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REFLECTION SPECTRA AND ELECTRICAL CONDUCTIVITY OF $(DBTTF)_8$-$(SnCl_6)_3$

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Optical reflection and dc conductivity measurements of $(DBTTF)_8$-$(SnCl_6)_3$ single crystals were carried out. The temperature dependence of the conductivity behaves as $(A/T^3)\exp(-E_g/2kT)$ in the temperature range above 85 K. The obtained activation energy Δ = 1010 K is fairly comparable with the result estimated by the optical study.

There has been considerable interest recently in a number of organic conductors which have highly anisotropic electrical, optical and magnetic properties. In all of these organic conductors, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is one of the system which have received the most detailed attention.[1] Accordingly many compounds with fulvalene rings in the TTF molecule were synthesized.[2] Dibenzotetrathiafulvalene (DBTTF) is one of them and it was found out by Aldoshina *et al.* to form the highly conductive complexes with the metal halides like $SnCl_4$.[3] In this paper, we report the temperature dependence of the electrical conductivity and the reflection spectra of the single crystal of $(DBTTF)_8(SnCl_6)_3$ complex.

The crystal of $(DBTTF)_8(SnCl_6)_3$ complex was prepared by the diffusion of DBTTF and $SnCl_6$ molecules in acetonitrile solution and it shows the dark and long needle crystals.[3] The single crystal of the complex consists of two staking layers for the molecules DBTTF and $SnCl_6^{2-}$ and the arrangement of each molecule is typically one-dimensional as is shown in Fig. 1.[4] The layers elongate along the c-axis and the period consists of 3 and 8 units of $SnCl_6^{2-}$ and DBTTF, respectively. Two of eight DBTTF molecules are neutral and six other molecules are oxidized to be the cation radicals. Thus, the complex of $(DBTTF)_8$-$(SnCl_6)_3$ shows the structural characteristic of organic conductor which consists of segregated columns of mixed valence donor stackings.

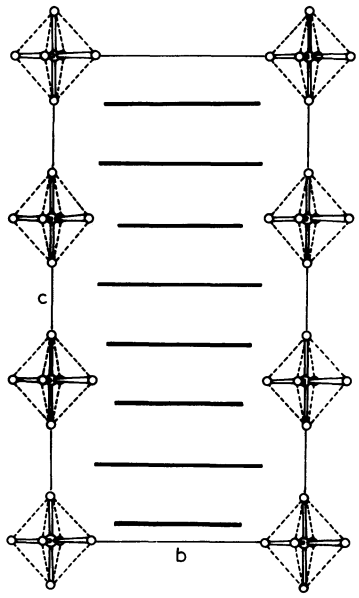

Fig. 1. Projection on the (bc)-plane of $(DBTTF)_8(SnCl_6)_3$.[4]

The experimental result of dc resistivity R(T) along the c crystalline axis was measured by the four probe method and is plotted in Fig. 2 as a function of $\ln T^3/R(T)$ vs. $1/T$ over the temperature range from 300 K to 85 K. The good straight line of the plot shows that the dc conductivity $\sigma(T)$ is well approximated by an equation given as

$$\sigma(T) = (A/T^3)\exp(-\Delta/T) = (A/T^3)\exp(-E_g/2kT) .$$

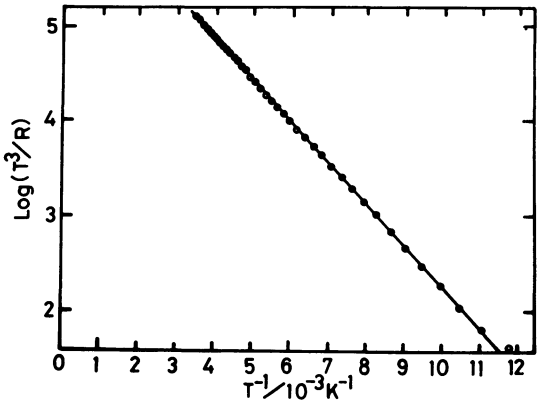

Fig. 2. Temperature dependence of the resistivity of $(DBTTF)_8-(SnCl_6)_3$.

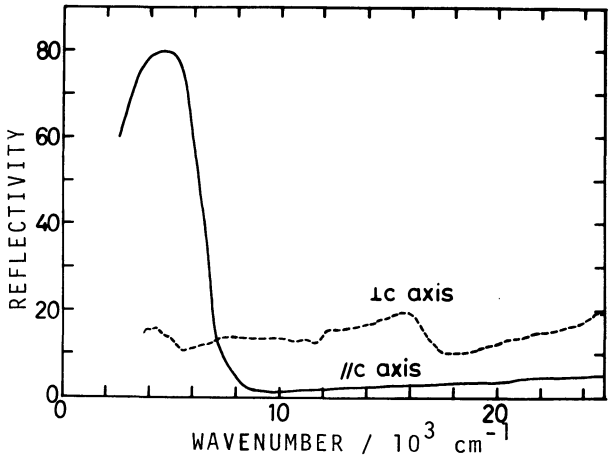

Fig. 3. Reflection spectra of $(DBTTF)_8-(SnCl_6)_3$.

This equation was suggested by Nagasawa[5] in order to explain the magnetic and electrical properties of $KCP[K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O]$. This equation means that the electron in the mixed valence state settles in the non-metallic ground state at low temperature and the thermally excited electron contributes to the transport phenomenon with the mobility of A/T^3. Nagasawa[6] explained such temperature dependence by the strong interaction between the conduction electron and the one-dimensional lattice vibration along the c-axis. That is, this effect may be characteristic of the crystals having the high one-dimensionality like KCP and $(DBTTF)_8(SnCl_6)_3$ complexes. The best fit to the equation gives $\Delta \simeq 1010$ K and $E_g \simeq 1400$ cm^{-1} and the room temperature conductivity $\sigma(RT)$ is about 100 $\Omega^{-1}cm^{-1}$. The crystalline reflection spectra are shown in Fig. 3. The band at 17000 cm^{-1} is found for the light polarized perpendicular to the c-axis and it can be assigned to the absorption band(L1) of DBTTF cation radical.[7] The c-axis absorption band does not mix with the intramolecular $\pi \rightarrow \pi^*$ transition bands of DBTTF molecule as is seen in Fig. 1. Therefore, the 5000 cm^{-1} band in the c-axis spectrum is assigned to the interband transition from the valence state to the conduction band created by the interaction between π-Mo's of DBTTF molecules in the stacking layer and the threshfold below 2000 cm^{-1} seems to correspond to the energy gap $E_g \simeq 1400$ cm^{-1} obtained by the conductivity measurement. Accordingly, this complex can be considered as the first organic conductor of the model suggested by Nagasawa.[5,6]

References

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