Low-temperature heat capacity of the quasi-one-dimensional organic metal $(TseT)_2Br$

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The heat capacity of the organic metal $(TSeT)_2Br$ is measured at temperatures between 1.8 and 7 K and between 16 and 40 K. A phase transition is observed at $T = 26$ K and is attributed to a change in the electron structure of the complex. The presence of the linear term in the expression for the heat capacity at low temperatures may point to the existence of a metallic or semimetallic electron system below the phase-transition point. An anomalously low Debye temperature is observed at 33 K.

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INTRODUCTION

The synthesis, structure, and certain properties of the organic high-conductivity complex $(TSeT)_2Br$ are described in Refs. 1 and 2. The structure of the complex is typical of quasi-one-dimensional organic metals. The projection of the unit cell of the crystal structure on the a–b plane is shown in Fig. 1 (Ref. 3).[1] The complete structure of the complex can be made up by translating this cell periodically a distance equal to the parameter c along an axis perpendicular to the plane of the figure. The TSeT molecules in the crystal form regular stacks directed along the c axis, and the interplanar distances between two neighboring molecules in the stack are shortened compared with the van der Waals radius. In the channels between the TSeT stacks are located bromine atoms. An analysis of the crystal structure shows that in the investigated compound there are four crystallographically independent TSeT molecules and two bromine atoms per unit cell.

We note an interesting property of this structure.[3] The distances between the selenium atoms of the neighboring stacks along the Se–Br–Se direction are greatly shortened in comparison with the sum of the van der Waals radii and approach the sum of the covalent radius of the selenium and of the ion radius of the bromine. This geometrical peculiarity of the crystal structure can disrupt to a certain degree the quasi-one-dimensionality of the electron system of the complex, increasing the transverse transport of carriers between stacks. This small effective three-dimensionalization of the system is apparently the most probable cause of the existence of new interesting properties of the isostructural complexes $(TSeT)_2Br$ and $(TSeT)_2Cl$, so that these substances, and several others,[1-5] can be treated as a new class of organic metals.

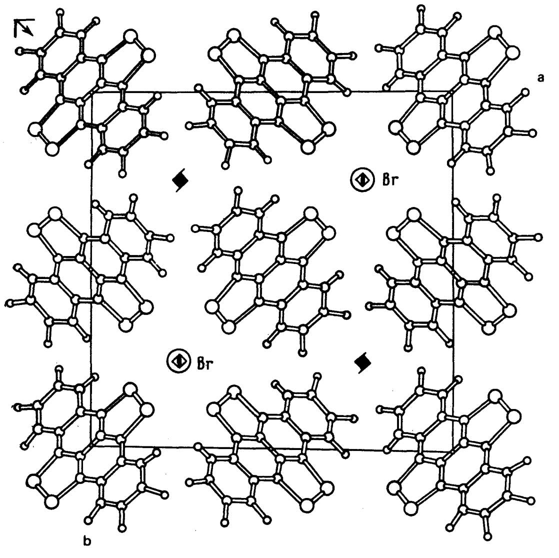

FIG. 1. Projection of unit cell of the crystal structure of $(TSeT)_2Br$ on the a–b plane.

The most important property of all the substances of this class is the absence of the complete dielectrization, typical of organic quasi-one-dimensional metals, of the electronic system of the complex when the temperature is lowered. Thus, the electroconductivity of $(TSeT)_2Br$ first increases when the temperature is lowered from room temperature, and then at $T = 34$ K it goes through a maximum and decreases quite rapidly to the room-temperature value, becoming practically constant at the lowest temperatures.[1]

The paramagnetic part of the susceptibility of the complex[2] changes little when the temperature is lowered in a wide range of temperatures, from room temperature to approximately 50 K, then decreases quite rapidly near $T = 30$ K, and tends to a finite constant value at lower temperatures. An analysis of the behavior of the conductivity and of the paramagnetic susceptibility indicates that in the absence of ordinary total dielectrization of the substance certain changes still take place in the electron system of the complex. The present paper is devoted to a study of the character of these changes and of the state of the electron and phonon systems of the complex at low temperatures, by measuring the temperature dependence of the heat capacity of the complex in the temperature intervals 1.8–7 K and 16–40 K.

EXPERIMENT AND MEASUREMENT RESULTS

We used for the measurements an adiabatic calorimeter with analog proportional-integral regulation of the temperature of adiabatizing screen of the "shield." The sample was a pressed pellet of single-crystals of the $(TSeT)_2Br$ complex with approximate mass 90 mg, glued with the aid of vacuum grease to a copper substrate, on which were mounted the heater, the resistance thermometer (in this calorimeter we used a carbon resistance thermometer made up of an Allen Bradley radio resistor). For measurements in the region of relatively high temperatures, 20–40 K, where the sensitivity of the carbon thermometer is low, we used a TSPN-2V platinum resistance thermometer taken outside the screen. The differential pickup for the detection of violation of thermal equilibrium between the screen and the calorimeter was an Au + 0.07 at.% Fe-chromel thermocouple.

The measurement of the heat capacity of small masses by the adiabatic method has a number of specific difficulties, which are considered in detail in Ref. 6. In our calorimeter the mass of the investigated material was lower by one order of magnitude than in the preceding variant.[6] Under these conditions, owing to purely technical difficulties, we did not succeed fully in maintaining as large a value of the main parameter of the adiabatic regime, namely the time of establishment of thermal equilibrium between the screen and the calorimeter. The shortening of this time led naturally to a certain lowering of the measurement accuracy. The random error of one measurement increased to 1.5% in the temperature interval 19–40 K and was approximately 10% in the interval 1.8–7 K. With decreasing mass of the investigated substance, as a rule, an increase takes place in the relative fraction of the contribution of the empty calorimeter to the total heat capacity. In our setup this fraction, at the very lowest temperatures, was approximately half the total heat capacity of the calorimeter.

It is seen from the measurement result that the decrease of the accuracy of the experiment is not very significant. On the other hand, the decrease of the mass of the investigated material to a value of the order of 100 mg has made it possible to use the result of one working synthesis of the organic metal and to avoid the laborious preparation of material for the sole purpose of measuring the heat capacity.

The results of the measurements of the heat capacity of $(TSeT)_2Br$ complex in the temperature interval 1.7–7 K are shown in Fig. 2. The measurement unit was the quantity Nk, where N is the number of elementary crystallographic cells in the entire sample and k is Boltzmann's constant. This scale corresponds to the heat capacity per unit cell, expressed in units of k. To separate the contribution of the electronic system and of the lattice vibrations, the traditional coordinates C/T and T^2 are used. It is seen from Fig. 2 that the heat capacity of the crystal, plotted in these coordinates, is well described at the lowest temperatures by the linear relation

$$C=\gamma T+\beta T^3, \tag{1}$$

and at $T \gtrsim 6$ K the experimental points deviate systematically downward from the straight line. Therefore, to choose the best line it is necessary to impose an upper limit on the temperature interval in which the measurement results are linearly interpolated. For the data shown in Fig. 2, the line was drawn b- least squares at temperatures lower than 5 K. The parameters γ and β are respectively $0.012 \pm 0.008\ Nk/K$ and $(0.66 \pm 0.05)10^{-2} Nk/K^3$. Figure 3 shows the measurements of the temperature dependence of the heat capacity of the complex and the temperature interval 18–36 K, in which the change of the metallic state of the complex is most probable. It is seen from the figure that near the temperature 26 K there the heat capacity exhibits a rather abrupt irregular behavior, which can be interpreted as a jump. The magnitude of the effect is approximately 4.5% of the total value of the heat capacity at this temperature, much higher than the limit

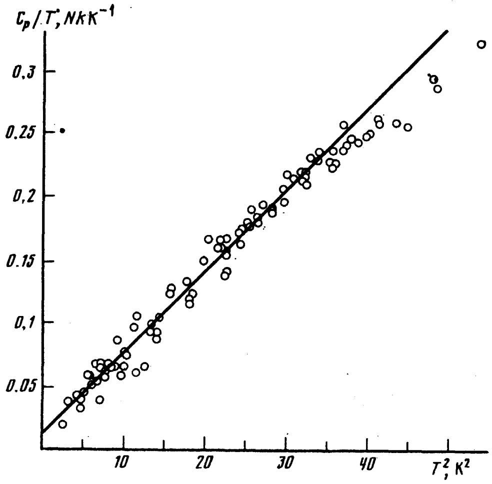

FIG. 2. Behavior of the heat capacity of the complex $(TSeT)_2Br$ in the temperature range 1.8–7 K, plotted in the coordinates C/T and T^2. The line is drawn by least squares in the interval 1.8–5.0 K.

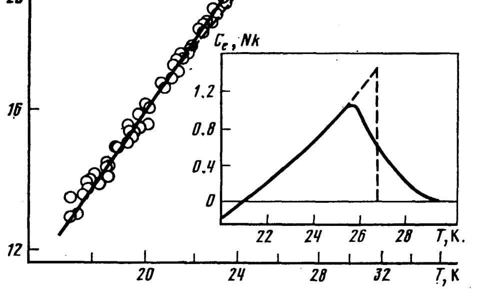

FIG. 3. Behavior of the heat capacity in the phase-transition region. The dashed line corresponds to the regular part. Inset: heat capacity near the transition after subtracting the regular part.

0.2% of the mean standard deviation from the smooth curve. Separation of the regular part of the heat capacity is a very difficult task, since we do not know the behavior of the lattice heat capacity in this temperature interval. To subtract the background we choose a temperature dependence corresponding, in a logarithmic scale, to a straight line that describes the high-temperature part of the experimental data (dashed line in Fig. 3). The results of such a subtraction are shown in the inset of Fig. 3. Approximating the obtained curve by a ramp function, as proposed in Ref. 7, we obtain for the jump an estimate $\Delta C = 1.6\,Nk$. We call attention to the difference between the scales of the heat capacity in Ref. 2 and in the present paper. The unit of measurement of the amount of matter in Ref. 2 was chosen to be the formal molecule $(\mathrm{TSeT})\mathrm{Br}_{0.5}$, while we used the crystallographic unit cell known from x-ray data, which corresponds to the formula $(\mathrm{TSeT})_4\mathrm{Br}_2$. The reasons for this choice will be discussed below.

DISCUSSION

It is natural to represent the total heat capacity of the crystal as a sum of the heat capacities of the lattice and of the electron system. The experimental data show that the behavior of the heat capacity in the temperature interval 1.8–7 K is well described by a sum of two terms with linear and cubic temperature dependences. The linear term can be interpreted as the heat capacity of the metallic system of the electrons. The existence of such a system at low temperatures in $(\mathrm{TSeT})_2\mathrm{Br}$ crystals can be expected on the basis of the analysis of the measurements of the conductivity and of the paramagnetic susceptibility.[1,2] The heat capacity of the metallic system of the noninteracting electrons is described at low temperatures by the known expression

$$C_e=\gamma T={}^1/_3\pi^2 N_e k g(\varepsilon_F)\,kT, \tag{2}$$

where N_e is the number of the carriers and $g(\varepsilon_F)$ is the state density on the Fermi level. If the paramagnetic susceptibility of the complex at low temperatures is regarded as the Pauli paramagnetism of the carriers

$$\chi_{\mathrm{para}}=N_e\mu_0^2 g(\varepsilon_F) \tag{3}$$

(μ_0 is the Bohr magneton), we can estimate from the susceptibility data[2] the coefficient γ of the linear term of the electronic heat capacity and compare it with the measured value. In this comparison, the coefficients agree within the limits of the mutual accuracy of the measurements, and this may be evidence of the existence of a system of electrons of metallic or semimetallic type at low temperatures.

The total heat capacity of the lattice can be represented as the sum of contributions from acoustic and optical phonons. To describe the former we can use the Debye approximation, which leads in the low-temperature limit to the following law:

$$C_D={}^{12}/_5\pi^4 N_D k (T/\Theta_D)^3; \tag{4}$$

N_D is the number of oscillators and Θ_D is the characteristic Debye temperature. The optical phonons can be regarded as oscillations of a set of Einstein oscillators, whose heat capacity at low temperatures is

$$C_E=N_E k(\Theta_E/T)^2\exp(-\Theta_E/T),$$

where Θ_E is the Einstein temperature.

The optical phonons arise only in complicated lattices and correspond to normal vibrations within the unit cell. Usually at helium temperatures the contribution of these degrees of freedom to the heat capacity is not noticeable, in view of their exponentially rapid freezing, since the frequencies of the optical vibrations are as a rule of the order of hundreds of degrees Kelvin. The frequencies of such oscillations in quasi-one-dimensional metals with their complex crystal cells consisting of very heavy organic molecules can be so low that their contribution to the total heat capacity of the crystal may turn out to be noticeable even at low temperatures. In this case, at certain temperatures, the observed increase of the lattice heat capacity with increasing temperature can be faster than the Debye T^3 law. Such an increase was actually observed in the heat capacity of the high-conductivity ion-radical salts $\mathrm{Qn(TCNQ)}_2$, NMP(TCNQ) and TTF(TCNQ).[8-10]

In the results shown in Fig. 2, this effect is missing; with increasing temperature, on the contrary, the experimental points deviate down from the straight line, as is typical of the pure Debye behavior of the heat capacity in that temperature region where the low-temperature approximation (2) no longer works. A similar phenomenon was observed in the behavior of the heat capacity of cation-radical salts $\mathrm{TTFBr}_{0.72}$, $\mathrm{TTFCl}_{0.67}$ and $\mathrm{TTF(SCN)}_{0.57}$ (Ref. 11).

It can be concluded from the presented results that in $(\mathrm{TSeT})_2\mathrm{Br}$, as well as in $\mathrm{TTFBr}_{0.72}$, $\mathrm{TTFCl}_{0.67}$ and $\mathrm{TTF(SCN)}_{0.57}$, in contrast to $\mathrm{Qn(TCNQ)}_2$, NMP(TCNQ) and TTF(TCNQ), there are apparently no optical modes with sufficiently low frequencies. It can be assumed that in ion-radical salts with an anion of the tetracyanquinodimethane type, low frequencies are possessed by optical phonons that correspond to normal vibrations of very massive cation-anion pairs. In cation-radical salts with inorganic anions, such pairs, owing to the low mass of anion, have excessively high energies, and their contribution to the lattice heat capacity at low temperatures is negligible. The validity of this assumption can be verified by direct measurements of the vibrational spectrum of the crystals.

Expression (2) contains the number of acoustic oscillators. Correct allowance for this number, generally speaking, plays an essential role in the determination of such a characteristic of the material as the Debye temperature. In the first studies of the heat capacities of organic metals at low temperatures[8,12,13] they measured as a rule the heat capacity per formal mole of the investigated material. The choice of this mole was in part arbitrary and consequently led to a number N equal to the number of total formal molecules of the complex, which does not necessarily coincide with the number of Debye oscillators. This question was first discussed in Ref. 9, where the authors suggested that in a complex ion-radical salt each cation and anion vibrate independently of each other, and the masses and elasticities of the oscillators are approximately equal. In this approach, the crystal structure is artificially reduced to a simple lattice whose sites are each cation and anion of the complex. In this case, first, it becomes difficult to explain the presence of a contribution of optical phonons to the heat capacity, since there can be no vibrations corresponding to optical phonons in a simple lattice, and second, the number of acoustic oscillators is overestimated.

To take correct account of the number of Debye oscillators it is necessary to assume that the total unit cell takes part as a unit in the acoustic vibrations of the crystal lattice. The composition of the crystallographic unit cell is known as a rule from x-ray structure analysis. Our results for $(TSeT)_2Br$, shown in Fig. 2, are represented in a scale where N is the number of unit cell in the sample, determined by x-ray measurements.[3] We note that the method of determining the number of Debye oscillators, either as proposed in Ref. 9 or per formal mole, leads to a calculated Debye temperature that is wrong by a factor $n^{1/3}$, where n is the number of molecules in the cell. This may turn out to be quite substantial for very complicated lattices. The Debye temperature determined by this method amounts to approximately 33 K for $(TSeT)_2Br$, which is anomalously low even for organic metals. Approximately the same values of the Debye temperatures are obtained for the related cation-radical salts TTT^2I_3 and $TSeT_2I$ (Refs. 14 and 15). Such a low Debye temperature of the crystals can explain in part why the resistance of these substances in the metallic phase depends practically linearly on the temperature. The temperature range of the existence of the metallic phase for these substances lies above 30–40 K. Such temperatures are still quite high for these crystals, the electrons are scattered mainly by phonons with Debye energy and momentum, and the number of such phonons is proportional to the temperature.

The results of the experimental study of the electric and magnetic properties of $(TSeT)_2Br$ show that at ~26 K changes take place in the electronic system of the complex. The heat-capacity measurement data shown in Fig. 3 confirm that these changes actually do take place and have the character of a phase transition. The transition point determined from the heat capacity (26 K) coincides with the interval of the fastest change of the paramagnetic susceptibilities[2] and with the temperature of the maximum of the logarithmic derivative with respect to the reciprocal temperature, if the data of Ref. 1 are used. We note that the phase-transition temperature coincides with the temperature of the maximum of the logarithmic derivative of the resistance also for other organic metals (see, e.g., Refs. 7 and 16). This agreement makes it possible to track the transition by following the behavior of the resistivity. This method of observation has obvious advantages over measurements of the heat capacity, namely, experimental simplicity and the absence of the unknown additive lattice contribution, which as a rule is very large for the heat capacity at temperatures above 4.2 K.

The question of the mechanism of the observed transition is far from trivial. Taking into account the aggregate of the known properties and the quasi-one-dimensional specifics of the investigated system, we can expect this transition to be of the Peierls type. One cannot call this a pure Peierls transition, if only because the complex preserves partially the metallic properties below the transition point. The possibility of such a transition with preservation of the metallic (more readily, semimetallic) properties is indicated in Ref. 17, where the properties of the complex $(TSeT)_2Cl$, which is isostructural to the material investigated in the present study, are analyzed. The cause of the partial stabilization of the metallic phase in the chloride and bromide of TSeT can apparently be the rather substantial three-dimensionality of crystal structure, which can lead to a certain bending of the initially flat Fermi surfaces of ideally one-dimensional strings. In the case of a slightly corrugated Fermi surface, the gap in the electronic states appears only on those sections of the surface which are made congruent by parallel transfer by the vector $2k_F$. In those momentum-space locations where there is no exact equality, pockets with conduction electrons may be produced, and it is these which will determine the properties of the material below the transition point.

A simple theory of the Peierls transition shows that the heat-capacity jump in the transition should be of the order of the entropy of the electronic system at the transition point, i.e.,

$$\Delta C \sim \gamma T_c.$$

The jump can then be estimated from the measured paramagnetic susceptibility, as was done in Ref. 2, or can be obtained from the low-temperature heat-capacity data given in the present paper. A comparison of these estimates with the experimentally measured heat-capacity jump shows that the latter is approximately one order of magnitude larger than the expected effect. We note that a similar discrepancy between a simple theoretical estimate and the experimentally measured heat-capacity jumps can be observed also in Refs. 7, 16, and 18 for the Peierls transition in the organic conductors TTF(TCNQ) and TTT_2I_3. One of the possible causes of this disparity may be the presence of an additional contribution to the heat capacity near the transition point from the fluctuations of the thermodynamic quantities, as is the case, e.g., in critical phenomena. So far, however, no critical behavior of any of the thermodynamic properties of one-dimensional organic metals has been observed in experiment, with the exception of the behavior of the logarithmic derivative of the resistivity of $TTF(TCNQ)_2$ in Ref. 19.

An attempt can be made to take into account the effect of fluctuations on the heat-capacity jump within the framework of the simple theory, as was done in Refs. 7 and 18. In this case the three-dimensional phase-transition point T_c in (6) should be replaced by the Peierls transition temperature in a one-dimensional string, which is four times larger. In Refs. 7 and 18 this approach led to satisfactory quantitative agreement; for our results, the expected value of the jump is as before smaller than the experimentally observed value by an approximate factor 2–2.5. We note that the quantitative agreement described in Refs. 7 and 18 can hardly serve as proof of the validity of the simple model, owing to the very large experimental error in the determination of the jump.

The relatively large jump of the heat capacity in the phase transition can be attributed also to the fact that the transition is of first order close to second, i.e., with small latent heat. It can then be assumed that in experiment we observe near the phase-transition point an infinite heat-capacity increase that is cut off by our measurement procedure. To verify this possibility we have plotted the time dependences of the calorimeter temperature with a pellet of the $(TSeT)_2Br$ complex at a constant heat supply under adiabatic conditions. Within the limits of our experiment no effects connected with the existence of latent heat of the transition, if it exists at all, were noted. At a dissipated power 10^{-5} W, a heating rate 4×10^{-2} K/min, and a thermometer-system sensitivity $\delta T\approx 10^{-3}$ K, the upper bound of the possible latent heat is approximately 15 μJ. This value corresponds to a phase-entropy difference of approximately 0.6 μJ/K. It is of interest to compare this value with the total entropy of the crystal at the transition point. The latter can be obtained by integrating the experimentally known temperature dependence of the heat capacity, cited in the present paper, with account taken of the main result of the Nernst theorem $C(0)=0$. This procedure leads to the value $S(T_c)=4.2$ mJ/K. We see that at the transition point the crystal entropy exceeds by almost four orders of magnitude the upper bound of the possible phase-entropy difference. The entropy of the electron system at the transition point exceeds by two orders the possible phase-entropy difference. Thus, if we assume that the described phase transition is of first order, its latent heat is vanishingly small.

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