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Comparative study of magnetotransport properties and structural features of the organic superconductors κ′-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, where X = Cl, Br

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Abstract

The crystal structure, the resistivity and the upper critical field of radical cation salts κ′-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, where X = Cl, Br (κ′-X hereafter), have been studied. Both κ′-Br and κ′-Cl samples were superconductors with T_c lying in the interval 11.3–11.9 K and had the unit cell volume smaller than that for κ-Br and κ-Cl, respectively. The temperature dependence of interlayer resistivity $\rho_\perp$ for κ′-Br is characterized by the hump lying in the temperature interval 35–100 K. For κ′-Cl $\rho_\perp$ is considerably smaller and goes down monotonously with the temperature. The curves $H_{cr}(T)$ for all crystals demonstrate a non-BCS-behaviour for both in-plane and out-of-plane magnetic field orientations.

Keywords: Organic conductors; Superconductivity

A quasi two-dimensional systems κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X are characterized by close proximity to the metal–insulator transition and one can get either metal or Mott insulator depending on the kind of the halogen atom X. For example, the cation-radical salt with X = Br is organic superconductor, while the salt with X = Cl is dielectric at ambient pressure and undergoes a transition to a superconducting state at a pressure of 0.3 kbar with the critical temperature $T_c = 12.8$ K. Recently a new approach to the synthesis of κ-Cl salt was proposed [1,2], as a result the modified κ′-Cl salts with new unexpected properties were synthesized. In particular, this salt was found to be the ambient pressure superconductor.

In this paper we present the results of comparative study of the crystal structure, the resistivity and the upper critical field of radical cation salts κ′-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, where X = Cl, Br (κ′-X hereafter). The crystals of κ′-Br salt were obtained by electrooxidation of BEDT-TTF (10^{-3} M/l) in 1.1.2-TCE-alcohol absolute (10 v/v%) medium in constant current conditions ($I = 0.3$–0.5 μA) at 20 °C. Mixture of the complex 18-cr-6, Na[N(CN)$_2$] and CuBr in a 1:1:1 molar ratio (4.5×10^{-3} M/l) with addition of M[N(CN)$_2$]$_2$ salts, M = Ni, Mn, Zn (20 mol% of CuBr concentration) was used as an electrolyte. X-ray analysis of obtained crystals defined that κ′-Br crystals were growing on a Pt anode together with those of the superconductor κ-Br. The κ′-Cl crystals were synthesized in the presence of only the Cu[N(CN)$_2$]$_2$ salt as an electrolyte [1,2]. For comparison, the deuterated d8-κ-Br salts, synthesized by traditional method [3], were also studied. Both κ′-Br and κ′-Cl samples were superconductors with T_c lying in the interval 11.3–11.9 K and had the unit cell volume smaller than that for κ-Br and κ-Cl.

According to our X-ray analysis, κ′-Cl and κ′-Br crystals have the same structure as correspondent κ-X salts, but there

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are two essential differences: (i) the deficiency ($\approx 7\%$) in the copper positions in κ′-Cl due to vacancies and (ii) smaller unit cell volume of both κ′-Cl and κ′-Br crystals ($\Delta V \approx 15$ Å^3) (see Ref. [2] for the unit cell parameters of κ′-Cl and the Table 1 for κ′-Br). Smaller unit cell volume of κ′-X salts with respect to κ-X salts may be ascribed to some effective "chemical" pressure, which, according to our measurements [2], is of the order of 600 bar for κ′-Cl.

The samples for transport measurements were thin plates with $1 \times 0.3 \times 0.02$ mm^3 characteristic sizes. The surface was oriented along conducting layers (the (*ac*) plane). The resistance was measured by a Lock-in detector at 20 Hz alternating current using a four-probe technique. Two contacts were prepared to each of two opposite sample surfaces with conducting graphite paste. Sample resistances $R_{\|}$ and $R_{\perp}$ were measured by sending the current either parallel ($\mathbf{J}\|(ac)$) or perpendicular ($\mathbf{J}\|\mathbf{b}$) to conducting layers, respectively. From these measurements two correspondent components $\rho_{\|}$ and $\rho_{\perp}$ of the resistivity tensor were calculated. The value of the current 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 the experiments in magnetic fields.

The temperature dependence of interlayer resistivity for κ′-Br and κ′-Cl samples is shown in Fig. 1. One can see that for all κ- and κ′-bromides $\rho(T)$ dependences are characterized by the hump lying in the temperature interval 35–100 K, which is well known for traditionally prepared κ-bromides. Usually the hump in κ-Br is observed at the temperature about 90 K and is attributed to some order–disorder transition in ET-ethylene groups (see, for example, Ref. [5]). Fig. 1 shows that the hump temperature may lie in the wide temperature region, which means that the hump nature is not still clear and requires further investigations. The resistivity of κ′-Cl is much smaller than that of κ- and κ′-Br in the whole temperature range between room temperature and T_c and, unlike to κ- and κ′-bromides, the temperature dependence $\rho(T)$ for κ′-Cl is monotonous.

The influence of magnetic field on the superconducting transition was studied for both in-plane ($\mathbf{B}\|(ac)$) and out-of-plane ($\mathbf{B}\|\mathbf{b}$) orientations of magnetic field by measurements of $R_{\perp}(T)$ dependences at different fixed magnetic field values. In these experiments the superconducting transition temperature T_c, determined at one half of the normal state resistance level, was measured as function of magnetic field. As a result, we have got the temperature dependences of the upper critical field $H_{cr}(T)$, shown in Fig. 2. One can see that the curves

Table 1
Unit cell parameters for the single crystals of κ- and κ′-(BEDT-TT)$_2$Cu[N(CN)$_2$]Br at room temperature (Space Group: *Pnma*, $Z = 4$)

	κ-Br [4]	κ′-Br(Ni)	κ′-Br(Zn)	d8-κ-Br
a, Å	12.942(3)	12.936(2)	12.931(2)	12.947(2)
b, Å	30.016(4)	29.930(4)	29.964(3)	29.998(3)
c, Å	8.539(3)	8.527(1)	8.5182(8)	8.5356(9)
V, Å^3	3317(1)	3301.6(9)	3300.4(6)	3314.9(7)

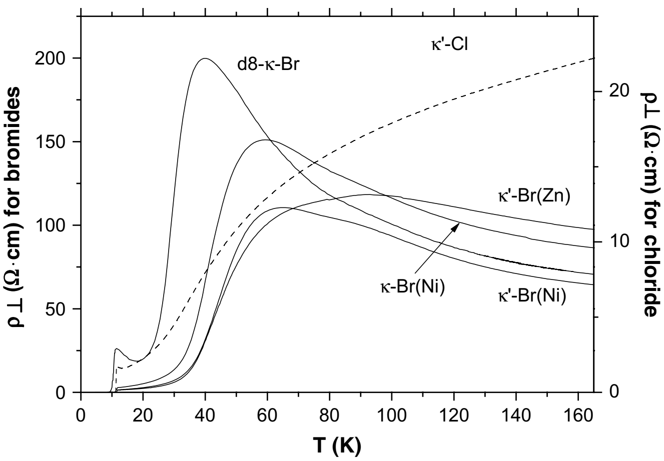

Fig. 1. Temperature dependences of the out-of plain resistivity for different κ- and κ′-salts.

$B_{cr}(T)$ for all crystals demonstrate a non-BCS-behaviour for both in-plane and out-of-plane magnetic field orientations. We would like to emphasize that H_{cr} values for all bromides including the deuterated samples are very close to each other and their temperature dependences are very similar. Moreover, $B_{cr}(T)$ dependences for κ′-Cl are also very similar to that for bromide samples.

In conclusion, we have studied the crystal structure, the resistivity and the temperature dependences of the upper critical field of new radical cation salts κ′-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, where X = Cl, Br. We have found that both κ′-Cl and κ′-Br crystals have smaller unit cell volume ($\Delta V \cong 15$ Å^3) with respect to that of the correspondent κ- salts, which is probably due to the deficiency in the copper positions. Unlike to traditionally synthesized κ-chloride samples, κ′-Cl is ambient pressure superconductors with $T_c = (11.3–11.9)$ K and exhibits metallic $\rho(T)$ dependence without "hump", which is characteristic for κ- and κ′-bromides. At the same time, we have not found any considerable difference in transport properties of κ- and κ′-bromides. Both κ′-Cl and κ′-Br samples demonstrate nontrivial temperature dependences of the upper critical field.

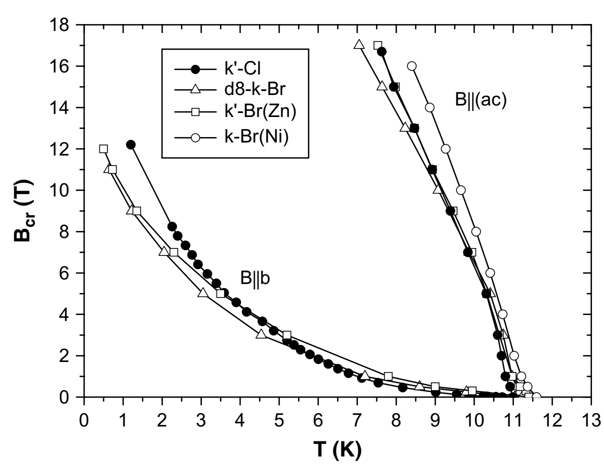

Fig. 2. Temperature dependences of the upper critical fields.

Acknowledgments

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