity (from the data of Reference 1). The linear portion follows Mott's law in the 20–70 K region.

cording to a fractional power law also confirms the essential role of disorder in $(TSeT)_4Hg_4I_9$. The analogous behavior of the susceptibility is observed in quasi-one-dimensional organic conductors with a different type of disorder: in complexes of TCNQ with asymmetric cations,[7] in irradiated samples of TTF–TCNQ,[8] and in $(TMTSeF)_2BrO_4$ compounds,[9,10] in which long-range order of the anions is absent. In $(TSeT)_4Hg_4I_9$ the source of disorder is the polymeric anionic chain. In spite of the fact that the cation stacks themselves are fully ordered, localization of the conduction electrons on them can arise due to the random potential created by electrostatic interaction with the anionic chain and by the shortened intermolecular Se–I–Se contacts.

Thus, the available data demonstrate that disorder in the anion sublattice leads to Anderson localization in $(TSeT)_4Hg_4I_9$ at low temperatures and to a variable-range-hopping conductivity.

We now attempt to estimate from the high-temperature data on thermopower and susceptibility the quantitative characteristics of the $(TSeT)_4Hg_4I_9$ energy spectrum. Since the unit cell contains 16 TSeT molecules, a detailed band-structure calculation is rather complicated. However, if we take into account the quite one-dimensional structure and the regularity of the TSeT stacks, we can arrive at a better approximation by taking the cation stacks to be independent. In this case we can apply simple formulae valid for the strictly one-dimensional case.

The thermopower of a one-dimensional metal in the strong-coupling approximation, for the case of an energy-independent relaxation time, is given by the formula[11]

$$S=\frac{2\pi^2}{3}\frac{k}{e}\frac{kT}{W}\frac{\cos(\pi\rho/2)}{\sin^2(\pi\rho/2)}, \tag{2}$$

where W is the bandwidth and ρ is the number of electrons per lattice unit. If the two types of cation stacks were identical they would have $\rho = 1.75$ (the anion Hg_4I_9 has charge -1). In this case we get from the high-temperature value of the thermopower in formula (2) $W = 3.4$ eV, which significantly exceeds the bandwidth in known organic metals (the maximum value is ~ 1 eV). Much more plausible is the assumption that one of the stacks has $\rho_1 = 1.5$ (which is generally typical of organic metals based on cation-radical salts) and the other is inert ($\rho_2 = 2$) and does not contribute to the conductivity. In this case we find the value $W_1 = 0.8$ eV for the bandwidth of the first type of stack. This is a completely reasonable value and is rather close to the corresponding figure for $(TSeT)_2\chi$ and $(TMTSeF)_2\chi$. It is obvious that the observed value of the thermopower would be very little changed if the second type of chain had a small charge and did not make a large contribution to the conductivity.

Assuming that $\rho_1 = 1.5$ and $\rho_2 = 2$, we find the value $W_2 = 0.4$ eV from the high-temperature paramagnetic susceptibility according to the value for a one-dimensional metal.[12] However, this is admittedly less accurate, as the possible existence of some charge on the second type of chains will lead to an additional term in the susceptibility.

We now examine the possible reasons for the suppression of the Peierls transition in $(TSeT)_4Hg_4I_9$. The authors of Ref. 2 proposed that the incorporation of the rigid polymeric anion chain into the structure could lower the transition temperature and, possible suppress it completely. In fact, an increase in lattice stiffness is equivalent to a decrease in the electron-phonon coupling constant λ and an exponential decrease of the critical temperature for the Peierls transition[13]:

$$T_P \sim T_F e^{-1/\lambda}, \tag{3}$$

where T_F is the Fermi temperature.

In the case of $(TSeT)_4Hg_4I_9$ we must take into account as well other factors which inhibit the Peierls transition. Undoubtedly, the transverse interactions between cation stacks weaken the tendency towards a Peierls instability. The presence of two types of cation stacks in the structure, in the case where both types participate in the conductivity, should cause competition between Peierls distortions with two different wave vectors, which could also inhibit the Peierls transition. **However, the principal reason for the suppression of the Peierls transition in $(TSeT)_4Hg_4I_9$ is the presence of lattice disorder. Analysis of a series of exactly soluble models within the molecular-field framework[13] has shown that the introduction into the lattice of various types of disorder lowers the Peierls transition temperature and, past a certain level, suppresses it completely.** A convenient criterion for comparison of different models of the suppression of the Peierls transition[13] is the electron localization length L, equal in the one-dimensional case for weak localization to twice the mean free path[14] l. Independent of the type of disorder, the Peierls transition is still possible if the localization length exceeds a critical value[13]:

$$L_c = cW/2kT_{P0}, \tag{4}$$

where c is the lattice constant and T_{P0} is the Peierls transition temperature in the absence of disorder. Taking for $(TSeT)_4Hg_4I_9$ a value of $W = 0.8$ eV for the bandwidth, and considering the upper limit for T_{P0} to have the value 100 K (the temperature of the conductivity maximum), we find the lower limit of L_c to be $L_c = 50c$. The magnitude of the mean free path can be found from the conductivity, which in the one-dimensional case from one-electron band theory is given by the simple formula[15]

$$\delta = 2e^2 l/\pi\hbar A, \tag{5}$$

where A is the cross-sectional area of a single conducting chain. Assuming[1] $\sigma(100\ \mathrm{K}) = 2\times10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$, and taking for A the cross-sectional area of one TSeT chain, we get $L = 2l = 25$ Å, or 5 repeat units of the cation sublattice. The resulting localization length is ten times less than the critical value for which the Peierls transition can occur. This means that the existing disorder in $(TSeT)_4Hg_4I_9$ is sufficient to suppress the Peierls transition.

Thus, the results of the present work demonstrate that disorder in the crystal lattice of $(TSeT)_4Hg_4I_9$ plays an essential role at low temperatures. However, it is necessary to point out the important qualitative difference in the behavior of $(TSeT)_4Hg_4I_9$ and other well-known quasi-one-dimensional disordered conductors, such as the salts of TCNQ having intrinsic structural disorder[7] or the Bechgaard salt[10] $(TMTSeF)_2BrO_4$, which are insulators at low temperatures. In contrast to these, $(TSeT)_4Hg_4I_9$ maintains a high conductivity all the way to 0.4 K.[1] In the region of temperatures $T < 20$ K, the conductivity decrease slows as temperature is reduced, while the thermopower deviates from its square-root dependence. Such behavior signifies a change in the conduction mechanism of $(TSeT)_4Hg_4I_9$ in this temperature region and is not completely understood. It is obvious that the conductivity in the region of very low temperatures proceeds by means of delocalized charge carriers (an indication of this near $10^3\ \Omega^{-1}\ cm^{-1}$, is the high, almost temperature-independent conductivity and the near-zero thermopower). In addition to this, the fractional-power growth of the magnetic susceptibility, continuing to 1.5 K, obviously takes place due to localized interacting spins.[7,8] The presence of two types of cation stacks in $(TSeT)_4Hg_4I_9$ permits us to explain such unusual behavior without contradiction. We must assume that at low temperatures the electrons on one type of stack are localized and make the principal contribution to the susceptibility, while on the stacks of the other type they are delocalized and provide a high metallic conductivity. The possibility that such a unique situation exists is very interesting and needs complete experimental confirmation.

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