CHEMISTRY LETTERS, pp. 1057-1060, 1988.

Valence State of Copper Atoms and Transport Property of an Organic Superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$, Measured by ESCA, ESR, and Thermoelectric Power

Hatsumi URAYAMA, Hideki YAMOCHI, Gunzi SAITO,* Tadashi SUGANO, Minoru KINOSHITA, Tamotsu INABE,+ Takehiko MORI,+ Yusei MARUYAMA,+ and Hiroo INOKUCHI+
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
+Institute for Molecular Science, Okazaki 444

ESCA, ESR, and thermopower were measured in crystals of an organic superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$ (Tc=10.4 K), to examine a valence state of Cu and a transport property. The Cu^{I} state was confirmed at 298 K by ESCA. ESR indicates a broad Lorentzian signal of a BEDT-TTF cation radical and no Cu^{II} signal at 298-4 K. The thermopower is anisotropic in the two-dimensional bc plane, which is originated from the anisotropy of the band structure.

Since the discovery of a high Tc superconductivity in the inorganic ceramic compounds, these copper-containing materials have been of great interests. An important role of copper atoms concerning with a mixed valence state and Jahn-Teller effect in these materials has been proposed.1) In organic compounds, on the other hand, we recently discovered the highest Tc (10.4 K) ambient pressure organic superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$, which contains a copper.2) The crystal structure reported in the previous paper showed a peculiar $Cu(NCS)_2$ sheet where a copper is coordinated by a sulfur as well as two nitrogen atoms to construct a one-dimensional polymer.3) Moreover, this salt has generated extensive interests in physical properties: the Shubnikov-de Haas effect,4a) the quasi two-dimensional reflectance spectra,4b) and the anomalous NMR relaxation.4c) In this paper we present ESCA, ESR, and thermopower measurements to investigate an electronic state of copper atoms and a transport property of this salt.

The ESCA spectra were recorded on a VG-1000 spectrometer with Mg K_α radiation under 5×10^{-8} Torr below. The sharp signals at 931.9 and 951.9 eV (Fig. 1) are attributed to Cu $2p_{3/2}$ and $2p_{1/2}$, respectively, and almost the similar ESCA spectrum was observed for CuSCN under the same conditions. These values of binding energies are reasonable for Cu^{I} species and neither shoulder peaks nor distinct shake-up satellites characteristic of Cu^{II} are observed.

The ESR data were obtained by utilizing a JEOL JES-FE1XG (9.2 GHz) spectrometer with a cylindrical cavity (TE_{011}) over the temperature range of 298-4 K on a single crystal ($2 \times 1 \times 0.04$ mm^3).5) The static field was always perpendicular to the b-axis. Li^+TCNQ^- (g=2.0026) was used as a standard sample of g-value. A broad Lorentzian signal is observed between room temperature and 4 K (Fig. 2). A sample-dependent additional peak appears at the center of the broad one below 30 K. With decreasing temperature the broad one becomes too wide to determine the linewidth ΔH and the sharp one becomes prominent (ΔH=10-20 G, g=2.0075). This g-value suggests that this sharp signal is not ascribed to Cu^{II} but to some imperfection of the crystal. The angular dependences of ΔH and g-values at 298 K are shown in Fig. 3. The g-value shows that the broad signal is originated from a BEDT-TTF cation radical; the directions at the maximum (2.0095) and minimum (2.0057) values are nearly parallel to the long molecular axis and tilted to the short molecular axis by 50°, respectively, in the crystal.

The temperature dependence of g-values is depicted in Fig. 4. The g-values are almost independent of temperature down to 20 K below which precise g-values cannot be obtained due to the broadening of the main signal and to the appearance of the sharp signal as mentioned above. The constant g-values (2.0078 - 2.0070) indicate that the molecular orientation of BEDT-TTF does not change substantially with respect to the crystal axes. The temperature independent g-values also confirm that there are nearly no spin-coupling between BEDT-TTF cation radical and Cu^{II} if any down to 20 K. Furthermore no localized Cu^{II} signal (g=2.05-2.50) was observed in the temperature range of 298-4 K within our experimental accuracy. Therefore these magnetic data strongly suggest that the copper atoms are in the diamagnetic Cu^I state in the crystal. The most striking feature of magnetic properties of this compound is that ΔH increases on decreasing temperature (Fig. 4). ΔH changes from 61 G (295 K) to 100 G (30 K) monotonically and then increases rapidly to 120 G (20 K). It was observed that the electrical resistivity of this salt decreases from room temperature to around 270 K slightly then increases very gradually down to around 90 K. After passing through the maximum at around 90 K the resistivity

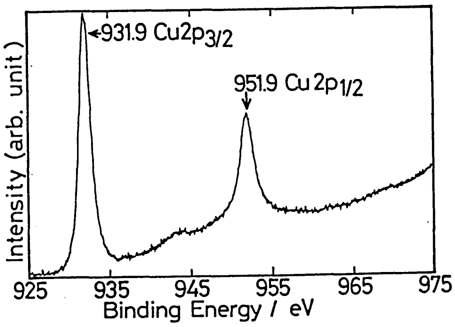

Fig. 1. ESCA spectrum for $(BEDT-TTF)_2Cu(NCS)_2$ at room temperature.

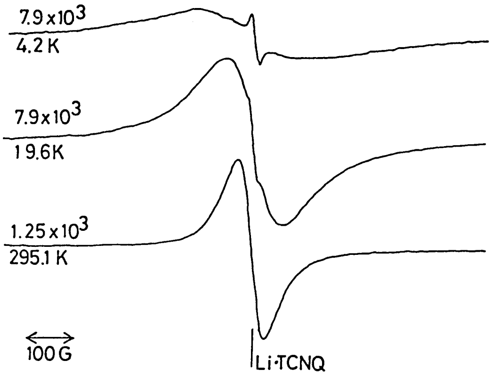

Fig. 2. ESR signals for a single crystal of $(BEDT-TTF)_2Cu(NCS)_2$ at 4.2, 19.6 and 295.1 K. Numbers mean relative intensities.

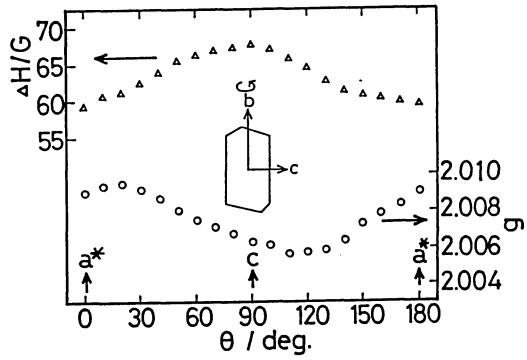

Fig. 3. Angular dependence of g-values and linewidth for a single crystal of $(BEDT-TTF)_2Cu(NCS)_2$.

decreases very rapidly.[2)] Therefore it is conceivable that ΔH increases due to the increasing scattering rate (τ^{-1}) of conduction electrons down to around 90 K, however, the pronounced increase below around 90 K is in contrast to the predictions of the Elliot formula for the spin relaxation in metals[6)]: $\Delta H=(\Delta g)^2\ \tau^{-1}/\gamma$, where spin-orbit coupling $\Delta g(=g-2.0023)$ is almost constant in the present salt and γ is the electron gyromagnetic ratio. At present the origin of the continuous increase of ΔH between 90 and 20 K cannot be explained.

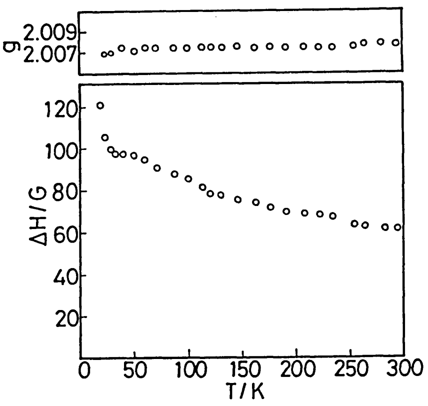

Fig. 4. Temperature dependence of g value and linewidth for a single crystal of $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu(NCS)}_2$.

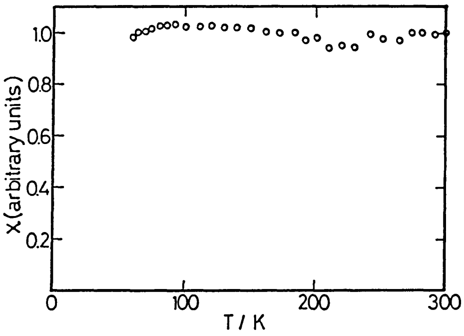

Fig. 5. ESR spin susceptibility vs. temperature for crystals of $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu(NCS)}_2$.

The ESR intensities were measured on single crystals with random orientation to have a satisfactory signal-to-noise ratio. The intensity is almost constant with some scattering down to 90 K followed by a slow decrease down to 60 K where the ESR signal diminished maybe due to the skin effect (Fig. 5). The intensity behavior is in good agreement with that observed by the d.c. susceptibility[2c)] and indicates the metallic nature of this salt in the measured temperature range. The spin susceptibility of 3.2×10^{-4} emu/mol at room temperature is close to that of the d.c. susceptibility, 4.6×10^{-4} emu/mol, and the transfer integral t of 0.06 eV is estimated by a tight-binding approximation for the two-dimensional quarter-filled band: $\chi_s=\mu_B{}^2N_A\cdot\pi^{1/2}\cdot\{\pi t\cdot\sin(\pi^{1/2})\}^{-1}$, where μ_B is the Bohr magneton and N_A is Avogadro's constant.

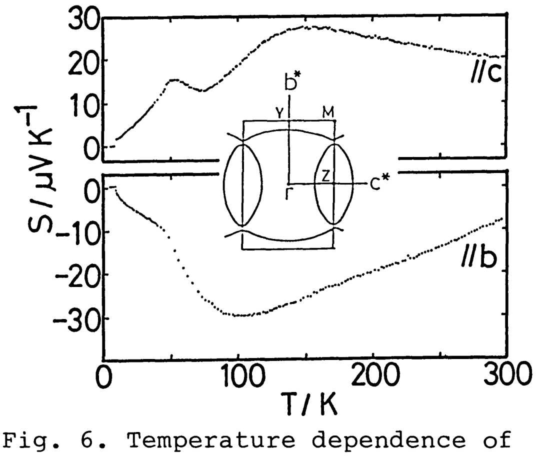

Fig. 6. Temperature dependence of thermopower along b and c axes and the band structure (inside) for $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu(NCS)}_2$.

The thermopower (S) was measured on a single crystal along the b- and c-axes. The crystal was mounted on a thin Au foil as an electrode in order to reduce a tension and the contacts were made by a gold paint. Figure 6 shows the results as a function of temperature from 300 to 4.6 K where S of a gold electrode is corrected. Quite surprisingly temperature dependences of S along two different directions exhibit completely opposite behaviors. S along the b-axis is negative and decreases linearly with decreasing temperature from -7 μV/K at 300 K to -30 μV/K at around 100 K then increases down to 10 K with a slight change of dS/dT at around 50 K. On the other hand, S along the c-axis is positive and increases from +20 μV/K (300 K) to +28 μV/K (around 150 K) then decreases down to 10 K with a hump at around 50 K.

Since the anion layer including copper atoms contains no conduction carriers as predicted from ESCA, ESR (vide supra), and structural analysis,3) the sign of S is expected to be positive due to the hole carriers in the BEDT-TTF sheets if a simple cosine-band is assumed. It has been proposed in the case of TMTSF • $CuBr_2$ that negative S is ascribed to a back electron transfer of about 10% from Cu^I to $TMTSF^+$ and this salt is assumed to be in a mixed-valence state of $[(TMTSF^+)_{0.9}(TMTSF)_{0.1}]\ [Cu^I{}_{0.9}Cu^{II}{}_{0.1}Br_2]$.7) However, such kind of back electron transfer was not observed in the present $Cu(NCS)_2$ salt. To the best of our knowledge, several BEDT-TTF cation radical salts in which a back electron transfer is not detected show negative thermopower in certain temperature range such as BF_4, I_3(β), Cu_5I_6, and Hg_3Cl_8 salts.8) Consequently the negative S is a rather common feature of BEDT-TTF cation radical salts. The temperature dependence of the negative S along the b-axis of the $Cu(NCS)_2$ salt was qualitatively explained on the basis of the band structure 4a) calculated on the extended Hückel method (Fig. 6). The band calculation indicates that the open Fermi surface near YM is electron-like, which makes $S_{//b}$ negative. The closed Fermi surface around the Z point is hole-like to make a positive contribution to $S_{//c}$. A little more quatitative calculation of S based on the Boltzmann equation by using this band structure will be published shortly.9) Therefore the peculiar behavior of the temperature dependences of S is the consequence of the complicated band structures of the $Cu(NCS)_2$ salt but not to a back electron transfer from Cu^I to BEDT-TTF. The additional hump at 50 K is not explained by the simple band theory, but can be ascribed to the phonon-drag. The superconducting transition is observed in the both directions at 10 K where the thermopower becomes zero.

References

1) J. G. Bednortz and K. A. Müller, Z. Phys. B, 64,189(1986).
2) a)H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett., 1988, 55; b)K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn., 57, 703 (1988); c)K. Nozawa, T. Sugano, H. Urayama, H. Yamochi, G. Saito, and M. Kinoshita, Chem. Lett., 1988, 617.
3) H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, Chem. Lett., 1988, 463.
4) a)K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, submitted to Phys. Rev. B; b)T. Sugano, H. Hayashi, H. Takenouchi, K. Nishikida, H. Urayama, H. Yamochi, G. Saito, and M. Kinoshita, submitted to Phys. Rev. B; c)T. Takahashi, T. Tokiwa, K. Kanoda, H. Urayama, H. Yamochi, and G. Saito, submitted to Phys. Rev. Lett.
5) The result of ESR work was presented at the Symposium of Molecular Structure, Kanazawa, October 1987. After the completion of our work, we obtained a paper which described different ESR behavior from ours though Tc is the same as our published data around 10 K: S. Gartner, E. Gogn, I. Heinen, H. J. Keller, T. Kultz, and D. Schweitzer, submitted to Solid State Commun.
6) R. J. Elliot, Phys. Rev., 96, 266(1954); A. W. Overhauser, ibid., 89, 689 (1953).
7) M. B. Inoue, C. Cruz-Vazguez, and M. Inoue, Synth. Metals, 22, 231(1988).
8) Int. Conf. on Electronics of Organic Materials, ELORMA 1987 Tashkent; K. Mortensen, J. M. Williams, and H. H. Wang, Solid State Commun., 56, 105(1985); V. A. Merzhanov, E. E. Kostyuchenko, O. E. Fabrt, I. F. Shchegolv, and E. B. Yagubskii, Zh. Eksp. Teor., Fiz., 89, 292(1985).
9) T. Mori et al., to be submitted.

(Received March 24, 1988)