

Superconductivity of κ -(BEDT-TTF)₂Cu[N(CN)₂]I under pressure

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The insulating state of κ -(BEDT-TTF)₂Cu[N(CN)₂]I salt appearing at ambient pressure at low temperatures is suppressed by hydrostatic pressure. The resistive measurements showed that in high-quality crystals the emerging metallic state reveals superconductivity. The superconducting state with the transition temperature of about 8 K is stable at pressures higher than 0.1 GPa.

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The salts of κ -(BEDT-TTF)₂Cu[N(CN)₂]X, with X standing for halogen atoms Cl, Br and I (in the following we designate the salts by their X as Cl, Br and I) form a homologous series of compounds [1]. All three salts are isostructural at room temperature and should possess metallic electronic structure according to a band structure calculation [2]. In reality the ground states for the salts are strikingly different. The Cl and Br salts are the highest T_c quasi-two-dimensional organic superconductors under hydrostatic (X = Cl, $T_c = 12.8$ K at 0.03 GPa) and ambient pressure (X = Br, $T_c = 11.6$ K), respectively. The third member of the family, I salt, is insulating at low temperatures at ambient pressure, similar to Cl salt, but does not undergo superconducting transition under hydrostatic pressure up to 0.5 GPa [1]. For I salt, however, traces of a superconducting phase with a T_c of about 8 K were reported in the modulated microwave absorption measurements [3, 4]. Since the volume fraction of these inclusions increases on long term annealing of the crystals [3], it was supposed that they represent an impurity phase of β_H -(BEDT-TTF)₂I₃, formed due to the thermolysis of κ -(BEDT-TTF)₂Cu[N(CN)₂]I.

In order to understand the mechanism of insulating state formation, we have recently studied the electronic transport properties and X-ray diffuse scattering in I salt [5]. We found that the metallic state realized at high temperatures in I salt is in agreement with the band structure calculation, while the insulating state is formed as a result of a structural transformation due to

ordering of the terminal ethylene groups of BEDT-TTF molecules.

Study of mixed of Br and Cl salts [6], and of Br and I salts [7] indeed showed a correlation between the electronic properties and conformational disorder present in the crystals [8]. Simultaneously, it was found that the degree of the conformational order may be influenced by the sample preparation technique. A similar effect of the crystal growth procedure on the conformational state of BEDT-TTF molecule in the lattice was first reported for β -phases [9]. Its influence may be also important for the closely related κ -(BEDT-TTF)₂Cu(NCS)₂, for which growth conditions strongly influence the shape of the resistivity temperature dependence [10–13]. Since the electrochemical synthesis of I salt is not easy, the typical crystals (we call them standard crystals in the following) are of rather low quality. This difficulty of sample preparation is the main reason why studies of I compound are scarce as compared to Cl and Br salts. Therefore, we considered the growth of high quality single crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]I an important goal.

In this letter we report the definitive observation of superconductivity in high quality crystals of I salt under a modest hydrostatic pressure of about 0.1 GPa. This observation shows that the superconducting properties of the compound are in line with the other members of the κ -(BEDT-TTF)₂Cu[N(CN)₂]X family. The transition temperature for I salt determined from resistive measurements is ~ 8 K. The small value of the critical pressure, required for inducing the superconductivity, allows

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us to reinterpret previous observations of superconducting inclusions in the salt [3, 4] as intrinsic and caused by local strain.

The crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]I were synthesized by the electrochemical oxidation of BEDT-TTF in a 1,1,2-trichloroethane medium. A mixture of (PPh₄)[N(CN)₂] and CuI was used as the electrolyte. The starting salts used for the preparation of the electrolyte were of high purity and did not contain any Cl or Br anions as adulterants²⁾. The typical applied current density was 3–5 $\mu\text{A}/\text{cm}^2$. The current density was reduced approximately twice after the nucleation of the crystals on the Pt electrode. The growth was performed during a period of 3 to 4 weeks. We refer to the crystals obtained by this route as to 'new crystals' in the following. The resultant new crystals had the usual shapes of a rhombus or distorted hexagon, however, contrary to the standard samples, they were free of the layered defects [5]. The two crystals studied had a size of $0.5 \times 0.5 \times 0.1 \text{ mm}^3$ and $0.6 \times 0.5 \times 0.12 \text{ mm}^3$. The sample resistance was measured by a standard four-probe technique with a current flowing along the highly conducting *ac*-plane. All four terminals were attached to the same sample surface. Measurements under quasi-hydrostatic pressure were performed in a beryllium copper clamp pressure cell with a silicon oil as a pressure medium. A pressure up to 0.4 GPa was applied at room temperature. The value of the pressure at low temperatures, presented here, was calculated using the results of Ref. [14]. The inplane resistance of the sample was found to decrease by a factor of 2 on loading from 0 to 0.4 GPa; no special features which could be ascribed to phase transitions under pressure were detected.

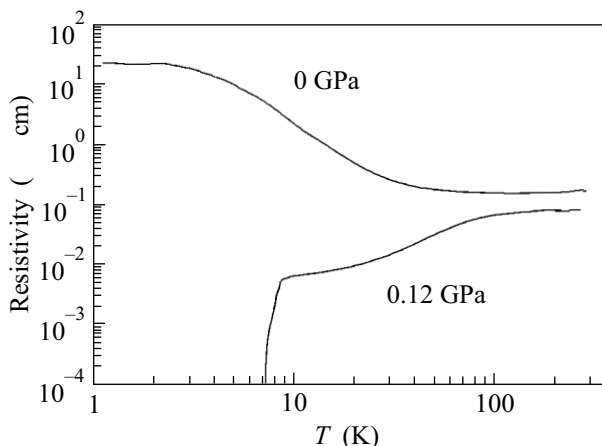


Fig.1. Resistivity temperature dependence for sample 1 at ambient pressure and under pressure of 0.12 GPa

²⁾The lack of Cl and Br impurities was confirmed by electron probe microanalysis measurements on the crystals.

In Fig.1 we show the temperature dependence of resistivity at ambient pressure and under a pressure of 0.12 GPa presented on a log-log scale. At ambient pressure the resistivity decreases upon cooling from room temperature down to 60 ~ 80 K (depending on the sample) and then shows a notable increase to low temperatures. Worth noting is that no resistivity decrease was found at ambient pressure down to 1.1 K. Under a pressure of 0.12 GPa, the sample shows a resistive transition into a superconducting state, with the transition onset at 8.2 K, midpoint at 7.7 K and zero resistive state achieved at 6.8 K (see Fig.2 for expanded view). To confirm the superconducting nature of this behavior, we

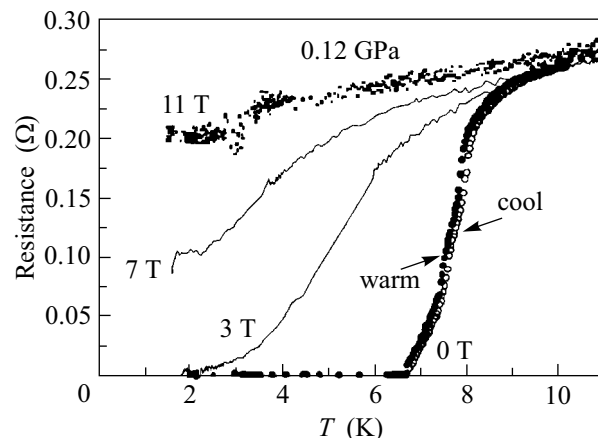


Fig.2. Resistance temperature dependence of sample 1 under hydrostatic pressure of 0.12 GPa in the vicinity of the superconducting transition as a function of magnetic field, applied at arbitrary direction with respect to the sample

show in Fig.2 the resistivity temperature dependence in the vicinity of the superconducting transition under a set of magnetic fields.

In order to understand the striking difference of our results and those previously reported for this compound, it is instructive to compare the properties of the two different sets of crystals. Both crystals were studied by an X-ray analysis and were confirmed to be isostructural at room temperature. The elemental composition of the crystals was studied using an electron probe microanalysis technique and no deviation from the chemical formula was found within the accuracy of the method. Besides, the ESR spectra of the new crystals were those typical for κ -phase salts [3]. They show *no* detectable inclusions of the β phase, possessing notably different ESR spectrum.

Some difference in the properties of the two sets of I crystals suggests that the main effect is coming from

an improved quality of the new samples. Although the resistivity temperature dependence of the new crystals is basically similar to that of the standard crystals [1, 5, 15], some small differences should be noticed. In the standard samples the resistivity starts to increase just below ~ 200 K, although this increase is very small down to 70 K. In addition, the overall resistance increase on cooling to 1.2 K in the standard samples (amounting to ~ 1000 times the value at room temperature) is notably higher than that in the new samples (200 to 500 times). Since both of the abovementioned features in the standard samples are due to disorder [2, 5], we conclude that the new crystals are characterized by a much higher degree of ordering at low temperature.

As can be seen from Fig.1, on application of pressure the resistance temperature dependence changes in a way very similar to that observed in Cl salt [16]. A resistivity maximum appears, signaling ethylene reordering taking place under pressure [17]. It is known that the resistance of Cl and Br salts is sensitive to thermal cycling [15, 17], due to a proximity to structural instability [18]. For the standard I salt this sensitivity is very small, indicating much higher lattice stability. In the samples under study the resistance hysteresis is almost of the same magnitude as in Cl salt. This finding shows that the samples are characterized by a soft lattice, prone to a structural transformation to the superconducting phase.

In conclusion, high quality single crystals of I salt show a clear superconducting transition under pressure, in contrast to the previous reports for this compound. This finding shows the crucial importance of crystal perfection for the occurrence of superconductivity in this family of materials.

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