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CARRIER-DOPING IN A MOTT-INSULATOR κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

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Abstract The first example, as an organic compound, of the realization of superconductivity by a carrier-doping into a Mott-insulating state is presented. Although κ- and κ'-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ have the same band structure, the former is a semiconductor, and the latter a metal at ambient pressure (AP). An extended Hückel band calculation and the spin susceptibility indicate that the κ-salt is a Mott-insulator with an exactly half-filled band. On the other hand, the κ'-salt shows an ESR signal of Cu^{2+} in addition to that of BEDT-TTF$^+$. It is found that the metallic state and the superconductivity at AP of the κ'-salt are realized by a carrier-doping by substituting Cu^+ with Cu^{2+}.

INTRODUCTION

The molecule bis(ethylenedithio)-tetrathiafulvalene (abbreviated as BEDT-TTF or ET) has afforded more than twenty superconductors. Among them, κ-(ET)$_2$Cu$_2$(CN)$_3$ was reported to show a superconducting transition at 2.8 K / 0.15 GPa.[2] At AP this salt is semiconducting. The origin of the semiconducting behavior is claimed to be its narrow band width, which is about a quarter of usual metallic ET salts; *i.e.*, κ-(ET)$_2$Cu$_2$(CN)$_3$ is a Mott-insulator. The anion layer of the κ-salt is made of two-dimensional polymeric anion with a honeycomb structure. One Cu atom is coordinated by CN^- in a triangular-planar form, which is usually seen for Cu^+. When all the copper is Cu^+, the oxidation state of the ET is +0.5. The ET-layer is formed by orthogonally-aligned ET$^{0.5+}$ dimers (κ-type structure).

On the other hand, κ'-(ET)$_2$Cu$_2$(CN)$_3$ is metallic and showed superconductivity at 3.8 K even at AP.[3] The crystal structure is the same as that of the κ-salt, except for the slight difference of the coordination angle around the Cu. Despite the same ET-layer structure as the κ-salt, the calculated band width was typical for metallic ET salts.

The considerable differences of the transport properties and the band calculations cannot be explained based only on the extremely simi-

lar crystal structures of them. In order to clarify what causes the dissimilarity, we re-examined the band calculation, and measured resistivity, ESR, and static magnetization of these salts.

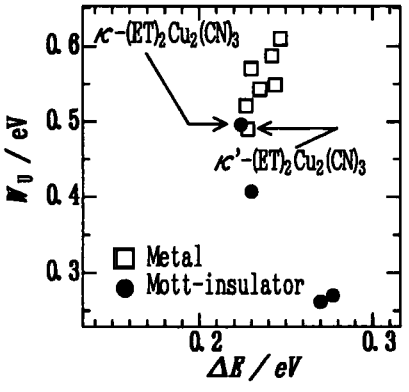
EXPERIMENTAL

The crystals of κ- and κ'-$(ET)_2Cu_2(CN)_3$ were prepared by an electrocrystallization of ET. The crystals of the κ'-salts were obtained only when $N(CN)_2^-$ was included in the supporting electrolytes. Extended Hückel tight-binding band calculations were carried out with a usual procedure[4] assuming a transfer integral $t = -10S$ eV, where S is the overlap integral. The ESR spectra and the magnetically modulated microwave absorptions (MMMA) were recorded with a JEOL JES-TE200 X-band ESR spectrometer. A Quantum Design MPMSR2 SQUID magnetometer was used to observe the diamagnetic shielding of the κ'-salt, with a field of 1 mT applied normal to the conducting plane of the zero-field-cooled sample. The resistivity under pressure was measured by a four-probe method using cramp-type pressure cell.

RESULTS AND DISCUSSION

Band Calculation

The HOMO bands of κ- and κ'-$(ET)_2Cu_2(CN)_3$ are split into a half-filled upper-band and a completely occupied lower-band due to the strong dimerization of the ET molecules. In contrast to Ref. 2, the band struc-



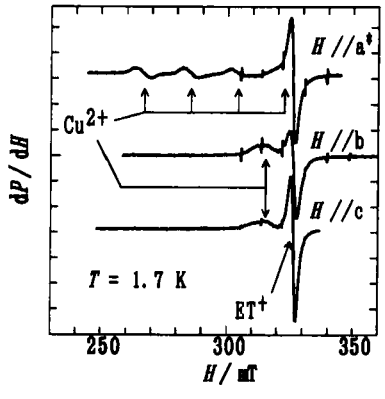


FIGURE 1(left) The ΔE - W_U phase diagram of ET salts. Squares and circles represent metals and Mott-insulators, respectively.

FIGURE 2(right) The ESR spectra of κ'-$(ET)_2Cu_2(CN)_3$ at 1.7 K.

tures are identical within a calculation error. Therefore, we can safely say that the difference between these results is derived from some different calculation procedures.

In Fig. 1, some ET salts with dimerized $ET^{0.5+}$ are plotted according to the upper-band width (W_U) and the dimerization energy (ΔE). The on-site Coulomb repulsion of a dimer is proportional to ΔE when $\Delta E \ll U_0$, where U_0 is the bear Coulomb repulsion of the constituent.[5] κ- and κ'-$(ET)_2Cu_2(CN)_3$ are located at the marginal region between Mott-insulators and metallic ET salts. Thus there is no difficulty in regarding κ-$(ET)_2Cu_2(CN)_3$ as a Mott-insulator. Then, why the κ'-salt is metallic?

Magnetic Properties

In addition to a narrow Lorentzian ESR signal of ET^+ observed at *ca.* 325 mT, four broad Gaussian absorptions split by an anisotropic hyperfine coupling with a nucleus having I=3/2 appear in the κ'-salt below 20 K (Fig. 2). Considering the nuclear spin and the anisotropy of the g-factor, the additional signal is ascribed to Cu^{2+} substituting the Cu^+. No such signals were observed for the κ-salt. These results suggest that the metallic and the superconducting states at AP of the κ'-salt are realized by the carrier-doping into the ET-layer from the Cu^{2+}. The concentration of the Cu^{2+} (x), which varies the oxidation state of the ET molecules as $+0.5(1-x)$, can be determined from the Curie-constant of the susceptibility. As shown in Tab. I, the longer the crystal-growth period, the lower the x becomes. The reason why $N(CN)_2^-$ is necessary to incorporate Cu^{2+} is thought to be that Cu^{2+} is stabilized by $N(CN)_2^-$, since $Cu(CN)_2$ is extremely unstable while $Cu[N(CN)_2]_2$ not.

TABLE I The crystal-growth conditions of κ- and κ'-$(ET)_2Cu_2(CN)_3$.

supporting electrolytes	solvent	period	x(ppm)
a KCN, CuCN, 18-Crown-6	$C_6H_5CN + H_2O$	10 days	0
b $NaN(CN)_2$, CuCN, 18-Crown-6	CH_3CN + EtOH	100 days	———
c $Cu[N(CN)_2]$, KCN, 18-Crown-6	$C_6H_5CN + H_2O$	94 days	88–340
d $Cu[N(CN)_2]$, KCN, 18-Crown-6	C_6H_5CN + EtOH	57 days	400–430
e $Cu[N(CN)_2]$, KCN, 18-Crown-6	C_6H_5CN + EtOH	51 days	480–580
f $Cu[N(CN)_2]$, KCN, 18-Crown-6	C_6H_5CN + EtOH	51 days	830
g $Cu[N(CN)_2]$, KCN, 18-Crown-6	C_6H_5CN + EtOH	51 days	1200

In Fig. 3a, the T_c's defined as the onset of MMMA as well as the

volume fractions (V_s) at 2 K are plotted against the x. Both the T_c and the V_s exhibit a maximum when x = 430 ppm and then decrease. The initial rise of them is considered to correspond to a reduction of the Hubbard gap due to the carrier-doping into the half-filled band. The rapid decrease of V_s above 430 ppm indicates that superconductivity disappears in the major part of the sample due to the pair-breaking effect of paramagnetic Cu^{2+}.

As shown in Fig. 3b, the χ_{spin}(RT) decreases with increasing x till about 580 ppm, where a jump of χ_{spin}(RT) is observed. The ratio between the observed χ_{spin} and that calculated based on the band calculation ranges from 3.9 (x = 530 ppm) to 5.3 (x = 0 ppm). Since the latter value is *ca.* 40 % larger than metallic ET salts, the κ-salt should have a stronger electronic correlation than them. Moreover, the enhancement of the χ_{spin} below x = 580 ppm is similar to that observed on carrier doping in Mott-type insulators based on transition-metal oxide, for example, $La_{1-x}Sr_xTiO_3$,[6] where effective mass of the charge carrier diverges as the Mott-transition approaches. Thus the Mott-insulating state of the κ-salt is confirmed.

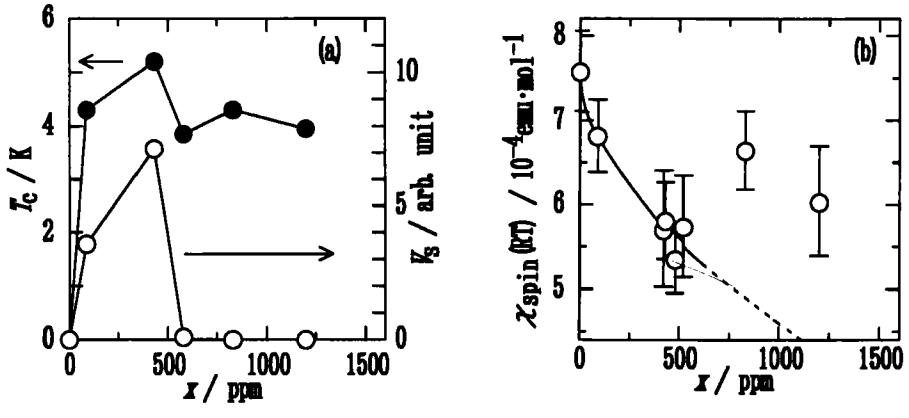


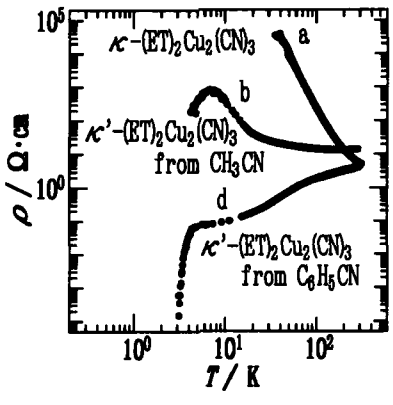
FIGURE 3 The dependencies on the content of Cu^{2+} (x) of (a) the superconducting transition temperature (T_c) and the volume fraction (V_s) and (b) the χ_{spin} at RT of ET molecules of κ'-$(ET)_2Cu_2(CN)_3$.

Resistivity

At AP, while the resistivity of the κ-salt is semiconductive, that of the sample (from batch c) of the κ'-salt is metallic (Fig. 4). The content of Cu^{2+} of the sample is 430 ppm. At AP the T_c of this sample is 4.1 K, which is higher than that reported previously (3.8 K).[3] The resistivity

of another sample grown in CH_3CN (batch b) shows a broad minimum at 150 K and a sharp peak at ~ 7 K. The x of this sample has not been determined because of its smallness. Similar resistivity behavior has been reported[7] for samples grown with Cl^-, which also stabilizes Cu^{2+}.

As shown in Fig. 5, below 0.1 GPa the T_c of κ-$(ET)_2Cu_2(CN)_3$ are just on the line reported by Geiser et al.[2] At higher pressure the T_c decreases with a faster rate. Although the κ'-salt has a slightly higher T_c than that of the κ-salt, they have exactly the same dT_c/dP.



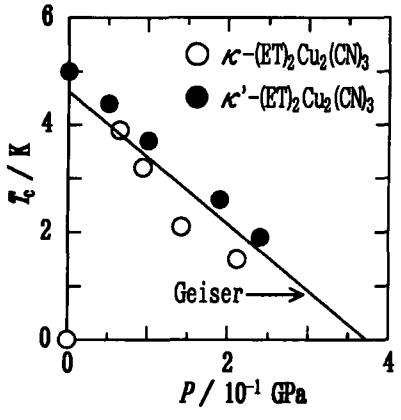


FIGURE 4(left) The temperature dependencies of the resistivity of κ- and κ'-$(ET)_2Cu_2(CN)_3$. Samples belong to the batches listed in TAB. I.

FIGURE 5(right) The pressure dependencies of the T_c of κ- and κ'-$(ET)_2Cu_2(CN)_3$.

SUMMARY

The comparative study of the calculated band parameters of ET salts suggested that at AP κ-$(ET)_2Cu_2(CN)_3$ is a Mott-insulator with a half-filled upper-band. This idea is supported by the results of the ESR and resistivity measurements. The ESR measurements revealed that the metallic state of κ'-$(ET)_2Cu_2(CN)_3$ at AP is brought about by an electron-doping into the ET layer from the Cu^{2+} in the anion layer.

An interesting point is that the T_c of κ'-$(ET)_2Cu_2(CN)_3$ is higher than that of κ-$(ET)_2Cu_2(CN)_3$ at all pressures. If this is the consequence of the positive effect of the carrier-doping on the superconductivity, then band-filling controls in other ET-based superconductors will

afford higher T_c. On the other hand, the decrease of the T_c in the over-doping region seems to be due to the pair-breaking effect of paramagnetic Cu^{2+}. Considering above two points, it is worth trying to incorporate diamagnetic divalent metal ions into κ-$(ET)_2Cu(NCS)_2$, κ-$(ET)_2Cu[N(CN)_2]Br$, *etc.*

Though a number of organic superconductors neighboring the Mott-insulating state are known, none of them are achieved by band-filling control. The reason is as follows: an attempt to dope carriers into a molecular conductor confronts a serious difficulty that not only the band-filling but also the arrangement of the conducting component is altered. This problem is now settled, considering the above results. By using a polymeric metal complex, the structure of conducting layers is retained even when the metal is substituted, as long as the coordination type of the substituent is alike. Also, when the polymeric anion has a cavity of sufficient size, alkali-metal or halogen doping into the cavity will also be possible.

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