Paramagnetic insulator–metal and metal–superconductor transitions in a quasi-two-dimensional organic complex (BEDT–TTF)$_2$Cu(NCS)$_2$

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The temperature dependences of the resistivity (at 10 GHz and under dc conditions), magnetic susceptibility, thermoelectric power, and resistivity anisotropy were determined for a new organic superconductor (BEDT–TTF)$_2$Cu(NCS)$_2$. An anomalous phase transition took place at $T = 45$ K from a high-temperature paramagnetic Mott–Hubbard insulator to a metallic state.

INTRODUCTION

A family of quasi-two-dimensional bis(ethylenedithiolo)-tetrathiofulvalene (BEDT–TTF) complexes with inorganic anions (BEDT–TTF)$_2$X, which includes organic superconductors with the highest critical temperature,[1] has recently increased by the addition of one further compound. A Japanese team reported synthesis of a (BEDT–TTF)$_2$Cu(NCS) complex which undergoes a transition to the superconducting state at $T_c = 10.4$ K under normal pressure.[2]

This new superconductor, similar to other members of the (BEDT–TTF)$_2$X family, has a quasi-two-dimensional crystal structure.[3] The conducting layer is formed by BEDT–TTF cation radicals bound by shortened intermolecular bonds in the bc plane. The conducting layers alternate along the *a* axis with nonconducting Cu(NCS)$_2$ anion layers bound along the *b* axis to form polymer chains. An unusual feature of (BEDT–TTF)$_2$Cu(NCS)$_2$ is a nonmonotonic temperature dependence of the resistivity.[2]

We shall report the results of a further study of the properties of this compound. An analysis of the temperature dependences of the resistivity at 10 GHz and under dc conditions, and of the magnetic susceptibility, thermoelectric power, and resistivity anisotropy shows that (BEDT–TTF)$_2$Cu(NCS)$_2$ is a high-temperature paramagnetic (Mott–Hubbard) insulator which undergoes an anomalous insulator–metal phase transition as a result of cooling to $T \approx 45$ K.

EXPERIMENTAL RESULTS

Our (BEDT–TTF)$_2$Cu(NCS)$_2$ crystals were prepared by electrochemical oxidation of BEDT–TTF in trichloroethane (2×10^{-3} mol/liter) using direct current and a platinum anode at a constant temperature. The current was varied from one experiment to another between 0.8 and 5.6 μA and the temperature was varied from 0 to 50 °C. Our electrolyte was a complex formed by CuSCN with KSCN or with NH$_4$SCN, prepared directly before the experiments in an electrochemical cell by dissolving CuSCN (5×10^{-3} mol/liter) in the presence of KSCN or NH$_4$SCN and the cyclic ester 18-crown-6 taken in the 1:1:1 ratio.

Irrespective of the values of the current, temperature, and electrolyte composition, in all cases crystals of just one phase, (BEDT–TTF)$_2$Cu(NCS)$_2$, were obtained although their shapes and dimensions differed. The resistivity and thermoelectric power measurements were made on selected single crystals in the form of platelets elongated along the *b* axis and with typical dimensions $2 \times 0.5 \times 0.05$ mm.

The temperature dependence of the electrical resistivity along the *b* axis was determined under dc conditions by the four-contact method (the contacts were bonded to a sample by a graphite paste) and the results are plotted in Fig. 1 (curve 1). The room-temperature resistivity was 0.05 Ω·cm. Cooling first reduced the resistivity slightly (by 5–10%), which reached its minimum value near $T = 270$ K; it then increased up to $T_{\max} \approx 80$–110 K [with the resistivity ratio $\rho(T_{\max})/\rho(300) = 2$–4, depending on the sample] and next fell steeply. This fall could be quite large, amounting to about three orders of magnitude between 90 and 12 K. In the range 12–25 K the resistivity obeyed a dependence of the $\rho = a + bT^2$ type. A superconducting transition occurred at $T_c \approx 9$–10.5 K. The width of this transition was 1 K for the best samples. The higher the maximum in the region of 90 K and the greater the fall of the resistivity between $T_{\max}$ and 12 K, the earlier the superconducting transition and the higher its temperature. Doping of (BEDT–TTF)$_2$Cu(NCS)$_2$ crys-

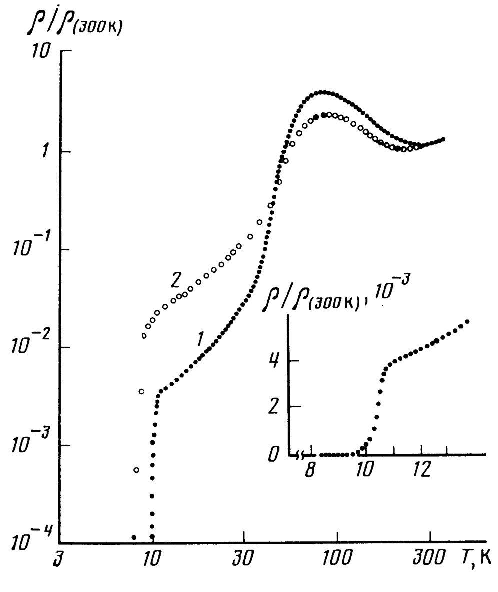

FIG. 1. Temperature dependence of the resistivity plotted using double logarithmic coordinates: 1) direct-current measurements; 2) measurements at 10 GHz. The inset shows the region of the superconducting transition.

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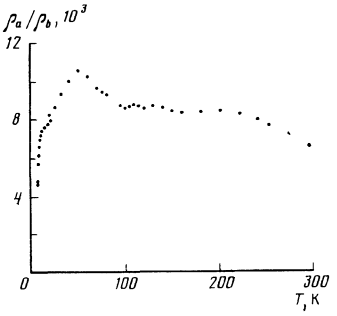

FIG. 2. Temperature dependence of the resistivity anisotropy.

tals with anions (by introducing a small amount of I_3^- or OCN^- anions into the solution during synthesis) reduced strongly the maximum resistivity, broadened the superconducting transition, and reduced its temperature. Detailed results of an investigation of the influence of doping will be published separately.

The temperature dependence of the resistivity along the *b* axis at 10 GHz, measured by a method described in Ref. 4, was somewhat different (curve 2 in Fig. 1). It was obtained for the same sample as curve 1. It is clear from Fig. 1 that although the basic behavior of the resistivity was the same under dc conditions and at 10 GHz, there were some differences and in particular the resistivity maximum was less at 10 GHz. This was true of all the investigated samples.

The resistivity anisotropy was investigated under dc conditions using an improved Montgomery method.[5] At room temperature the resistivity anisotropy was fairly strong and the ratio ρ_a/ρ_b ranged from 3000 to 7000, depending on the sample. At temperatures $T > 50$ K this ratio depended weakly on temperature (Fig. 2), but cooling below ~ 50 K reduced the ratio approximately twofold near the superconducting transition.

The thermoelectric power was measured along the *b* axis employing a method usually applied to organic single crystals. The temperature dependence of the thermoelectric power was determined (Fig. 3). This power was $-8\,\mu$V/K at room temperature, rose smoothly (in the absolute sense) as a result of cooling, reached a maximum at $T = 90$–100 K, and then began to decrease. Near $T = 50$ K there was an inflection in the temperature dependence of the thermoelectric power; below this temperature a further reduction of the thermoelectric power right down to $T \approx 12$ K was a linear function of temperature. The inset in Fig. 3 shows the behavior of the thermoelectric power in the region of the superconducting transition.

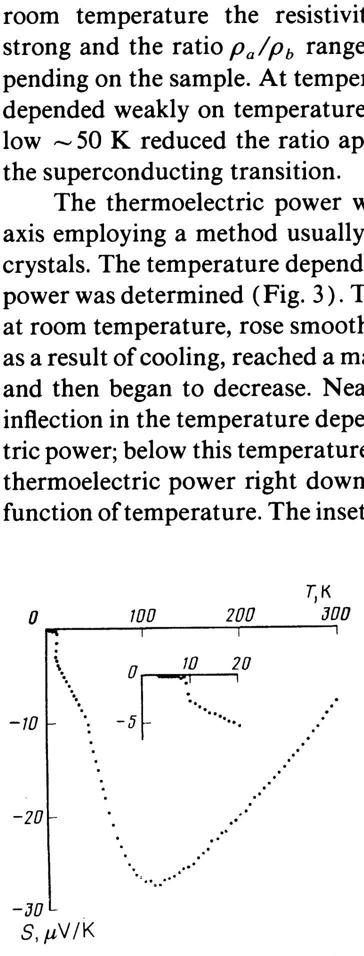

FIG. 3. Temperature dependence of the theromoelectric power. The inset shows the low-temperature parts of the dependence.

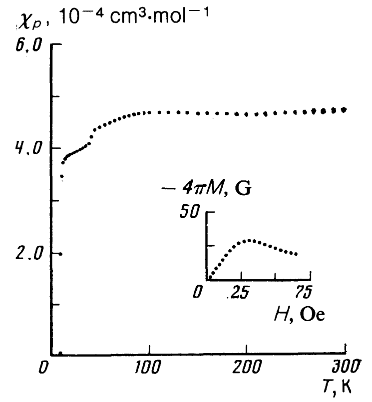

FIG. 4. Temperature dependence of the paramagnetic susceptibility. The inset shows the magnetization curve at $T = 4.2$ K.

The magnetic susceptibility was determined by the Faraday method. A sample was a set of randomly oriented single crystals with a total mass of 20 mg. Figure 4 shows the temperature dependence of the paramagnetic component of the susceptibility determined in a field $H = 8$ kOe. The measured susceptibility was corrected to allow for the diamagnetic contribution of the lattice, -4.56×10^{-4} cm^3 M/mol, determined using the Pascal rules. It is clear from Fig. 4 that at about 100 K the magnetic susceptibility was almost constant. Below 100 K it fell slightly and at $T = 45$ K there was a large (about 10%) jump.

At $T < 11$ K the susceptibility included a considerable diamagnetic contribution associated with the superconductivity. Below 9 K the susceptibility measured in a field of 8 kOe became negative and at $T = 4.2$ K its value reached -1.4×10^{-2} cm^3/mol.

We determined the magnetization curve at 4.2 K between 0 and 200 Oe (inset in Fig. 4). This curve had a maximum at $H = 35$ Oe. In the linear part of the dependence $M(H)$ we found that dM/dH was close to $-1/4\pi$.

DISCUSSION OF RESULTS

We shall first consider the behavior of $(\text{BEDT-TTF})_2\text{Cu(NCS)}_2$ at low temperatures. The temperature dependence of the resistivity (inset in Fig. 1) shows that the superconducting transition in the best samples begins at 11 K and is completed at 9.5 K. The critical temperature, deduced from the middle of the resistive transition region, was 10.5 K. The superconducting transition, deduced from the thermoelectric power, was also complete at 9.5 K, below which the thermoelectric power vanished (as expected for a superconductor).

The magnetic susceptibility and the Meissner effect in $(\text{BEDT-TTF})_2\text{Cu(NCS)}_2$ had already been investigated.[6] Our data indicate that the superconducting transition was manifested more clearly in the magnetic susceptibility than in Ref. 6. The total susceptibility measured in a field of 8 kOe became neqative already at $T < 9$ K (according to Ref. 6, it became negative only below 2 K in a field 30 kOe). At $T = 4.2$ K the slope of the magnetization curve corresponded to total diamagnetic screening, indicating that the transition was of bulk nature and the sample consisted of a single phase. (A study of diamagnetic screening[6] yielded the values 83% at 2 K and 56% at 4.2 K.) The first critical field, deduced from the maximum of the magnetization curve at $T = 4.2$ K, agreed with Ref. 6 and was $H_{c1} = 35$ Oe.

The compound $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ was quasi-two-dimensional and its resistivity anisotropy was strong. It was reported in Ref. 7 that the anisotropy ratio was $\rho_a/\rho_b \approx 600$ at room temperature. Our results indicated that this ratio was even higher, ranging from 3000 to 7000, depending on the sample. Such a discrepancy could indicat also some difference between the quality of the samples (this was probably because of the difference between the methods used to measure the anisotropy).

The paramagnetic susceptibility of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ near T_c could be used to estimate the density of states at the Fermi level, $N(E_F) \approx 7\ \mathrm{eV}^{-1}\cdot\mathrm{spin}^{-1}$ per molecule (without allowance for the exchange enhancement). A similar value of $N(E_F)$ had been reported, for example, for $(\mathrm{BEDT{-}TTF})_2\mathrm{I}_3$ in Ref. 8. On the whole, the behavior of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ at low temperatures was typical of metals and superconductors based on BEDT–TTF: the resistivity obeyed a quadratic law,[9] whereas the thermoelectric power was negative and linear as a function of temperature.

In addition to the record critical temperature of the superconducting transition, the $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ compound was distinguished amongst other organic conductors by an unusual behavior at high temperatures, particularly by the resistivity maximum at $T \approx 90$ K. A maximum of similar type had been reported for $(\mathrm{DMET})_2\mathrm{AuBr}_2$ at $T = 180$ K (Ref. 10) and attributed to a semiconductor–metal transition at this temperature. Moreover, the temperature dependence of the resistivity of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ included also a shallow minimum at $T = 270$ K. It was reported in Ref. 2 that the high-temperature state of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ could be regarded as metallic, the temperature-independent paramagnetic susceptibility was treated as of the Pauli type, and the increase in the resistivity at temperatures $T < 270$ K was attributed to the influence of a disorder in the anion layer. A similar treatment could also account for the difference between the behavior of the resistivity at 10 GHz and under dc conditions observed in our experiments. However, a more detailed x-ray structure investigation[3] demonstrated that there was no disorder at $T = 104$ K in $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$.

We found that both below and above $T_{\min} = 270$ K, namely in the interval 160–400 K, the temperature dependence of the resistivity obeyed well a single relationship $\rho = \rho_0 T^{\alpha} \exp(\Delta/T)$, where $\alpha = 3.3$ and $\Delta = 850$ K. Such a temperature dependence was incompatible with the metallic state and suggested the existence of a gap $2\Delta = 1700$ K in the spectrum of electron excitations (the term T^{α} represents the temperature dependence of the mobility). The paramagnetic susceptibility was found to have a constant and finite value in this range, i.e., the spectrum of spin excitations had no gap. Therefore, we had to assume that the activation energy of the resistivity was due to electron correlation effects, i.e., it was a Mott–Hubbard gap. Such a state of a paramagnetic insulator had been observed in many quasi-one-dimensional organic compounds such as $(\mathrm{TMTTF})_2\mathrm{SCN}$ (Ref. 11). The high-temperature insulator state of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ was also attested to by the behavior of the thermoelectric power which increased in the absolute value as a result of cooling down to 100 K. The proposed behavior is confirmed also by the fact that doping lowers the resistivity maximum, which is difficult to explain by postulating a metallic state at high temperatures.

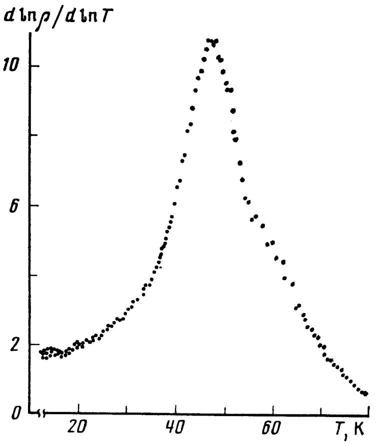

FIG. 5. Temperature dependence of the logarithmic derivative of the resistivity.

Therefore, at temperatures $T \gtrsim 100$ K the compound $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ behaves as a Mott–Hubbard paramagnetic insulator. Below ~ 90 K the behavior of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ changes considerably: the resistance begins to fall, the magnetic susceptibililty also decreases somewhat, and the thermoelectric power approaches zero. Further cooling gives rise to a number of anomalies of the physical properties of $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ in the region of $T = 45$ K. At this point there is an abrupt change in the susceptibility and an inflection in the thermoelectric power. The resistivity anisotropy begins to decrease below 50 K. The most significant anomaly is observed in the logarithmic derivative $d\ln\rho/d\ln T$ of the resistivity (Fig. 5), which has a sharp peak at $T = 47$ K. The results taken as a whole can be regarded as evidence that at this point the compound $(\mathrm{BEDT{-}TTF})_2\mathrm{Cu(NCS)}_2$ undergoes a phase transition. This is a transition from an insulator to a metal and it occurs as a result of cooling. Such a transition is anomalous and is difficult to explain convincingly. It may be a transition of the Mott type and the reason for the appearance of the metallic state at low temperatures may be an increase in the width of the conduction band because of compression of the crystal lattice and a corresponding increase in the overlap integrals. This is a fairly unique situation. It is also possible that the transition is due to purely structural changes. The true cause of this transition cannot be identified without investigations of the low-temperature crystal structure.

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