Electrical and Magnetic Properties of $(BEDT\text{-}TTF)_4Ni(CN)_4$ Complex

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The electrical conductivity and the ESR spectra of the single crystal of $(BEDT\text{-}TTF)_4Ni(CN)_4$ complex were measured. This crystal exhibits a metal–insulator transition at 160 K. The ESR signals show the presence of the $[Ni^{III}(CN)_4]^-$ anion in addition to the BEDT-TTF cation radical. The spin concentration of Ni(III) ion was estimated to be 0.01 of the total Ni ions from the temperature dependence of the spin susceptibility of these components. The X-ray photoelectron spectra were also taken.

The discovery of superconductivity in β-$(BEDT\text{-}TTF)_2I_3$ at T_c=1.3 K under ambient pressure[1–3] has promoted the preparation of radical salts of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) with the linear triatomic anion such as I_2Br^- [4] and AuI_2^-.[5] After that, the studies of many complexes including the metal salts as the counter anion were made and the stable organic superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$, exhibiting complete superconductivity around 10 K at ambient pressure was discovered.[6] Such charge transfer complexes between BEDT-TTF and metal salts are interesting on magnetic properties in addition to electrical properties, because the metal ion can have the incompletely occupied electron shell. From this point of view, we investigated the magnetic and electronic properties of $(BEDT\text{-}TTF)_2CuCl_2$[7] and obtained the result that the Cu atoms in $(BEDT\text{-}TTF)CuCl_2$ are in a mixed-valence state consisting of mono and bivalent cations. In the present paper, we report the complex of $(BEDT\text{-}TTF)_4Ni(CN)_4$.

Experimental

Black plate-like crystals were grown by the electrochemical crystallization of BEDT-TTF in 1,1,2-trichloroethane by using $K_2Ni(CN)_4$ as a supporting electrolyte. The electrical conductivity of the single crystal was measured by the four probe method using gold paste as a contact. The ESR spectra were taken by a Varian E112 at X-band with a continuous helium flow cryostat and a rectangular microwave cavity. The crystal was rotated around the a axis and was measured over a temparature range of 4—300 K. The X-ray photoelectron spectra were recorded on a VG ESCALAB MkII. Mg $K\alpha$ radiation (1253.6 eV) was used as the X-ray excitation source and the measurements were carried out at 10^{-7} Torr (1 Torr≈133.322 Pa) or below.

Results and Discussion

Figure 1 shows the temperature dependence of electrical conductivity of the single crystal. The room temperature conductivity was about 20 S cm^{-1}. The crystal was metallic between 230 and 300 K and became

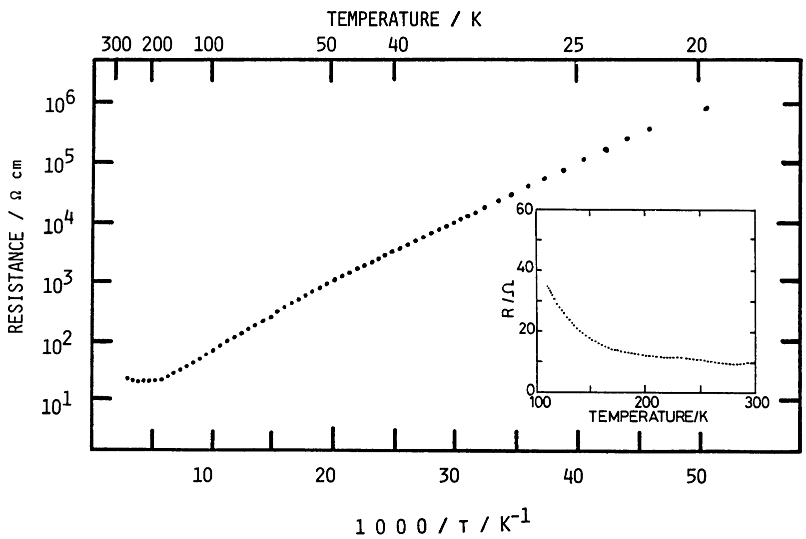

Fig. 1. Temperature dependence of the a axis electrical conductivity of the single crystal of $(BEDT\text{-}TTF)_4Ni(CN)_4$.

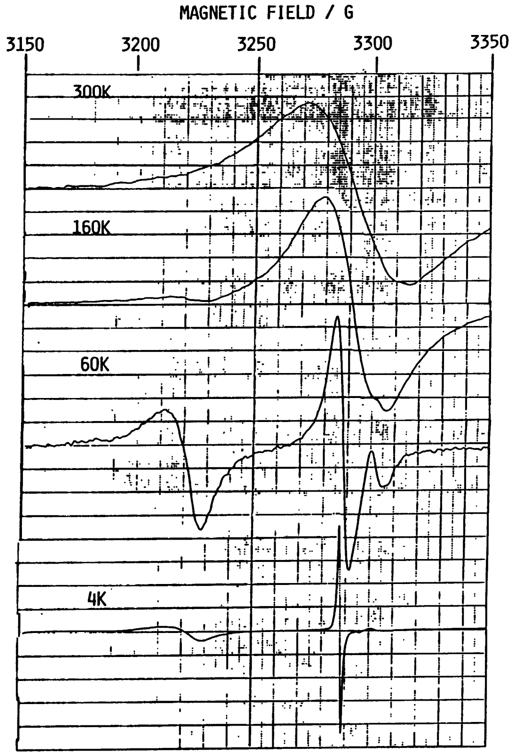

Fig. 2. ESR spectra of (BEDT-TTF)$_4$Ni(CN)$_4$ for the field direction giving the maximum *g* value around the *a* axis.

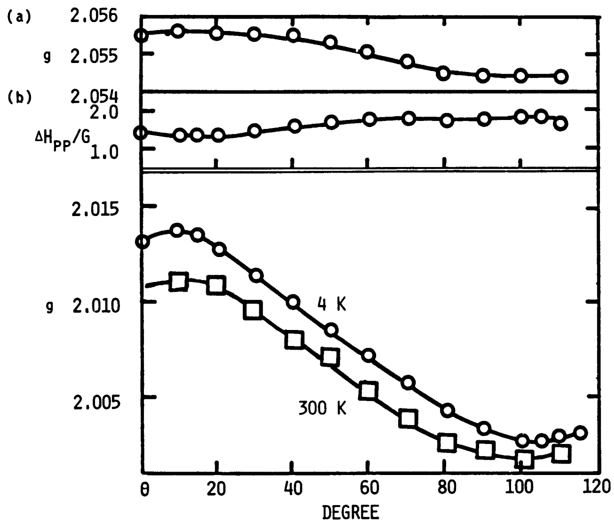

Fig. 3. Angular dependence of the *g* value around the *a* axis. The field is perpendicular to the *ac* plane at 0 degree. (a) Weak band at 4 K (—○—○—). (b) Strong band at 4 K (—○—○—) and 300 K (—□—□—).

semi-conductive with the energy gap of 100 K below 160 K after the temperature dependence of the conductivity was not observed between 160 and 230 K. This kind of resistance behavior may be explained by the phase transition of the crystal between 160 and 230 K.

The ESR spectra of the single crystal of (BEDT-TTF)$_4$Ni(CN)$_4$ are shown in Fig. 2. The angular dependence of the *g* value and linewidth for the strong and weak bands at 4 and 300 K is shown in Fig. 3. The *g* value exhibits the maximum for the field applied nearly perpendicular to the ac plane. As is shown in Fig. 4, the molecular plane of BEDT-TTF is almost normal to the ac plane and the Ni(CN)$_4$ anion is located in the ac plane.[8] Accordingly the direction of the maximum *g* value is in accordance with the direction normal to the Ni(CN)$_4$ anion plane or parallel to the long axis of BEDT-TTF molecule.

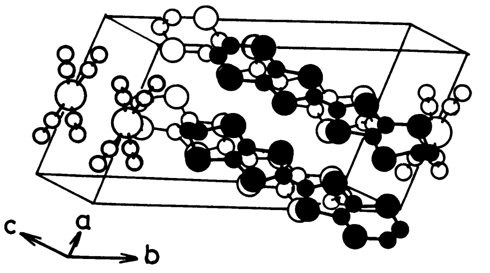

Fig. 4. Crystal structure of (BEDT-TTF)$_4$Ni(CN)$_4$.[8]

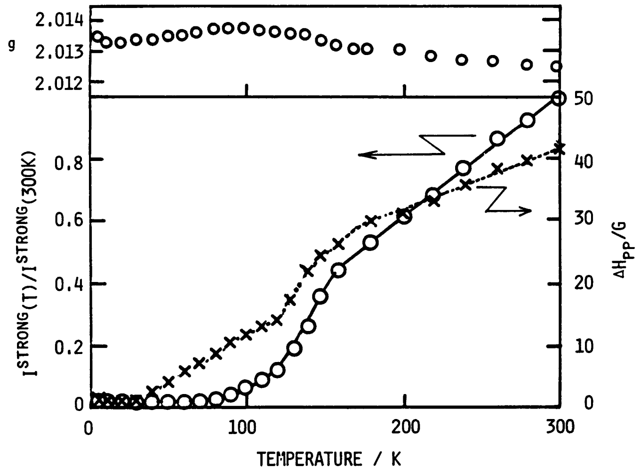

Fig. 5. Temperature dependence of the *g* value, the linewidth and the absorption intensity of the ESR spectra of the strong band for the field giving the maximum *g* value.

The ESR spectrum at 4 K consists of the strong band at g=2.013 (3300 G; 1G=10^{-4} T), the weak band at g=2.056 (3220 G) and the satellite band at g=2.004 (3305 G). The strong band is assigned to the unpaired π-electron of the BEDT-TTF cation radical.[7] The weak band can be assigned to the d electron of $[Ni^{III}(CN)_4]^-$ in a square planar arrangement.[9]

Figure 5 shows the temperature dependence of the *g* value, the linewidth ΔH_{pp} and the absorption intensity of the ESR spectra of the strong band for (BEDT-TTF)$_4$Ni(CN)$_4$. The magnetic susceptibility $\chi^{strong}(T)$ at temperature T is given by the absorption intensity of the ESR signal,

$$\chi^{strong}(T) = C\{I^{strong}(T)/I^{strong}(300\text{ K})\}. \quad (1)$$

The coefficient C may be estimated with the observed static magnetic susceptibility at room temperature of 9×10^{-4} emu mol^{-1}. This value was corrected by considering the diamagnetic effect of the constitution atoms. The magnetic susceptibility and the linewidth of the strong band decrease almost linearly with decreasing temperature between 300 and 160 K and exponentially below 160 K. The activated behavior below 160 K corresponds to that of the electrical conductivity and means the occurence of the metal–semiconductor transition. If the susceptibility at room temperature may be described by the Pauli paramagnetism of the tight binding model, the calculated susceptibility is given the simple equation,[10]

$$\chi = \frac{N_0 \mu_B^2}{\pi t \sin(\rho\pi/2)}, \qquad (2)$$

where N_0 is Avogadro's number, μ_B is the Bohr magneton and t is the transfer integral. The degree of the charge transfer (ρ=1/2) per BEDT-TTF molecule and the observed susceptibility of 9×10^{-4} emu mol^{-1} gives t=0.016 eV.

The temperature dependence of the absorption intensity of the weak band can be depicted by the Curie law as shown in Fig. 6. The magnetic susceptibility of $[Ni(III)(CN)_4]^-$ ion is given by the next equation,

$$\chi^{weak}(T) = n_{Ni} \frac{N_0 g_{Ni}^2 \mu_B^2}{3kT} s(s+1) \qquad (3)$$

$$= C\{I^{weak}(T)/I^{strong}(300\text{ K})\}. \qquad (4)$$

Then, the number of spins per $[Ni(CN)_4]^-$ anion is estimated to be n_{Ni}=0.01.

Figure 7 shows the X-ray photoelectron spectra (ESCA) of $(BEDT\text{-}TTF)_4Ni(CN)_4$ complex and $K_2Ni(CN)_4$. The Ni 2p3/2 and Ni 2p1/2 peaks were observed in both components and no difference of the

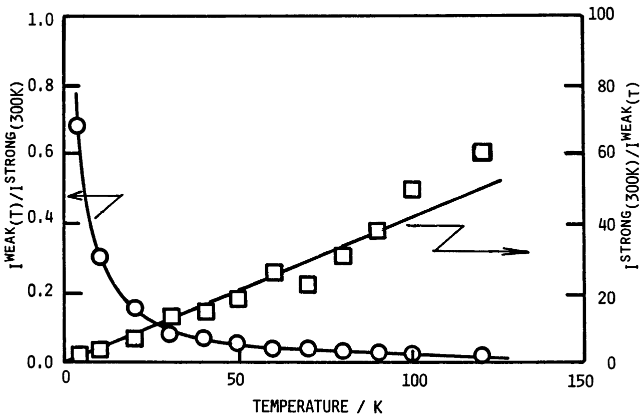

Fig. 6. Temperature dependence of the absorption intensity of the ESR spectra of the weak band.

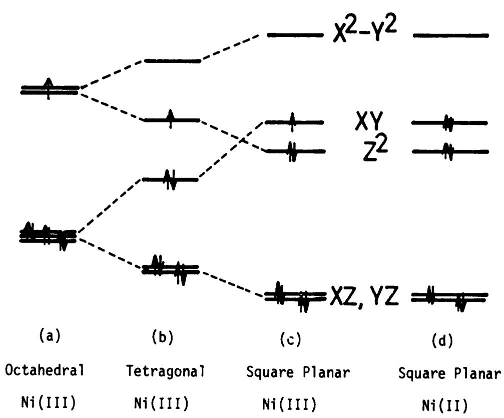

Fig. 8. Energy level diagram for Ni(III) and Ni(II) ions. The z axis is normal to the $Ni(CN)_4$ plane.

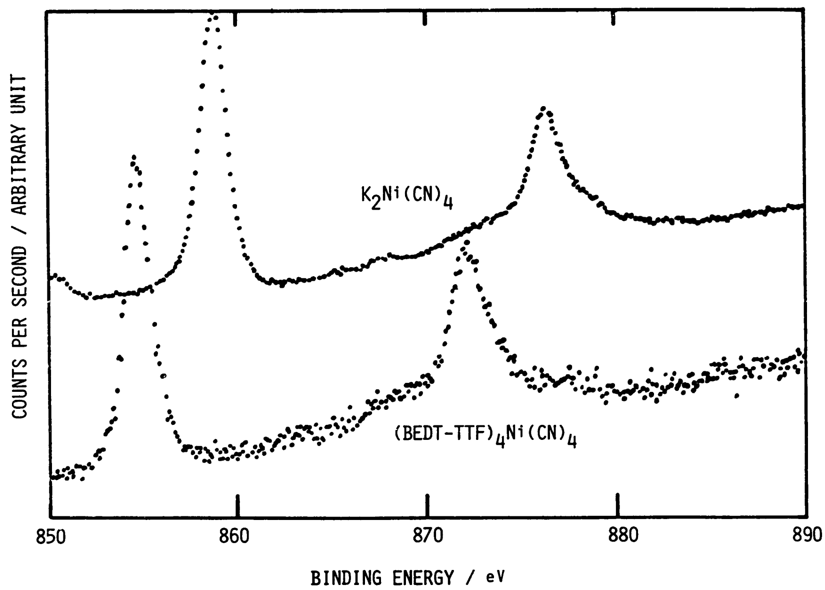

Fig. 7. X-Ray photoelectron spectra (ESCA) of $(BEDT\text{-}TTF)_4Ni(CN)_4$.

line shape and the intensity ratio is found between them. That is, most parts of the Ni atoms in $(BEDT\text{-}TTF)_4Ni(CN)_4$ complex are in the bivalence state and the low spin d^8 configuration of Ni(II) ion forms the closed shell in the square-planar arrangement as is shown in Fig. 8, while a few Ni(III) complexs prepared by the electrochemical oxidation have the unpaired electron in the d_{xy} orbital. Such mixed valence state of the metal ion in the BEDT-TTF complex was observed for the Cu ion in $(BEDT\text{-}TTF)_2CuCl_2$.[7] These ESR spectra consist of both signals of BEDT-TTF cation and metal ion. This fact shows the possibility of the coexist of the free carrier in the conducting BEDT-TTF band and the paramagnetic electron in the metal ion.

The above-mentioned results about the magnetic and electrical measurements show that the electrical conductivity of $(BEDT\text{-}TTF)_4Ni(CN)_4$ complex is metallic at room temperature and the metal–insulator transition occurs at 160 K by the dimerization of the BEDT-TTF molecules.

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References

1) E. B. Yagubskii, I. F. Schegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. L. Buravov, *Sov. Phys. JETP Lett.*, **39**, 12 (1984).

2) J. M. Williams, T. J. Emge, H. H. Wang, M. A. Beno, P. T. Copps, L. N. Hall, K. D. Carlson, and G. W. Crabtree, *Inorg. Chem.*, **23**, 2558 (1984).

3) H. Schwenk, C. P. Heidmann, F. Gross, E. Hess, K. Andres, D. Schweitzer, and H. J. Keller, *Phys. Rev. B*, **31**, 3138 (1985).

4) T. J. Emge, H. H. Wang, M. A. Beno, P. C. W. Leung, M. A. Firestone, H. C. Jenkins, J. D. Cook, K. D. Carlson, J. M. Williams, E. L. Venturini, L. J. Azedo, and J. E. Schirber, *Inorg. Chem.*, **24**, 1736 (1985).

5) H. H. Wang, M. A. Beno, U. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, and J. E. Schirber, *Inorg. Chem.*, **24**, 2465 (1985).

6) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **1988**, 558.

7) M. Tanaka, A. Kawamoto, J. Tanaka, M. Sano, T. Enoki, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **60**, 2531 (1987).

8) A. Kawamoto, M. Tanaka, and J. Tanaka, *Chem. Lett.*, to be submitted.

9) A. G. Lappin, C. K. Murray, and D. W. Margerum, *Inorg. Chem.*, **17**, 1630 (1978).

10) J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, *Phys. Rev. B*, **15**, 4738 (1977).