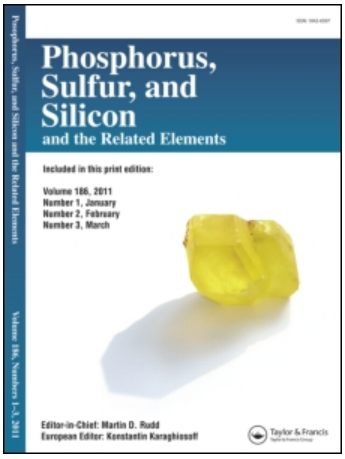

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Organic Superconductors Based on Sulfur and Selenium Compounds

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ORGANIC SUPERCONDUCTORS BASED ON SULFUR AND SELENIUM COMPOUNDS

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Abstract This paper describes brief background and outline of the organic superconductors based on TMTSF and BEDT-TTF. Especially we discuss the structural and physical properties of the specific organic superconductors $(TMTSF)_2ClO_4$ and κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, emphasizing their dimensionality characteristics.

INTRODUCTION

More than forty organic superconductors so far prepared are of charge transfer (CT) type and are classified into eight families on the basis of the organic species; namely TMTSF (7 members with the highest Tc of 3K at 5kbar), BEDT-TTF (22, 12.8K at 0.3kbar), DMET (7, 1.9K), MDT-TTF (1, 5K), BEDO-TTF (2, 1K), dmit (4, 6K at 19kbar) and C_{60} (5, onset 33K[1]). Except C_{60} compounds, all of them are TTF related conductors. Though the total number of organic superconductors is still less than 1% and the maximum Tc is lower than that of inorganic systems, the organics have provided many interesting features both in the normal and superconducting phases.

BRIEF OUTLINE FROM ORGANIC CONDUCTORS TO ORGANIC SUPERCONDUCTORS

History

Organic conductors started in mid 50s by the discovery of the cation radical salt of perylene•bromide by Akamatu, Inokuchi and Matsunaga.[2] In 1960 an excellent acceptor TCNQ was synthesized in the course of the cyanocarbon chemistry conducted by Du pont group.[3] The Little's theory for high Tc organic superconductor based on the electron-exciton interactions accelerated the study of organic conductors to great extent in 60s.[4] In 1970 a good electron donor ability of TTF was demonstrated by Wudl et al.[5] Soon after that the first organic metal TTF•TCNQ was discovered by Cowan's group[6] and others. Since then more than 150 organic

metals and highly conductive organic conductors were accumulated in 70s. As a result of the extensive efforts of chemists, the first organic superconductor emerged in 1980 with Tc of 0.9K at 12kbar.[7]

From the practical point of view, the starting point of organic superconductors was to find a way to suppress the metal-insulator (MI) transition observed in the organic metal such as TTF·TCNQ complex. TTF or TCNQ molecules form segregated uniform stack in the complex by making overlap of their π-electrons to each other. So the complex is inevitably low-dimensional and shows a MI transition characteristic to low dimensionality.

Theoretically it has been predicted that a low-dimensional metal exhibits one of three possible low-temperature phases. The first one is the Peierls transition due to the electron-phonon coupling and the system has a MI transition. The second is the SDW state due to the spin-spin antiferromagnetic interaction and the system becomes an insulator too. The third one is the superconducting state due to the formation of Cooper pair. In the case of the BCS superconductor, the Cooper pair is formed by the electron-phonon interaction with singlet spin.

Almost all organic metals prepared during 70s were found to be the Peierls insulators and consequently finding a way to eliminate such MI transition became the most urgent subject in order to stabilize the superconducting state.

Tactics in the k-Space to Suppress MI Transition

In one-dimensional metal the energy dispersion of the electrons can be depicted schematically as Fig. 1a. The energy dispersion along the k_y direction is flat and the Fermi surfaces are represented by two straight lines with a separation of $2k_F$ in the k_x-k_y plane. These Fermi surfaces can overlap completely by a $2k_F$ modulation along the k_x and this perfect nesting is the origin of the MI transition. A few methods have been proposed to avoid the perfect nesting, among which to have an increased dimensionality in the Fermi surface (Fig. 1b,1c) was found to be the most effective way to suppress the MI transition and induce the superconducting state. But at the same time such method sometimes gives only a stable two-dimensional (2D) metallic state.

Tactics in the Real Space to Suppress MI Transition

One may use selenium or tellurium analogues of TTF to increase the

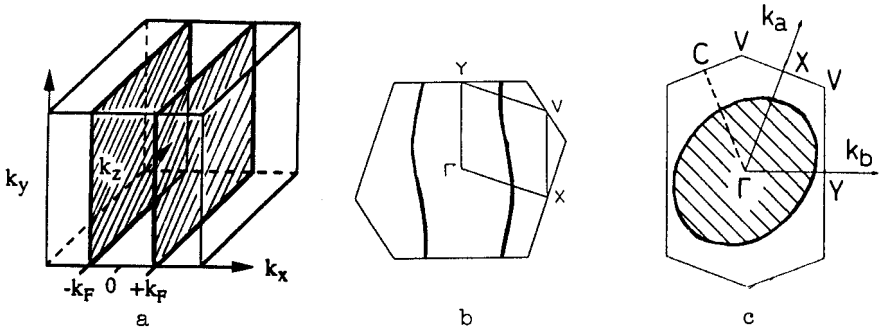

Figure 1 Fermi surfaces of one-dimensional metal (a), $(TMTSF)_2X$ (b) and β-$(BEDT\text{-}TTF)_2I_3$ (c).

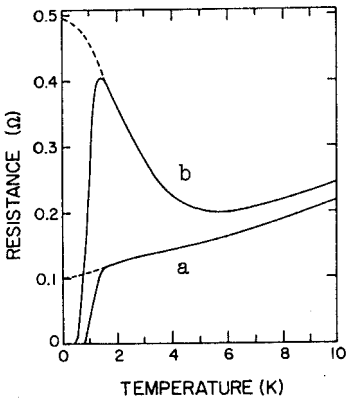

Figure 2 Temperature dependence of resistivity (//a) of $(TMTSF)_2ClO_4$ at slow (a) and intermediate (b) cooling rate [14].

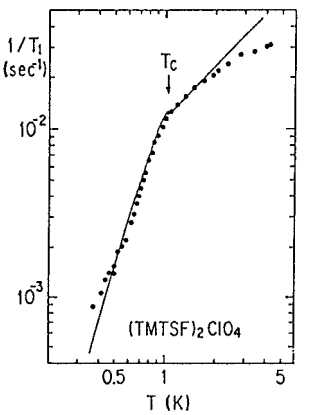

Figure 3 Temperature dependence of ^1H-NMR relaxation rate $1/T_1$ of $(TMTSF)_2ClO_4$ [20]. The solid curve shows the theoretically calculated one for the gapless superconductor (normalized to the experimental data at Tc) [21].

interstack interaction because of the larger van der Waals (vdW) radius of Te (2.06A) or Se (1.90A) than that of S (1.80A).[8] Also the larger atomic polarizability of Te or Se than S is a favorable factor to reduce the on-site Coulomb repulsive energy in a CT complex. According to this 'atomic substitution method' TMTSF superconductors and organic metals based on TTeF or HMTTeF have been developed.[7,9] The Fermi surface of the TMTSF system turned out to be not closed 2D but 1D with fairly warping (Fig. 1b).

A simple consideration in the framework of the BCS theory tells us the disadvantage of using heavier molecules or atoms to raise Tc since $Tc=M^{-1/2}$, if we suppose the phonon mode is associated with the molecular weight M. We have proposed an idea to add appropriate substitutional groups to TTF moiety to increase dimensionality and prepared 2D BEDT-TTF organic metal which did not exhibit MI transition.[10] Since then BEDT-TTF molecule, which has ethylenedithio groups to the two ends of TTF molecule and firstly synthesized by Mizuno et al.,[11] became the center of the 2D organic metals and superconductors which have a closed Fermi surface (Fig. 1c).

The organic superconductors so far prepared have been developed on the basis of the concept of increased dimensionality by chemical method (above mentioned) with or without physical method (pressure).

$(TMTSF)_2ClO_4$ [12,13]

Black shinny single crystals with needle shape ($30\times0.7\times0.1mm^3$) of $(TMTSF)_2ClO_4$ were prepared by the electrochemical oxidation of TMTSF in the presence of TBA(tetrabutylammonium)ClO_4 from THF. Other TMTSF superconductors $(TMTSF)_2X$ were also prepared by using TBA.X and they are isostructural to each other. TMTSF molecules form a 1D zigzag columns along the a axis which are separated by the anion columns along the c axis. So the a axis is the most conductive and the c axis is the least conductive. Considerably short Se..Se atomic contacts which connect the conducting 1D columns are easily recognizable along the b axis when the anion is small. The typical intermolecular interactions along each axis are $t_a:t_b:t_c$=ca. 0.25eV:ca. 0.025eV:ca. 0.0015eV=10:1:0.06. So the energy dispersion is approximately represented as $E_k=-2t_a cosak_a-2t_b cosbk_b$. The Fermi surface of TMTSF system is not closed but

opened along the k_b axis since t_b is not so big (Fig. 1b). If t_b reaches more than ca. 30% of t_a, the Fermi surface becomes a closed cylindrical one. The degree of warping of the Fermi surface is proportional to t_b or roughly to the strength of Se..Se interactions.

Although these Fermi surfaces cannot overlap by the $2k_F$ modulation along the k_a direction, they can overlap completely by the shift of $Q_o=(2k_F, \pi/b)$. This is the reason why TMTSF system is susceptible to MI transition even though they have 2D character. For example, the ClO_4 salt exhibits anion disorder-order transition at 24K with the appearance of the superstructure (ax2bxc). Since the nesting vector corresponds a lattice modulation of (2ax2b), the anion disorder-order transition of ClO_4 does not lead an insulating state. If the sample crystal is cooled very rapidly, e.g. 50K/min, through 24K, the anion disorder is frozen which results in an SDW state below 5K and no superconducting state appears. On the other hand, if the cooling rate is very slow, e.g. 0.1K/min, above 24K, a complete anion order occurs resulting in an appearance of superconducting state with Tc=1.2K. The intermediate cooling rate will cause the appearance of SDW below 5K and superconducting state below 1.2K (Fig. 2).[14]

One of the most exciting properties of TMTSF salts is the field induced SDW observed under high magnetic field applied perpendicular to the ab plane.[15] Since the electrons near the Fermi surface move along the open orbit with a periodic modulation of G=eHb/hc under magnetic field H, this system is susceptible to the SDW instability with a wave vector $Q_x=2k_F+nG$, where c is velocity of light, h is Planck's constant, and n is an integer. An SDW phase appeared above at a certain threshold magnetic field (e.g. 6T at 1.5K for ClO_4 salt) and several different semimetallic (except n=0 sub-phase which is insulating) SDW phases follow successively then seems to return to the normal state at around 28T.[16] The boundary between the normal and FISDW states is in the shape like a bell with a maximum at ca. 17T and ca. 5.5K in the magnetic field and temperature diagram. A nonlinear transport behavior was observed in the semimetallic sub-phases suggesting a sliding of SDW.[17]

Many of the superconducting characteristics of the ClO_4 salt such as the specific heat jump[18] and the energy gap[19] deduced from tunneling spectroscopy are consistent with the simple BCS theory. However, a microscopic investigation by proton NMR pointed out the unconventional

nature of the superconductivity of this salt.[20] The temperature dependence of the relaxation rate (T_1) of protons at zero magnetic field indicates that $1/T_1$ decreases rapidly just below Tc (Fig. 3) in contrast to the typical superconductors with isotropic gap where $1/T_1$ increases below Tc reaching maximum at T=ca. 0.9Tc. Theoretically the temperature dependence of $1/T_1$ for the singlet or triplet state with anisotropic gap is known to behave that $1/T_1$ reaches maximum around T=ca. 0.99Tc and has 5% larger value than that at Tc, then varies approximately as T^3 down to 0.5Tc and deviates to lower values at lower temperatures.[21] This theoretically derived behavior coincide with the observed one fairly well suggesting that the ClO_4 salt has an anisotropic order parameter having lines of zero on the Fermi surface.

The followings are the summary of Tc, upper critical field (Hc_2), critical current (Jc) of $(TMTSF)_2ClO_4$: Tc=1.2K (ambient pressure, slow cooled sample); Hc_2(0K)=2.8(//a), 2.1(//b), 0.16T(//c);[22] Jc(0.5K)=ca. 0.1A/cm^2(//c) which is one order of magnitude smaller than Jc(//a).[23]

BEDT-TTF SALT[13,24]

In spite of the non-planar molecular conformation of neutral BEDT-TTF, it becomes almost flat except terminal ethylene group(s) on the formation of CT complexes. BEDT-TTF molecules in a complex may pile up by minimizing the steric hindrance caused by the ethylene group(s), leaving cavity along the direction of molecular long axis. This tendency prevent the proximate face-to-face approach of BEDT-TTF molecules along the stacking axis. Instead of that, BEDT-TTF molecules have strong tendency to form proximate intermolecular atomic contacts of sulfur along the side-by-side direction (molecular short axis). These two kinds of intermolecular interactions bring about the characteristics of BEDT-TTF complexes such as two-dimensionality and polymorphism.

A linear anion I_3 is the typical one to exhibit remarkable polymorphism. More than 10 kinds of I_3 salts have been known, among which β- and κ-phases are worth mentioning in connection with the following discussion. There are at least three b-phase salts with Tc of 1.5K (low Tc β),[25] 2K[26] and 8.1K (high Tc β),[27] and the highest Tc in the high Tc β-phase is attributed to the absence of both of the disorders due to incommensurate superlattice modulation and the ethylene conformation.[28] In the β-phase salt, all of the donor

molecules are oriented parallel to each other to form a stack. Short S..S intermolecular contacts are located between donor molecules on neighboring stacks. These features provide 2D closed Fermi surface in this salt (Fig. 1c).[29] In the κ-phase salt, on the other hand, two donor molecules form a face-to-face dimer.[30] Dimers are oriented with approximately orthogonal alignment with respect to their neighboring dimers and form 2D conduction network. The Fermi surface estimated for this salt is a circle. The 2D conducting donor layer is sandwiched between the insulating layers composed of the anion I_3. Even though the anion is the same between β- and κ-I_3 (Tc=3.6K) salts, Tc's of them are quite different. Within the β-phase salts derived from the structurally related anions; IBr_2, I_2Br, and AuI_2, Tc's of them are quite different; 2.7K, no Tc, and 3.4-4.9K, respectively.[31]

To explain the size effect of the linear anion on Tc within the β-phase salts, few interesting correlations have been proposed between Tc and structural parameters, such as lattice pressure,[32] unit cell volume[33] or anion length.[34] All these correlations suggest the use of longer symmetric linear anion than I_3 in order to have higher Tc than that of the high Tc β-I_3 salt. Since triiodide is the longest one (10.1A) among the symmetric linear polyhalides, we have searched for appropriate anions among a variety of metal halides and metal pseudohalides. In the course of this search, the $Cu(NCS)_2$ salt was discovered but it turned out that the anion was neither symmetric nor linear and furthermore the salt was not the β-phase.[35]

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ Salt[35]

Single crystals of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ are hexagonal thin plates with the dimension of 2-3mm along the b axis, 1-2mm along the c axis and 0.05-0.1mm along the a* axis. They were prepared by the electrocrystallization of BEDT-TTF in the presence of CuSCN, KSCN and 18-crown-6 ether from 1,1,2-trichloethane. The crystal is monoclinic and the largest plane corresponds to the bc plane. Within the bc plane, donor molecules form dimers which are orthogonally aligned to construct 2D conducting layer. This type of donor packing is not the β-type but the κ-type (Fig. 4). There are no inversion center at the center of the dimer which is contrast to the case of the κ-I_3 salt. There are short inter- and intradimer S..S contacts giving 2D conducting character to the bc plane. Every conducting layer is sandwiched between the

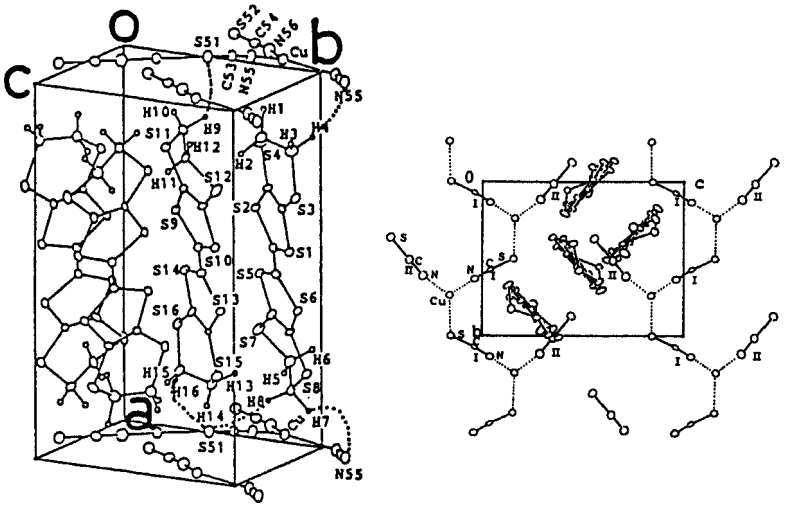

Figure 4 Crystal structure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (dextrorotatory form). The dotted lines show short atomic contacts between BEDT-TTF molecule and anion.

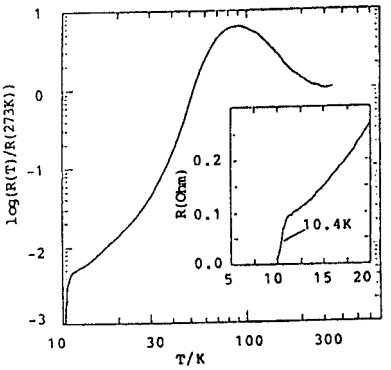

Figure 5 Temperature dependence of resistivity (//b) of κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$.

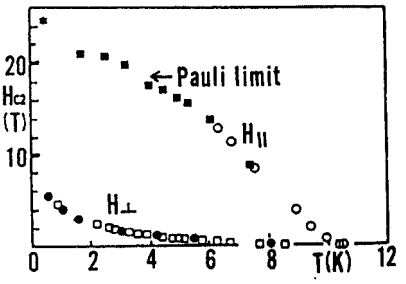

Figure 6 Temperature dependence of upper critical field (Hc_2) of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Hc_2 values were determined by the midpoint of resistive recovery with magnetic field.

insulating anion $Cu(NCS)_2$ along the a-axis. The anion $Cu(NCS)_2$ is asymmetrically bent as a V shape where the dihedral angle of SCN-Cu-NCS is 121°. The anions are linked one after the other to form a zigzag 1D flat polymer. There are two crystallographycally independent NCS groups. SCN(I) and Cu^{+1} form infinite chain SCN(I)..Cu..SCN(I) along the b axis and the other ligand NCS(II) is bonded to Cu to complete triangular coordination. Every polymer orients in the same direction to construct an insulating sheet in the bc plane. So the crystal does not have an inversion center and is optically active. Figure 4 is the structure of the dextro rotatory form. The crystal is not active in the second harmonic generation but is active in the third order.[36]

There are no short atomic contacts between the neighboring anion polymers. However, hydrogen atoms on the ethylene groups of BEDT-TTF molecule form short atomic contacts with N and S atoms of SCN(I). So a 2D conducting layer of BEDT-TTF molecules is connected to both of the above and below 2D conducting layers by these short C-H..N and C-H..S contacts through the thin insulating layer, that gives 3D nature to this salt. In the sense of the electron density, the terminal ethylene groups are not much important at all, because electrons are crowded in the central C_6S_8 moiety. But the replacement of hydrogens with deuterium atoms has big effect on its superconductivity (vide infra).

The conductivity at room temperature (σ_{RT}) is 10-40Scm^{-1} (//b). The conductivity anisotropy is $\sigma_{a*}:\sigma_b:\sigma_c$=1/600:1:1.2. The temperature dependence of conductivity (Fig. 5) shows a semiconductive behavior between 270K and 90K, which is not intrinsic since the magnetic properties showed metallic nature in this region. The semiconductive behavior was almost identical between those within the 2D plane and perpendicular to it. This is in contrast to that of the κ-$Cu[N(CN)_2]Br$ salt which showed considerable anisotropy of the semiconductive behavior.

Superconductivity starts at 11K and Tc defined by the midpoint of resistive transition is 10.4K. We have compared isotope effect on Tc by using three kinds of BEDT-TTF molecules. One is the normal BEDT-TTF, the second is ^{13}C molecule in which carbon atoms of ethylene groups are substituted by ^{13}C and the third is the fully deuterated BEDT-TTF. Both the four-probe conductivity and SQUID magnetic measurements revealed that Tc of this salt increases in the order of H-salt, ^{13}C-salt and D-salt. This isotope effect is opposite to what to be expected from the

simple BCS theory. According to the simple BCS theory Tc is proportional to one over square root of isotope mass M. Since we do not know the superconducting mechanism of this material, we do not know what is the appropriate parameter for M. If we use molecular weight as M, Tc of the deuterated salt should be lowered to 10.3K but the observed Tc was 11.1K and higher than those of H- and ^{13}-salts. This inverse isotope shift has not been rationalized yet, though we expect that CH vibrations or CH..anion stretchings somehow contribute to the superconductivity of this salt.

Figure 6 shows the temperature dependence of Hc_2 values defined by the midpoint of resistance increase by the magnetic field. At 0.5K Hc_2 values are 5.5T along the a* axis and 24.5T within the bc plane. The value in the bc plane is more than that of Nb-Ti and it is noticeable that Hc_2 values below 3K are more than the Pauli limited value (H_p), which is calculated by a simple correlation between Tc and the magnetic field which breaks singlet Cooper pair ($H_p(T)=1.84Tc$). In the conventional superconductors, Hc_2 values are limited by H_p. So the big enhancement of Hc_2 observed here is a further question.

But the Hc_2 values determined here are not plausible. We have used the resistance recovery curve with magnetic field to determine the Hc_2 values in Fig. 6. The observed recovery curves were very broad for the transition, which is reminiscent to those of oxide superconductors, suggesting either a flux-flow effect or distribution of Tc.[37] If the flux-flow effect is dominant, the previously obtained Hc_2 values are underestimated. At present the intrinsic Hc_2 values are not decisive.

The magnetoresistance showed Shubnikov-de Haas oscillations below ca. 1K and above ca. 8T. This was the first observation of such quantum oscillations in organic conductors and a conclusive evidence of the existence of the 2D closed Fermi surface. From the oscillation period, the area of the extremal orbit of the Fermi surface was evaluated as 18% of the first Brillouin zone. This is in perfect agreement with the calculated 2D Fermi surface (Fig. 7). The band calculation based on the extended Huckel MO indicated the 1D open Fermi surface together with the 2D closed one. The coexistence of the 1D and 2D Fermi surfaces has been confirmed by the observation of the magnetic break down oscillations under high magnetic field (>20T).[38]

The temperature dependence of the penetration depth deduced by

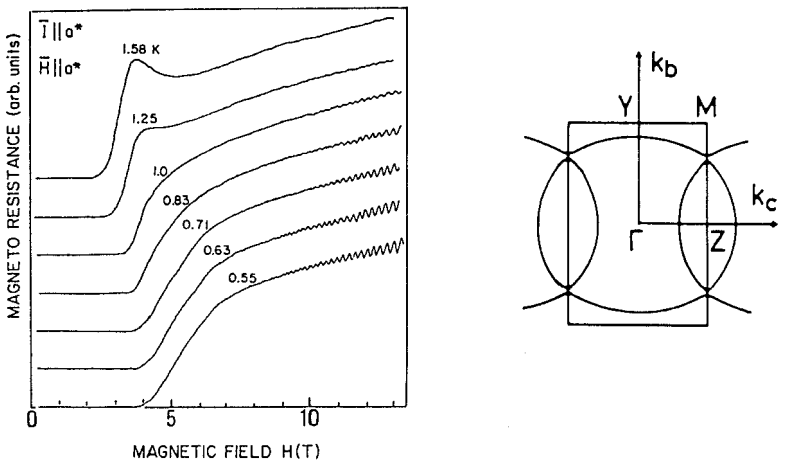

Figure 7 Shubnikov-de Haas signals and Fermi surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

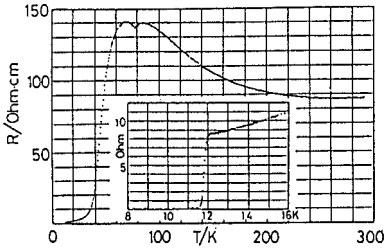

Figure 8 Temperature dependence of resistivity (//b) of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br.

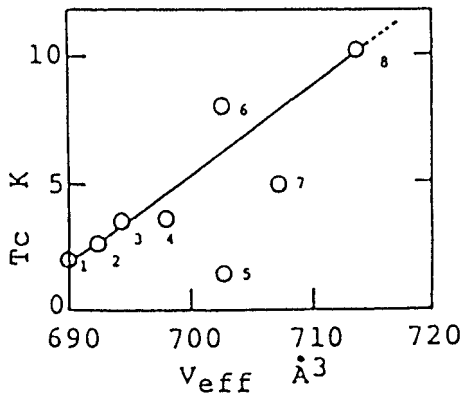

Figure 9 Effective volume (V_{eff}) dependence of Tc of (BEDT-TTF)$_2$X: 1:ReO_4, 2:β-IBr_2, 3:κ-I_3, 4:θ-I_3, 5:low Tc β-I_3, 6:high Tc β-I_3, 7:β-AuI_2, and 8:κ-Cu(NCS)$_2$ salts.

both the complex susceptibility[39] and μSR[40] measurements suggest anisotropic superconductivity of gapless nature, although there are some experimental results[41] of other groups which are in accord with the conventional BCS type which has a finite superconducting gap.

The followings are the summary of Tc, Hc_2 and Jc of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt: Tc=10.4K (normal BEDT-TTF), 11.1K (deuterated BEDT-TTF); Hc_2(0.5K, tentative)=24.5T(//c), 5.5T(//a*); Jc=10^2-10^3A/cm^2.

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br Salt

The characteristics of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt have stimulated to create new organic superconductors by modifying the anion which is composed of transition metal and (pseudo)halide. $NH_4Hg(SCN)_4$,[42] $Ag(CN)_2H_2O$[43] and Cu[N(CN)$_2$]X (X=Cl, Br)[44] anions are among them. α-(BEDT-TTF)$_2$$NH_4Hg(SCN)_4$ has much strong 2D character since the 2D conducting layers are separated by the very thick 2D polymerized anion of $NH_4Hg(SCN)_4$.[42] The considerable suppress of Tc in this salt (Tc=0.8K) by increasing the thickness of the anion layer may suggest the importance of the 3D character or inter-donor-layer interactions to realize sizable Tc.

The efficiency of the ligand $N(CN)_2$ was demonstrated by the preparation of κ-phase superconducting salts of Cu[N(CN)$_2$]X (X=Cl Tc=11.6K, Br Tc=12.8K at 0.3kbar) by Williams et al. recently.[44] The anion layer is composed of 1D infinite chains of ..Cu..NCNCN..Cu.. and Cu^{+1} is further coordinated by X. Since there are weak inter-anion-chain interactions in the κ-Cu[N(CN)$_2$]Br salt, the dimensionality of the anion layer is somewhat higher than the $Cu(NCS)_2$ salt. Figure 8 shows the temperature dependence of the κ-Cu[N(CN)$_2$]Br salt prepared in our group.[35c,45] The κ-Cu[N(CN)$_2$]Br salt exhibits semiconductive behavior between 270K and 70K, which is very reminiscent to that of the $Cu(NCS)_2$ salt. There is a dip at ca. 80K with two resistivity maximum at around 70K and 90K. These positions of the maximum and dip show anisotropy. The conductivity anisotropy is $\sigma//:\sigma_\perp$=200:1, so the magnitude of 3D seems to be a little higher than that of the κ-$Cu(NCS)_2$. Tc was 11.7K in our sample with a transition width of 0.5K. Hc_2 values were considerably higher than those of the $Cu(NCS)_2$ salt. At 1.5K Hc_2 values are 7.4T($\perp$) and 30.6T(//), the latter exceeds the Pauli limited value. Here also the broadening of the resistivity recovery curves by the magnetic field was outstanding indicating these Hc_2 values are not

intrinsic and underestimated. Shubnikov-de Haas oscillations were not observed yet in this salt. The deuteration of the terminal ethylene groups of this salt lowered Tc by 0.4-0.5K which is in contrast to that observed inverse isotope shift in the κ-$Cu(NCS)_2$ salt.[45]

A Relation Between Tc and Effective Volume

A linear correlation between Tc's of several BEDT-TTF salts of different phases and the effective volume of one carrier in a unit cell was observed (Fig. 9).[35b] The effective volume is defined as [(unit cell volume)-(anion volume)]/(number of formal carriers in a unit cell) and may correlate with the density of state. On the basis of the effective volume consideration, the following guide lines are withdrawn:

1) Comparison of the β-phase and κ-phase I_3 salts indicates that the β-phase has bigger effective volume by ca. $10A^3$ which corresponds to the Tc difference of ca. 3K. This means that the donor molecules in the β-phase salt are packed more loosely than the κ-phase salt. Therefore it is desirable to find suitable large anion which fit β-type (or loose) packing of donor molecules.

2) The use of large anion increases unit cell volume that usually results in large effective volume. But bulky anion increases anion volume that will decrease effective volume. For example, the κ-I_3 and κ-$Cu(NCS)_2$ salts have almost the same unit cell volume but the effective volume is smaller by ca. $10A^3$ in the I_3 salt because I_3 is thick compared to $Cu(NCS)_2$ (vdW radius I=1.98, S=1.80, C=1.70, N=1.55A). Therefore it is desirable to use thin anion layer composed of big anion unit. The use of thin anion layer may correspond to the increase of the three-dimensionality in the anisotropy of the electrical conductivity.

3) The thermal contraction of organic superconductor is quite large. For example from room temperature to around 10K the unit cell volume of the κ-$Cu(NCS)_2$ salt decreases by $60A^3$,[46] which corresponds to the decrease of effective volume of $30A^3$ or 10K in Tc. So it is very crucial to avoid the thermal contraction of organic crystals in order to have high Tc. The comparison of the temperature dependences of the lattice parameters of κ-$Cu(NCS)_2$ and κ-$Cu[N(CN)_2]Br$ salts revealed that the magnitude of thermal contraction along a certain direction depends on whether there is tight intermolecular atomic contacts or not.[35c] For

example, since there are short atomic contacts between donor ethylene groups and $Cu(NCS)_2$ anion along the a axis, a thermal expansion instead of contraction of the lattice was observed in this salt. The anion..anion interactions play an important role in the thermal contraction. The b axis of the κ-$Cu(NCS)_2$ salt where $Cu(NCS)_2$ anions are bonded to each other shows very small thermal contraction. On the other hand, since the anion polymers are isolated to each along the c axis, the contraction of this axis is large. The anion polymers of the κ-$Cu[N(CN)_2]Br$ salt are connected to each other by weak Br..N atomic contacts, so the contraction along this direction is not so large. Therefore, in order to keep the thermal contraction small, it is desirable to use a structurally two-dimensional anion layer which is able to provide short anion..donor contacts.

As a consequence, the summary of the anion designing is as follow: use big anion which forms thin two-dimensional anion layer and provides both the loose donor packing and strong anion..donor atomic contacts.[47] This statement is equal to find more three-dimensional, loosely packed and thermally hard organic superconductor.

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47. Accordingly it is of interest to use CN instead of Br of the $Cu[N(CN)_2]Br$ salt since CN is thinner and longer anion than Br (vdW=1.85A). We have prepared a new ambient pressure organic superconductor (Tc=10.7K) using CuCN and tetraphenylphosphonium $N(CN)_2$ as the electrolyte [T.Komatsu, T.Nakamura, N.Matsukawa, H.Yamochi, G.Saito, H.Ito, T.Ishiguro, M.Kusunoki, K.Sakaguchi, Solid State Commun., submitted]. The fact that Tc of this salt is lower than that of the $Cu[N(CN)_2]Br$ suggests larger thermal contraction of the former salt than the latter. A precise crystallographic examination to prove this is underway.