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Reflection Spectra of $(DBTTF)_4\cdot(BF_4)_2\cdot EtOH$ Complex

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The polarized reflection spectra of the crystal of $(DBTTF)_4\cdot(BF_4)_2\cdot EtOH$ complex were measured and the optical parameters were determined by the simulation of the observed reflection spectra. The theoretical analysis of the observed spectra shows that the electronic structure of DBTTF cation molecules is typical of the island type configuration. The 4000 and $11500\,cm^{-1}$ bands polarized parallel to the stacking axis were assigned to the CT_2 and CT_1 bands, and the parameters U and t of the Hubbard Hamiltonian were estimated to be $U=8950\,cm^{-1}$ and $t=1250\,cm^{-1}$.

There has been considerable interest recently in organic conductors which have highly abnisotropic electrical, optical and magnetic properties. Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is one of them which received the most detailed attention. After the discovery of the TTF-TCNQ complex, many compounds with fulvalene rings were synthesized to obtain the radical salts with highly electrical conductivity. Dibenzotetrathiafulvalene (DBTTF) is one of those compounds[1] and the direct oxidation of DBTTF by halogens and metal halides were reported to yield radical salts such as $(DBTTF)_2$-I_3,[2] $(DBTTF)_8(SnCl_6)_3$,[3] and $(DBTTF)_3(SnBr_6)$,[3] $(DBTTF)_2(Cu_2Cl_6)$,[4] and $(DBTTF)_2(Cu_2Br_6)$.[5] The employment of tetrafluoroborate as an oxidant was reported to yield the ion-radical salt $(DBTTF)(BF_4)_{0.8}$ showing a high conductivity up to 180 K.[6] We repored the crystal structure of another complex $(DBTTF)_4(BF_4)_2$ EtOH.[7] In the present paper, the reflection spectra of the crystal of $(DBTTF)_4\cdot(BF_4)_2\cdot EtOH$ complex are reported and the results of the theoretical analysis are presented by using the Hubbard approximation.

Experimental

The crystal of $(DBTTF)_4\cdot(BF_4)_2\cdot EtOH$ complex was prepared in an ethanol solution. The reflection spectra of the single crystal at the normal incidence were measured over the range of 5000—$25000\,cm^{-1}$ by means of a reflection spectrophotometer made in our laboratory. All calculations for the analysis of the experimental data were made on a FACOM M382 computer of Nagoya University.

Theoretical

For the island type system[8] of $[(DBTTF)_3]^{2+}$ cations the Hamiltonian H may be given by the Hubbard Hamiltonian as follows,

$$H = -t\sum_{i}\sum_{\sigma=\alpha,\beta}(a^{+}_{i,\sigma}a_{i+1,\sigma}+a^{+}_{i+1,\sigma}a_{i,\sigma}) + U\sum_{i} n_{i,\alpha}n_{i,\beta} \tag{1}$$

where $a^{+}_{i,\sigma}$ and $a_{i,\sigma}$ are the creation and anihilation operators of the π-electron occupying HOMO of the DBTTF molecule at the i-th site, σ represents the spin of π-electron, $n_{i,\sigma}=a^{+}_{i,\sigma}a_{i,\sigma}$ is the number of π-electron on the i-th site, t is the electron transfer integral and U the intramolecular Coulomb integral. Then, the ground and lower excited configuration functions for the singlet state are taken into account for the calculation of the electronic states of the island type system.[8]

$$\Phi^{1,2} = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{2,\alpha}-a_{1,\alpha}a_{2,\beta})\Phi_{HF} \tag{2}$$

$$\Phi^{2,3} = \frac{1}{\sqrt{2}}(a_{2,\beta}a_{3,\alpha}-a_{2,\alpha}a_{3,\beta})\Phi_{HF} \tag{3}$$

$$\Phi^{1,3} = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{3,\alpha}-a_{1,\alpha}a_{3,\beta})\Phi_{HF} \tag{4}$$

$$\Phi^{CT}_{1} = a_{3,\alpha}a_{3,\beta}\Phi_{HF} \tag{5}$$

$$\Phi^{CT}_{2} = a_{1,\alpha}a_{1,\beta}\Phi_{HF} \tag{6}$$

$$\Phi^{CT}_{3} = a_{2,\alpha}a_{2,\beta}\Phi_{HF} \tag{7}$$

Here, Φ_{HF} means the Hartree–Fock wave function of the neutral trimer of DBTTF. The energy of the island type system is calculated by diagonalizing the secular determinant for the symmetrical and the antisymmetrical states as is shown in the next equations,

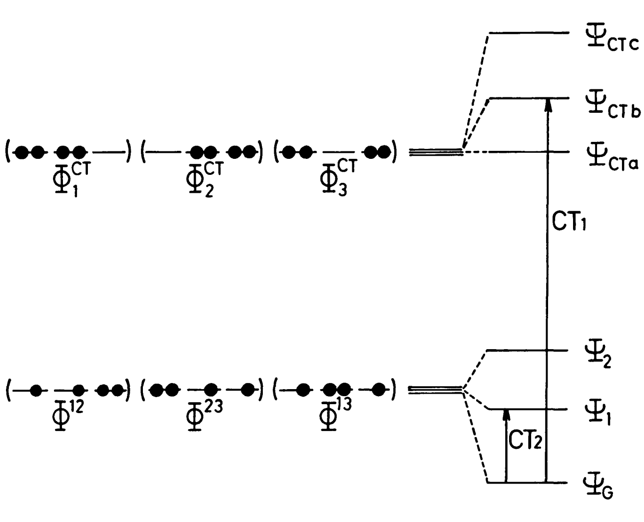

Fig. 1. Energy diagram of the island trimer type configuration.

$$\begin{array}{l|ccc|}
\Phi^{1,3} & 0 & \sqrt{2}t & 0 \\
\frac{1}{\sqrt{2}}(\Phi^{1,2}+\Phi^{2,3}) & \sqrt{2}t & 0 & -\sqrt{6}t \\
\frac{1}{\sqrt{2}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}+2\Phi_3^{\mathrm{CT}}) & 0 & -\sqrt{6}t & U
\end{array}, \tag{8}$$

and

$$\begin{array}{l|ccc|}
\frac{1}{\sqrt{2}}(\Phi^{1,2}-\Phi^{2,3}) & 0 & \sqrt{2} & 0 \\
\frac{1}{\sqrt{2}}(\Phi_1^{\mathrm{CT}}-\Phi_2^{\mathrm{CT}}) & \sqrt{2}t & U & 0 \\
\frac{1}{\sqrt{3}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}-\Phi_3^{\mathrm{CT}}) & 0 & 0 & U
\end{array}. \tag{9}$$

Then, the eigenvalues and eigenfunctions are obtained as follows and the energy diagram of the cation trimer system is depicted in Fig. 1.

$$\begin{aligned}
\Psi_G &= c_0\left\{\frac{1}{2}(\Phi^{1,2}+\Phi^{2,3}-\sqrt{2}\Phi^{1,3}) + \frac{\sqrt{3}t}{U-\sqrt{2}t}\frac{1}{\sqrt{6}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}+2\Phi_3^{\mathrm{CT}})\right\}, \\
E_G &= -\sqrt{2}t - \frac{3t^2}{U+\sqrt{2}t},
\end{aligned} \tag{10}$$

$$\begin{aligned}
\Psi_1 &= \frac{b_1}{\sqrt{2}}(\Phi^{1,2}-\Phi^{2,3}) + \frac{b_2}{\sqrt{2}}(\Phi_1^{\mathrm{CT}}-\Phi_2^{\mathrm{CT}}), \\
E_1 &= \frac{U-\sqrt{U^2+8t^2}}{2},
\end{aligned} \tag{11}$$

$$\begin{aligned}
\Psi_2 &= c_1\left\{\frac{1}{2}(\Phi^{1,2}+\Phi^{2,3}+\sqrt{2}\Phi^{1,3}) + \frac{\sqrt{3}t}{U-\sqrt{2}t}\frac{1}{\sqrt{6}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}+2\Phi_3^{\mathrm{CT}})\right\}, \\
E_2 &= \sqrt{2}t - \frac{3t^2}{U-\sqrt{2}t},
\end{aligned} \tag{12}$$

$$\begin{aligned}
\Psi_{\mathrm{CT},a} &= \frac{1}{\sqrt{3}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}+\Phi_3^{\mathrm{CT}}), \\
E_{\mathrm{CT},a} &= U,
\end{aligned} \tag{13}$$

$$\begin{aligned}
\Psi_{\mathrm{CT},b} &= -\frac{b_2}{\sqrt{2}}(\Phi^{1,2}-\Phi^{2,3}) + \frac{b_1}{\sqrt{2}}(\Phi_1^{\mathrm{CT}}-\Phi_2^{\mathrm{CT}}), \\
E_{\mathrm{CT},b} &= \frac{U+\sqrt{U^2+8t^2}}{2},
\end{aligned} \tag{14}$$

$$\begin{aligned}
\Psi_{\mathrm{CT},c} &= c_2\left\{\frac{1}{\sqrt{6}}(\Phi_1^{\mathrm{CT}}+\Phi_2^{\mathrm{CT}}+2\Phi_3^{\mathrm{CT}}) - \frac{\sqrt{3}t}{U+\sqrt{2}t}\frac{1}{2}(\Phi^{1,2}+\Phi^{2,3}-\sqrt{2}\Phi^{1,3}) - \frac{\sqrt{3}t}{U-\sqrt{2}t}\frac{1}{2}(\Phi^{1,2}+\Phi^{2,3}+\sqrt{2}\Phi^{1,3})\right\}, \\
E_{\mathrm{CT},c} &= U + \frac{3t^2}{U+\sqrt{2}t} + \frac{3t^2}{U-\sqrt{2}t}.
\end{aligned} \tag{15}$$

Here, c_0, c_1, c_2, b_1, and b_2 are given by the following equations,

$$\begin{aligned}
c_0 &= \left\{1+\frac{3t^2}{(U+\sqrt{2}t)^2}\right\}^{-1/2}, \\
c_1 &= \left\{1+\frac{3t^2}{(U-\sqrt{2}t)^2}\right\}^{-1/2}, \\
c_2 &= \left\{1+\frac{3t^2}{(U+\sqrt{2}t)^2}+\frac{3t^2}{(U-\sqrt{2}t)^2}\right\}^{-1/2}, \\
b_1 &= \left\{\frac{1}{2}\left(1+\frac{U}{\sqrt{U^2+8t^2}}\right)\right\}^{-1/2},
\end{aligned}$$

and

$$b_2 = -\left\{\frac{1}{2}\left(1-\frac{U}{\sqrt{U^2+8t^2}}\right)\right\}^{-1/2}. \tag{16}$$

The optically allowed transitions are the CT_2 transition from Φ_G to Φ_1 and the CT_1 transition from Φ_G to $\Phi_{\mathrm{CT},b}$, and their transition energies are given by

$$\Delta E_{\mathrm{CT}_2} = E_1 - E_G = \frac{U-\sqrt{U^2+8t^2}}{2} + \sqrt{2}t + \frac{3t^2}{U+\sqrt{2}t}, \tag{17}$$

and

$$\Delta E_{\mathrm{CT}_1} = E_{\mathrm{CT},b} - E_G = \frac{U+\sqrt{U^2+8t^2}}{2} + \sqrt{2}t + \frac{3t^2}{U+\sqrt{2}t}. \tag{18}$$

The transition moments of these two bands may be expressed as follows,

$$\langle\Psi_G|M|\Psi_1\rangle = c_0\left\{\frac{b_1}{\sqrt{2}} - \frac{2tb_2}{U+\sqrt{2}t}\right\}\boldsymbol{R}, \tag{19}$$

and

$$\langle\Psi_G|M|\Psi_{\mathrm{CT},b}\rangle = c_0\left\{-\frac{b_2}{\sqrt{2}} - \frac{2tb_1}{U+\sqrt{2}t}\right\}\boldsymbol{R}, \tag{20}$$

were $\boldsymbol{R}$ is the vector between the nearest neighboring DBTTF molecules. Then, the oscillator strengths of the CT_2 and CT_1 bands are given by the next equations,

$$f_{\mathrm{CT}_2} = 3 \times 1.09 \times 10^{11} \times \Delta E_{\mathrm{CT}_2} \times |\langle\Psi_G|M|\Psi_1\rangle|^2, \tag{21}$$

and

$$f_{\mathrm{CT}_1} = 3 \times 1.09 \times 10^{11} \times \Delta E_{\mathrm{CT}_1} \times |\langle\Psi_G|M|\Psi_{\mathrm{CT},b}\rangle|^2. \tag{22}$$

Here U and t are in cm^{-1} and $\boldsymbol{R}$ is in cm.

The optical reflectivity R can be expressed by the following equation

$$R = \frac{1+|\varepsilon|-\sqrt{2(|\varepsilon|+\varepsilon_1)}}{1+|\varepsilon|+\sqrt{2(|\varepsilon|+\varepsilon_1)}}. \tag{23}$$

and the dielectric function $\varepsilon(\omega)$ are approximated by the semiclassical Lorentz model,

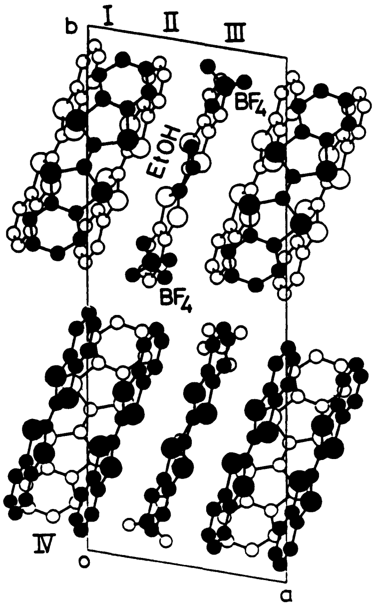

Fig. 2. The projection of the structure of $(DBTTF)_4 \cdot (BF_4)_2 \cdot EtOH$ along the *c* axis.

$$\varepsilon(\omega) = \varepsilon_{core} + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}$$
$$= \varepsilon_1(\omega) + i\varepsilon_2(w), \quad (24)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function of the DBTTF cation trimers, and $|\varepsilon| = \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}$. The oscillator strength f is determined by using the equation,

$$f = \frac{m_e}{4\pi N e^2} \Omega_j^2. \quad (25)$$

Here, m_e is the electron mass and N is the number density of DBTTF molecule. By fitting the above-mentioned equations of the reflectivity R to the observed values, the optical parameters of the complexes $(DBTTF)_4 \cdot (BF_4)_2 \cdot EtOH$ may be obtained and their energy structure can be determined.

Results and Discussion

$(DBTTF)_4 \cdot (BF_4)_2 \cdot EtOH$ crystallizes in the form of the dark blue needle and the space group is monoclinic *C*2/*m*.[7] The projection of the structure along the c axis is shown in Fig. 2. The structure consists of two crystallographically independent stacks. The DBTTF molecules (I, II, and III) are stacked parallel to each other in columns along the a axis. The angles between the mean planes of these DBTTF molecules and the a axis are almost equal and the mean interplanar spacing is 3.6A. The fourth DBTTF (IV) and ethanol and two BF_4^- anions form another sheet along the same direction. The molecular plane of DBTTF (IV) is almost perpendicular to the column of the other three DBTTF (I, II, and III) molecules.

On the other hand, Raman spectra of the complex shows that the DBTTF ν_5 band (totally symmetric streching vibrational mode of the central C=C bond) are observed at three Raman frequencies of 1540, 1442, and 1400 cm^{-1}.[9] The ν_5 band at 1540 cm^{-1} corresponds to that of the neutral DBTTF molecule and another one at 1400 cm^{-1} to the fully ionized cation radical $DBTTF^+$. The third band (ν_5=1442 cm^{-1}) is located intermediately between those of the neutral and cation molecules.

The above consideration suggests that the molecule (IV) is neutral and the other three molecules (I, II, and III) are ionized. Then, the island type model may be used to the analysis of the reflection spectra. The reflection spectra were observed for the polarizations

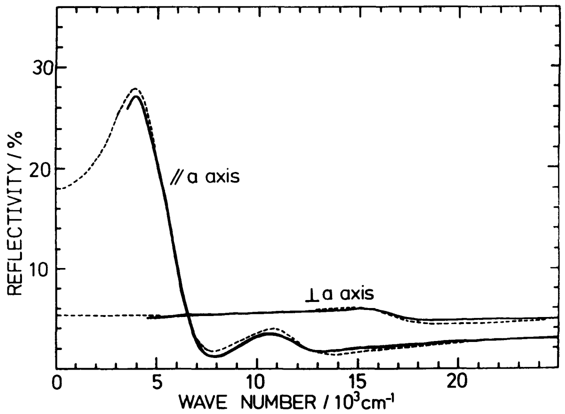

Fig. 3. Observed and calculated reflection spectra of the crystal of $(DBTTF)_4 \cdot (BF_4)_2 \cdot EtOH$ on the ac plane. (——: obsd, ----: calcd)

Table 1. Dielectric Parameters of the Lorentz Fits of Reflectivity Data for $(DBTTF)_4 \cdot (BF_4)_2 \cdot EtOH$

	//*a* spectrum		⊥*a* spectrum
ε_{core}	2.1		2.5
Ω_j/cm^{-1}	7500	5000	5000
ω_j/cm^{-1}	3800	11500	16500
γ_j/cm^{-1}	2500	3000	4000
f	0.32	0.14	0.14

Table 2. Hubbard Parameters (*t* and *U*) Determined by the Analysis of the Reflection Spectra of Various DBTTF Crystals[11,12]

Type	Compound	t/cm^{-1}	U/cm^{-1}
Alternant	$(DBTTF)_3(SnBr_6)$	2000	
Dimer	$(DBTTF)_2(Cu_2Cl_6)$	2200	6500
	$(DBTTF)_2(Cu_2Br_6)$	2300	7700
Island	$(DBTTF)_4(BF_4)_2EtOH$	1250	8950

parallel and perpendicular to the a axis on the ac plane as is shown in Fig. 3. The 4000 cm^{-1} band in the a axis spectrum can be assigned to the CT_2 band and the 11000 cm^{-1} band to the CT_1 band. The 16000 cm^{-1} in the $\perp a$ axis spectrum are assigned to the short axis component of the LE band of DBTTF$^+$ cation radical.[10]

The best fit of Eq. 23 to the observed reflectivity is obtained and the calculated reflection spectra are depicted in Fig. 3 in order to compare with the observed ones. The obtained parameters Ω_j, ω_j, γ_j, and $\varepsilon_{\mathrm{core}}$ are shown in Table 1 together with the oscillator strength determined by Eq. 25. Then, the experimental data (ΔE_{CT_1}=11500 cm^{-1}, f_{CT_1}=0.14, ΔE_{CT_2}=3800 cm^{-1}, f_{CT_2}=0.32, and R=3.6 A) give U=8950 cm^{-1} and t=1250 cm^{-1} which correspond to the calculated values (ΔE_{CT_1}=11500 cm^{-1}, f_{CT_1}=0.04, ΔE_{CT_2}=1900 cm^{-1} and f_{CT_2}=0.41). The obtained parameters (t and U) are shown in Table 2 together with those estimated by the analysis of other crystals ($(DBTTF)_3(SnBr_6)$,[11] $(DBTTF)_2(Cu_2Cl_6)$,[12] and $(DBTTF)_2(Cu_2Br_6)$[12]). In these crystals, the interplanar distances between DBTTF's are almost same (3.6 A) but the stacking behaviors are different. Therefore, the smaller t and the larger U values for $(DBTTF)_4\cdot(BF_4)_2\cdot EtOH$ may be explained by the comparison of the overlap integrals between the HOMO's of DBTTF in the crystals.

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