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Pressure-temperature phase diagram of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I

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The pressure-temperature phase diagram of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I determined by resistive measurements is presented. Under a hydrostatic pressure of about 1 kbar an insulating state is transformed into a metallic state, showing superconductivity with a transition temperature T_c up to 8 K. A resistivity maximum develops in the boundary region of insulator-metal transformation and its position gradually shifts to high temperatures with pressure. These properties of the salt are in line with the generic phase diagram for κ-phase materials, although the salt is located deep in the insulating domain of the phase diagram, contrary to the expectation based on the ionic radius of the halogen atom. We show the relation of the shape of the phase diagram to the degree of structural order in the material.

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I. INTRODUCTION

Variation of the lattice parameters with chemical substitution or physical pressure (P) brings about modification of the band structure and allows us to figure out important parameters for the description of the electronic properties. This approach is especially useful for organic materials, which have soft lattice and thus are very sensitive to pressure.[1–3] Recently, several attempts were made to determine the generic pressure-temperature (P-T) phase diagram for the family of the highest transition temperature (T_c) quasi-two-dimensional organic superconductors κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, with X standing for halogen atoms Cl, Br, and I or their mixtures (in the following we designate the salts by their X as Cl, Br, and I).[4–9] The κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X salts share the same crystal lattice structure at room temperature,[10] and the metallic state is predicted for all of them according to the band-structure calculation.[11] In view of the fact that at ambient pressure several members of the family (Cl and I salts, and Br salt with deuterium isotope substitution in BEDT-TTF molecule, d-Br) are insulators, and magnetic order is found in some of them [Cl (Refs. 12, 6, and 7) and d-Br salts (Ref. 7)], the crucial role of the electronic correlation was discussed.[13]

Until recently the experimental studies of this family were restricted mainly to Cl and Br salts. The third member of the family, I salt, was initially reported to be nonsuperconducting up to pressure of 5 kbar.[10] Since information about this salt was scarce, the reason for the lack of superconductivity was not clear. It was thought as due to crystal imperfection, like disorder[11] and superstructurelike effects,[14] or as being intrinsic and caused by modification of the band structure, as proposed based on the consideration of a Mott-Hubbard scheme on the triangular lattice.[15]

Very recently, we succeeded in the preparation of high quality single crystals of I salt,[16] which showed clear superconductivity under hydrostatic pressure with T_c up to about 8 K, and confirmed the intrinsic nature of superconducting inclusions observed previously in several studies.[17,18] This finding naturally led us to determine the phase diagram for I salt, for which the mechanism of insulating state formation is reasonably understood in terms of structural transformation.[14]

In this paper we report the P-T phase diagram for I salt determined from resistance measurements and the upper critical fields (H_{c2}) for the superconducting state. We found that the insulator-to-metal transformation of I salt under pressure is very similar to that of Cl salt, although it proceeds at slightly higher P values. This finding shows that (i) the properties of the salt are in line with a generic P-T phase diagram for the κ phases; (ii) the salt is occupying a place at the low-pressure side of the phase diagram, contrary to the expectation based on ionic radii of halogen atoms; (iii) the T_c of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X salts is systematically decreasing with the ionic radius of halogen atoms. The sensitivity of the pressure coefficient of T_c and of the shape of the phase diagram to the degree of disorder in the crystal and the wave vector of the low-temperature superstructure, together with the irregular change of the ground state with ionic radius contrary to the superconducting T_c, imply a notable involvement of the structural transformations in the insulating state formation, as was shown at ambient pressure from systematic study of transport properties.[14]

II. EXPERIMENT

We performed the study on samples obtained by two different synthetic routs. The first one was used in our recent study,[16] the second one was corresponding to the procedure described in Ref. 10. We refer to the crystals obtained by these two routs as ‘‘new’’ and ‘‘old’’ in the following. The old crystals were synthesized several years ago and characterized comprehensively at ambient pressure by transport and x-ray measurements[14] and by ESR measurements.[19] To our surprise, we found a complete resistive transition to the superconducting state in all the samples from both batches, which is contrary to previous reports for this compound.

The new crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I were prepared by the electrochemical oxidation of BEDT-TTF in a 1,1,2-trichloroethane medium.[16] Since the composition of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X crystals can be strongly changed even by small contamination of the starting reagents by Cl and Br impurities,[20] special care was taken to prevent it. We used starting reagents of the highest possible grade and the lack of contamination was confirmed by electron probe microanalysis measurements on the grown crystals. We found no traces of Cl and Br within the accuracy of the method, i.e., below approximately 0.1%. The resultant new samples were of much higher quality than the old ones. This can be seen directly in the width of x-ray spots at room temperature and becomes prominent at 4.2 K (see below). An x-ray analysis was performed at room temperature and confirmed the crystals to be isostructural to usual κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I. X-ray diffuse scattering measurements were made using the fixed-sample, fixed-film monochromatic Laue method.[21] An imaging plate was used instead of a photographic film used in our previous study; for other experimental details, see Ref. 14.

The electrical resistivity was measured by a conventional four-probe technique with an electrical current flowing along the highly conducting ac plane. A quasihydrostatic pressure was created by a beryllium copper clamp pressure cell with a silicon oil as the pressure medium. A pressure up to 7 kbar was applied at room temperature. The pressure dependence of resistance taken at room temperature on loading did not indicate any phase transition with pressure. The pressure at low temperatures, discussed throughout this paper, was calculated using the results of Ref. 22. This value is believed to be accurate with an uncertainty of ± 0.2 kbar for $P > 1$ kbar, while a large uncertainty is inevitable at low-pressure values.

We studied resistivity of five new crystals and two old crystals. The resistivity value at room temperature $\rho(295\ \mathrm{K})$ was the same within the experimental scatter for old and new samples and equal $(8 \pm 3) \times 10^{-2}\ \Omega$ cm. All of the samples showed complete resistive superconducting transition under pressure above 1.2 kbar, although the midpoint T_c and the resistive transition width showed notable (up to 3 and 5 K, respectively) variation from crystal to crystal. On the contrary, the onset of resistive transition was always in a range 6.5–8.2 K. For the most perfect sample, having the sharpest transition, an onset junction point was at 8.2 K, midpoint at 7.7 K, and an end-junction point at 6.8 K. Since this width of the resistive transition is notably less than in another crystals and is usual for κ-phase salts, we consider this value as intrinsic for this material.

Measurements of the H_{c2} were performed in a 15-T superconducting solenoid. The pressure cell was rotated by a double axis rotator system and aligned with an accuracy of better than 0.1° with respect to the field. The measurements were made by making temperature sweeps under fixed magnetic fields. The resistive transition did not broaden much on field application, therefore for determination of T_c we used an onset junction point, which is least sample dependent.

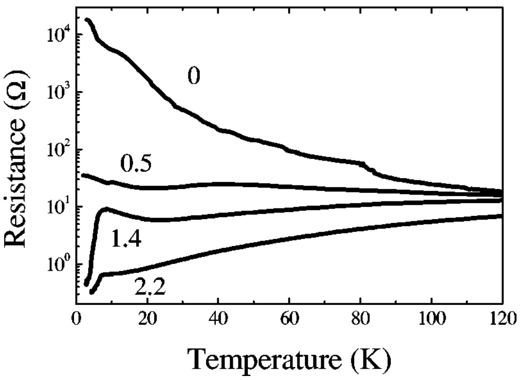

FIG. 1. Temperature dependence of the resistance for new samples for a series of increasing hydrostatic pressures (the depicted values indicate the pressure in kbar at low temperatures).

III. RESULTS AND DISCUSSION

In Fig. 1 we show resistivity ρ temperature dependence at ambient and under several hydrostatic pressures for new samples. The behavior of the old samples was essentially the same, with some difference in pressure scale (see below). At ambient pressure ρ decreases slightly down to 200 K (not shown) and then gradually increases to 1.2 K, the lowest temperature in our study. The rate of ρ increase gets higher below about 80–100 K, while the $\rho(T)$ curve flattens below 10–20 K (depending on a sample).

Upon application of pressure, the resistivity decreases gradually, with the change being larger towards the lowest temperatures. At the boundary of the metallic and insulating behavior, $R(T)$ curve shows a maximum, followed by a minimum at low temperatures (Fig. 1). In the same P range a slight $R(T)$ decrease starts to develop at T_c, although the resistance does not reach zero. Both of these features, the formation of the resistance maximum[23,24] and the incomplete superconducting transition in $R(T)$ (Ref. 5) in the transformation range, are typical for Cl salt and can be understood as coexistence of insulating and metallic (superconducting) phases in the transformation range.[25,9] With pressure increase the maximum is transformed into a notable slope change, and its position on the temperature scale shifts rapidly to high T. In Fig. 2 we show the P-T phase diagram determined from these resistance measurements. The vertical lines show the boundary pressure range in which incomplete superconducting transition in $R(T)$ is observed. We show only the lines relevant to the phase transformation from the insulating to the superconducting state, omitting detailed features related to the formation of the insulating state, characterized in our previous study on old samples.[14] Except for an approximately 0.5-kbar shift on the pressure scale, this phase diagram is *identical* to the phase diagram of Cl salt,[23] determined in the same way (from resistance measurements under liquid pressure).

The shape of the diagram was essentially the same for all

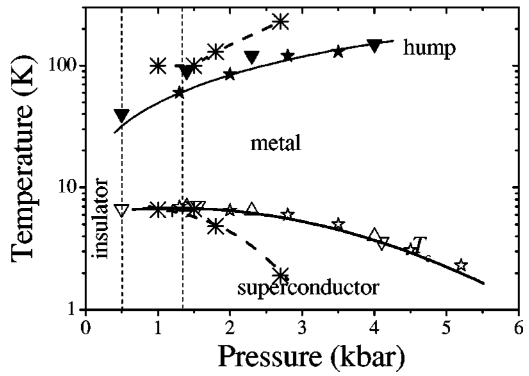

FIG. 2. Pressure-temperature phase diagram of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I determined from the resistance measurements. The vertical dashed lines show boundaries of the range in which incomplete transition is observed in $R(T)$. Two sets of data correspond to old (crosses with dashed lines) and new (solid lines, different symbols correspond to several samples) samples.

new samples, despite the difference in the sharpness of the superconducting transition. In the old samples, however, there is a notable, although not precisely characterized, difference in the pressure scale for the same features. This regards first of all the width of the pressure range in which the superconductivity is observed. Because of difficulty of pressure control in the low-pressure region it is impossible to compare precisely the values of the threshold pressure for insulator-to-metal transformation, although a trend for lower values in the old samples seems to be present.

The difference in the width of the pressure range where superconductivity is observed is directly related to a notable difference in the pressure coefficient of T_c. The new samples show superconductivity in a broader P range and are characterized by a relatively small pressure coefficient of T_c, dT_c/dP, about -1.7 K/kbar (Fig. 3). This value is more than two times lower than that for the old samples, about -4 K/kbar. The relevant values for Cl and Br salts lie between these two extremes. The pressure coefficient of T_c for Cl salt was reported as -3.6 K/kbar and -3.2 K/kbar from gas[24] and liquid[23] pressure measurements, respectively. For Br salt the respective values were reported as -2.8 K/kbar under gas pressure[26] and -2.4 K/kbar from liquid pressure[27] experiments. From consideration of the shape of $T_c(P)$ curve, it seems that for some pressure range the T_c is not changing in new samples. This feature is reminiscent of the behavior observed in mixed κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_{0.9}$I$_{0.1}$ crystals, in which T_c shows a shallow maximum with pressure increase.[28]

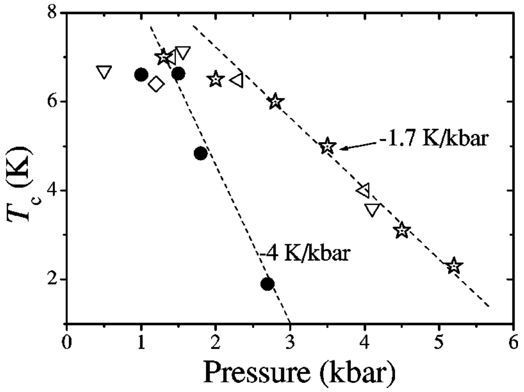

FIG. 3. Pressure dependence of the superconducting transition temperature for new samples (open symbols, different symbols correspond to different samples) and one old sample (solid square). The solid line is a guide for eyes, the dashed lines show the approximated pressure dependence of T_c.

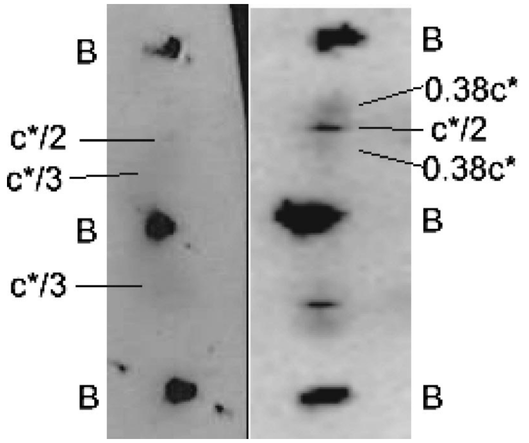

FIG. 4. A part of x-ray Lauegram showing superstructure spots in old (left) and new (right) crystals. $T=4.6$ K. Note much larger amplitude of $c^*/2$ superstructure reflex in new crystals and difference in the wave vector of second superstructure. B's correspond to ordinary Bragg peaks due to main lattice.

To understand the origin of the difference in the properties of the samples we show in Fig. 4 a part of a Lauegram, containing the most characteristic features, taken at 4.6 K. The two outer spots and the central spot (marked with B in Fig. 4) are due to the main lattice. In addition, in both old and new samples we can see a double superstructural transformation. In old samples the first transformation takes place at ~ 200 K resulting in the $c^*/2$ superstructure, while the second starts at around 100 K, where a short-range order with diffuse reflex centered at around $c^*/3$ is formed (left panel in Fig. 4). In the new samples the $c^*/2$ superstructure is formed as well, and it is characterized by a much better defined reflex. However, the main difference between the samples comes from the second (low-temperature) superstructural transformation. The diffuse $c^*/3$ spot typical for old crystals is transformed into a relatively sharp spot, corresponding to the wave vector $0.38c^*$, so the second superstructure is incommensurate. In addition, as can be seen from the figure, the new crystals have much higher crystal perfection, revealed in the width of both the superstructural spots in the Lauegram measured along the c^* axis, along which the system has the highest resolution.

In view of this finding, it is natural that the crystals may have different compressibility of the lattice, caused by the presence of the superstructure. This in turn can lead to the difference of the pressure coefficient of T_c. Since formation of the insulating state is correlated with low-temperature superstructural transformation,[14] it can be expected that at metal-insulator boundary the $c^*/3$ superstructure is sup-

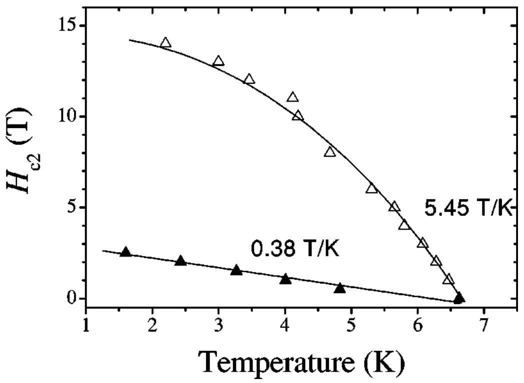

FIG. 5. The temperature dependence of H_{c2} for new samples under pressure 1.2 kbar in magnetic fields oriented parallel (open symbols) and perpendicular (solid symbols) to the conducting plane. The lines are guides for eyes.

pressed. In this case the $c^*/2$ superstructure should be present in the superconducting state (as is indeed observed in Br salt via the reconstruction of the Fermi surface[29]), and determine the stiffness of the lattice. It is an open question, if the suppression of superconductivity is related to some transformation of this $c^*/2$ superstructure.

The H_{c2} for the superconducting state of the I salt was measured under a pressure of 1.2 kbar, in the region of the highest T_c just on the boundary of the superconducting domain. The measurements were made under the magnetic fields H oriented perpendicular ($H_{c2\perp}$) and parallel ($H_{c2\parallel}$) with respect to the highly conducting plane of the crystal on one of the new samples. The H-T phase diagram is shown in Fig. 5. The $H_{c2\perp}$ is comparable with that for Cl salt [about 3 T at 0.7 kbar (Ref. 30)], but is notably lower than for Br salt at ambient pressure [above 10 T (Ref. 31)]. The value of $H_{c2\parallel}$ is also notably lower than in the Br salt [about 35 T (Ref. 31)]. The slope of the H_{c2}(T) curves near T_c, in the region of validity of Ginzburg-Landau theory, allows us to determine the coherence lengths for I salt, using the formulas

$$\mu_0 T_c \frac{dH_{c2\parallel}(T)}{dT} = \frac{\Phi_0}{2\pi\xi_\perp(0)\xi_\parallel(0)},$$

$$\mu_0 T_c \frac{dH_{c2\perp}(T)}{dT} = \frac{\Phi_0}{2\pi\xi_\parallel(0)^2},$$

where $\xi_\parallel(0)$ and $\xi_\perp(0)$ are the coherence lengths parallel and perpendicular to the layer, respectively, μ_0 is the magnetic constant, and $\Phi_0 = 2.07\times10^{-15}$ Wb is the magnetic flux quantum. The values of the coherence length were determined for new samples as $\xi_\parallel(0) = 11.3$ nm and $\xi_\perp(0) = 0.8$ nm.

IV. CONCLUSION

As can be seen from the above description, the properties of I salt are in reasonable correspondence with those for related Cl and Br compounds. It is not clear at the moment, whether magnetic ordering is typical for I salt at ambient pressure, similar to Cl salt, although, except for the large difference in the magnitude,[32,14] the resistance relaxation induced by cycling the magnetic field seems to be very similar. More detailed studies on this subject are under way.

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