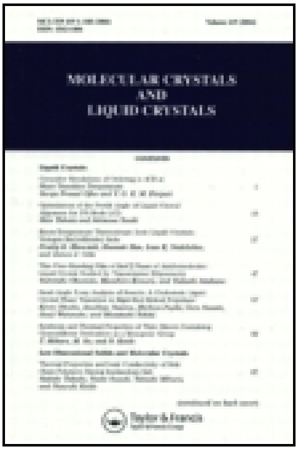


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# Superconductivity of a θ-type et salt prepared using CuCN AND PH 4 PN(CN) 2 as electrolyte

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# SUPERCONDUCTIVITY OF A θ-TYPE ET SALT PREPARED USING CuCN AND $PH_4PN(CN)_2$ AS ELECTROLYTE

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*A θ-type ET salt $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ has been obtained by electro-cystallization in PhCN, using $Ph_4N[N(CN)_2]$ and CuCN as electrolytes. Some of them showed anomalous behaviors for Low-Field-Microwave-Absorption (LFMA) measurements, which were one of the characteristics of super-conductivity. However, the others did not show the LFMA signals, indicating that there are two phases in this compound having different electronic states at low temperature.*

Keywords: $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$; Mott insulator; LFMA; superconductivity; SQUID magnetometry

## INTRODUCTION

A θ-type ET salt $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ (ET = bis(ethylenedithio)-tetrathiafulvalene) is a co-product of two superconductors $\kappa$-$(ET)_2$-$Cu(CN)[N(CN)_2]$ ($T_c = 11.2$ K for ET-h8 salt and 12.3 K for ET-d8 salt) and $\kappa'$-$(ET)_2Cu_2(CN)_3$ ($3\,K < T_c < 11\,K$) [1]. The crystal structure and the physical properties of this compound have been reported [2]. The cystal-lographically equivalent $ET^{+0.5}$ molecules form uniform segregated stacks along the c-axis with herring-born structure, so called θ-type arrangement. The anion and the donor layers pile up alternatingly along the b-axis. The anion layer consists of the double helices of (-Cu-NCNCN-) infinite

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chains bridged by CN groups. Although the calculated Fermi surface is two-dimensional, the material is semiconducting below 400 K with a semiconductor-semiconductor transition at 220 K ($T_{ss}$). The spin susceptibility is expressed by quadratic-layer Heisenberg antiferromagnet model between 32.6 K and $T_{ss}$. Therefore the semiconductive nature can be ascribed to the strong electron-electron correlation that becomes more distinct below $T_{ss}$. Together with the appearance of the very weak 0.5c* superstructure at low temperatures, the compound is regarded as a Mott insulator at least below $T_{ss}$.

We found an anomalous behavior of this compound at low temperature during the study of the superconductivity of $\kappa$-$(ET)_2Cu(CN)[N(CN)_2]$ and $\kappa'$-$(ET)_2Cu_2(CN)_3$. We report here the LFMA study of single crystals of the compound and discuss about the superconductivity.



## EXPERIMENTAL

Black flattened needles having a rhombus section of $\theta$-$(ET)_2$-$Cu_2(CN)[N(CN)_2]_2$ were prepared by the electrooxidation of ET-h8 and ET-d8 (deuterated) using $Ph_4N[N(CN)_2]$ and CuCN as supporting electrolytes in a mixed solvent of PhCN and ca. 10 vol% ethanol or methanol. We have obtained 129 batches so far. The SQUID magnetometer was used to detect superconductivity for each batch and predict what kind of salts harvested from the $T_c$. In order to detect superconductivity for the individual single crystals, we measured the temperature dependence of the LFMA signals using the usual EPR device, because LFMA is much more sensitive than SQUID magnetometry. After cooling the crystal without fields, the DC magnetic field applied parallel to the *a*-axis was swept from −250 G to 250 G during the LFMA measurements with the microwave power (0.1 mW) and modulation field (100 kHz, 10 G). We identified the crystals from the lattice parameters by the X-ray diffraction measurement with graphite monochromated Mo K$\alpha$ radiation on a four-circle diffractometer.

## RESULTS AND DISCUSSION

In this study, we investigated a batch (ET-d8 salts, labeled #*d*4), which showed superconductivity by the SQUID measurement (onset $T_c = 10$ K). The calculated volume fraction of the superconductivity was 9% at 1.9 K. Most of the crystals in #*d*4 had needle like shape that is typical for $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$, while the co-product superconductors are plate like shape.

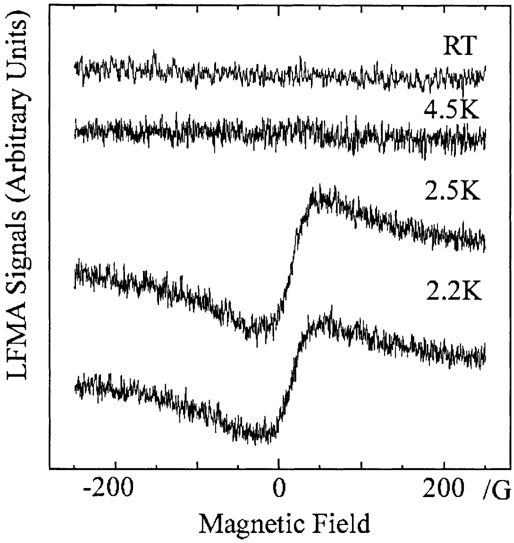


**FIGURE 1** Temperature dependence of LFMA signals of $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ (#d4-0).

Figure 1 shows the temperature dependence of the LFMA signals of a needle-like single crystal (labeled #*d*4-0), of which lattice parameters (orthorhombic, mmm, a = 11.04(2), b = 38.81(2), c = 4.208(4) Å V = 1803(3) $Å^3$, and Z = 2) were almost the same as those of the previously reported $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$. The signal appeared below 2.5 K and almost disappeared at 4.5 K, indicating that a phase transition occurred around the temperature. The shape of the signal of this crystal below 2.5 K is similar to that of superconductor [3]. However, the SQUID measurement of #*d*4-0 could not detect the superconducting behavior below the $T_c$. These results indicate that either the crystal size or the volume fraction of superconductivity is too small to detect the diamagnetism by SQUID measurement, or it is not a superconductor.

We have obtained the other needle-like crystals that showed LFMA signals below 10 K, but could not determine the lattice parameters by the X-ray diffraction measurement, probably due to cracking of the crystal by rapid cooling for LFMA measurement. There are also several crystals in the batch #*d*4 identified as $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ by the X-ray diffraction measurements but they did not exhibit any LFMA signals. Therefore, it is natural to consider that there are two kinds of $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ having a similar crystal structure but different electronic states at low temperature, as long as the LFMA measurements are concerned, although so far, there are a few crystals which showed the LFMA signals.

Then, what makes the difference between these two states? One possible reason is that the change of the band filling by carrier doping transforms this compound into a metallic one and superconducting state at low temperature. In the case of $\kappa'$-$(ET)_2Cu_2(CN)_3$ [4], it is said that the partial substitution of $Cu^{2+}$ for $Cu^{+}$ caused a Mott insulator into superconductor. Concerning to #*d*4-0, however, no EPR signals originated from $Cu^{2+}$ was detected down to 2.2 K. Another is that there is a fraction of the co-product superconductors on the crystal of a Mott insulator $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$. Actually, the presence of crystals of $\kappa$-$(ET)_2Cu(CN)[N(CN)_2]$ in the batch #*d*4 was confirmed by the Raman spectra. However, for the EPR measurements of *d*4-0, there is only one Lorentzian signal from RT to 2.2 K and the line width rapidly decreased to zero at low temperatures which is in fair agreement with that of the previously reported $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$, while that of $\kappa$-$(ET)_2Cu(CN)[N(CN)_2]$ is quite different [5]. As the results, we conclude that #*d*4-0 is a mono-crystal of $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$.

It is important to note that there are generally other origins of LFMA signals except for superconductor. However, it is said that the clock-wise hysteresis between the upward sweep and the backward sweep of the magnetic field is unique to superconductors. Therefore, we are planning to detect the hysteresis of the LFMA signals for the crystal of $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$.

## CONCLUSION

We detected LFMA signals for several needle-like crystals of a batch #*d*4. One of them was identified as $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ by X-ray diffraction measurement. However, there was also more crystals identified as $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ that did not show the LFMA signal. It indicates that there are two kinds of $\theta$-$(ET)_2Cu_2(CN)[N(CN)_2]_2$ having a similar crystal structure but different electronic states at low temperature, as long as the LFMA measurements are concerned. The origin of the LFMA signal and the difference of these two states are not clear at the present stage.

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