

Transport properties and structural features of the ambient-pressure superconductor κ' -(BEDT-TTF)₂Cu[N(CN)₂]Cl

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The crystal structure and low-temperature transport properties of the recently synthesized κ' -(BEDT-TTF)₂Cu[N(CN)₂]Cl radical cation salt are investigated. The crystals exhibit metallic conductivity and are ambient-pressure superconductors with critical temperature in the range (11.3–11.9) K. The crystals show some distinctions in structure as compared to that of the Mott insulator κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl: smaller size of the unit cell and deficiency in the occupancy of the copper positions. Anisotropy of superconducting properties as well as a nontrivial temperature dependence of the upper critical field were observed.

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I. INTRODUCTION

The determination of the conditions giving rise to superconductivity in quasi-two-dimensional organic conductors based on radical cation salts of BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] and its derivatives is one of the main objectives in understanding the physics of these strongly correlated electronic materials.^{1,2} The BEDT-TTF donor is a main building brick for constructing layered organic metals and superconductors. The molecule contains eight sulfur atoms and saturated nonplanar CH₂CH₂ groups. The S atoms promote the formation of multiple side-by-side S··S contacts in radical-cation layers, while the ethylene groups create some steric hindrances for face-to-face π -intermolecular interactions providing the increment of electronic dimensionality in BEDT-TTF salts. Among this class of salts, the superconductors with the highest transition temperatures T_c at ambient and mild pressure are those of the κ -(BEDT-TTF)₂Cu[N(CN)₂]X family, with X standing for halogen ions Cl, Br, and I, or their mixtures.^{3–12}

These compounds are built of conducting radical-cation BEDT-TTF layers, which alternate with dielectric ones composed of single-charged Cu[N(CN)₂]X anions (Fig. 1). The anion sheet consists of polymerized zig-zag chains extended along the *a* direction and involving a flat three-coordinated Cu¹⁺ atom with two bridged [(NC)N(CN)][−] dicyanoamide (dca) groups and a terminal halogen X[−] ion. The radical-cation layer is formed by pairs of BEDT-TTF molecules with an average +0.5 charge per molecule, which are packed perpendicular to each other in the crystal. The proximity of dimeric units in all directions is sufficient to yield a two-dimensional sulfur network in the plane of the BEDT-TTF layers. According to band-structure calculations,¹³ these κ phases are expected to be metals. However, different ground states are found within this family: while the salts with X = Br, Br_{0.5}Cl_{0.5}, and Br_{0.7}Cl_{0.3} are ambient-pressure superconductors with T_c near 11.5 K,^{3,8,10} those with X = Cl, Br_{0.9}I_{0.1}, and I are insulators, which display a great sensitivity to pressure.^{4–7,9,11,12} The application of small hydrostatic pressure makes them superconducting with $T_c = 12.8$ K and 3.5 K

at $P = 0.3$ kbar and 8 K at 1.2 kbar, respectively. On cooling at ambient pressure, the salt with X = Cl (denoted as “ κ -Cl” hereafter) reveals weakly temperature-dependent resistivity behavior down to 100 K. Below 100 K, resistance starts to increase and finally the “ κ -chloride” undergoes a transition to an antiferromagnetic insulating (AFI) state.^{14,15} Through the observation of the proton nuclear spin-lattice relaxation, an antiferromagnetic ordering is observed at 27 K. The AFI phase shows weak ferromagnetism below 23 K due to spin canting.¹⁵ It is suggested that the magnetic order is driven by strong electron correlations and that the κ -Cl salt is a Mott insulator. When pressure is varied over a range of a few hundred bars, the κ -Cl salt displays a very rich phase diagram with paramagnetic insulating, antiferromagnetic insulating, metallic, and superconducting phases.^{6,16–18} It is considered that the pressure induces the Mott transition from insulator to metal in κ -Cl.^{17–19} According to current views, the ground state of the dimeric κ -type BEDT-TTF salts with a half-filled conducting band is determined by the ratio between an effective on-dimer Coulomb interaction U_{eff} and the width of the conduction band W .²⁰ If Coulomb interactions become too large (especially the intradimer Coulomb repulsion) in comparison with the bandwidth, the carriers are localized on the dimers and the metallic state is destroyed in favor of a Mott-Hubbard state where the spins of the localized carriers are antiferromagnetically ordered. The bandwidth can be changed by hydrostatic pressure or chemical substitutions (X), which explains the wide variety of electron properties and the great sensitivity to pressure of κ -X salts.

Recently we have synthesized the κ' -(BEDT-TTF)₂Cu[N(CN)₂]Cl salt (denoted as “ κ' -Cl” hereafter) which, in contrast to the Mott insulator κ -Cl, is a metal at ambient pressure and undergoes a superconducting transition with $T_c \approx 11.5$ K.²¹ In this work, we report on some peculiarities of the crystal structure of κ' -Cl as compared with κ -Cl, transport and magnetotransport properties of the κ' -Cl crystals as a function of the current and magnetic field direction.

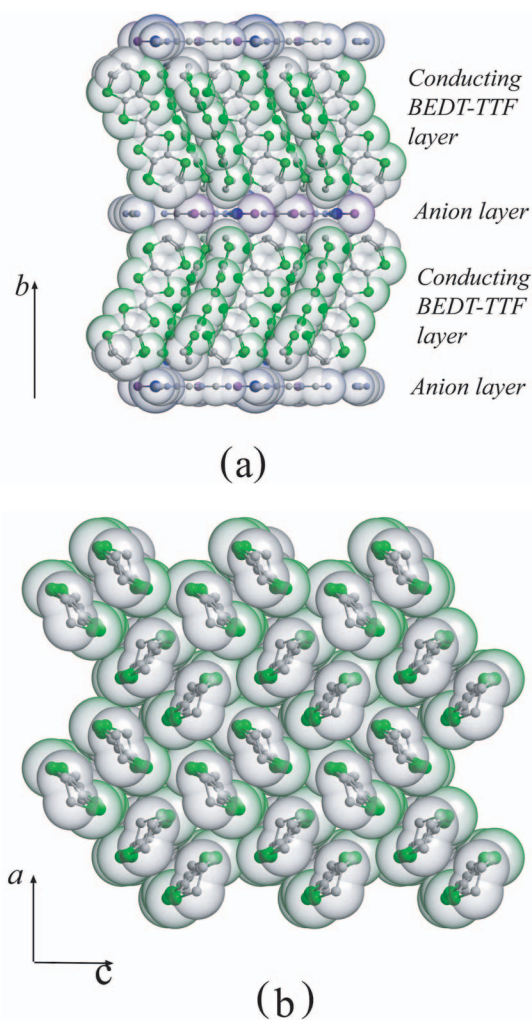


FIG. 1. (Color online) Structure of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl crystals: (a) a view along the layers and (b) a conducting radical-cation layer.

II. EXPERIMENT

A. Sample synthesis

The standard method for the preparation of the κ -Cl crystals consists of electro-oxidation of BEDT-TTF under constant current in a 1,1,2-trichloroethane (TCE)+10% (vol.) absolute ethanol in the presence of either two- or three-component electrolytes containing Cu^+ salts [CuCl or Cu(dca)].^{4,5,22} In the course of our investigations related to the synthesis of BEDT-TTF salts with magnetic-coordination anions based on dicyanamide complexes of divalent transition metals, we studied the electro-oxidation of BEDT-TTF in the presence of Mn(dca) $_2$ and Cu(dca) $_2$ in TCE with ca. 10% (vol.) ethanol. For Mn dicyanamide, the crystals of BEDT-TTF salt with a paramagnetic [Mn(dca) $_3$] $^-$ anion, (BEDT-TTF) $_2$ [Mn(dca) $_3$], were obtained, while in the case of Cu dicyanamide the crystals of κ' -Cl salt were formed together with those of κ -Cl (see Sec. II C) and (BEDT-TTF) $_2$ CuCl $_2$ ones²³ as a minor product. The generation of Cu^+ cations, which are necessary to form a Cu[N(CN) $_2$]Cl anion, is probably due to the chemical oxidation of BEDT-

TTF by Cu(dca) $_2$. It is known that Cu^{2+} oxidizes BEDT-TTF.²⁴ To slow down chemical oxidation, BEDT-TTF and Cu(dca) $_2$ were placed in different compartments of an electrochemical cell. TCE was the source of Cl^- anions as it has already happened in the synthesis of some BEDT-TTF salts.^{25,26} It should be noted that because of the low solubility of Cu^{2+} dicyanamide, the currents which could be passed through the cell were very low (0.1–0.3 μA). For the comparative study of the crystal structure and transport properties of the κ' -Cl and κ -Cl crystals, the latter have also been synthesized using the standard procedure:²² the electro-oxidation of BEDT-TTF in TCE with 10% (vol.) absolute ethanol in the presence of the electrolyte composed of CuCl, PPh $_4$ [N(CN) $_2$], and N(hexyl) $_4$ Cl.

B. X-ray study and band-structure calculations

In order to clarify what causes the considerably different transport properties of κ' -Cl and κ -Cl salts, we have carried out comparative x-ray crystal-structure studies of these salts. Selected experimental parameters and crystal data for κ' -Cl at 293 K (1) and κ -Cl at 293 K (2), 90 K (3) as well as at 90 K under small pressure (4) are listed in Table I. To create the pressure the samples were coated with the drop of silicon organic liquid, polyethylsiloxane (PES); the pressure value is estimated to be about (300–400) bar (see the next paragraph). Intensity data for κ' -Cl were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK $_{\alpha}$ radiation in an ω -scan mode. Cell parameters were obtained by the least-squares refinement method with 25 reflections measured in an ω -2 θ mode under the same experimental conditions. All the x-ray data for κ -Cl salt were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo K $_{\alpha}$ radiation in ϕ and ω scans and using an Oxford Cryostream for low-temperature measurements. Bruker SMART and SAINT utilities were used for data collection and reduction. Structures were solved by direct methods and refined using the SHELXL-97 programs.²⁷

The tight-binding band-structure calculations for (1)–(4) were based upon the effective one-electron Hamiltonian of the extended Hückel method.²⁸ The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg-Helmholz formula.²⁹ All valence electrons were explicitly taken into account in the calculations and the basis set consisted of double- ζ Slater-type orbitals for C and S and single- ζ Slater-type orbitals for H. The exponents, contraction coefficients, and atomic parameters for C, S, and H were taken from the previous work.³⁰

C. Transport measurements

Sample resistance was measured using a four-probe technique by a lock-in detector at (20–75) Hz alternating current. The samples were thin plates with $0.50 \times 0.30 \times 0.02$ mm 3 characteristic size. The largest surface of plate was oriented along conducting layers (the ac plane). Two contacts were prepared to each of two opposite sample surfaces with conducting graphite paste. In the experiment we

TABLE I. Unit-cell parameters and structure-refinement details for the single crystals of κ' -(BEDT-TTF)₂Cu[N(CN)₂]Cl and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (space group: *Pnma*, *Z*=4).

	κ' -Cl	κ -Cl		
Temperature, K	(1) 297	(2) 293	(3) 90	(4) 90+ <i>P</i>
<i>a</i> , Å	12.929(1)	12.963(2)	12.8983(5)	12.8932(4)
<i>b</i> , Å	29.879(2)	29.897(4)	29.5320(11)	29.5137(10)
<i>c</i> , Å	8.457(1)	8.467(1)	8.3957(3)	8.3913(3)
<i>V</i> , Å ³	3267.0(5)	3281.5(1.3)	3198.0(4)	3193.1(3)
Size, mm	0.50 × 0.30 × 0.017	0.20 × 0.12 × 0.12	0.20 × 0.12 × 0.12	0.20 × 0.12 × 0.12
Number of unique reflections	2872	5295	5246	5167
Number of observed reflections $I > 2\sigma(I)$	2056	4416	4995	4940
$2\theta_{max}$, °	50	64.28	64.54	64.22
$R_1, F > 4\sigma(F)$	0.038	0.037	0.018	0.023
R_2 , all <i>F</i>	0.065	0.047	0.019	0.024
GOF	1.014	1.084	1.129	1.197

could measure either $R_{\parallel} = V_{12}/J_{34}$ or $R_{\perp} = V_{24}/J_{13}$ when the current was run mainly parallel [$\mathbf{J} \parallel (ac)$] or perpendicular [$\mathbf{J} \perp (ac)$] to conducting layers, respectively (see Fig. 2). The value of the current *J* running through the sample was fixed and did not exceed 10 μ A. The measurements of the sample resistance in the temperature range 1.2–300 K were carried out in the cryostat with a superconducting solenoid, which generated the field of up to 17 T.

We have tested more than ten samples obtained in the course of the same synthesis. Some of them were not uniform, containing parts with metallic κ' -Cl phase as well as parts with transport properties similar to those of the κ -Cl crystals. The nonuniform samples had the characteristic shape of a feather (see Fig. 3). They were big enough (3 × 0.5 mm²) so we had an opportunity to make the samples for the measurements by cutting the small plates from the different parts of the as-grown sample to measure local-lattice parameters and transport properties. It has been established that the parts with the unit-cell volume *V*

= 3267(1) Å³ always had transport properties of metal-like κ' -Cl and the parts with $V = 3282(1)$ Å³ were semiconductor-like κ -Cl crystals. For both types of the cut samples, complete structural research has been carried out. It is worth noting that the results of the structural analysis of κ -Cl crystals, obtained in conditions of our synthesis and synthesized by the traditional one,²² completely coincided. In this paper we present the results obtained on the uniform samples, which had metallic-like *R*(*T*) dependence at ambient pressure. All of them were superconductors with a smooth and narrow superconducting transition; the transition 10–90 % width did not exceed 0.5 K. The data for different metallic κ' -Cl samples were similar.

$R_{\parallel}(T)$ and $R_{\perp}(T)$ dependencies are shown in Fig. 2 for one of the samples. The temperature dependencies had a positive derivative in the whole temperature range below 300 K for both longitudinal and transverse resistances. A small portion with a negative derivative was observed only at low temperature near a superconducting transition for transverse resistance $R_{\perp}(T)$.

The components ρ_b and ρ_{ac} of the resistivity tensor calculated for the same sample by the modified Montgomery method³¹ as well as the resistivity-anisotropy value ρ_b/ρ_{ac} are shown in Fig. 4 as a function of the temperature. The resistivity anisotropy ρ_b/ρ_{ac} was found to be within 200–400 depending on the sample at *T*=300 K and monotonically increased with the temperature decrease attaining a value of 1000–1400 at *T* ≈ 15 K. The extrapolation of $\rho(T)$ depen-

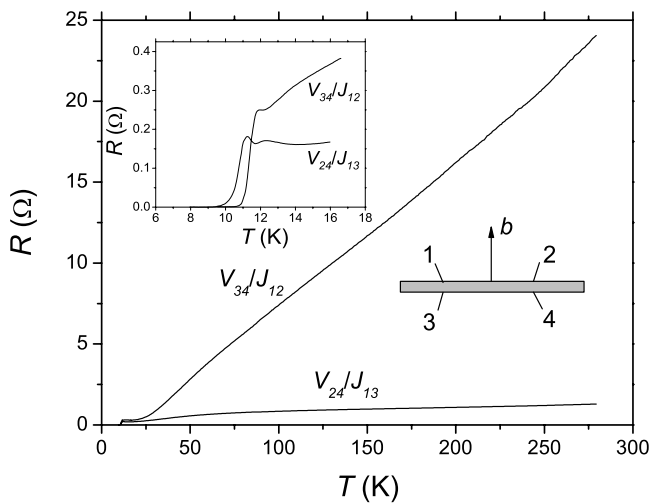
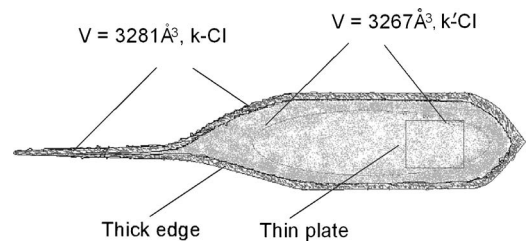

 FIG. 2. Temperature dependencies for the longitudinal $R_{\parallel}(T)$ and transversal $R_{\perp}(T)$ sample resistances.


FIG. 3. The shape of one of the nonuniform samples. The parts of the sample with different properties are indicated.

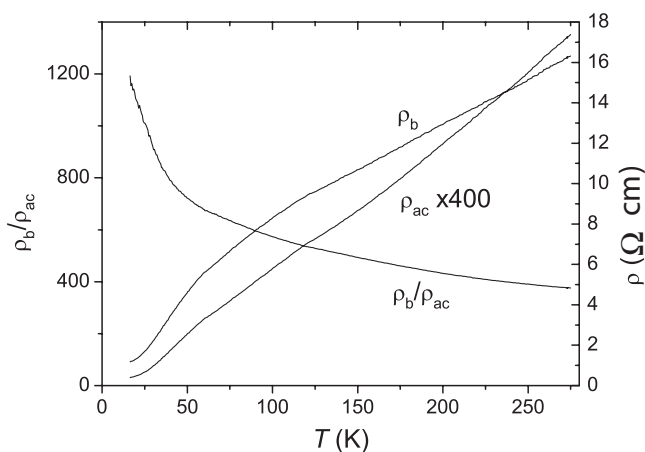


FIG. 4. Temperature dependencies for the longitudinal- and transversal-resistivity tensor components ρ_{ac} , ρ_b , and for the resistivity anisotropy ρ_b/ρ_{ac} .

dence to the low-temperature region gives the residual in-plane resistivity value (0.5–0.7) m Ω cm and the RRR value in the limits 70–100. These parameters together with the narrow superconducting transition testify that we deal with rather high-quality and uniform samples.

The superconducting transition temperature T_c determined at one half of the normal-state resistance level for different κ' -Cl samples was found to lie in the interval 11.3–11.9 K. The T_c value proved to be slightly dependent on the current orientation. This effect is demonstrated in Fig. 2 for the sample with $T_c \approx 11.5$ K measured at $\mathbf{J} \parallel (ac)$. As seen from the inset, for the $\mathbf{J} \perp (ac)$ T_c value proved to be about 0.6 K smaller. We would like to emphasize that this result does not depend on the current value at small currents 1–10 μ A. This means that this effect has nothing to do with the electron system overheating, which could take place because of the difference in the power dissipation for longitudinal and transversal geometries.

Since the crystal-structure measurements revealed a difference in the unit-cell volume of κ' -Cl crystals in comparison with that of κ -Cl, we found it interesting to investigate the influence of external pressure on the transport properties of our samples. As a rough check we have applied the pressure by cooling the sample immersed into a PES drop. The result of this experiment is shown in Fig. 5. In the temperature region 300–120 K the curve $R(T)$ for the sample immersed into a PES drop coincides with that obtained without it because at $T > 120$ K the drop is in the liquid state³² and does not create any pressure. When the temperature becomes smaller than 120 K the freezing liquid starts to compress the sample and its resistance diminishes because of the contraction of intermolecular S \cdot ·S contacts. As seen from the inset, the pressure leads to a decrease in the critical temperature by about 0.6 K. For different κ' -Cl samples the pressure effect was similar but in some cases it was hardly detectable because of the transition broadening. For comparison, the result of a similar experiment on a κ -Cl sample is presented in Fig. 6. One can see the semiconductor-like $R(T)$ dependence at ambient pressure similar to that observed earlier (see, for example, Refs. 4, 5, and 7). Under the pressure created by

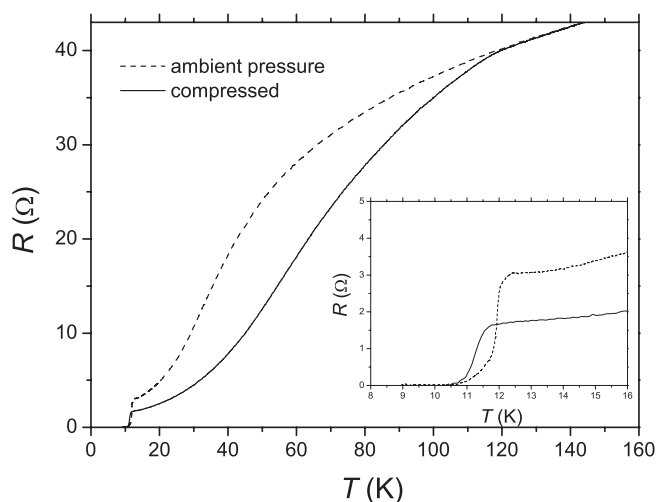


FIG. 5. Influence of the pressure on the temperature dependence of the sample resistance for κ' -Cl.

the PES drop the sample resistance at $T < 120$ K diminishes considerably and at $T \approx 12.4$ K the superconducting transition occurs. Using the pressure dependence of T_c for κ -Cl (Refs. 4, 6, and 33) we have estimated the pressure created by the drop of PES. It proved to be in the limits of 300–400 bars.

Let us now turn to the effect of a magnetic field, which proved to be dependent from both the field orientation and the current direction in the sample. The application of a magnetic field resulted in a lowering T_c and an essential broadening of the superconducting transition took place at $\mathbf{J} \parallel (ac)$ geometry. However, at $\mathbf{J} \perp (ac)$ the transition shifted to lower temperatures and no considerable broadening was observed (Figs. 7 and 8). At the same time one can see a rise of the measured transversal resistance R_{\perp} with the temperature drop just before the superconducting transition. This part of the $R(T)$ curve with $dR/dT < 0$ may be considered as an evolution of a small portion with a negative derivative observed near the superconducting transition at $B=0$. We explain this growth by the increase of the resistivity anisotropy

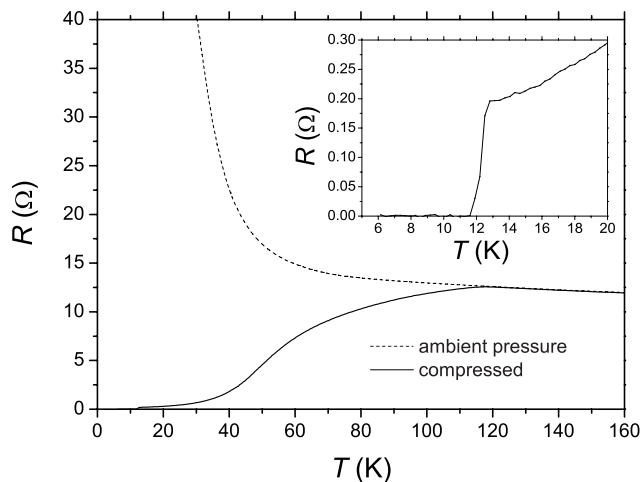


FIG. 6. Influence of the pressure on the temperature dependence of the sample resistance for κ -Cl.

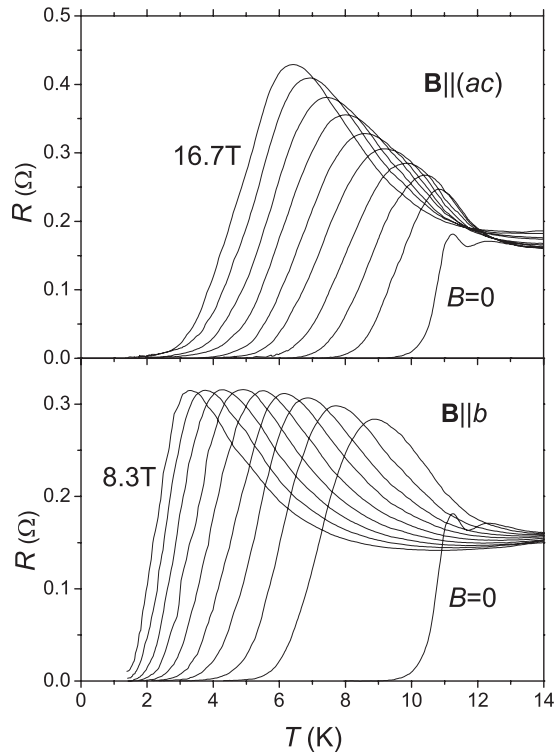


FIG. 7. Influence of magnetic field on the superconducting transition detected by transversal resistance for two different orientations of magnetic field. For each set of the curves the field changes by a constant interval within the shown limits.

near T_c . To check this statement we have calculated the ρ_b and ρ_{ac} values in the vicinity of the superconducting transition in the presence of the magnetic field (see Fig. 9). As shown in the figure, the ρ_b value is almost temperature independent above T_c , while ρ_{ac} goes down with the temperature decrease leading to an increase of the ρ_b/ρ_{ac} value. At fixed ρ_b the smaller is the longitudinal resistivity, the greater is the transversal voltage, and, consequently, the greater is the mea-

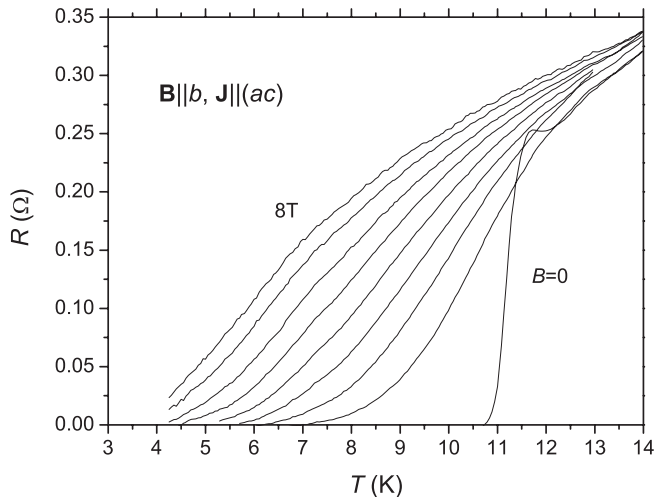


FIG. 8. Influence of magnetic field on the superconducting transition detected by longitudinal resistance. The field changes by a constant interval within the shown limits.

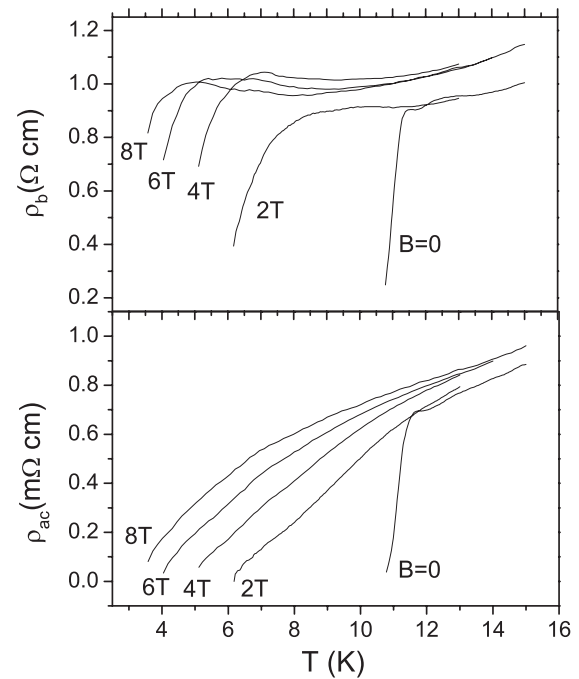


FIG. 9. Influence of magnetic field on the resistivity-tensor components ρ_{ac} and ρ_b in the vicinity of the superconducting transition.

sured R_{\perp} value. At $B=0$ a negative portion on $R_{\perp}(T)$ dependence near T_c appears because the superconducting transition starts for R_{\parallel} at a higher temperature than for R_{\perp} . This leads to the increase of the anisotropy and to the growth of R_{\perp} with the temperature decrease. At $B \neq 0$ this effect becomes more pronounced (Figs. 7 and 8) and the temperature interval for the portion with $dR/dT < 0$ becomes wider.

III. DISCUSSION

The crystal structure of the organic metal κ' -Cl has been found to be identical with that of the Mott insulator κ -Cl⁴ (Fig. 1). It is known that the BEDT-TTF molecule has some conformational degree of freedom of the terminal ethylene groups, which are basic units of a hydrogen-bond network linking the donor and counterion species. These two terminal groups can adopt either eclipsed (*e*) or staggered (*s*) configurations (see Fig. 10). The *e* and *s* configurations are energetically very similar for the isolated BEDT-TTF molecule. In the BEDT-TTF-based radical-cation salts one of the conformations may become preferred because of the particular cation-anion interactions. In most of the BEDT-TTF salts some disordering pattern is observed at room temperature due to the presence of both conformations. This conformational feature of the BEDT-TTF donor may be the reason underlying some specific physical properties of the BEDT-TTF-based conductors. In the present case we initially assumed that the κ' -Cl crystals were more ordered than those of κ -Cl because the degree of disorder of the ethylene groups exerts an important control of the superconductivity in these materials. Our results indicate that there is some disorder in the radical-cation layer of both κ -Cl and κ' -Cl crystals at room temperature. The ratio of the *e* and *s* conformations of

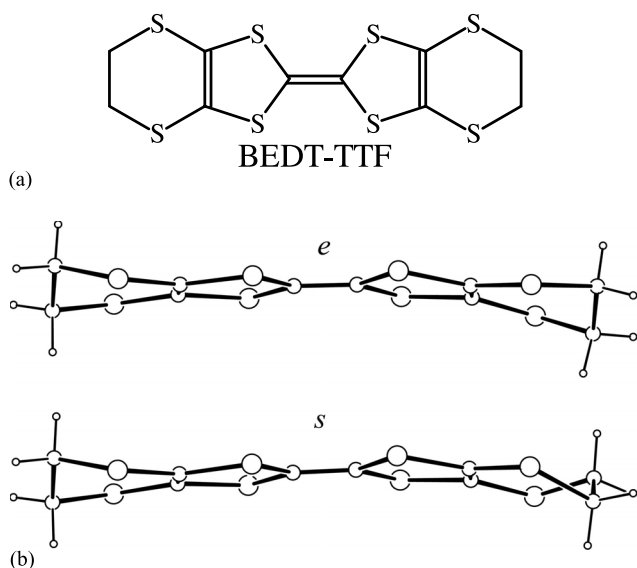


FIG. 10. Molecule of BEDT-TTF (a) and two possible conformations of the ethylene groups: eclipsed (*e*) and staggered (*s*) (b).

terminal ethylene groups is the same, 0.8:0.2. There is an ordering tendency towards the eclipsed conformation at low temperatures although it is not complete even at 90 K. The ratio of *e*:*s* conformations in the κ -Cl salt is 0.93:0.07, 0.98:0.02, and 0.98:0.02 at 150 K, 90 K (3), and 90 K+*P* (4), respectively. This observation is in agreement with the results of the thermal expansion measurements³⁴ and those of the specific heat studies³⁵ of κ -Cl single crystals, which imply that the ordering process of the ethylene groups is not completed at about 80 K (temperature of a glass-like transition).

The only feature definitely detected is that the unit-cell volume for the superconducting sample (κ' -Cl) is smaller than that for the nonsuperconducting one (κ -Cl) (Table I). It should be noted that the Argonne group had κ -Cl single crystals with the different unit-cell volumes: 3299(1) Å³ in Refs. 4, 13, and 15 and 3289.1(4) Å³ in Ref. 36. The unit-cell volume of our κ -Cl single crystals 3281.5(1.3) Å³ is close to the latter magnitude. An analysis of the intermolecular contacts in κ' -Cl crystals shows that their lattice is compressed as compared to that of κ -Cl ones (the difference in the unit-cell volumes of our κ' -Cl and κ -Cl crystals reaches 14.5 Å³). All intermolecular S··S contacts in the conducting layer are a little bit shorter, which results in enhanced intermolecular interactions and, consequently, wider partially filled bands. At this point we must consider what is the reason for the “chemical pressure”-like effect in two compounds with the same composition. We attempted to refine the occupation factor of Cu in the structures. A tendency towards larger Cu deficiency in the superconducting sample (7% as compared with only 1.5% in the nonsuperconducting one) was observed. We believe that it is the origin of the chemical pressure effect. Additionally, since the κ' -Cl crystals grow in the presence of Cu²⁺ dicyanamide, the incorporation of Cu²⁺ ions in the anion sheets seems to be quite plausible. The N(CN)₂[−] anion coordinating to a Cu²⁺ may stabilize the higher oxidation state of copper. The presence of Cu²⁺ ions

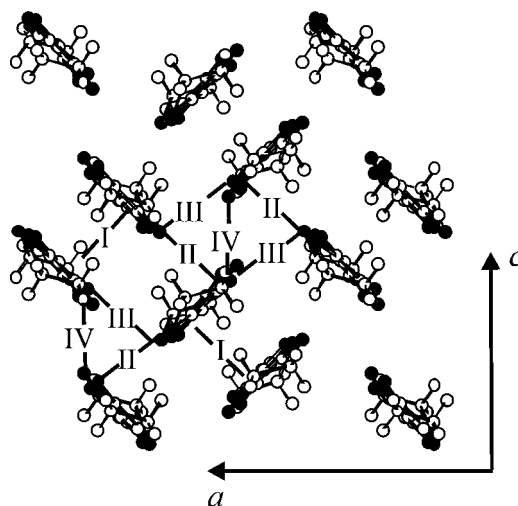


FIG. 11. Donor layer with labeling of the interactions.

contributes to lattice contraction too, as a consequence of the smaller ion radius of Cu²⁺ (0.80 Å vs 0.98 Å for Cu¹⁺). Besides, the partial substitution of Cu¹⁺ with Cu²⁺ as well as Cu deficiency results in a change in the number of electrical carriers, or, in other words, the doping of the Mott dielectric state (κ -Cl). The occurrence of the metallic state and superconductivity in the κ' -Cl crystals is possibly associated with this effect, as it occurs, for instance, in the κ' -(BEDT-TTF)₂Cu₂(CN)₃ superconductor³⁷ or in copper-oxide superconductors. It is well known that the metallic and superconducting states in the copper-oxide systems are realized as a consequence of the carrier doping in the antiferromagnetic insulating state.

Tight-binding band-structure calculations for (1)–(4) show that the differences in the band structures and Fermi surfaces are indeed very small. The Fermi surface consists of overlapping distorted circles and therefore is two-dimensional in nature, as in the case of other κ -phase salts.¹³ Because of the similarity with those for other κ phases, these results are not reported here. A more sensitive measure of the differences in the electronic structure is provided by a comparison of the different HOMO··HOMO interactions occurring in the donor layers. The strength of such interactions in salts (1)–(4) may be evaluated from the so-called $\beta_{\text{HOMO-HOMO}}$ interaction energies³⁸ (see Fig. 11 for the labeling) reported in Table II. Those for the room-temperature structures of κ' -Cl (1) and κ -Cl (2) are very similar. In addition, those for κ -Cl show the expected trend of a slight increase (interactions I, II, and IV) because of the thermal contraction. Although there also occurs a decrease of interaction III, the former dominates and leads to a slight decrease of the density of states at the Fermi level. Let us note that the intradimer interaction (I), which may be related to the on-dimer Coulomb interaction, is larger [and $n(e_f)$ is also larger as corresponds to weaker interdimer interactions] for the Mott insulator κ -Cl than for the organic metal κ' -Cl at the same temperature. According to the Kino-Fukuyama prediction³⁹ the Mott-insulator state is stabilized for larger intradimer interactions.

The transport properties of the κ' -Cl samples exhibit some interesting features. First of all we note the difference

TABLE II. Values of the $|\beta_{\text{HOMO-HOMO}}|$ for the different interactions and density of states at the Fermi level $n(e_f)$ [electrons/(eV·unit cell)] in the four structures.

Structure	$ \beta_{\text{HOMO-HOMO}} /\text{eV}$				$n(e_f)$
	I	II	III	IV	
1	0.4503	0.1909	0.0591	0.1308	7.21
2	0.4521	0.1904	0.0581	0.1294	7.32
3	0.4700	0.2066	0.0540	0.1411	6.83
4	0.4717	0.2070	0.0557	0.1416	6.78

in the superconducting transition temperature measured at different current orientations (see Fig. 2). The same, but much more pronounced effect was observed earlier in the layered high- T_c superconductors.^{40,41} The possible physical reason for the different T_c values obtained from longitudinal and transversal resistance measurements is a layer-decoupling transition, the so-called ‘‘Friedel transition,’’⁴² which occurs for a disordered layer array.⁴³

Another very interesting and intriguing feature is the strikingly different behavior of the $R(T)$ dependencies in the presence of a magnetic field for $\mathbf{J}\parallel(ac)$ and $\mathbf{J}\perp(ac)$ (compare Figs. 7 and 8). For $\mathbf{J}\parallel(ac)$ one can see a ‘‘fan-shaped’’ broadening which is typical for high- T_c superconductors and is attributed to the mechanism of dissipative interaction of the current with the Abrikosov vortices. We believe that in our samples the broadening for $\mathbf{J}\parallel(ac)$ occurs because of the same mechanism as in high- T_c superconductors despite the much smaller T_c values. This is supported by the observations⁴⁴ of very feeble pinning effects in organic superconductors due to the breakup of the three-dimensional vortex lines into the uncorrelated two-dimensional pancakes. As for the $\mathbf{J}\perp(ac)$ geometry, the dissipative effects seem to be suppressed probably because the pancakes in the conducting layers interact dissipatively mainly with the current component parallel to the layer. The absence of noticeable broadening in a magnetic field at $\mathbf{J}\perp(ac)$ allows us to determine the resistive upper-critical-field value B_{cr} and to plot $B_{cr}(T)$ dependencies from the set of the curves $R_{\perp}(T)$ at different B [or $R_{\perp}(B)$ at different T]. The $B_{cr}(T)$ dependence for two magnetic-field orientations is shown in Fig. 12. All points but one were obtained from the $R(T)$ curves at fixed B . The last point in the bottom curve was obtained from the $R(B)$ curve at fixed $T=1.2$ K. Of special note is the positive curvature of the $B_{cr}(T)$ dependencies and the fact that for $\mathbf{B}\parallel b$ the derivative dB_{cr}/dT is very small at $B=0$. Nevertheless, as seen from the inset, this derivative is finite and is equal to $dB_{cr}/dT|_{B=0}=-0.075$ T/K. When the magnetic field is along the (ac) plane, this value is about 18 times greater and equals -1.36 T/K. Taking into account that for the $\mathbf{J}\perp(ac)$ geometry the dissipative interaction of the vortices with the current is suppressed, i.e., we deal with the superconducting transition rather than with the points on the ‘‘irreversibility line’’ of the B - T -vortex phase diagram, we can consider that $B_{cr}(T)$ dependencies in Fig. 12 correspond to the temperature dependencies of the upper critical field $B_{c2}(T)$.

The positive curvature of $B_{c2}(T)$ dependencies was observed earlier in organic superconductors $\beta_{\text{H}}(\text{BEDT}$

-TTF)₂I₃, κ -(BEDT-TTF)₄Hg_{2.89}Br₈,⁴⁵ and κ -(BEDT-TTF)₂X, where $X=\text{Cu}(\text{NCS})_2$, $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$, $\text{Cu}[\text{N}(\text{CN})_2]\text{CN}$,⁴⁶ in layered low-temperature superconductors TaS₂ and NbSe₂,⁴⁷ in high-temperature superconductors Y-Ba-Cu-O, Tl-Ba-Cu-O, Bi-Sr-Cu-O (Ref. 48) and in some other superconductors. This behavior cannot be explained in the frame of the BCS theory. Despite numerous theoretical models the adequate theory for this phenomenon still does not exist.

Although the crystal and calculated band structures of κ' -Cl and κ -Cl salts are practically identical, the former is a metal at ambient pressure; in contrast, the latter is a semiconductor. The most direct way to explain the main properties of the κ' -Cl crystals is to suppose that it is identical to κ -Cl, compressed by some pressure sufficient to transform it from the Mott-insulator to metal state. Within this model the compression, determined by the chemical-pressure effect, may be estimated from the comparison of the transport properties of the κ' -Cl samples with that of compressed κ -Cl ones. Taking into account the results of Refs. 4, 6, and 33, and we can state that both the metalliclike $R(T)$ dependence at $T < 100$ K and the $T_c \approx 11.5$ K value for κ' -Cl correspond to compressed κ -Cl at about 500–600 bar pressure. Another way to estimate the effective pressure within this model is to compare the lattice parameters of κ' -Cl with those in κ -Cl

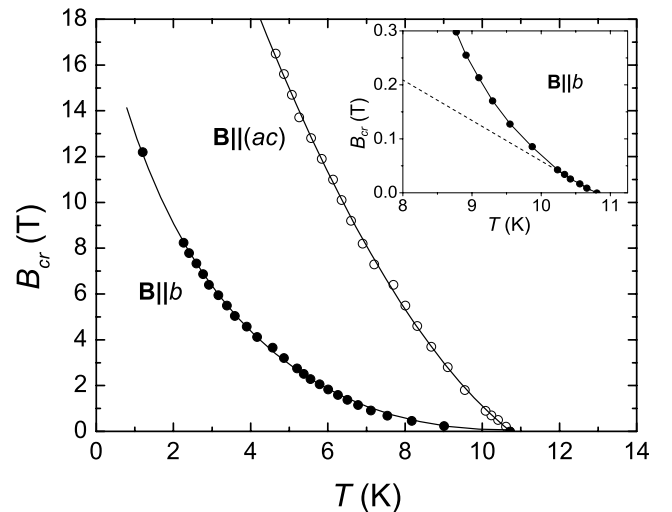


FIG. 12. Dependencies $B_{cr}(T)$ for the magnetic-field orientation in the plane of the conducting layers and along the normal to these layers.

under pressure. Using the data of Ref. 36 we get approximately the same value. Unfortunately this simple model does not take into account two circumstances. First, since κ' -Cl salt is Cu deficient and probably contains a small amount of Cu^{2+} instead of Cu^{1+} , the band filling will be somewhat different. Second, the presence of paramagnetic impurities (Cu^{2+}) may affect the T_c value.^{37,49} One can assume that the content of Cu^{2+} may be different for different κ' -Cl samples, which could be the reason for the observed difference in T_c values. It is interesting to note that (i) in contrast to the ambient-pressure superconducting κ -Br crystals, which show the resistivity maximum around 90 K,⁵⁰ the resistivity of κ' -Cl does not pass through maximum under the cooling and (ii) the temperature dependencies of the upper-critical field $B_{c2}(T)$ for κ' -Cl differ markedly from those for κ -Cl under pressure.⁵¹ The analysis outlined above provides some valuable insights into the factors that could control transport properties of κ' -Cl crystals although more complete studies are necessary and they are underway.

IV. CONCLUSION

In conclusion, we have performed transport measurements, x-ray study, and band-structure calculations on the

κ' -Cl and κ -Cl single crystals. These studies show that they are isostructural, and consequently their electronic structures are very similar. At room temperature there is the same disorder in the radical-cation layer: the ratio of e and s conformations of terminal ethylene groups of the BEDT-TTF molecule is 0.8:0.2 in both κ' -Cl and κ -Cl crystals. However, the two salts differ in their transport properties. At ambient pressure, κ -Cl is a Mott insulator and κ' -Cl is a superconductor with a critical temperature lying in the range 11.3–11.9 K. Two parameters, which can be responsible for the difference in transport properties of these salts were found: the smaller unit-cell volume and the greater deficiency of Cu in κ' -Cl in comparison with κ -Cl. The transport measurements reveal an anisotropy of superconducting properties as well as a non-trivial temperature dependence of the upper critical field.

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- ¹T. Ishiguro, K. Yamaji, and G. Saito, in *Organic Superconductors*, 2nd ed., edited by P. Fulde, Springer Series in Solid State Science Vol. 88 (Springer, Berlin, 1998).
- ²R. H. McKenzie, *Science* **278**, 820 (1997); *Comments Condens. Matter Phys.* **18**, 309 (1998); B. J. Powell and R. H. McKenzie, *Phys. Rev. Lett.* **94**, 047004 (2005).
- ³A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, and M.-H. Whangbo, *Inorg. Chem.* **29**, 2555 (1990).
- ⁴J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M.-H. Whangbo, *Inorg. Chem.* **29**, 3272 (1990).
- ⁵H. H. Wang, K. D. Carlson, U. Geiser, A. M. Kini, A. J. Schultz, J. M. Williams, L. K. Montgomery, W. K. Kwok, U. Welp, K. G. Vandervoort, S. J. Boryschuk, A. V. Strieby Crouch, J. M. Kommers, D. M. Watkins, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M.-H. Whangbo, *Synth. Met.* **41–43**, 1983 (1991).
- ⁶J. E. Schirber, D. L. Overmyer, K. D. Carlson, J. M. Williams, A. M. Kini, H. H. Wang, H. A. Charlier, B. J. Love, D. M. Watkins, and G. A. Yaconi, *Phys. Rev. B* **44**, 4666 (1991).
- ⁷Yu. V. Sushko, V. A. Bondarenko, R. A. Petrosov, N. D. Kushch, and E. B. Yagubskii, *J. Phys. II* **1**, 1015 (1991).
- ⁸N. D. Kushch, L. I. Buravov, A. G. Khomenko, E. B. Yagubskii, L. P. Rozenberg, and R. P. Shibaeva, *Synth. Met.* **53**, 155 (1993).
- ⁹N. D. Kushch, L. I. Buravov, A. G. Khomenko, S. I. Pesotskii, V. N. Laukhin, E. B. Yagubskii, R. P. Shibaeva, V. E. Zavodnik, and L. P. Rozenberg, *Synth. Met.* **72**, 181 (1995).
- ¹⁰R. P. Shibaeva, S. S. Khasanov, N. D. Kushch, E. B. Yagubskii, K. Boubekour, P. Batail, and E. Canadell, in *Supramolecular Engineering of Synthetic Metallic Materials, Conductors and Magnets*, edited by J. Veciana, C. Rovira, and D. B. Amabilino, NATO Advanced Studies Institute Series C518 (Kluwer Academic Publishers, Dordrecht, 1999), p. 409.
- ¹¹N. D. Kushch, M. A. Tanatar, E. B. Yagubskii, and T. Ishiguro, *Pis'ma Zh. Eksp. Teor. Fiz.* **73**, 479 (2001) [*JETP Lett.* **73**, 429 (2001)].
- ¹²M. A. Tanatar, T. Ishiguro, S. Kagoshima, N. D. Kushch, and E. B. Yagubskii, *Phys. Rev. B* **65**, 064516 (2002).
- ¹³U. Geiser, A. J. Shultz, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M.-H. Whangbo, *Physica C* **174**, 475 (1991).
- ¹⁴U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, *Phys. Rev. Lett.* **69**, 840 (1992).
- ¹⁵K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, *Phys. Rev. Lett.* **75**, 1174 (1995).
- ¹⁶H. Ito, T. Ishiguro, M. Kubota, and G. Saito, *J. Phys. Soc. Jpn.* **65**, 2987 (1996).
- ¹⁷P. Limelette, P. Wzietek, S. Florens, A. Georges, T. A. Costi, C. Pasquier, D. Jérôme, C. Mézière, and P. Batail, *Phys. Rev. Lett.* **91**, 016401 (2003).
- ¹⁸F. Kagawa, T. Itou, K. Miyagawa, and K. Kanoda, *Phys. Rev. B* **69**, 064511 (2004).
- ¹⁹F. Kagawa, K. Miyagawa, and K. Kanoda, *Nature (London)* **438**, 534 (2005).

- ²⁰K. Miyagawa, K. Kanoda, and A. Kawamoto, Chem. Rev. (Washington, D.C.) **104**, 5635 (2004).
- ²¹E. B. Yagubskii, N. D. Kushch, A. V. Kazakova, L. I. Buravov, V. N. Zverev, A. I. Manakov, S. S. Khasanov, and R. P. Shibaeva, Pis'ma Zh. Eksp. Fiz. **82**, 93 (2005) [JETP Lett. **82**, 99 (2005)]; Proceedings of ISCOM'2005 [J. Low. Temp. Phys. (to be published)].
- ²²H. H. Wang, U. Geiser, J. M. Williams, K. D. Carlson, A. M. Kini, J. M. Mason, J. T. Perry, H. A. Charlier, A. V. S. Crouch, J. E. Heindl, M. W. Lathrop, B. J. Love, D. M. Watkins, and G. A. Yaconi, Chem. Mater. **4**, 247 (1992).
- ²³U. Geiser, H. H. Wang, C. E. Hammond, M. A. Firestone, M. A. Beno, K. D. Carlson, L. Nunez, and J. M. Williams, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **43**, 656 (1987).
- ²⁴M. Kurmoo, D. Talham, P. Day, J. A. K. Howard, A. Stringer, I. Parker, A. Obertelli, and R. H. Friend, Synth. Met. **22**, 415 (1988).
- ²⁵T. Naito, T. Inabe, K. Takeda, K. Awaga, T. Akutagawa, T. Hasegawa, T. Nakamura, T. Kakiuchi, H. Sawa, T. Yamamoto, and H. Tajima, J. Mater. Chem. **11**, 2221 (2001).
- ²⁶R. M. Lobkovskaya, R. P. Shibaeva, E. E. Laukhina, and A. V. Zvarykina, Zh. Strukt. Khim. **31**, 31 (1990) [J. Struct. Chem. **31**, 687 (1991)].
- ²⁷G. M. Sheldrick, *SHELXL-97* (University of Göttingen, Göttingen, 1997).
- ²⁸M.-H. Whangbo and R. Hoffmann, J. Am. Chem. Soc. **100**, 6093 (1978).
- ²⁹J. Ammeter, H.-B. Bürgi, J. Thibeault, and R. Hoffmann, J. Am. Chem. Soc. **100**, 3686 (1978).
- ³⁰A. Pénicaud, K. Boubekur, P. Batail, E. Canadell, P. Auban-Senzier, and D. Jérôme, J. Am. Chem. Soc. **115**, 4101 (1993).
- ³¹L. I. Buravov, Zh. Tekh. Fiz. **59**, 138 (1989) [Sov. Phys. Tech. Phys. **34**, 464 (1989)].
- ³²A. S. Kirichenko, A. V. Kornilov, and V. M. Pudalov, Instrum. Exp. Tech. **48**, 813 (2005).
- ³³Yu. V. Sushko and K. Andres, Phys. Rev. B **47**, 330 (1993).
- ³⁴J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A. M. Kini, and T. Sasaki, Phys. Rev. B **65**, 144521 (2002).
- ³⁵H. Akutsu, K. Saito, and M. Sorai, Phys. Rev. B **61**, 4346 (2000).
- ³⁶A. J. Shultz, H. H. Wang, J. M. Williams, L. W. Finger, R. M. Hazen, C. Rovira, and M.-H. Whangbo, Physica C **234**, 300 (1994).
- ³⁷T. Komatsu, N. Matsukawa, T. Inoue, and G. Saito, J. Phys. Soc. Jpn. **65**, 1340 (1996).
- ³⁸M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, and H. H. Wang, Inorg. Chem. **24**, 3500 (1985). Since overlap is explicitly included in extended Hückel calculations, these interaction energies (β) should not be confused with the conventional transfer integrals (t). Although the two quantities are obviously related and have the same physical meaning, the absolute values of β are somewhat larger than those of t .
- ³⁹H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 2158 (1996).
- ⁴⁰V. L. Arbutov, O. M. Bakunin, A. E. Davletshin, S. M. Klotsmanet, and M. B. Kosmyna, JETP Lett. **48**, 440 (1988).
- ⁴¹V. N. Zverev, D. V. Shovkun, and I. G. Naumenko, JETP Lett. **68**, 332 (1998).
- ⁴²J. Friedel, J. Phys. (Paris) **49**, 1561 (1988).
- ⁴³M. Dzierzava, M. Zamora, D. Baeriswyl, and X. Bagnoud, Phys. Rev. Lett. **77**, 3897 (1996).
- ⁴⁴S. L. Lee, F. L. Pratt, S. J. Blundell, C. M. Aegerter, P. A. Patenden, K. H. Chow, E. M. Forgan, T. Sasaki, W. Hayes, and H. Keller, Phys. Rev. Lett. **79**, 1563 (1997); L. Ya. Vinnikov, T. L. Barkov, M. V. Kartsovnik, and N. D. Kushch, Phys. Rev. B **61**, 14358 (2000).
- ⁴⁵I. F. Schegolev, Jpn. J. Appl. Phys., Suppl. **26**, 1972 (1987).
- ⁴⁶K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 730 (1988); W. K. Kwok, U. Welp, K. D. Carlson, G. W. Crabtree, K. G. Vandervoort, H. H. Wang, A. M. Kini, J. M. Williams, D. L. Stupka, L. K. Montgomery, and J. E. Thompson, Phys. Rev. B **42**, 8686 (1990); T. Nakamura, T. Komatsu, G. Saito, T. Osada, S. Kagoshima, N. Miura, K. Kato, Yu. Maruyama, and K. Oshima, J. Phys. Soc. Jpn. **62**, 4373 (1993).
- ⁴⁷D. E. Prober, R. E. Schwall, and M. R. Beasley, Phys. Rev. B **21**, 2717 (1980); R. A. Klemm, A. Luther, and R. M. Beasley, *ibid.* **12**, 877 (1975).
- ⁴⁸V. F. Gantmakher, L. P. Kozeeva, A. N. Lavrov, and G. E. Tsydynzhapov, JETP **88**, 148 (1999); D. D. Lawrie, J. P. Franck, J. R. Beamish, E. B. Molz, Wei-min Chen, and M. J. Graf, J. Low Temp. Phys. **107**, 491 (1997); A. P. Mackenzie, S. R. Julian, G. G. Lonzarich, A. Carrington, S. D. Hughes, R. S. Liu, and D. C. Sinclair, Phys. Rev. Lett. **71**, 1238 (1993); M. S. Osofsky, R. J. Soulen, Jr., S. A. Wolf, J. M. Broto, H. Rakoto, J. C. Ousset, G. Coffe, S. Askenazy, P. Pari, I. Bozovic, J. N. Eckstein, and G. F. Virshup, Phys. Rev. Lett. **71**, 2315 (1993).
- ⁴⁹O. Drozdova, G. Saito, H. Yamochi, K. Ookubo, K. Yakushi, M. Uruichi, and L. Ouahab, Inorg. Chem. **40**, 3265 (2001).
- ⁵⁰C. Strack, C. Akinci, V. Pashchenko, B. Wolf, E. Uhrig, W. Assmus, M. Lang, J. Schreuer, L. Wiehl, J. A. Schlueter, J. Wosnitza, D. Schweitzer, J. Müller, and J. Wykhoff, Phys. Rev. B **72**, 054511 (2005).
- ⁵¹Y. Shimojo, T. Ishiguro, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **71**, 1716 (2002).