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Organic Superconductor κ-(BEDT-TTF)$_2$[CU(NCS)$_2$] and Its Related Materials

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ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] AND ITS RELATED MATERIALS

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Abstract The chemical, physical and structural features of an organic superconductor, κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$], and an organic metal, (BEDT-TTF)$_2$[KHg(SCN)$_4$], are described. The isotope effect, H_{c2} value, ^{1}H-NMR relaxation rate, and energy gap of the former are not explained by the simple BCS theory. The Shubnikov-de Haas effect and angle-dependent quantum oscillation were observed in the latter.

INTRODUCTION

Among the organic superconductors so far prepared, κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] (abbreviated to κ-Cu(NCS)$_2$ salt hereafter) has the highest Tc (10.4-11.1K). Extensive chemical and physical studies on this compound have been carried out,[1] but as yet the difinite picture on the mechanism of superconductivity of this material is not clear since various transport and magnetic properties in the superconducting phase cannot be explained by the simple BCS theory. Here we will overview the characteristic features of κ-Cu(NCS)$_2$ salt stressing the anomalous behaviors on the inverse isotope effect, superconducting critical fields, superconducting energy gap, etc.

Very recent progress in the organic conductors came from the observations of the Fermi surface of several organic conductors and superconductors.[2] κ-Cu(NCS)$_2$ salt was the first organic compound on which the Shubnikov-de Haas(SdH) effect was observed. The angle-dependent quantum oscillation of megnetoresistance has been also reported for some BEDT-TTF conductors.[2c,3] We have prepared (BEDT-TTF)$_2$[KHg(SCN)$_4$] (KHg(SCN)$_4$ salt) as a modification of κ-Cu(NCS)$_2$ salt. KHg(SCN)$_4$ salt was found to be a typical two-dimensional organic metal and to show the angle-dependent quantum oscillation of magneto-resistance in addition to the SdH effect.[5]

CRYSTAL GROWTH OF κ-$Cu(NCS)_2$ SALT AND $KHg(SCN)_4$ SALT

The electrochemical oxidation of BEDT-TTF(30mg) in 100ml of 1,1,2-trichloroethane(TCE) in the presence of CuSCN(70mg), KSCN(130mg) and 18-crown-6 ether(200mg) afforded black shinny single crystals of κ-$Cu(NCS)_2$ with a typical dimension of $3x2x0.05mm^3$. Thicker and longer crystals were obtained in the mixture of TCE and ethanol (1-10 W%) but twins appeared frequently. By using the reaction product (white plates) of KSCN, CuSCN and 18-crown-6 ether as the supporting electrolyte, the same κ-$Cu(NCS)_2$ crystals were obtained from TCE, dichloromethane or 1,2-dichloroethane, but a mixture of κ-$Cu(NCS)_2$ and (BEDT-TTF)[$Cu_2(SCN)_3$] was harvested from tetrahydrofuran.

By employing $Hg(SCN)_2$ instead of CuSCN in the supporting electrolyte in the above electrolysis, black thick plates ($1.5x0.3x0.2 mm^3$) of the K^+ containing $KHg(SCN)_4$ salt were grown from the mixed solvent of TCE and 10 vol% of ethanol. K^+ ions in the crystals can be replaced by NH_4 ions by the same electrocrystallization method when NH_4SCN is used instead of KSCN. This salt, (BEDT-TTF)$_2$[$NH_4Hg(SCN)_4$], exhibited almost the same crystal structure and electrical properties as those of $KHg(SCN)_4$ salt. Different polymorphs of BEDT-TTF salts with mercury thiocyanate have been also prepared under the different conditions of electrolysis.[6]

CRYSTAL AND ELECTRONIC STRUCTURES

κ-$Cu(NCS)_2$ Salt

Figure 1 shows the crystal structures of κ-$Cu(NCS)_2$ salt? Two crystallographycally independent BEDT-TTF molecules form a dimerized pair and the dimers are arranged almost perpendicularly to each other. Since the corresponding bond lengths and bond angles of two independent donors are almost the same, it is reasonable to predict that every donor molecules have the same formal charge of +0.5. A number of short S..S atomic contacts were observed both between dimers and within a dimer. This sort of atomic contacts together with the special arrangement of the donors in the crystal lead to the two-dimensional electronic structure within the bc plane. The two-dimensional layer composed of donor molecules is sandwitched by the insulating anion layers along the a axis. The anion layer has a very unique structure.

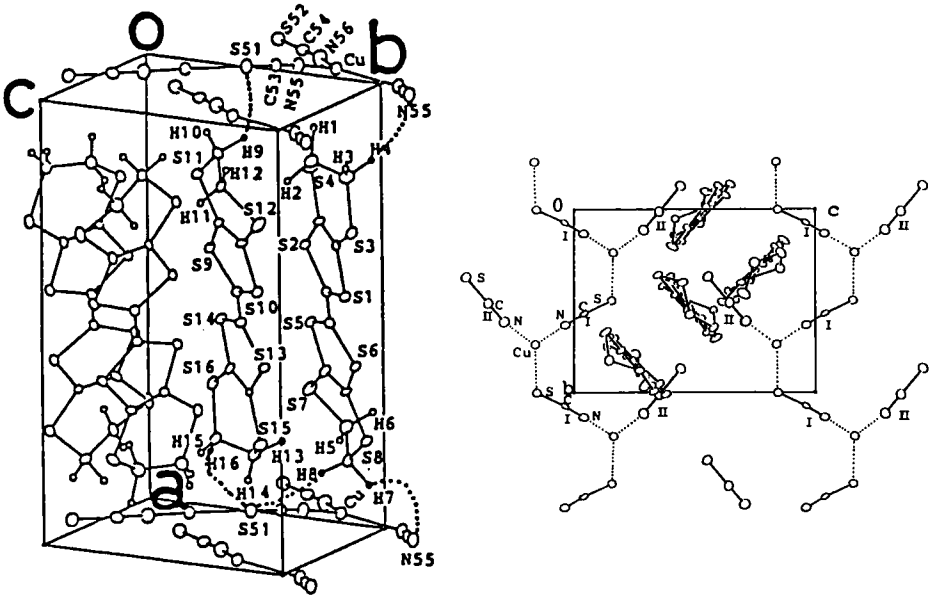

FIGURE 1 Crystal structure of κ-(BEDT-TTF-h_8)$_2$[Cu(NCS)$_2$] at 104K (dextrorotatory form). Dotted lines indicate short atomic contacts between BEDT-TTF and anion. (monoclinic, $P2_1$, a=16.382, b=8.402, c=12.833A, β=111.33°, V=1645.3A^3, Z=2)[7]

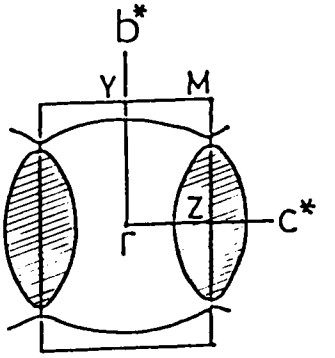

FIGURE 2 Fermi surface of κ-(BEDT-TTF-h_8)$_2$[Cu(NCS)$_2$] calculated by the tight-binding method based on the srystal structure at RT. Shaded regions indicate hole-like parts.[2a]

$Cu(NCS)_2$ anion is asymmetrically bent like a boomerang where two independent NCS groups (I and II) are almost linear (∠SCN(I)-Cu-NCS (II)=121° at RT, 118° at 104K). The repeating unit, SCN(I)-Cu-NCS(II), is linked one after the other along the b-axis to form a zigzag one-dimensional flat polymer; $-(-SCN(I)-Cu-)_n-$.
NCS(II)

Both of the nitrogen and sulfur atoms of the ligand NCS(I) can coordinate to copper cation (Cu^+), but it is the nitrogens of the ligand NCS(II) which are directed towards Cu^+. Every polymer aligns in the same direction to form insulating sheets in the bc plane. A number of short atomic contacts are present between the both terminal ethylene groups of BEDT-TTF molecules and the nitrogen and sulfur atoms of the ligand NCS(I). Therefore every two-dimensional conducting layer is linked to each other through these short atomic contacts.

The calculated Fermi surface by T.Mori on the basis of the extended Hückel MO exhibits the complicated features; both a cylindrical closed surface which is hole-like and a modulated open surface which is electron-like construct the Brillouin zone (Fig.2).[2a]

$KHg(SCN)_4$ Salt

Figure 3 shows the crystal structures of $KHg(SCN)_4$ salt.[4] There are three crystallographycally independent BEDT-TTF molecules, A, B and C, and they have the same formal charge of +0.5. BEDT-TTF molecules form two different kinds of segregated columns along the c axis. One of them is composed of equivalent BEDT-TTF molecule A, and the other is made of B and C. The dihedral angles between the molecules in the neighboring columns are 75.7° and 81.9°. Since there are a number of short S..S atomic contacts along the a axis, a two-dimensional conducting sheet is constructed within the ac plane.

The anion $KHg(SCN)_4$ forms polymer but the polymeric structure is much different from that observed in the $Cu(NCS)_2$ salt. Every sulfur and nitrogen atoms of every ligand are linked to K or Hg as is shown in Fig.3 schematically, where K^+ ions are electrostatically linked to four SCN groups with nitrogens to form a pyramid while the softer Hg^{+2} ions are coordinated to four SCN ligands with sulfurs tetrahedrally. Consequently two-dimensional anion network is constructed within the ac plane (Fig.4). The anion-layer thickness is 6.8Å and is much larger than other BEDT-TTF compounds, so that the strong two-dimensionality

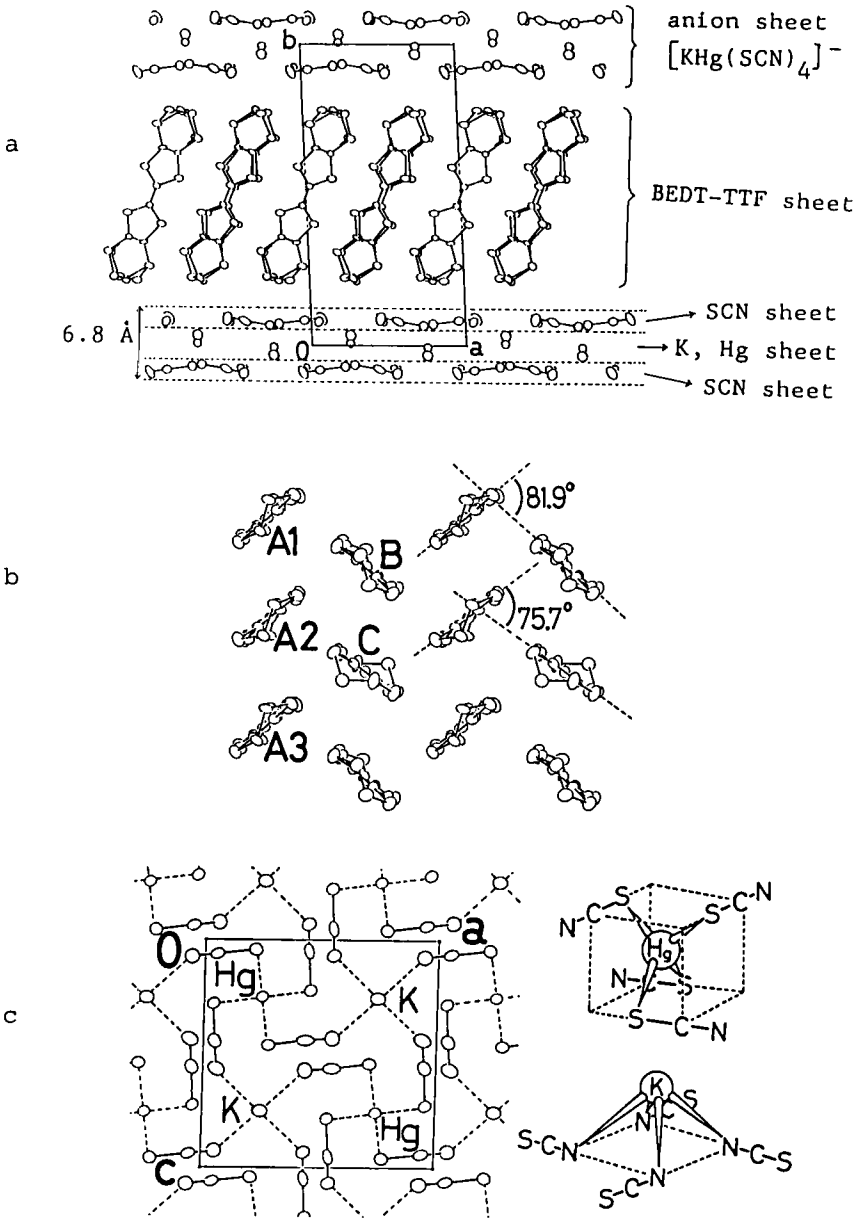

FIGURE 3 Crystal structures of (BEDT-TTF)$_2$[KHg(SCN)$_4$] at RT. a)along the c axis, b)molecular stacking of BEDT-TTF, c)polymeric structure of anion KHg(SCN)$_4$ and schematic structures of its component clusters. (triclinic, P$\bar{1}$, a=10.082, b=20.565, c=9.933A, α=103.70, β=90.91, γ=93.06°, V=1997A^3, Z=2)[4]

due to weak interlayer couplings is expected.

The conducting BEDT-TTF layer and the insulating anion layer repeat alternatingly along the b axis. Several short atomic contacts between the ethylene groups of BEDT-TTF and carbon, nitrogen and sulfur atoms of SCN were observed at low temperatures.

The calculated Fermi surface based on the extended Hückel MO consists of both the hole pockets at the corner of the Brillouin zone and a modulated one-dimensional open surface along ZΓ (Fig.5).[8]

ELECTRICAL PROPERTIES OF κ-Cu(NCS)$_2$ SALT[7a,9]

The conductivity at RT is not so high (10-40Scm^{-1}) which is normal for many BEDT-TTF superconductors. The conductivity anisotropy at RT is $\sigma_{a*}:\sigma_b:\sigma_c$=1/600:1:1.2 (the longest axis of the crystal corresponds to the b-axis and the developed face is the bc plane). A metallic temperature dependence was observed above 270K and below 90K, but the conductivity is thermally activated between them (Fig.6). The activation energy in the semiconductive-like region differs from sample to sample, and the magnetic measurements by ESR and ac spin susceptibility indicate a metalli property, hence the semiconductive-like behavior in this region is still unexplained. This kind of big enhancement of resistivity has been observed in several organic metals.

The mid-point of the resistivity jump at the superconducting transition (Tc) is 10.4K for the κ-Cu(NCS)$_2$ salt of protonated BEDT-TTF. If the Tc is determined by the simple BCS theory in which the molecular weight of donor molecule (M) is regarded as the isotope mass;

$$Tc \propto M^{\alpha}, \quad \alpha = -1/2 \qquad (1)$$

the Tc of the κ-Cu(NCS)$_2$ of the deuterated BEDT-TTF should be at around 10.3K. Contrary to this prediction the Tc of the κ-Cu(NCS)$_2$ salt of the deuterated BEDT-TTF was found to be somewhat higher than that of the protonated BEDT-TTF (inverse isotope effect). Tc is very sensitive to the chemical and physical purity of the salt, and the Tc of 11.1K was observed in the very pure deuterated compound by four-probe method (Fig.7). It has been known that the Tc of κ-Cu(NCS)$_2$ salt was suppressed very quickly by pressure (-1.3K/kbar), and this sensitivity makes the comparison of Tc only by four-probe method very unreliable. We have compared the Tc of the protonated and deuterated salt by the RF

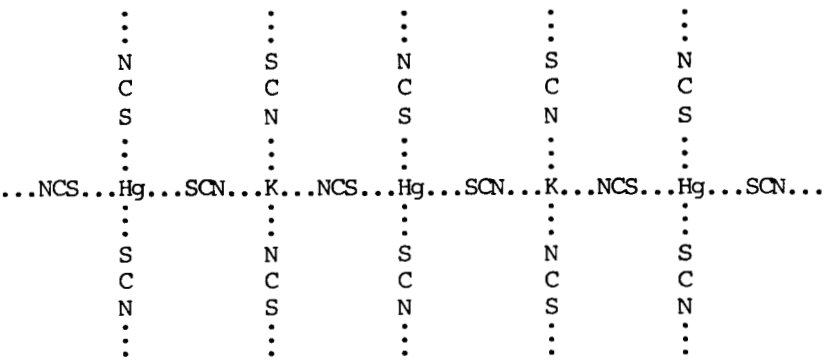

FIGURE 4 Schematic structure of two-dimensional anion network of $KHg(SCN)_4$.

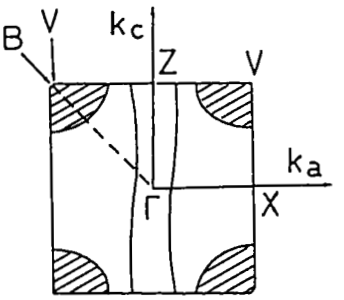

FIGURE 5 Fermi surface of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$ calculated by tight-binding method based on the crystal structure at RT. Shaded regions indicate hole-like parts.[8]

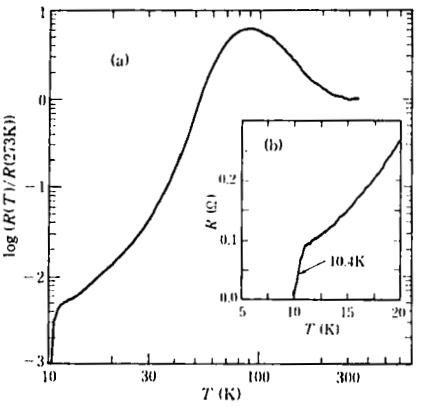

FIGURE 6 Temperature dependence of electrical resistivity of κ-(BEDT-$TTF\text{-}h_8)_2[Cu(NCS)_2]$.[7a]

penetration depth measurements, in which electrical contacts are not needed, and confirmed that the Tc of the deuterated salt is higher by about 0.6K than that of the protonated salt. Since the terminal hydrogens of BEDT-TTF are involved in the formation of the short atomic contacts with ligand SCN, the inverse isotope effect may indicate that the superconductivity of this salt is somewhat associated with the increase of the electron-phonon coupling in the deuterated salt through the short atomic interaction. We have measured the Tc of the salt κ-$Cu(^{15}NCS)_2$, in which ^{14}N atoms were substituted by ^{15}N, and found that its Tc is almost identical to that of κ-$Cu(NCS)_2$ salt within an experimental error. Then a salt of κ-$Cu(NCS)_2$ with ^{13}C-BEDT-TTF was prepared, where only four terminal ethylene carbons of BEDT-TTF were replaced by ^{13}C. A comparison of Tc by SQUID is underway.

Very recently Tc of 12.8K was observed in only one deuterated single crystal out of several in one batch.[10] But the crystal was broken by the thermal treatment during the process to check the reproducibility, so it is not identified yet whether the higher Tc is intrinsic or due to misread of temperature, or the Tc increase is due to the negative lattice pressure.[11]

MAGNETORESISTANCE OF κ-$Cu(NCS)_2$ SALT[9a,b,12]

The temperature dependence of the upper critical field is shown in Fig.8. The GL coherence lengths were calculated by using H_{c2} values near Tc and the following relation;

$$H^i_{c2}(T) = \Phi_0/2\pi\xi_j(T)\ \xi_k(T) = [\Phi_0/2\pi\xi_j(0)\xi_k(0)][(Tc-T)/Tc] \quad (2)$$

where Φ_0=hc/2e is the flux quantum, as $\xi_{//bc}:\xi_{a*}$=182A:9.6A=19:1. It is noteworthy that the coherence lengths are very two-dimensional and ξ_{a*} is less than the length of the interlayer distance along the a axis. This situation is similar to that of the high Tc oxide superconductors; ξ_c=3.8-6.3A (c≃11.6A) and ξ_{ab}=23-35A were deduced at 0K in YBCO.[13]

H_{c2} in the bc plane showed no saturation below 1K and H_{c2} values at low temperatures exceeded Pauli limited value (Hp);

$$Hp(kOe) = 18.4Tc. \quad (3)$$

H_{c2} value along the a* axis also showed no saturation and an upturned behavior was seen at low temperatures. The exceeded H_{c2} value in the bc plane for spin pair breaking, upturned behaviors and no saturation at

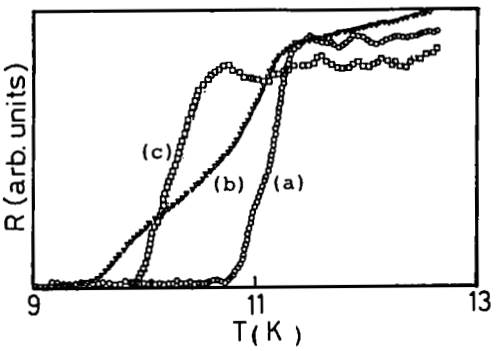

FIGURE 7 Superconducting transition of κ-(BEDT-TTF-d_8)$_2$[Cu(NCS)$_2$] with various purity; a)most purified, b)moderately purified, and c)no purified samples.[9d]

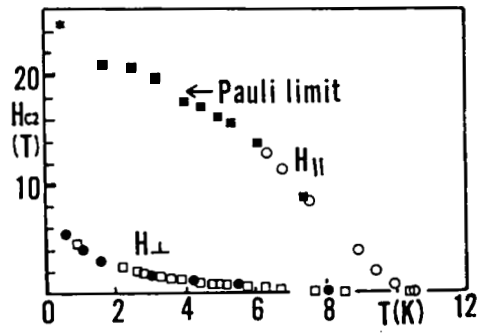

FIGURE 8 Temperature dependence of upper critical field of κ-(BEDT-TTF-h_8)$_2$[Cu(NCS)$_2$]. Pauli limit is indicated by an arrow.[9a,12]

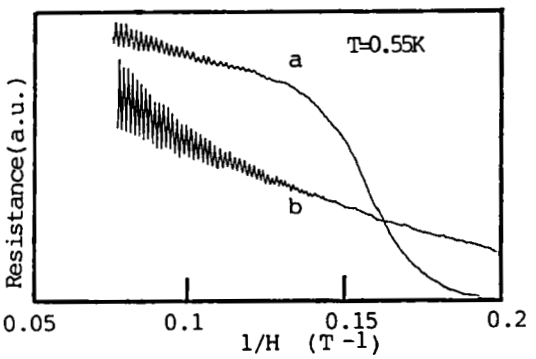

FIGURE 9 Shubnikov-de Haas signals of κ-(BEDT-TTF-d_8)$_2$[Cu(NCS)$_2$](H,I // a*); a)1bar and b)8kbar.[9]

low temperatures cannot be interpreted by the simple BCS theory.

SdH oscillation was observed (Fig. 9, T<~1K, H>~8T) indicating the existence of the closed Fermi surface. The oscillation of $\Delta(1/H)= 0.0015T^{-1}$ corresponds to the area of the extremal orbit of $S=6.37\times10^{14}$ cm^{-2} from $S = 2\pi e/\Delta(1/H)\hbar c$. The area corresponds to 18% of the first Brillouin zone. This is quantitatively equal to that of the calculated cylindrical Fermi surface in Fig. 2. SdH oscillation also gave an effective mass of $m/m^*=3.5$ at the Fermi level.

At higher pressure the magnitude of oscillation enhanced considerably. The effective mass decreased to $m/m^*=2.4$ at 8kbar and SdH oscillations indicated the coexistence of two other very small pockets, which correspond to 1 and 2% of the first Brillouin zone.[14]

^{1}H-NMR RELAXATION RATE OF κ-Cu(NCS)$_2$ SALT[15]

A Korringa relation was observed between 77K and 10K in the ^{1}H-NMR measurements on polycrystals indicating that the salt is metallic in this region. In the superconducting region, however, $1/T_1$ values started to deviate from the Korringa relation at around 7-8K and showed a big enhancement with a peak at considerably lower temperature than Tc (Fig. 10). The peak height is about 30 times than that of the normal state at 3.28KOe and peak position depends on the applied magnetic field. In a typical BCS superconductor, $1/T_1$ starts to increase just below Tc, reaching a maximum at around T=0.9Tc with the peak height of about twice of that of the normal state, and then decreases exponentially due to finite gap opening. Hasegawa and Fukuyama theory[16] for the anisotropic superconductors of quasi-two-dimension predicts eight types of possible superconductivity, three of which are spin singlet states and the rest five are triplet. However, the observed features in Fig.10 are far from the predictions of their theory and are unexpected for usual superconductors to date. ^{13}C-NMR measurements on the ^{13}C-enriched κ-Cu(NCS)$_2$ salt are underway to investigate the curious behavior above mentioned more precisely.

SUPERCONDUCTIVITY GAP OF κ-Cu(NCS)$_2$ SALT[17]

The tunneling spectroscopic measurements on a junction of κ-Cu(NCS)$_2$ salt/Al_2O_3/Au revealed that no reliable spectra were obtained at

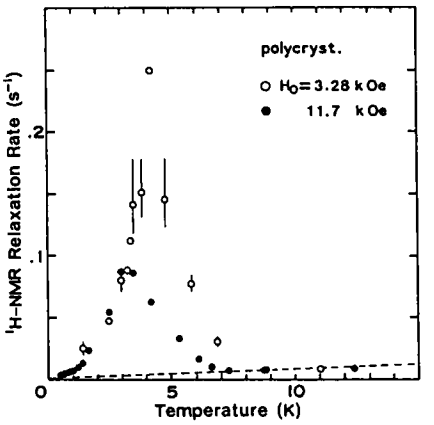

FIGURE 10 ^{1}H-NMR relaxation rate $1/T_1$ of κ-(BEDT-TTF-h_8)$_2$[Cu(NCS)$_2$] at low temperatures. The broken line indicates the Korringa behavior determined at high temperatures.[15]

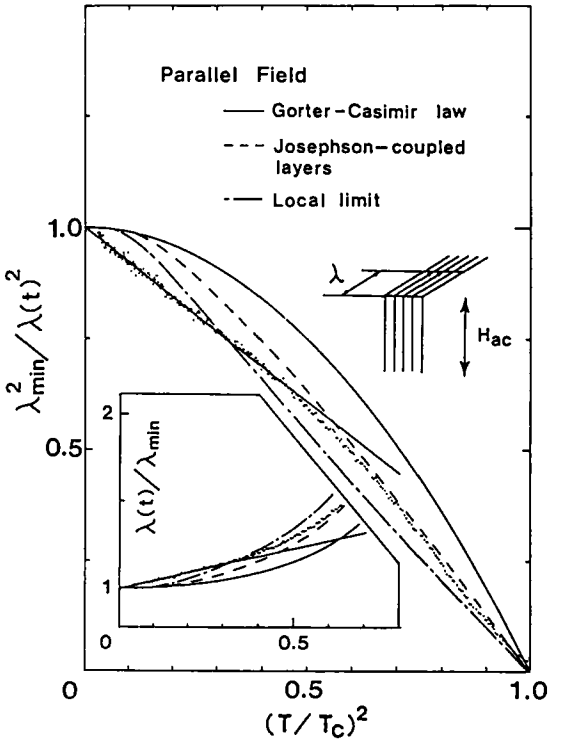

FIGURE 11 Temperature dependence of the penetration depth of κ-(BEDT-TTF-h_8)$_2$[Cu(NCS)$_2$], λ_{min} is the penetration depth at the lowest temperature studied in this work(1.5K).[17c-e]

temperatures above 4.2K. Furthermore the obtained spectra well below Tc do not coincide with each other. One of the gap data gave 4.5 for the $2\Delta_o/k_BTc$ ($2\Delta_o$=4meV and Tc=10.4K) which is a little larger than that of the BCS ratio, 3.52, where $2\Delta_o$ is the superconducting energy gap. The other samples showed much smaller gap structure, less than 1meV. A similar measurements for a deuterated salt has revealed that there seem to be three different superconducting gaps, 0.8, 2.1 and 4.3meV in the tunneling spectrum. Therefore at the moment we may postulate that the superconducting gaps of this salt are anisotropic.

The magnetic field penetration depth; λ, was deduced by the complex susceptibility measurements for single crystals in order to investigate the gap. The absolute value of λ was determined with the external ac field parallel to the crystal surface as λ=1.2mm at 1.5K, where the penetration is dominant in the direction of the two-dimensional layer. This value is extremely larger than those of the conventional superconductors, and also greater than that for $(TMTSF)_2ClO_4$ (170μm).[18]

The temperature dependences of λ with the ac field either parallel or perpendicular to the crystal surface showed $[\lambda(0)/\lambda(T)]^2=1-0.8x(T/Tc)^2$ (or $\lambda(T)/\lambda(0)=1+0.4(T/Tc)^2$), Fig.11, at low temperatures. This T^2 dependence is completely different from the exponential temperature dependence predicted by the simple BCS theory (in Fig.11 some theoretical and empirical predictions for conventional BCS type superconductors are compared). The power law dependence indicates that the superconducting energy gap of this salt is anisotropic with nodes on the Fermi surface as has been observed in the heavy electron systems.

ELECTRICAL PROPERTIES AND MAGNETORESISTANCE OF $KHg(SCN)_4$ SALT[5,19]

The electrical conductivities within the conducting plane (ac plane) at RT (20-100Scm^{-1}) and the temperature dependences vary from sample to sample. Some sample showed a big enhancement or a weak shoulder of resistivity at around 130K and some did not. In any case the compound is metallic at low temperatures but the conductivity increased only an order of magnitude compared to the RT value. The conductivity anisotropy is much larger than that of κ-$Cu(NCS)_2$ salt; σ_c/σ_b is more than 2000 at 4.2K where σ_b is the conductivity along the b* axis perpendicular to the conducting ac plane.

A typical result of the transverse magnetoresistance measurements

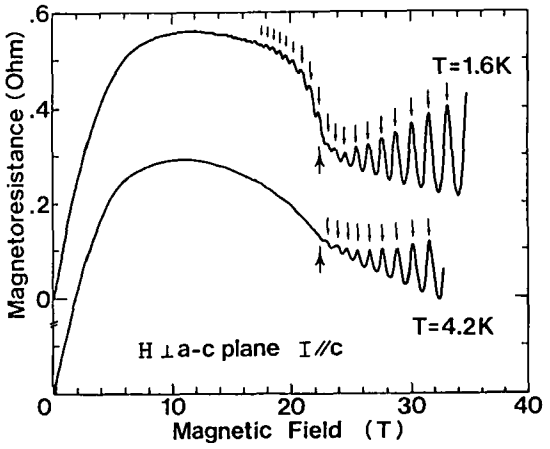

FIGURE 12 Transverse magnetoresistance of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$; the kink structure and the oscillation peaks are marked by arrows.[54]

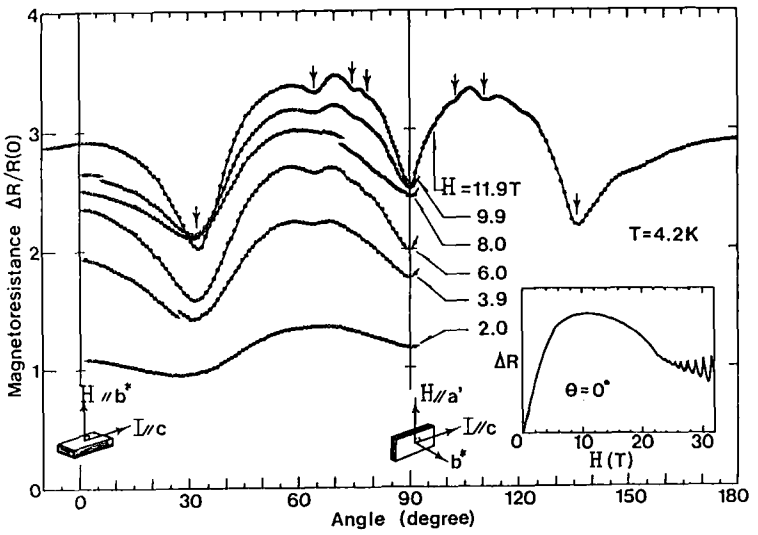

FIGURE 13 Angle-dependent quantum oscillations of magnetoresistance of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$; oscillation dips are indicated by arrows.[19]

is shown in Fig.12 where the external magnetic field is perpendicular to the ac plane and the current is parallel to the c axis. The magnetoresistance increased with increasing magnetic fields and showed saturation at around 10T. Then it showed an unusual negative slope above 10T. A sharp kink appeared at around 22.5T, the position of which is independent on temperature. SdH oscillations were superposed on this background magnetoresistance and the amplitude of the oscillations were largely enhanced above the kink. The oscillation period $0.0015T^{-1}$ corresponds to 16% of the first Brillouin zone which is comparable to that of the closed Fermi surface in Fig.5 (19%).

When the applied field is parallel to the a' axis, neither SdH oscillations nor kink structures were observed. The angle dependence of the magnetoresistance is shown in Fig.13 where the magnetic fields are tilted from the b* direction in the a'b* plane. The angle dependent quantum oscillations were observed as a series of dips, the positions of which are almost periodic against $\tan\theta$ where θ represents the angles between the field and the b* axis. The angle dependent oscillations indicate the existence of the weakly warped cylindrical Fermi surface according to the Yamaji's model.[20] The observed periods of $\Delta(\tan\theta) \simeq 1.5$ (magnetic fields are in the a'b* plane) and $\Delta(\tan\theta) \simeq 3$ (magnetic fields are in the b^*c plane) gave the Fermi wave numbers of $k_{Fa} \simeq 0.1A^{-1}$ and $k_{Fc} \simeq 0.05A^{-1}$, respectively, indicating a strong anisotropy in the cross-section of the cylindrical Fermi surface in the ac plane ($\simeq$2:1).

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