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Superconductivity at Normal Pressure in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ Crystals

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Single crystals of the κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ cation-radical salt are obtained. These crystals exhibit metallic properties and pass to a superconducting state with T_c = 11.5 K at ambient pressure. © *2005 Pleiades Publishing, Inc.*

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Isostructural cation-radical salts of the κ-(BEDT–TTF)$_2$Cu[N(CN)$_2$]X family, where BEDT–TTF is the organic π donor bis(ethylenedithio)tetrathiafulvalene, (X = Br, Cl, I, $Br_{1-x}Cl_x$, and $Br_{1-x}I_x$) have been the subject of numerous investigations in recent years [1–14]. These compounds exhibit a wide diversity of electronic properties in spite of the similarity of their crystal structures. These are layered materials constructed of conducting BEDT–TTF cation-radical layers alternating with insulating layers of singly charged $\{Cu[N(CN)_2]X\}^-$ anions (Fig. 1a). The anionic layer consists of polymer zigzag chains stretched along direction **a** and including a planar three-coordinate Cu^{1+} atom with two bridging $[(NC)N(CN)]^-$ dicyanamido groups and a terminal halogen atom X. The cation-radical layer is formed from pairs of BEDT–TTF molecules with an average charge of +0.5 per molecule packed in the crystal perpendicularly to each other (Fig. 1b). The overlapping of molecular orbitals of donor molecules in the layers leads to the formation of broad electron energy bands in the crystal. According to the theoretical band-structure calculations [1–3], these materials must be metals. It has been found that the cation-radical salts with X = Br, $Br_{0.5}Cl_{0.5}$, and $Br_{0.7}Cl_{0.3}$ are organic superconductors at ambient pressure with T_c = 11.6 K [2, 5], while the salts with X = Cl and $Br_{0.9}I_{0.1}$ [4, 5] undergo a transition to a superconducting state at a pressure of 0.3 kbar with T_c = 12.8 and 3.5 K, respectively, and the salt with X = I passes to a superconducting state at a pressure of 1.2 kbar with $T_c \approx 8$ K [6, 7]. At ambient pressure, the cation-radical salt with X = Cl (designate it as κ-Cl) retains its semiconducting properties to a temperature below 100 K. A transition to an insulating state, which is identified as an antiferromagnetic transition, occurs in the region of 40 K, and weak ferromagnetism is detected in these crystals below 22 K [4, 8, 9]. When the pressure is varied above several hundreds of bars, crystals of the κ-Cl salt demonstrate a rich phase diagram with paramagnetic insulating, antiferromagnetic insulating, metallic, and superconducting phases [8–12]. In addition, it was found by x-ray diffraction that two structural phase transitions occur in these crystals at a high pressure and room temperature: a reversible transition with a reduction of symmetry at a pressure of 8.8 kbar and the second transition at 12 kbar characterized by the disappearance of Bragg reflections and possibly associated with amorphization under pressure [13].

In this work, it is shown that new intriguing properties are added to the whole diversity of the properties of the Cl–cation radical salt: single crystals of this salt (designate it as κ'-Cl) have been obtained, which, as distinct from the κ-Cl Mott dielectric described above, have metallic properties and pass to a superconducting state with T_c = 11.5 K at ambient pressure. An x-ray diffraction study of these crystals has been performed, and their transport properties have been investigated.

The measurements of the electrical resistance were performed with a 20-Hz alternating current using a four-contact method with a synchronous detector. The samples were made as thin plates with characteristic sizes of 1 × 0.3 × 0.02 mm whose surface was oriented along the conducting layers (the ac plane). A couple of contacts were made on each of the two opposite surfaces of the sample using a conducting carbon paste. The resistance of the sample was measured by passing a current both along ($J \parallel (ac)$) and across ($J \parallel b$) of the conducting layers. The magnitude of the current J passing through the sample was fixed and did not exceed 10 μA. For experiments in a magnetic field, a superconducting solenoid creating a field of up to 17 T was used.

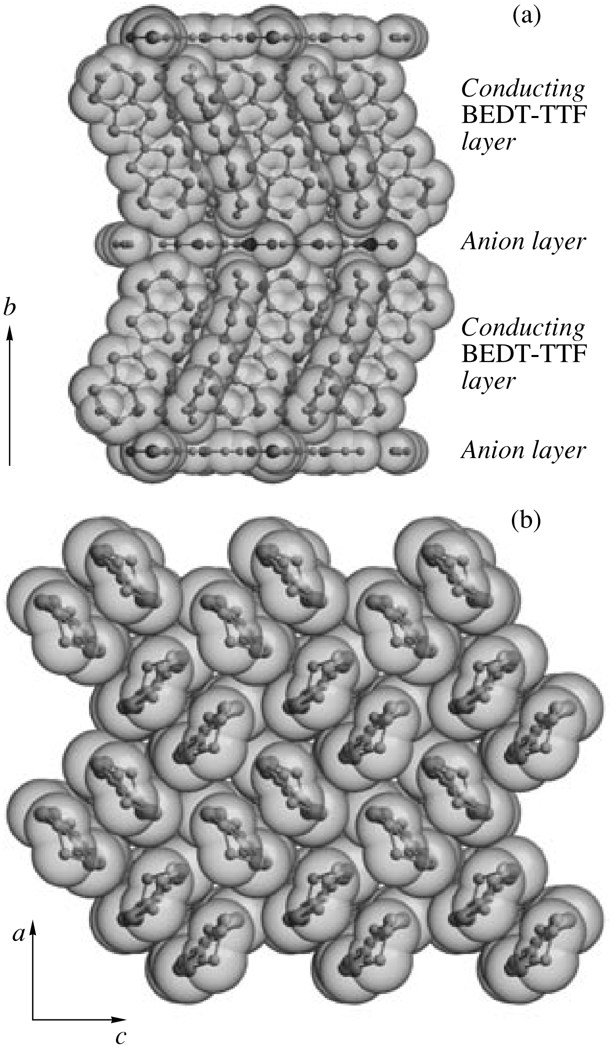

Fig. 1. Structure of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl crystals: (a) a view along the layers and (b) a conducting cation-radical layer.

In test experiments, the dynamic susceptibility at a frequency of 100 kHz was also studied.

The resistivity anisotropy (ρ_b/ρ_{ac}) calculated by the modified Montgomery method [14] was in the range 200–400 at T = 300 K for various samples and increased monotonically with decreasing temperature, reaching values of 1000–1400 at $T \approx 15$ K. The temperature dependence for both longitudinal and transverse resistances had a positive derivative in the entire temperature range below 300 K. A small region with a negative derivative occurred only at a low temperature in the vicinity of the superconducting transition and was more pronounced for a transverse resistance. We investigated several samples obtained in the course of one synthesis. The results obtained with different samples were similar. Given below are the results for one of them.

The dependence $R(T)$ obtained in the case of current passage along the conducting layers and the temperature dependence of the dynamic susceptibility at $T <$ 15 K are presented in Fig. 2. It is evident in the figure that a transition to a superconducting state with the critical temperature T_c = 11.5 K determined by the middle of the transition is observed in the dependence $R(T)$. For the same sample, the transition detected by the dynamic susceptibility starts at approximately 11 K.

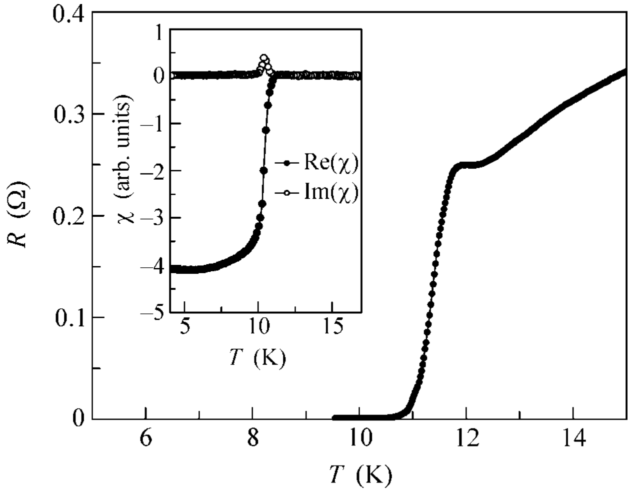

Fig. 2. Superconducting transition detected on a sample of κ'-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl by the temperature dependences of the resistance and (inset) dynamic susceptibility.

The application of a magnetic field led to a decrease in T_c; in this case, a considerable broadening of the superconducting transition occurred in the $J \parallel$ (ac) geometry while the transition at $J \perp$ (ac) did not broaden but displaced to the region of lower temperatures. For this reason, the dependences $H_{c2}(T)$ presented below were constructed by measuring the transverse resistance, that is, for the case when the current was passed along the normal direction to the conducting layers. The absence of a notable broadening in a magnetic field suggests that we are dealing with the dependence $H_{c2}(T)$ rather than with an “irreversibility line.” In Fig. 3, the dependence $H_{c2}(T)$ is presented for two orientations of the magnetic field. All the points except one were obtained from the curves $R(T)$ at fixed values of the field H. The last point in the lower curve was obtained from the curve $R(H)$ at the fixed temperature T = 1.2 K. Attention is attracted by the positive curvature of the $H_{c2}(T)$ dependences and also by the fact that for $H \parallel b$ the derivative dH_{c2}/dT is close to zero at the point $T = T_c(0)$. For the case when the magnetic field lies in the (ac) plane, this derivative is finite and equal to $dH_{c2}/dT|_{T_c(0)} = -1.36$ T/K.

The main crystallographic data are as follows: rhombic (C$_{10}$H$_8$S$_8$)$_2$Cu[N(CN)$_2$]Cl crystals, sp. gr. *Pnma*, a = 12.932(2) Å, b = 29.877(5) Å, c = 8.458(1) Å, V = 3267.8(9) Å^3, and Z = 4. Experimental data for 4567 independent reflections with $I \geq 2\sigma(I)$ were

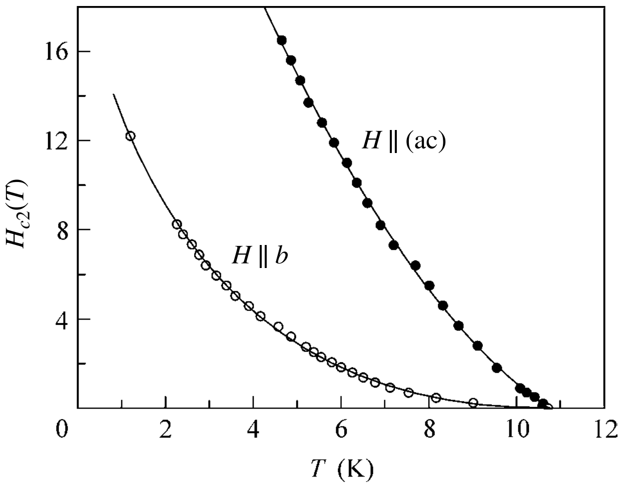

Fig. 3. Dependences $H_{c2}(T)$ for the magnetic field orientation in the plane of the conducting layers and along the normal to these layers.

obtained on an Enraf-Nonius CAD4 diffractometer (MoKa radiation, ω scan, $2\theta_{\max} = 50°$, the size of the crystal was $0.5 \times 0.2 \times 0.02$ mm, absorption correction was introduced). The structure was determined by the direct method and was refined by the least-squares method in an anisotropic approximation to $R_1 = 0.056$. Crystals of the organic metal κ'-Cl exhibit almost the same structure as the Mott dielectric κ-Cl [4].

A preliminary analysis of the κ'-Cl crystal structure at room temperature showed the following differences between κ'-Cl and κ-Cl:

1. It is found that certain disorder exists at room temperature in κ-Cl crystals caused by the fact that the presence of two conformations (eclipsed and staggered) of terminal ethylene groups in the BEDT–TTF molecule is equiprobable. At a low temperature, these groups become fully ordered and the BEDT–TTF molecule assumes only the eclipsed conformation [15]. The ratio of the eclipsed and staggered conformations in κ'-Cl crystals equals 0.8 : 0.2; that is, the proportion of the eclipsed conformer, which is the conformer typical of the low-temperature state of κ-Cl crystals, is larger in the case of κ'-Cl crystals even at room temperature.

2. The volume of the unit cell in κ'-Cl crystals $V = 3267.8(9)$ Å^3 is smaller than that in κ-Cl crystals $V = 3299(1)$ Å^3 [4] and even smaller than the corresponding volume in the latter crystals $V = 3285.2(8)$ Å^3 under a pressure of 1.2 kbar [13]. Correspondingly, all the intermolecular S…S contacts in the conducting layer are shorter, which enhances intermolecular interactions and, as a consequence, increases the width of the conduction band. This effect is equivalent to chemical compression.

3. In the refinement of the structure, an incomplete occupation of the position of the copper atom was revealed (a deficit of ~5%) with the complete occupation of the positions of the other atoms. This may indirectly indicate that the anionic layer contains Cu^{2+} along with Cu^{1+}. Then, it might be suggested that the superconductivity of κ'-Cl crystals occurs through the doping of carriers into the κ-Cl Mott dielectric. A similar situation was observed in the case of the κ-(BEDT–TTF)$_2$Cu$_2$(CN)$_3$ cation-radical salt [16].

Subsequently, we plan to perform detailed synthetic, structural, and physical investigations with the aim of tracing the structure–property relationships and elucidating the nature of the superconducting state in these crystals.

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