Effect of fluctuations on the Peierls transitions in the organic metal (dibenzotetrathiafulvalinium)$_{2.67}$SnCl$_6$ [(DBTTF)$_{2.67}$·SnCl$_6$]

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We have investigated the temperature dependences of the conductivity and of the magnetic susceptibility of the new organic conductor (DBTTF)$_{2.67}$·SnCl$_6$. The conductivity of the single crystals at room temperature is 250–550 Ω^{-1}cm^{-1}. According to the theory of Lee, Rice, and Anderson, a Peierls transition takes place in the system at the temperature $T_P \approx 330$ K, followed by a dip in the state density on the Fermi surface when the temperature is lowered. At $T_{3d} \approx 115$ K, three-dimensional ordering takes place in the system, with formation of an energy gap, with activation energy $E \approx 590$ K. The conductivity activation energy agrees with the activation energy determined from the susceptibility. The ratio of the energy gap $2\Delta(0)$ to the temperature of the Peierls transition is $2\Delta(0)/T_P \approx 3.5$, in accord with the exact calculation within the framework of the molecular field.

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Observation of high conductivity in charge-transfer salts containing tetra-cyanquinodimethan (TCNQ)[1,2] has stimulated great interest in the investigation of the electronic properties of quasi-one-dimensional systems. It can be regarded as established that many interesting properties, in many respects not yet understood, of compounds of this type are the consequence of their crystal structure and of the degree of electron transfer from the donor to the acceptor.[3] Among the most investigated organic metals are salts in which the electron acceptor is TCNQ or its derivatives, and the donors are molecules of tatrathiafulvalene (TTF)[4] or tetrathiatetrazene (TTT)[5] and their derivatives.[6] The conduction in this family of salts is both along the anion and cation stacks. The interpretation of the experimental data for salts in which there are two conducting stacks is quite complicated, since the contribution of these stacks to the physical properties of the system is unknown and the theoretical models used to explain the measurement results are ambiguous.[7] Metal-dielectric transitions, which differ in character from both the Mott transition and the Peierls transition, are possible in these systems.[8] Simpler for the interpretation of the physical properties are the quasi-one-dimensional systems with one conducting stack.[9-12]

We report here on the conductivity and magnetic susceptibility of a new organic metal (DBTTF)$_{2,67}$ · SnCl$_6$, in which the conducting cation-radical stack is made up of molecules of dibenzotetrathiafulvalenium (DBTTF).[13] The complex (DBTTF)$_{2,67}$ · SnCl$_6$ in the form of thin long brittle needles is produced by interaction of DBTTF with an excess of SnCl$_4$ in boiling acetonitryl. A characteristic feature of the structure is the presence of stacks made up of DBTTF molecules and (SnCl$_6$)$^{-2}$ octahedra. The stacks are arranged along the c axis of the crystal, with three units of (SnCl$_6$)^3 and 8 units of DBTTF per period. A projection of the structure of the complex along the stack direction is shown in Fig. 1. The DBTTF molecules are shown here in the central position, although in fact they are slightly rotated relative to one another around a twofold axis. The planes of the DBTTF molecules are parallel to the ab plane and the distances between them along the stack axis are all equal at 3.49 Å. The (DBTTF)$_{2,67}$ · SnCl$_6$ axes belong to tetragonal syngony with unit-cell parameters $a = 14.991$ Å, $b = 14.991$ Å, $c = 27.885$ Å and space group $P42_1c$. The DBTTF molecules of neighboring stacks are separated by at least 4.13 Å the shortest distance between the carbon and sulfur in the DBTTF molecules in neighboring stacks).

According to x-ray structure data, one unit cell along the conduction axis contains 8 units of DBTTF and 3 units of (SnCl$_6$)$^{-2}$, and two electrons go from each anion to the cation stack. It was shown by the nuclear gamma resonance (NGR) method that the investigated complex contains only tetravalent tin atoms, so that the reverse transfer of electrons from (SnCl$_6$)$^{-2}$ to the cation radical is negligibly small. Thus, the conduction in the investigated complex was only along one cation-radical stack, the degree of filling of which is easy to calculate. When the complex is formed, each DBTTF molecule losses on the average 3/4 of an electron. Assuming that the conduction along the DBTTF stack is described by the simple band model with two states per molecule, we have a band filled to 5/8.

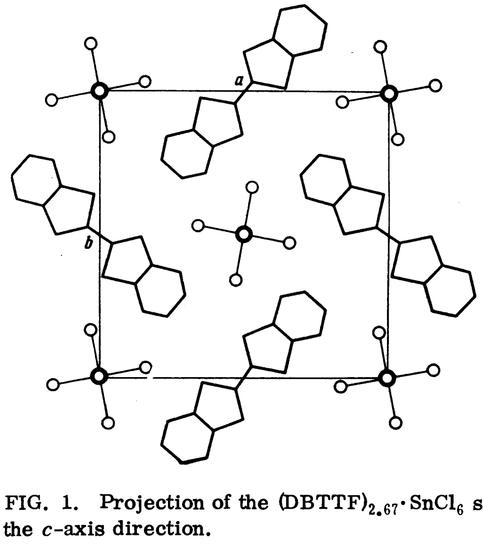

FIG. 1. Projection of the (DBTTF)$_{2.67}$·SnCl$_6$ structure along the c-axis direction.

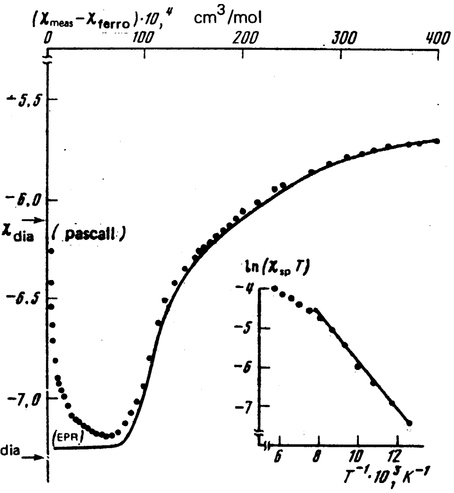

FIG. 2. Temperature dependence of the magnetic susceptibility after subtrating the contribution from the ferromagnetic impurities (points) and from the ferro- and paramagnetic impurties (solid line). Inset—plot of ln $(\chi_{sp}T)$ against T^{-1}.

The magnetic susceptibility χ was measured with a magnetic balance of the Faraday type[14] in the temperature range 1.3–400 K. The points in Fig. 2 show the measured susceptibility after subtracting the ferromagnetic impurities, which were determined from the dependence of χ on the magnetic field. The concentration of these impurities was 8 parts per million. In all the investigated temperature range the susceptibility decreases with decreasing temperature, and only below 60 K does it begin to increase. This low-temperature growth is as a rule typical of all organic high-conductivity salts and is due to the admixture of localized paramagnetic centers or to structure defects. The low-temperature suceptibility varies in accord with the Curie law, $\chi = CT$, with a paramagnetic-center concentration corresponding to 0.13%. The solid line in Fig. 2 shows the measured susceptibility from which the low-temperature contribution has been subtracted. The diamagnetism of the core is determined from the Pascal rule ($\chi_{dia} = -610 \cdot 10^{-6}$ cm^3/mol) and from measurement of the components of the investigated salt ($\chi_{dia} = -650 \cdot 10^{-6}$ cm^3/mol). It can also be determined by extrapolating the low-temperature increase of χ into the region $T^{-1} \rightarrow 0$. This extrapolation, for five measurements on five synthesized batches of $(DBTTF)_{2,67} \cdot SnCl_6$, yielded $\chi_{dia} = -725 \cdot 10^{-6}$ cm^3/mol. This value differs somewhat from the χ_{dia} values obtained above, but lies within the 20% accuracy of the determination of the Pascal constants.

The EPR signal obtained from the single crystals for the investigated complex consists of a single symmetrical line with a width 20 Oe between the peaks of the derivative. The spin susceptibility determined by EPR is $\chi_{sp} = 150 \cdot 10^{-6}$ cm^3/mol at room temperature, yielding $\chi_{dia} = -728 \cdot 10^{-6}$ cm^3/mol.

The conductivity of the crystals, with typical dimensions 4×0.04×0.03 mm, were measured by a four-contact method. The single crystals were glued with graphite paste to the unsecured ends of four gold or platinum wires of 30 μm diameter. This method of fastening the sample makes it relatively easy to glue the contacts to crystals of arbitrary length and remove it from the module should further investigations of the crystal is necessary. Since the $(DBTTF)_{2,67} \cdot SnCl_6$ crystals are very thin, correct measurement of their conductivity in a direction perpendicular to the conducting axis was impossible. However, the conductivity of pressed pellets is smaller by three orders of magnitude than the conductivity along the needle axis. This attests to a strong anisotropic character of the conductivity of the investigated complex.

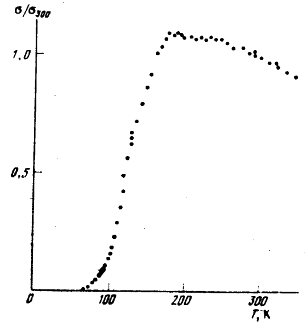

FIG. 3. Conductivity along the c axis for typical $(DBTTF)_{2.67} \cdot SnCl_6$ single crystals as a function of temperature.

The conductivity along the conducting axis c is shown in Fig. 3. In the temperature interval 350–200 K it is metallic and its room-temperature value is 250–550 Ω^{-1}cm^{-1}. Below the temperature T_{max} at which the conductivity reaches its highest value and which ranges for various samples between 180 and 200 K, the conductivity begins to decrease abruptly in accord with the activation law (Fig. 4), with an activation energy 0.05 eV.

Some information on the character of the conductivity can be obtained from the electron mean free path determined within the framework of the simple band model: $\lambda = \sigma\pi\hbar/2e^2S$, where e is the electron charge, σ is the conductivity of the crystal, and S is the number of conducting filaments per square centimeter. At room temperature the value of λ for the salt $(DBTTF)_{2,67} \cdot SnCl_6$ is 1.8–3.96 Å or 0.5–1.14 times the near distance between the DBTTF electrons. For comparison we can cite the electron mean free paths of other well-conducting organic salts with one-dimensional packing of the molecules into stacks. Thus, λ is 2.1–2.8 times the nearest distance for TTT_2I_3,[15], 1.6–2.5 times the distance for HMTSeF-TCNQ (HMTSeF-hexamethylenetetraselenofulvalene),[16] 0.4–0.6

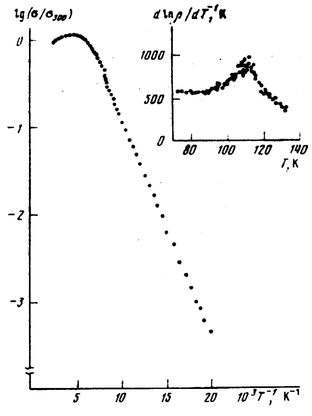

FIG. 4. Logarithmic dependence of the conductivity of the reciprocal temperatures. The inset shows the logarithmic derivative of the resistance as a function of temperature.

the distance for TTF-TCNQ,[17] 0.6 the distance for $K_2Pt(CN)_4 \cdot Br_{0,3} \cdot 3H_2O$,[18] and ~0.15 the distance for $Qn \cdot (TCNQ)_2$ (Qn-quinoline).[19] If we compare these quantities with, say, the mean free path in metallic nickel, namely $\lambda = 60$ Å or 24 nearest distances, it becomes obvious that for most organic conducting salts the concept "metallic conductivity" is quite arbitrary.

In the intermediate temperature region (above 100 K) the plot of $\log(\delta/\sigma_{300})$ against T^{-1} (Fig. 4) derivates from a straight line, thus pointing to a temperature dependence of the activation energy, which tends to zero above 150 K. It can be assumed that in this temperature region the system goes over into a metallic state. The inset in Fig. 4 shows the dependence of the logarithmic derivative of the resistance $d\ \ln(R/R_0/d(T^{-1})$ on T, calculated from the data of Fig. 3 and describing the connection between the conductivity activation energy and the temperature. It is seen from the figure that the logarithmic derivative has a peak at 115 K.

It has been shown[20] that in a large number of quasi-one-dimensional salts in which a metal-insulator transition occurs the position of the temperature corresponding to the maximum conductivity changes substantially from sample to sample, whereas the temperature that characterizes the peak of the logarithmic derivative depends little on the samples. From the data on the specific heat[21] of the TTF-TCNQ salt it follows that the thermodynamic transition coincides with the peak of the logarithmic derivative of the resistance. For the investigated salt $(DBTTF)_{2,67} \cdot SnCl_6$, the maximum of the conductivity of the various samples occurs at temperatures 180–220 K, and the maximum of the logarithmic derivative of the resistance lies in the interval 113–117 K.

From theoretical premises[22] within the framework of the molecular-field model for one-dimensional systems it is known that the activation energy of the conductivity in a Peierls transition is constant at low temperatures and tends to zero with an infinite derivative at the transition temperature (T_P). It has also been shown that the ratio of the gap $2\Delta(0)$ at zero temperature to the transition temperature T_P is constant and its value is $2\Delta(0)/T_P = 3.5$. However, for most salts which are related only by their quasi-one-dimensional packing of the molecules in the crystal, this ratio lies in the interval 8–10 (Ref. 20).

For $(DBTTF)_{2,67} \cdot SnCl_6$ salt, the ratio is $2\Delta(0)/T_P \approx 10$. This discrepancy between the theory and experiment can be understood by taking into account the effect of fluctuations on the Peierls transition.[23] It follows from this consideration that in quasi-one-dimensional systems the temperature of the three-dimensional ordering (T_{3d}) is much lower than the transition temperature (T_P) determined within the framework of the molecular field for isolated one-dimensional chains.

According to Lee, Price, and Anderson,[23] allowance for the fluctuations in a Peierls transition in a quasi-one-dimensional system leads at T_P to a dip in the state density on the Fermi surface. This dip increases with decreasing temperature and becomes appreciable only in the temperature region $T_{3d} \approx 1/4T_P$. An energy gap is formed in this temperature region. At tempertures $T \leqslant T_{3d}$ the correlation length along the stack becomes very large and increases exponentially with decreasing temperature. It is therefore assumed that at T_{3d} three-dimensional ordering of the system sets in and a true energy gap is formed. Information on the appearance of the dip in the state density is obtained by measuring the paramagnetic susceptibility.

It is seen from the temperature dependence of the paramagnetic susceptibility of the salt $(DBTTF)_{2,} \cdot SnCl_6$ (Fig. 2) that at temperatures slightly higher than room temperature this susceptibility tends to a certain constant value. Assuming that in this temperature region the susceptibility is of the Pauli type, we can determine the width dt of the band (t is the transition interval) within the framework of the tight-binding model for the non-interacting electrons. The susceptibility of one conducting chain at zero temperature is then given by[24]

$$\chi_P(0) = \frac{N\mu_B{}^2}{\pi t \sin(^1/_2\pi\rho)},$$

where N is Avogadro's number, μ_B is the Bohr magneton, and ρ is the number of electrons per DBTTF (it equals 5/4). It follows therefore that the width of the band is $4t \approx 0.3$ eV.

With decreasing temperature, the paramagnetic susceptibility begins to decrease, thus attesting to a lowering of the state density on the Fermi surface. In accord with Ref. 23, this decrease is due to the Peierls transition. The solid line in Fig. 5 shows the theoretical plot of the susceptibility against temperature, obtained with account taken of the effect of the fluctuations on the Peierls transition.[23] It is seen that the experimental values fit the theoretical curve quite well. From the superposition of these two curves it follows that the Peierls-transition temperature of the $(DBTTF)_{2,67} \cdot SnCl_6$ salt is $T_P \approx 330$ K. The temperature of the three-dimensional ordering should in this case equal[23] $1/4T_p \approx 85$ K and, according to the theory, the susceptibility should decrease sharply in the temperature region $1/4T_P < T < 1/2T_P$. It is seen from Fig. 2 that the experimental curve drops steeply in the temperature interval 80–160 K.

The activation energy calculated from the susceptibility at low temperatures inset in Fig. 2) is $E_a \approx 630$ K.

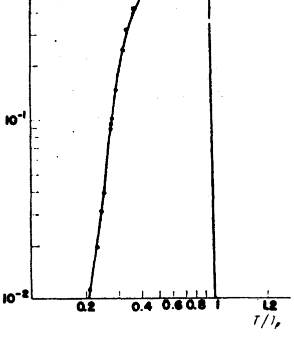

FIG. 5. Measured spin susceptibility (points), and the theoretical Pauli spin susceptibility normalized to the susceptibility in the metallic state as a function of T/T_P.[23]

It should be noted that in accord with the susceptibility data the gap begins to decrease when the temperature rises above $T\approx 116$ K, and it is precisely in this region that the logarithmic derivative of the resistance has a maximum. It was noted above that the activation energy of the conductivity is $E_a\approx 5.90$ K, in good agreement with the susceptibility data. Thus, for the obtained values of the energy gap ($2E_a\approx 1180$ K) and of Peierls transition temperature ($T_P\approx 330$ K) we get $2\Delta(0)/T_P\approx 3.5$, which agrees with the exact calculation within the framework of the molecular field approximation.

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Metamagnetic phase transitions and instability of magnetic structure in rare-earth orthoferrites

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We have investigated the metamagnetic and spin-reorientation transititions that occur in $TbFeO_3$ in an external magnetic field when **H** is parallel to the *a* axis of the crystal and when it is parallel to the *b* axis. We detected anomalies, corresponding to these transitions, on the magnetostriction field-dependence curves (one anomaly for $\mathbf{H}\|a$ and two for $\mathbf{H}\|b$). We estimated the R–R and R–Fe interaction constants in $TbFeO_3$. It is shown that these phase transitions may be regarded as transitions of the Jahn-Teller type.

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1. INTRODUCTION

Certain rare-earth ions (RI) behave, in crystals at low temperatures, like Ising ions; that is, their magnetic moment is directed along a definite crystal axis for arbitrary directions of the field acting on them. Such, for example, are the Dy^{3+}, HO^{3+}, and Tb^{3+} ions in orthoaluminates and orthoferrites.

Metamagnetic transitions in Ising anti-ferromagnets have been investigated in detail[1,2] only in those with a single rare-earth subsystem ($TbAlO_3$, $DyAlO_3$, etc.).