Ambient Pressure Superconductivity in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl Single Crystals

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Single crystals of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl radical cation salt possessing metallic properties and showing a superconducting transition with T_c = 11.5 K at ambient pressure were first prepared. PACS numbers: 61.10 Nz, 72.80 Le, 74.70. Kn

1. INTRODUCTION

Isostructural radical cation salts of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X family, where BEDT-TTF is an organic π-donor, bis(ethylenedithio)tetrathiafulvalene, X = Br, Cl, I, Br$_{1-x}$Cl$_x$, Br$_{1-x}$I$_x$, have intensely been studied over past years[1-12]. They demonstrate a wide variety of electron properties despite of their similar crystal structures. These compounds are layered materials built of conducting radical cation BEDT-TTF layers, which alternate with dielectric ones composed of single-charged {Cu[N(CN)$_2$]X}$^-$ anions[1-5]. The anion sheet consists of polymeric zig-zag chains extended along the *a* direction, which involve a flat three-coordinated Cu$^+$ ion with two bridged [(NC)N(CN)]$^-$ dicyanamide (dca) groups and a terminal halogen X atom. The radical cation layer is formed by pairs of the BEDT-TTF molecules with average +0.5 charge per molecule, which are packed perpendicular to each other in a crystal. According to theoretical calculations of band structure[1-3], these materials are expected to be metals. It was found that radical cation salts with X=Br, Br$_{0.5}$Cl$_{0.5}$ and Br$_{0.7}$Cl$_{0.3}$ are ambient pressure organic superconductors with T_c = 11.6 K[1,5], while salts with X= Cl and Br$_{0.9}$I$_{0.1}$ undergo a superconducting transition at 0.3 kbar with T_c = 12.8 K and 3.5 K, respectively[4,5], and a salt with X = I exhibits a superconducting transition at 1.2 kbar with T_c ≈ 8 K[6]. A radical cation salt with X = Cl (hereinafter denoted as "κ-Cl") retains its semiconducting properties below 100 K at ambient pressure, and near 40 K

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it undergoes a dielectric transition identified as an antiferromagnetic one, and below 22 K these crystals were found to exhibit weak ferromagnetism[4,7,8]. When varying pressure above several hundreds of bars, the crystals of the κ-C1 salt showed a rich phase diagram with a paramagnetic dielectric, antiferromagnetic dielectric, metallic and superconducting phases[7,9-11]. Moreover, the existence of two structural phase transitions at room temperature and high pressure was found for these crystals by an X-ray diffraction method: a reversible transition accompanied by symmetry lowering at pressure of 8.8 kbar and the second transition at ~ 12 kbar, characterized by a reversible disappearance of Bragg reflections consistent with pressure-induced amorphization[12].

Here, we present new intriguing properties of the κ-C1-salt: single crystals of the salt were prepared (hereinafter denoted as "κ'-C1"), which in contrast to the described Mott insulator κ-Cl have metallic properties and undergo a superconducting transition with T_c = 11.5 K at ambient pressure. X-ray analysis of these crystals was performed and transport properties were studied.

2. RUSULTS AND DISCUSSION

The κ-Cl crystals are conventionally synthesized using the method of electro-oxidation of BEDT-TTF in a 1,1,2-trichloroethane (TCE) – absolute ethanol (9:1) mixture in the presence of either two- or three-component electrolytes comprising Cu$^+$ salts (CuCl or Cu(dca))[4,13]. In the course of our investigations related to the synthesis of BEDT-TTF salts with magnetic coordination anions of dicyanamide complexes of divalent transition metals (Mn^{2+}, Cu^{2+}, Co^{2+}), we studied the electro-oxidation of BEDT-TTF in the presence of Mn(dca)$_2$ and Cu(dca)$_2$ in TCE containing 10 vol% of 96% ethanol at a current of 0.3-0.5 μA. For Mn dicyanamide, the crystals of the BEDT-TTF salt with a paramagnetic [Mn(dca)$_3$]$^-$ anion, (BEDT-TTF)$_2$[Mn(dca)$_3$], were obtained, whereas in the case of Cu dicyanamide the crystals of κ'-Cl salt were formed together with the (BEDT-TTF)$_2$CuCl$_2$ ones[14] as a minor product. The generation of Cu$^+$ cations, which are necessary to form the {Cu[N(CN)$_2$]X}$^-$ anion, is probably due to the chemical oxidation of BEDT-TTF by Cu(dca)$_2$. It is known that Cu^{2+} oxidizes BEDT-TTF[15]. To slow down the possible chemical oxidation, the BEDT-TTF and Cu(dca)$_2$ were placed in different compartments of an electrochemical cell. The source of Cl$^-$ anions was TCE[16,17].

The main crystallographic parameters for κ'-C1 are: rhombic symmetry, space group *Pnma, a* = 12.932(2) Å, *b* = 29.877(5) Å, *c* = = 8.458(1) Å, *Z* = 4, *V* = 3267.8(9) Å^3. 4567 independent reflections with $I \geq 2\sigma(1)$ were collected on a Enraf-Nonius CAD4 diffractometer. The structure was

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solved by a direct method and refined by the least-square method in anisotropic approximation to R_1 = 0.056. The crystals of κ'- Cl have almost the same structure as the Mott insulator κ-Cl[4]. The analysis of the crystal structure of κ'-Cl at room temperature revealed the following differences between κ'-Cl and κ-Cl.

1. It is known that there is some disordering in the radical cation layer in κ-Cl crystals at room temperature, which is due to the equiprobable presence of two conformations (eclipsed and staggered) of terminal ethylene groups of the BEDT-TTF molecule. Full ordering of these groups takes place at low temperature and the BEDT-TTF molecule has only eclipsed conformation[3]. The ratio of eclipsed and staggered conformations in κ'-Cl crystals is 0.8:0.2 at room temperature.

2. The unit cell volume of κ'-Cl crystals, V = 3267.8(9) Å^3, is less than that of κ-Cl crystals[4], V = 3299(1) Å^3, and is even less than the volume of the latter ones, V = 3285.2(8) Å^3, at 1.2 kbar pressure[12]. Correspondingly, all intermolecular S...S contacts are shorter in a conducting layer that results in enhanced intermolecular interactions and, as a consequence, to a wider conductivity band. This effect is equivalent to chemical compression.

3. The refinement of the structure revealed incomplete population of the position of a Cu atom (~ 5%) at completely populated positions of other atoms. This can testify that Cu^{2+} is present in addition to Cu$^+$ in the anion sheets of κ'- Cl crystals.

The electroresistance was measured using a four-probe technique by a lock-in detector at 20 Hz alternating current. The samples were thin plates with 1 x 0.3 x 0.02 mm^3 characteristic sizes. The surface was oriented along conducting layers (the *ac* plane). Two contacts were made to each of two opposite sample surfaces with conducting graphite paste. Sample resistance was measured when current was passed both parallel ($J\|(ac)$) and perpendicular ($J\|b$) to conducting layers. The value of the current (J) running through the sample was fixed and was not higher than 10 μA. A superconducting solenoid, which generated the field of up to 17 T was used for experiments in magnetic fields. In test experiments a dynamic susceptibility was also studied at 100 kHz frequency.

The resistivity anisotropy (ρ_b/ρ_{ac}) calculated by the modified Montgomery method[18] was found to be within 200-400 depending on the sample at T = 300 K and monotonically increased with the temperature decrease attaining the value of 1000-1400 at $T \approx 15$ K (Fig.1). The temperature dependences had a positive derivative in the whole temperature range below 300 K for both longitudinal and transverse resistances (Fig.1). A small portion with a negative derivative was observed only at low temperature near a superconducting transition and was more clearly pronounced for transverse

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resistance. We tested several samples obtained during the same synthesis. The data obtained for different samples were similar. The data for one of these samples are presented below.
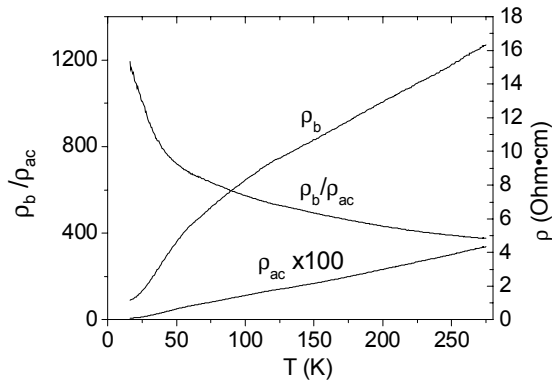

Fig.1. Temperature dependences for longitudinal (ρ_{ac}) and transverse (ρ_b) resistivities and the resistivity anisotropy (ρ_b/ρ_{ac}).

Fig.2 shows the *R(T)* dependence at current running along conducting layers and the temperature dependence of dynamic susceptibility at *T* < 15 K. It is seen that there is a superconducting transition in the *R(T)* dependence with the critical temperature T_c = 11.5 K determined at one half of the normal state resistance level. A dynamic susceptibility transition starts approximately at 11 K in the same sample.
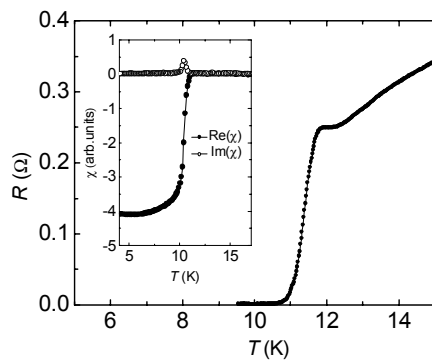

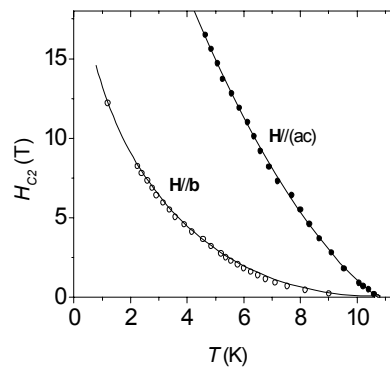Fig.2. Superconducting transition in κ'-C1 registered by resistance and dynamic susceptibility (in insert).

Fig.3. $H_{c2}(T)$ curves for the field both parallel and perpendicular to conducting layers.

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The application of magnetic field resulted in lowering T_c, and an essential broadening of a superconducting transition took place in $J\|(ac)$ geometry, while at $J\perp(ac)$ the transition shifted to lower temperatures and no noticeable broadening was observed. For this reason, the $H_{c2}(T)$ dependences presented above were plotted for transverse resistance measurements, i.e. when the current was passed along the normal direction to the conducting layers. The absence of a notable broadening in a magnetic field suggest that we deal 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 $R(T)$ curves at fixed H. The last point in the lower curve was obtained from the $R(H)$ curve at $T = 1.2$ K. Of special attention is a positive curvature of the $H_{c2}(T)$ dependences and the fact that at $H\|b$ the dH_{c2}/dT derivative is close to zero at the point $T = T_c(0)$. When magnetic field is along the (ac) plane, this derivative is finite and equal to $dH_{c2}/dT|_{Tc(0)} = -1.36$ T/K.

The appearance of superconductivity in the κ'-C1 crystals is probably due to the effect of "chemical compression". However, it should be noted that a possible presence of Cu^{2+} in the anion sheets can also result in the changes in a conductivity band filling as it was found in the case of the superconducting κ'-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ salt[19]. The study of the EPR spectra of κ'-C1 can provide with the information on the presence of Cu^{2+} in these crystals. The EPR investigations are in progress.

3. CONCLUSIONS

For the first time the crystals of κ'-(BEDT-TTF)$_2$Cu[N(CN)$_2$]C1 (κ'-C1) radical cation salt, which exhibit metallic conductivity and are ambient pressure superconductors, were synthesized. The crystals showed some distinctions in structure as compared to that of the Mott insulator κ-Cl: smaller size of the unit cell - "chemical compression" and deficiency ($\approx 5\%$) of the occupancy of copper positions. The appearance of superconductivity in the κ'-C1 crystals is probably due to the effect of "chemical compression". A nontrivial temperature dependence of upper critical field was observed for κ'-C1 ones: the $H_{c2}(T)$ curves have positive curvature with field directed both in the conducting plane and perpendicular to it.

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