Anisotropic resistivity and thermopower of the organic superconductor (ET)2Cu[N(CN)2] Br

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Anisotropic resistivity and thermopower of the organic superconductor $(ET)_2Cu\,[N(CN)_2]\,Br$

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Abstract. — We have measured the temperature dependence of the resistivity of $(ET)_2Cu$ $[N(CN)_2]\,Br$ in three crystallographic directions and the thermopower in the **a** and **c** directions. The resistivity has two maxima - at 75 and 95 K. The value of the resistivity anisotropy is rather large: ρ_b/ρ_a is about 10^3 at the ambient temperature and increases with lowering temperature below 50 K. The temperature derivative of resistivity exhibits a strong maximum at 50 K. Thermopower is positive for the **a** direction, while it is negative for the **c** direction. We have concluded, that $(ET)_2Cu\,[N(CN)_2]\,Br$ undergoes insulator-metal transition near 50 K similarly to $(ET)_2Cu(NCS)_2$.

1. Introduction.

At present, the organic compound $(ET)_2Cu\,[N(CN)_2]\,Br$ [1] has the highest $T_c(\approx 12\ K)$ at ambient pressure among ET-based organic superconductors. Besides its prominent superconducting transition temperature, $(ET)_2Cu\,[N(CN)_2]\,Br$ retains from its predecessor, $(ET)_2Cu(NCS)_2$, another distinct feature - the anomalous resistivity behaviour [2].

$(ET)_2Cu\,[N(CN)_2]\,Br$, as well as its relative compound $(ET)_2Cu\,[N(CN)_2]\,Cl$ [3], belongs to the family of ET salts with a so-called κ-type crystal structure [4]. It is formed by two-dimensional conducting sheets of ET molecules, located in the **ac** plane and composed of ET dimers, alternating with polymer anion chains extending along the **a** direction [1].

In this paper we describe the way of synthesis of high quality single crystals of $(ET)_2Cu$ $[N(CN)_2]\,Br$ and the results of temperature investigations of resistivity and thermopower in different crystallographic directions.

2. Experimental.

2.1 SYNTHESIS. — The $(ET)_2Cu[N(CN)_2]Br$ crystals were prepared by electro-chemical oxidation on Pt electrodes of ET $(2 \times 10^{-3}$ M$)$ under the galvanostatic regime at the constant temperature (20 °C). The electrolyte used was the mixture of CuBr $(5 \times 10^{-3}$ M$)$, $NaN(CN)_2$ $(5 \times 10^{-3}$ M$)$ and 18- crown-6 ether $(5 \times 10^{-3}$ M$)$ or CuBr and $Ph_4P[N(CN)_2]$. The solvents were 1,1,2-trichloroethane (TCE), TCE with an addition of 10% of ethanol, and nitrobenzene. The magnitude of the current, applied to different cells, was between 0.2 and 0.6 μA.

The quality of single crystals, determining their superconducting transition temperature T_c and transition width δT_c, depends significantly on the synthesis conditions: the magnitude of the current, and the kind of the solvent and dicyanamide salt used. The most perfect crystals were produced in the pure TCE without absolute ethanol, by using $NaN(CN)_2$, at the electrocrystallization current of 0.5 μA (the anode current density of 1.4 – 1.5 $\mu A/cm^2$). At these conditions the crystals grew on the anode in 12-14 days and were quite uniform. The crystals had the shape of plates with typical dimensions $1 \times 1 \times 0.05$ mm^3.

2.2 RESISTIVITY AND ANISOTROPY. — The temperature dependence of the electrical resistivity was measured by the four probe method with both d.c. and a.c. techniques. Contacts to the sample were made by graphite paste using 10 μm diameter platinum wires. The values of ρ_b/ρ_a and ρ_b/ρ_c were large enough to perform direct measurements of ρ_b, assuming the uniform distribution of current in the sample, when voltage is applied normally to the conducting plane. The resistivity anisotropy was measured also using an improved Montgomery method [7].

At the ambient temperature the value of the resistivity in the **ac** plane varies in the range 0.02-1 Ωcm for different batches depending on synthesis conditions. Usually crystals with lower ρ(295 K) had higher T_c and lower δT_c. For the best crystals, having perfect superconducting transition, the typical resistivity values at the ambient temperature are: $\rho_a = 4 \times 10^{-2}$ Ωcm, $\rho_b = 50$ Ωcm, $\rho_c = 6 \times 10^{-2}$ Ωcm. A typical temperature dependence of the resistivity of $(ET)_2Cu[N(CN)_2]Br$ in all directions is shown in the figure 1. At first it lowers slightly with the diminishing of the temperature, having a broad minimum of around 250 K, then grows down approximately 100 K. Then the resistivity passes through the two maxima - at 95 K and 75 K, the former being higher than the latter. These two maxima, not equally pronounced in different directions, are well reproduced in different samples. After this, the resistivity drops about 50 times until the beginning of the superconducting transition. The insert of figure 1 shows the region of the superconducting transition. It occurs at $T_c = 11.7$ K (the midpoint of the transition) with a width, determined as $\delta T_c = T_{0.9} - T_{0.1}$ being less than 0.4 K. The temperature derivative of ρ_a, ρ_b and ρ_c exhibits a strong maximum at 50 K (Fig. 2). The overall behaviour of the resistivity in all directions is qualitatively similar.

Temperature dependences of calculated resistivity anisotropy ρ_b/ρ_a and ρ_b/ρ_c for the same crystal are shown in figure 3. Both values do not change significantly in the region above 50-60 K. With further lowering the temperature ρ_b decreases slower, than other components, so both ρ_b/ρ_a and ρ_b/ρ_c increase noticeably. Measurements of the resistivity anisotropy by the improved Montgomery method [7] gave essentially the same temperature dependence, but the values of $\rho_b/\rho_a \approx 3000$ in the range 70-295 K were more typical.

2.3 THERMOPOWER. — Thermopower was measured by standard for an organic crystals method [8]. The temperature dependence of thermopower measured in directions **a** and **c** on the same crystal is shown in the figure 4. The thermopower has different signs for different

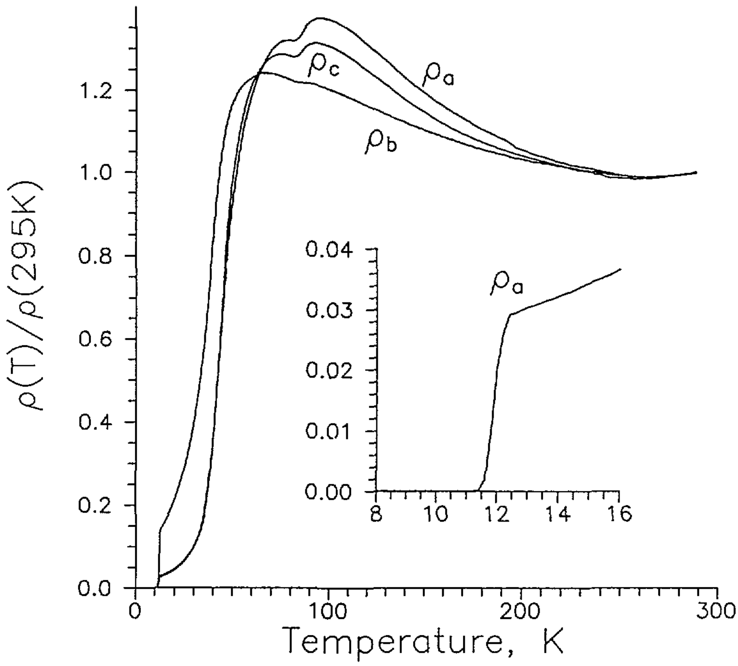

Fig. 1. — The temperature dependence of the normalized resistivity in the **a**, **b** and **c** directions. Insert shows the superconducting transition.

directions. For the **a** direction the thermopower is positive in the whole temperature range. It has a value of about $+20\ \mu V/K$ at the ambient temperature, then increases slightly with the lowering of the temperature and then, after a broad maximum around 130 K, decreases towards zero almost linearly. Similarly, for the **c** direction the thermopower is negative with the value of $-18\ \mu V/K$ at the ambient temperature and has an extremum at 120 K. Remarkably, it has a well pronounced peak at 70 K, followed by a minimum at 50 K, this feature being reproduced on all measured samples. Below approximately 10 K both components of thermopower are very close to zero.

3. Discussion.

Superconducting transition, occuring at $T_c = 11.7$ K, is in agreements with previous results [1]. Small observed δT_c reflects high quality of our crystals. The value of the resistivity at ambient temperature is somewhat higher than it was reported earlier [1]. It should be also noted, that in spite of very sharp superconducting transition the residual resistance ratio in $(ET)_2Cu[N(CN)_2]Br$ is relatively low ($\rho(75\text{ K})/\rho(12\text{ K}) \approx 50$).

As it was mentioned, the temperature derivative of the resistivity exhibits a strong peak at 50 K for all directions. As in the case of $(ET)_2Cu(NCS)_2$ [6], it can be an argument for the existence of a phase transition in $(ET)_2Cu[N(CN)_2]Br$ at this temperature. This transition should be of an anomalous insulator-metal type, since the low-temperature state is metallic and superconducting, and the high-temperature one is semiconducting. The reasons for such transition, as in the case of $(ET)_2Cu(NCS)_2$ [6], is presumably the change of the band structure

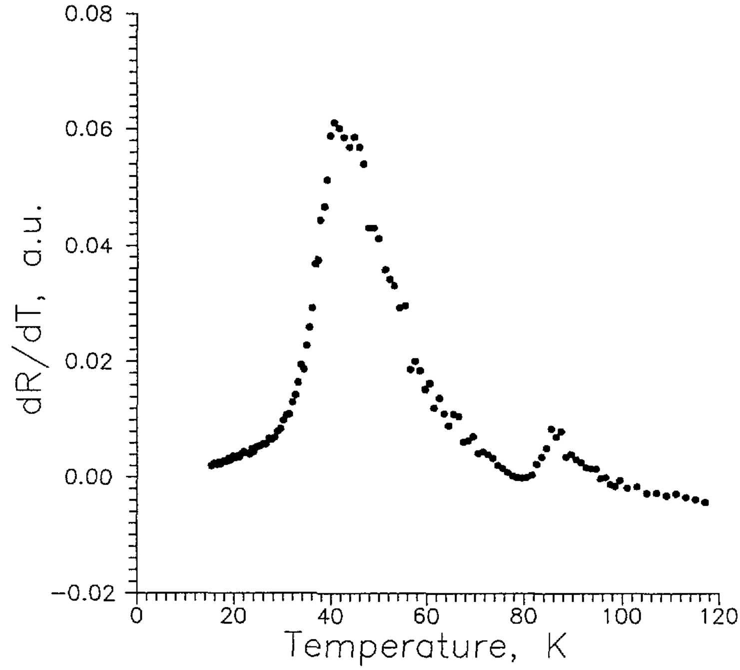

Fig. 2. — The temperature derivative of the resistivity in the **a** direction.

occuring with lowering the temperature due to the contraction of the lattice. The increase of the transfer integrals resulting from the lattice contraction might change the state from a Mott-Hubbard insulator to metal. The quantitative analysis of the resistivity temperature dependence in this model was successfully carried out for $(ET)_2Cu(NCS)_2$ [10]. Similar analysis can be done for $(ET)_2Cu[N(CN)_2]Br$ as soon as more structural data (under the pressure or at low temperature) is available.

The resistivity behaviour of $(ET)_2Cu[N(CN)_2]Br$ resembles very much that of $(ET)_2Cu(NCS)_2$, whose one of the most interesting features is the resistivity maximum near 100 K. In the case of $(ET)_2Cu[N(CN)_2]Br$ this maximum is split into two, located at 75 and 95 K. The latter is most clearly visible in the **a** direction and is almost absent in the **b** direction. Therefore, it may be concerned with another phase transition, presumably involving some kind of moderate change in the cation subsystem, rather than any change in the interlayer interaction.

The behaviour of thermopower is similar to that found in $(ET)_2Cu(NCS)_2$. The difference in the thermopower sign for the **a** and **c** directions can be explained in terms of a simple single-band model [9], though this model does not account for the phase transition, probably occuring at 50 K. The probable phase transition at 95 K manifests itself in change of thermopower behaviour below $\approx$ 100 K. There was recently published a paper by Yu *et al.* [11], concerning the temperature dependence of the thermopower of $(ET)_2Cu[N(CN)_2]Br$ in the **ac** plane. Their results are very similar to ours, and some difference can be explained by uncertainties in crystallographic orientation of the samples.

In summary, we have measured the temperature dependence of the resistivity of $(ET)_2Cu[N(CN)_2]Br$ in three crystallographic directions and the thermopower in the **ac** plane. We found the large value of the resistivity anisotropy $\rho_b/\rho_a \approx 10^3$, a strong peak in the temperature

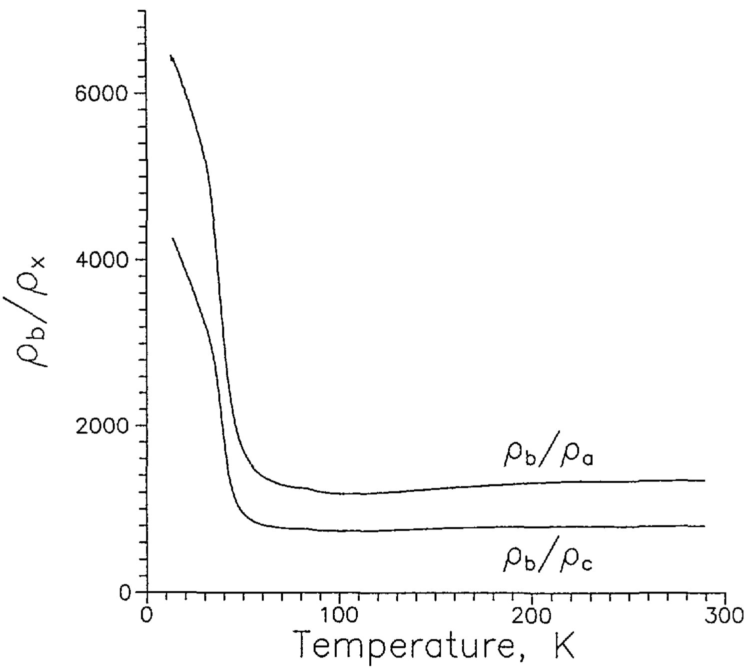

Fig. 3. — The temperature dependence of the resistivity anisotropy.

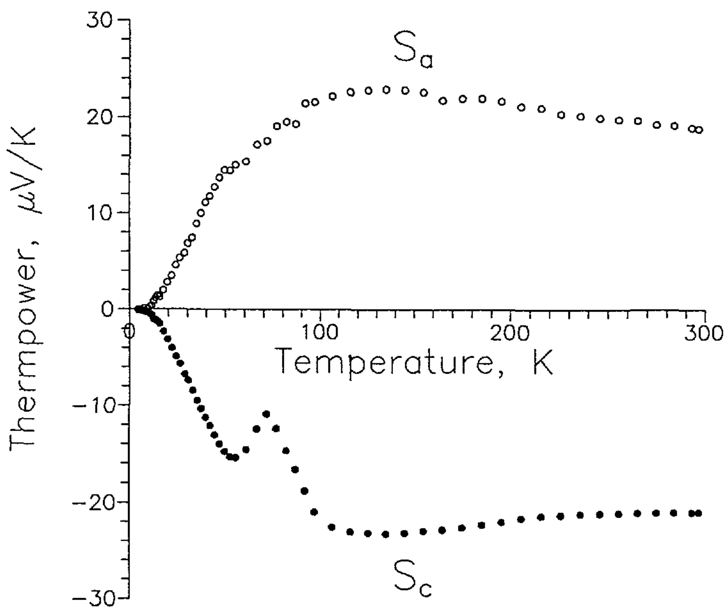

Fig. 4. — The temperature dependence of the thermopower measured in the a and c directions.

derivative of the resistivity occuring at 50 K, and different signs of the thermopower in the **a** and **c** directions. We have concluded, that $(ET)_2Cu[N(CN)_2]Br$ undergoes an insulator to metal transition near 50 K similarly to $(ET)_2Cu(NCS)_2$. The additional anomaly observed at ≈ 95 K may be concerned with another phase transition.

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