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Molecular Metals Based on BETS and Magnetic Anions-λ-and κ-$BETS_2FeCl_4$ and θ-$BETS_4Cu_2Cl_6$

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Abstract Novel electric, magnetic and structural properties of molecular metals based on BETS (=Bis(ethylenedithio)tetraselenafulvalene) molecules and magnetic anions such as $FeCl_4^-$ and $Cu_2Cl_6^{2-}$ were reported. $BETS_2FeCl_4$ has two modifications (κ and λ). Unlike κ-$BETS_2FeCl_4$ with stable metallic state down to 2 K, λ-$BETS_2FeCl_4$ exhibited a cooperative electric (metal-insulator) and magnetic (paramagnetic-antiferromagnetic) transition at 8 K. $BETS_4Cu_2Cl_6$ with θ-type arrangement of BETS molecules is metallic down to 4 K. Two Cu^{2+} ions are bridged by two Cl atoms to form binuclear magnetic anion $Cu_2Cl_6^{2-}$. The Crystal structure and the temperature dependence of the magnetic susceptibility were briefly described.

INTRODUCTION

It is well known that the structure chemical concept of the design of molecular metals with two-dimensional (2D) stable metal bands has been established in 1980s.[1] And the numbers of molecular metals and superconductors are now rapidly increasing. However almost all the molecular metals examined so far are simple π electron systems. Several

years ago, we tried to prepare another type of organic metals, where π metal electrons coexist with magnetic moments of counter anions at very low temperature. These compounds have two kind of open-shell electronic orbitals, which will play important roles to determine the electric and magnetic properties of the systems. An excellent prototypical example may be the DCNQI-Cu compounds with π metal electrons of interacting d-electrons of mixed-valent Cu ions,[2,3] which has presented a good hint to develop new types of molecular conducting systems with "multi-frontier electronic structures" including π molecular metals with magnetic ions.

Of course, the preparation of molecular conductors with magnetic counter ions is not so difficult. But in order to obtain molecular metals, where π metal electron can survive down to low temperature at ambient pressure, the suitable choice of constituent molecules (especially donor molecules) becomes important. We adopted BETS molecule because BETS is an exceptionally good donor molecule to prepare stable 2D π metal systems (BETS (=bis(ethylenedithio)tetraselenafulvalene)[4-6] and tried to prepare Bechgaard type salts $(BETS)_2MX_4$ ($M=Mn^{2+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}; X=Cl, Br) by electrocrystallization.[7,8] Of course, the interaction between π metal electrons and 3d electrons of magnetic ions will be not so strong in this type of molecular metals. But we thought that the control of the π-d interaction would be the next step of this study. In this paper, physical properties of BETS metals with magnetic Fe^{3+} and Cu^{2+} ions will be presented.

$BETS_2FeCl_4$ SALTS

Crystals of $BETS_2FeCl_4$ salt prepared by using $[Et_4N]FeCl_4$ as electrolyte have two modifications. The plate crystal belongs to Orthorhombic system with space group Pnma and well-known κ-type 2D molecular arrangement similar to those of κ-type BEDT-TTF (or ET) superconductors : a=11.693 Å, b=35.945, c=8.491, V=3569 $Å^3$.[8] As was expected, metal electrons and magnetic moments coexist in this system at low temperature(Fig. 2). Resistivity decreases with lowering temperature down to 2K,

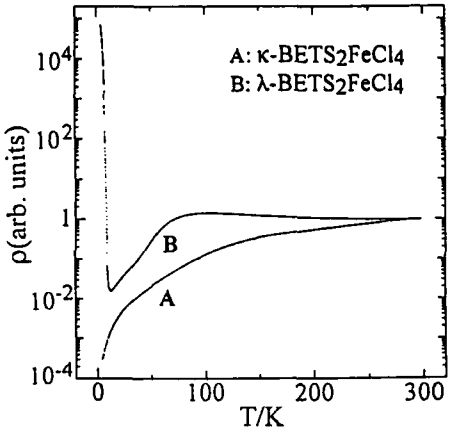
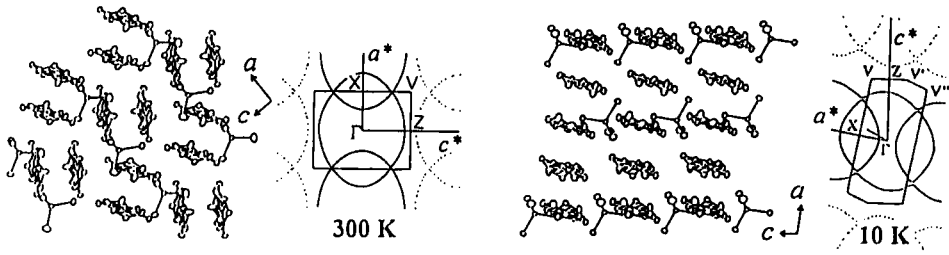


FIGURE 1 Resistivity of $BETS_2FeCl_4$.



κ-$BETS_2FeCl_4$ λ-$BETS_2FeCl_4$

FIGURE 2 Molecular Arrangement and 2D Fermi surfaces of κ- and λ-$BETS_2FeCl_4$.

where resistivity was less than $5x10^{-6}$ Ωcm. At first we considered that κ-$BETS_2FeCl_4$ might be the first π molecular metal with π metal electrons and localized magnetic moments at very low temperature and ambient pressure.[7] However recently we have found that similar conducting system $(BEDT\text{-}TTF)_3CuCl_4 \cdot H_2O$ has been reported by Day et al.[9] Tight-binding band calculation gave 2D Fermi surfaces (Fig. 2).[10]

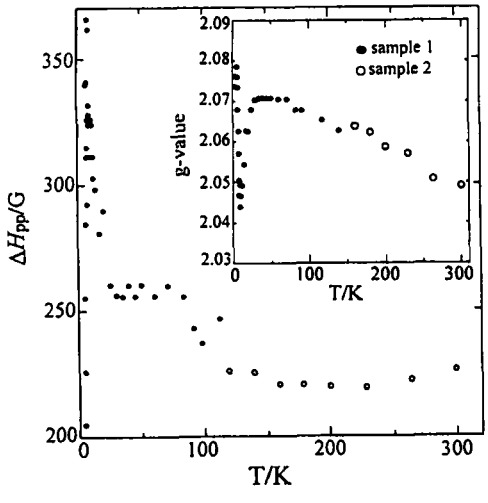
The needle crystal of $FeCl_4$ salt λ-$BETS_2FeCl_4$ belong to triclinic system with space group $P\bar{1}$: a=16.164 Å, b=18.538. c=6.593, α=98.40°, β=96.69, γ=112.52, V=1173 $Å^3$.[8] Unlike κ-type salt with stable metallic state, λ-$FeCl_4$ salt undergoes a sharp metal-insulator (MI) transition at 8 K (Fig. 1). Compared with TMTSF salts with the similar magnitude of MI transition temperature (T_{MI}), the resistivity increase below T_{MI} was much larger, suggesting the development of large energy gap.

Interestingly, isostructural λ-type salt with nonmagnetic anion $GaX_{4-z}Y_z$ (X,Y=F, Cl, Br) exhibited superconducting transition below 8 K.[11] The striking contrast in the ground states indicates that the existence of the magnetic moments in anion sites is essential for the MI transition.

As shown in Fig. 1, the resistivity of λ-$BETS_2FeCl_4$ shows a characteristic round maximum around 90 K, indicating the strong correlation of π metal electrons in BETS layers. The resistivity maximum was suppressed at high pressure and the MI transition temperature was decreased with increasing pressure. The metallic state was stabilized above 4 kbar.[8]

The spin density of λ-$BETS_2FeCl_4$ estimated from ESR intensity at room temperature was about one order of magnitude larger than the Avogadro number, which suggested that Fe^{3+} ions are in high-spin states.[8] Since the accuracy of the ESR data obtained before[8] seemed to be insufficient especially at low temperature, the temperature dependence of ESR intensity was recently reexamined below 150 K, which reconfirmed satisfactorily the Curie-Weiss law indicating the antiferromagnetic (AF) interaction between Fe^{3+} ions (Fig. 3). The Weiss temperature was fairly large, -23K, which was

FIGURE 3 Temperature dependence of ESR signal of λ-BETS2FeCl4.



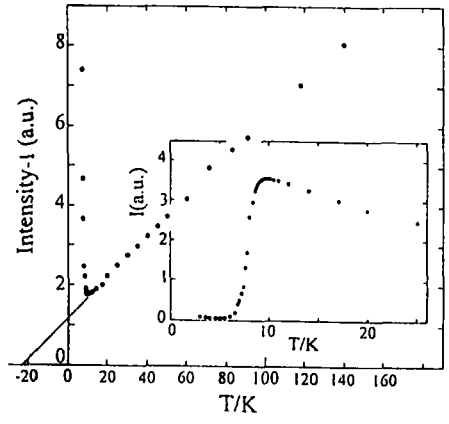


FIGURE 4 Temperature dependence of ESR line width and g-value of λ-BETS2FeCl4.

lower than the previously obtained value, -15 K.[8] The ESR signal observed in the metallic phase rapidly disappeared below 8 K, clearly showing that the magnetic transition and MI transition take place cooperatively (Fig. 3).

Goze et al. have found a new interesting phenomenon that the insulating phase was suppressed under high magnetic field.[12] For example, at 4 K, where the system is in the insulating state, the metallic state is recovered above 9 T. The resistivity of "the field restored highly conducting state (FRHCS)" is strongly dependent on the direction of magnetic field. When the magnetic field was perpendicular to the conduction plane (//(010)), the large resistivity was observed. Brossard et al. have suggested the possibility that all the magnetic moments of Fe^{3+} ions are arranged ferromagnetically in this FRHCS. The molecular crystal with π metal electrons and ferromagnetically arranged magnetic moments may be a new situation in the organic metal systems.

Recently Tokumoto et al. have measured the anisotropy of magnetization of λ-BETS2FeCl4 by using fairly oriented thin needle crystals sealed in a quartz capillary.[13] The anisotropy at low magnetic field clearly shows the AF nature of the insulating ground state. The line width of ESR signal gave a sharp enhancement around the transition

temperature (Fig. 4), which also suggests the MI transition and AF transition take place cooperatively at 8 K. The g-value showed a fairly large temperature dependence around T_{MI} (see the inset of Fig. 4). The cooperative electric and magnetic transition around 8 K indicates that the additional potential produced by the development of AF spin structure in anion sites is strong enough to vanish 2D Fermi surface of the π metal electrons in BETS layers.

Since Fe ion is in high-spin state, it may be possible that the magnetic moments tend to be parallel to the magnetic field around 10T at low temperature. Therefore, as pointed out by Brossard, it might be possible that the high-spin Fe^{3+} moments are arranged ferromagnetically in FRHCS. At the same time it should be pointed out that the most prominent feature of the metallic state of this system may be large paramagnetism due to the high spin Fe^{3+} ions and relatively small susceptibility in the insulating AF state, which will mean that the high magnetic field favor the metallic state.[8] The magnetic properties of this system are strongly affected by π metal electrons of donor layers. There exists a clear T-H phase boundary curve where the AF spin structure in the anion sites disappears and the π metal electrons will be recovered.

The sharp decrease of M/H for the magnetic field parallel to the needle axis[13] suggests the easy axis to be parallel to the c axis of the crystal along which FeCl4 anions are arranged regularly (see Fig. 1). Large Fe..Fe distance[14] and fairly large Weiss temperature (-23 K) suggests that the direct magnetic dipole-dipole interaction cannot be a candidate of the main origin of AF spin ordering. The antiferromagnetic interaction seems to be mediated by BETS molecules. There are many short Cl···Se or Cl···S contacts in the λ-type salts, which will play an important role.[8]

The microscopic mechanism of π-d interaction will be a new important problem in the organic π metals at low temperature. λ-FeCl4 salt will be a good system to make clear this interesting problem.

θ-$BETS_4Cu_2Cl_6$ SALT

Crystals were grown electrochemically from BETS (6mg) at a current of 0.9 μA using tetrahydrofuran (17ml) as solvent and $[Et_4N]_2CuCl_4$ (57mg) as the supporting electrolyte.[15] Although we used $CuCl_4^{2-}$ as supporting electrolyte, the structural and magnetic properties examined afterward revealed that the crystal has the binuclear magnetic anion, $Cu_2Cl_6^{2-}$.[8] The electrical resistivity measurement showed that $(BETS)_4Cu_2Cl_6$ remains metallic down to 4 K ($\sigma(RT)=10^2$ Scm^{-1}). The resistivities

decrease monotonously with lowering temperature and the resistance ratio of ρ(300K)/ρ(4K) was about 20 (Fig. 5).

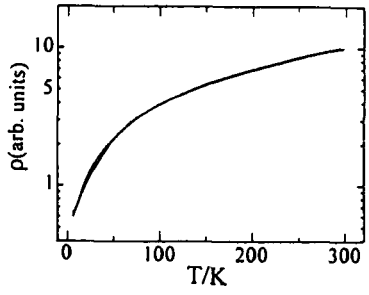


FIGURE 5
Resistivity of θ-$BETS_4Cu_2Cl_6$

The crystals belong to orthorhombic Pbcn. The lattice constants are a=9.583(2) Å, b=34.897(8), c=20.043(4), V=6674.2(2.6) $Å^3$ and Z=4. The structure of $BETS_4Cu_2Cl_6$ was determined on the basis of 2340 independent intensity data ($I>3\sigma(I)$) collected by a four-circle diffractometer (Rigaku AFC-7R) with rotating anode. The final R and R_W values were R=0.092 and R_W=0.073.

The unit cell structure and the molecular arrangement of $BETS_4Cu_2Cl_6$ are shown in Figs. 6 and 7. The molecular arrangement of BETSs is that of θ-type one first found in the organic superconductor, θ-ET_2I_3 (ET=BEDT-TTF).[16] The θ-type BETS arrangement has been found also in other BETS salts: θ-$BETS_2PF_6$,[4] θ-$BETS_2TaF_6$[6] and θ-$BETS_4HgBr_4(C_6H_5Cl)_x$.[5] The former two with monoclinic lattices and space group of C2/c are almost isostructural to that of θ-MT_2AsF_6[17] and exhibit metal–semi-metal transition around 30K. θ-$BETS_4HgBr_4(C_6H_5Cl)_x$ with tetragonal lattice is metallic down to 4K. Every BETS molecule in θ-$(BETS)_4Cu_2Cl_6$ is surrounded by six neighbouring BETS molecules as if the system has a 2D hexagonal packing structure in the ac plane. One BETS molecules(A) and two one-half of them(B,C) are crystallographically independent (Figs. 6 and 7). Dihedral angles between molecules A and B is 76.3°, molecules A' and C is 81.7°, molecules B and C is 5.5°. The interplanar distance of B···C is 4.036 Å, A···A' and A···A" are 3.799 Å and 3.814 Å respectively. The binuclear $Cu_2Cl_6^{2-}$ anion has a

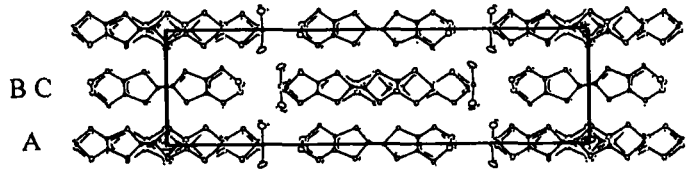


FIGURE 6
Crystal structure of θ-$BETS_4Cu_2Cl_6$.

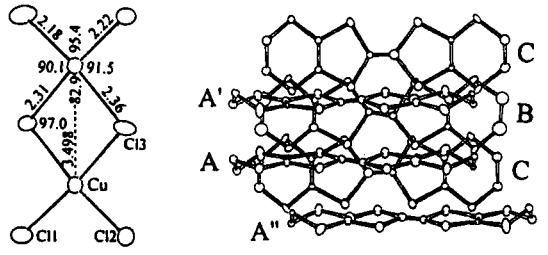


FIGURE 7 Bond lengths (Å) and angles (°) of $Cu_2Cl_6^{2-}$ and arrangement of BETS molecules.

twofold symmetry and is almost planar. The deviation of the Cu atom from the plane formed by Cl1,Cl2,Cl3 atoms is 0.029 Å. The bond length of Cu-Cl(bridging) (2.33 Å) is longer than Cu-Cl(non-bridging) (2.20 Å). The Cl(bridging)-Cu-Cl(bridging) angle (82.9°) is much smaller than the Cl(non-bridging)-Cu-Cl(non-bridging) angles (95.4°). The shortest intermolecular Cu···Cu distance is 8.211Å. The shortest Se···Se, Se···S and S···S distances are 3.73Å, 3.50Å and 3.48 Å, respectively. The shortest contacts of S···Cl between BETS and anion is 3.64Å and Se···Cl is 5.80 Å.

Magnetic susceptibility measurements showed a broad maximum around 200K, where susceptibility is about $6.5x10^{-4}$ emu/mole($BETS_2CuCl_3$) (Fig.8). This temperature dependence of the susceptibility indicates that two paramagnetic Cu^{2+} ions in $Cu_2Cl_6^{2-}$ are coupled antiferromagnetically to give the susceptibility explained by "singlet-triplet model"(J=163K). By measuring the diamagnetism of neutral BETS, Pauli paramagnetic contributions of π metal electrons was derived (ca. $2x10^{-4}$ emu/mol $(BETS)_2CuCl_3$), which seems to be smaller than other BETS metals such as κ- and λ-BETS2GaCl4.[19]

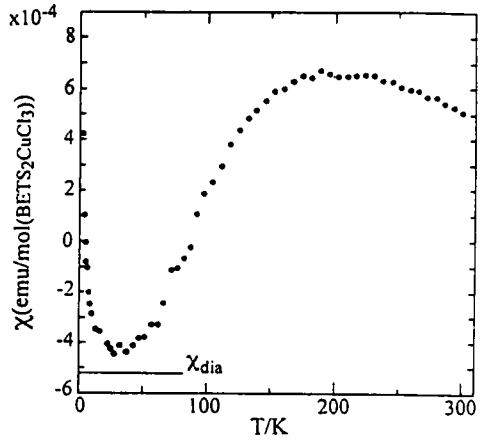


FIGURE 8 Susceptibility of θ-$BETS_4Cu_2Cl_6$.

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