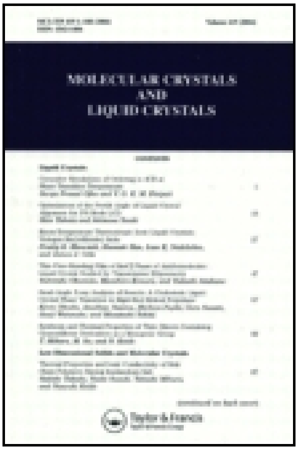

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Reflectance Spectra of Bedt-Ttf salts

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REFLECTANCE SPECTRA OF BEDT-TTF SALTS

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Abstract The polarized reflectance spectra were measured on four BEDT-TTF salts. The results clearly show the effects of intermolecular S-S interaction which gives more or less two dimensional character in their band structures. The observed infrared maxima in the conductivity spectra are concluded to be attributable mainly to the inter-band excitation.

INTRODUCTION

Recently, it has been revealed that the charge-transfer salts of BEDT-TTF show several unique features in the electrical properties.[1-7] This is considered to be associated with the presence of a relatively strong intermolecular S-S interaction along the direction normal to BEDT-TTF stack. In order to understand their unique behaviors, it is of great importance to accumulate information concerning their electronic structures. One of the most direct ways for this purpose is to investigate the optical properties on their single crystals. We report here the optical properties of four BEDT-TTF salts; β-

$(BEDT\text{-}TTF)_2PF_6$, $(BEDT\text{-}TTF)_2\cdot ClO_4\cdot(C_2H_3Cl_3)_{0.5}$, $(BEDT\text{-}TTF)_3\cdot(ClO_4)_2$ and β-$(BEDT\text{-}TTF)_2I_3$.

EXPERIMENTAL

The polarized reflectance spectra in the infrared and visible regions were measured, mostly at room temperature, by means of microspectrophotometric technique. We used an infrared microspectrophotometer JASCO MIR-300 for the region below 5000 cm^{-1}, and a modified Olympus MMSP-RK microspectrophotometer for the region of 5000-25000 cm^{-1}.

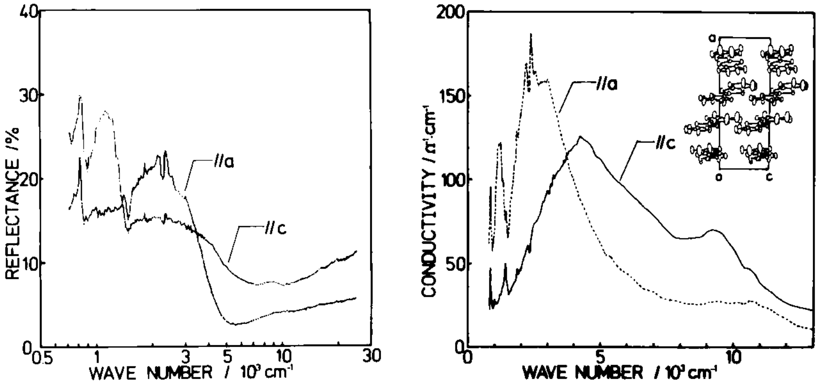
RESULTS

1) β-$(BEDT\text{-}TTF)_2PF_6$

In this salt, BEDT-TTF molecules are stacked along the a-axis with a periodicity composed of four molecules[8] (see the inset of Fig. 1(b)). There exist several short S-S contact between molecules along the c-axis. This salt is known to show metal-insulator (M-I) transition at 297 K.[3,8] At 297 K, the DC conductivity is about 10 $ohm^{-1}\cdot cm^{-1}$ along the c-axis, and its anisotropic ratio $\sigma(//c)/\sigma(//a)$ is about 50.

As shown in Fig. 1(a), both the //a and //c reflectance spectra show an infrared dispersion, but the reflectance value is quite low in comparison with what is usually found for a typical 1-D organic metal. The // a and // c conductivity spectra obtained by the Kramers-Kronig transformation of reflectance data, are shown in Fig. 1(b).

For both polarizations, the conductivity shows a broad maximum and falls down at lower frequency, the maximum being at 2400 cm^{-1} (0.36 eV) and 4300 cm^{-1} (0.54 eV) for the //a and //c polarizations, respectively. We calculated plasma frequency $\omega_{p\alpha}$ by use of the following equation (α denotes the polarization direction).



(a) (b)

Figure 1 Reflectance spectra of β-$(BEDT-TTF)_2 \cdot PF_6$, (a), and conductivity spectra, (b).

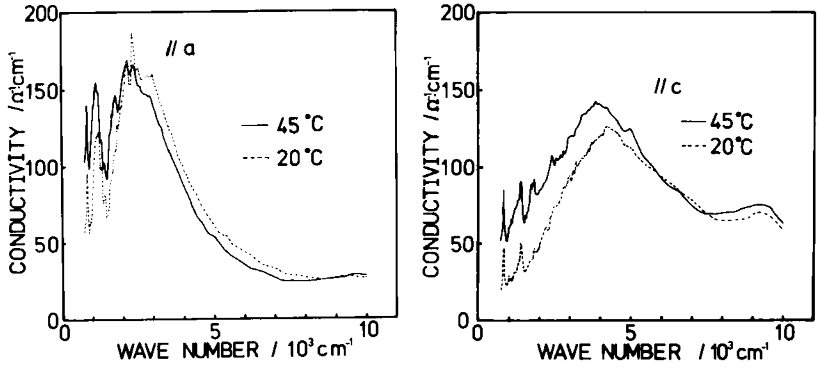


Figure 2 Conductivity spectra of β-$(BEDT-TTF)_2 \cdot PF_6$ above and below M-I transition

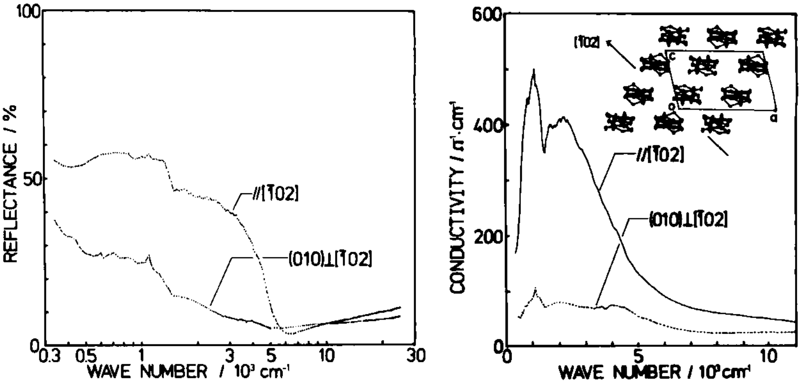
$$\omega_{p\alpha}^{2} = 8\int\sigma_{\alpha}(\omega)\,d\omega \qquad (1)$$

The obtained values were 5.1×10^3 and 5.3×10^3 cm^{-1} for the //a and //c polarizations, respectively. Figure 2 shows the conductivity spectra at the temperatures below and above the M-I transition. The general features of the spectra little change on going from the insulting phase to the metallic phase except a small shift of the maximum in the //a spectrum and an slight increase of the //c conductivity at low frequency.

2) (BEDT-TTF)$_2$·ClO$_4$·(C$_2$H$_3$Cl$_3$)$_{0.5}$

This salt is reported to be metallic down to 1.8 K, the conductivity at room temperature being about 20 ohm^{-1}·cm^{-1} with small anisotropy within the (010) plane.[3]

The infrared reflectance measured on the (010) crystal face is highest for the light polarization parallel to the



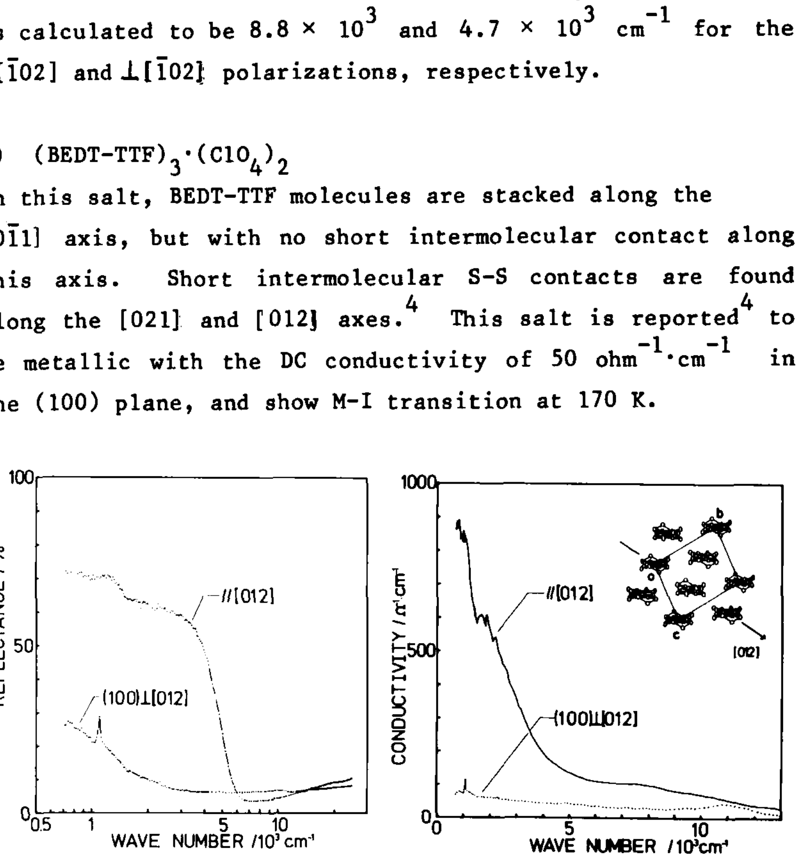
(a) (b)

Figure 3 Reflectance spectra of (BEDT-TTF)$_2$·ClO$_4$·(C$_2$H$_3$Cl$_3$)$_{0.5}$, (a), and conductivity spectra, (b).

$[\bar{1}02]$ axis, which is nearly perpendicular to the stacking axis of BEDT-TTF, and along which there exist short intermolecular S-S contacts.[4] Both the //$[\bar{1}02]$ and ⊥$[\bar{1}02]$ reflectance spectra show a broad infrared dispersion, the reflectance value around 300 cm^{-1} being about 60 and 30 % for the //$[\bar{1}02]$ and ⊥$[\bar{1}02]$ polarizations, respectively. As shown in Fig. 2(b), the $[\bar{1}02]$ conductivity clearly show a maximum at about 1300 cm^{-1} (0.17 eV). The plasma frequency is calculated to be 8.8×10^3 and 4.7×10^3 cm^{-1} for the //$[\bar{1}02]$ and ⊥$[\bar{1}02]$ polarizations, respectively.

3) $(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2$

In this salt, BEDT-TTF molecules are stacked along the $[0\bar{1}1]$ axis, but with no short intermolecular contact along this axis. Short intermolecular S-S contacts are found along the [021] and [012] axes.[4] This salt is reported[4] to be metallic with the DC conductivity of 50 $ohm^{-1} \cdot cm^{-1}$ in the (100) plane, and show M-I transition at 170 K.



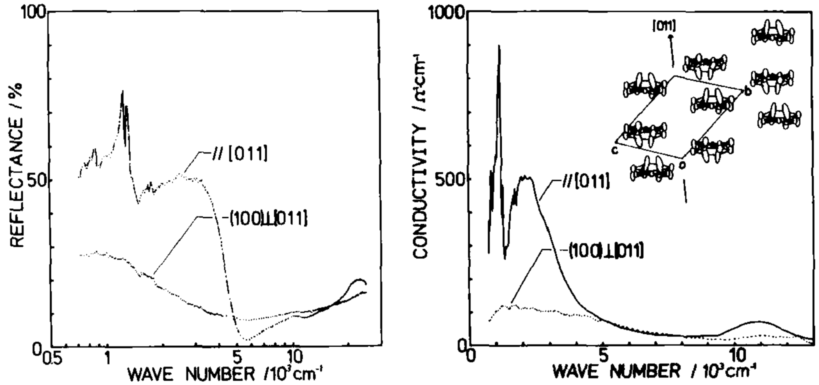
(a) (b)

Figure 4 Reflectance spectra of $(BEDT\text{-}TTF)_3 \cdot (ClO_4)_2$, (a), and conductivity spectra, (b).

The infrared reflectance measured on the (100) crystal face is significantly stronger for the //[012] polarization than for the ⊥[012] polarization, as shown in Fig. 4(a). This feature resembles to what is often found for an organic 1-D metal. But it should be noted that the [012] axis is not the direction of BEDT-TTF stack. As shown in fig. 4(b), the //[012] conductivity does not exhibit a maximum at least within the observed frequency region. But it is likely to fall down at lower frequency because the DC conductivity is only 50 $ohm^{-1}\cdot cm^{-1}$. The plasma frequency is calculated to be 10.5×10^3 and 4.4×10^3 cm^{-1} for the //[012] and ⊥[012] polarizations, respectively.

4) β-$(BEDT\text{-}TTF)_2I_3$

This modification of $(BEDT\text{-}TTF)_2I_3$ is reported to be superconductive below 1.4 K, although the DC conductivity at room temperature is only 30 $ohm^{-1}\cdot cm^{-1}$ with little anisotropy within the (100) plane.[5-7] Infrared reflectance



(a) (b)

Figure 5 Reflectance spectra of β-$(BEDT\text{-}TTF)_2\cdot I_3$, (a), and conductivity spectra, (b).

measured on the (100) crystal face was found to be highest for the polarization parallel to the [011] axis which nearly corresponds to the stacking direction of BEDT-TTF.[10]

Figure 5 shows the // [011] and ⊥[011] reflectance spectra. The // [011] conductivity clearly shows a broad maximum at 2200 cm^{-1} and falls down in the region below 1000 cm^{-1} in agreement with the low DC conductivity. The plasma frequency is calculated to be 8.5×10^3 and 5.3×10^3 cm^{-1} for the // [011] and ⊥[011] polarizations, respectively.

DISCUSSION

For all the four BEDT-TTF salts studied here, the optical conductivity in the infrared region is significantly higher than the DC conductivity, and falls down at lower frequency, often showing a maximum in the region of 2000-6000 cm^{-1}. Another important feature is that the polarization direction which gives high infrared conductivity is not necessarily parallel to BEDT-TTF stack, and rather in the direction of strong intermolecular S-S interaction. These feature are quite different from those found in $(TMTSF)_2X$.

Within the framework of single-particle excitation, we calculated the conductivity spectra which were expected from the band structures of BEDT-TTF salts.[9] We used the following formula in calculating the optical conductivity for the α polarization.

$$\sigma_{\alpha}(\omega) = \mathrm{Re}\left\{\frac{1}{i\Omega\hbar^{3}}\sum_{n}\frac{\omega}{\omega_{n0}}\,\frac{2\,[H,P_{\alpha}]_{0n}\,[H,P_{\alpha}]_{n0}}{\omega^{2}-\omega_{n0}^{2}+i\,\omega\Gamma}\right\} \qquad (2)$$

where P_{α} is the projection of the dipole operator **P** along the α direction, Ω is the crystal volume, Γ is the electronic relaxation rate, which was tentatively assumed to be 0.1 eV, and 0 and n stand for the ground and excited states, respectively. The Hamiltonian and dipole operators are expressed as follows

$$H = \Sigma\,\Sigma\, t_{p\ell,qm}\, a^{+}_{p\ell} a_{qm} \qquad (3)$$

$$\mathbf{P} = e \sum_{p}\sum_{\ell}(\mathbf{R}_{p\ell}-\mathbf{G})\, a^{+}_{p\ell} a_{p\ell} \qquad (4)$$

where $a^{+}_{p\ell}$ and $a_{p\ell}$ are the creation and annihilation operators of electron at the ℓ-th site in the p-th unit cell, $t_{p\ell,qm}$ is transfer integural, $\mathbf{R}_{p\ell}$ is the position vector and **G** is the vector of the center of mass. Figure 6 shows the calculated conductivity spectra. Since the contribution of the intra-band excitation was calculated to be lower than that of the inter-band excitation, we omitted here the former contribution. Note that the main features of the observed conductivity spectra are well reproduced in these calculated conductivity spectra. This fact indicates that the observed high infrared reflectance is mainly associated with the inter-band excitation in the case of the BEDT-TTF salts. In contrast with this, a similar calculation showed that the infrared reflectance was mainly due to the intra-band excitation in the case of

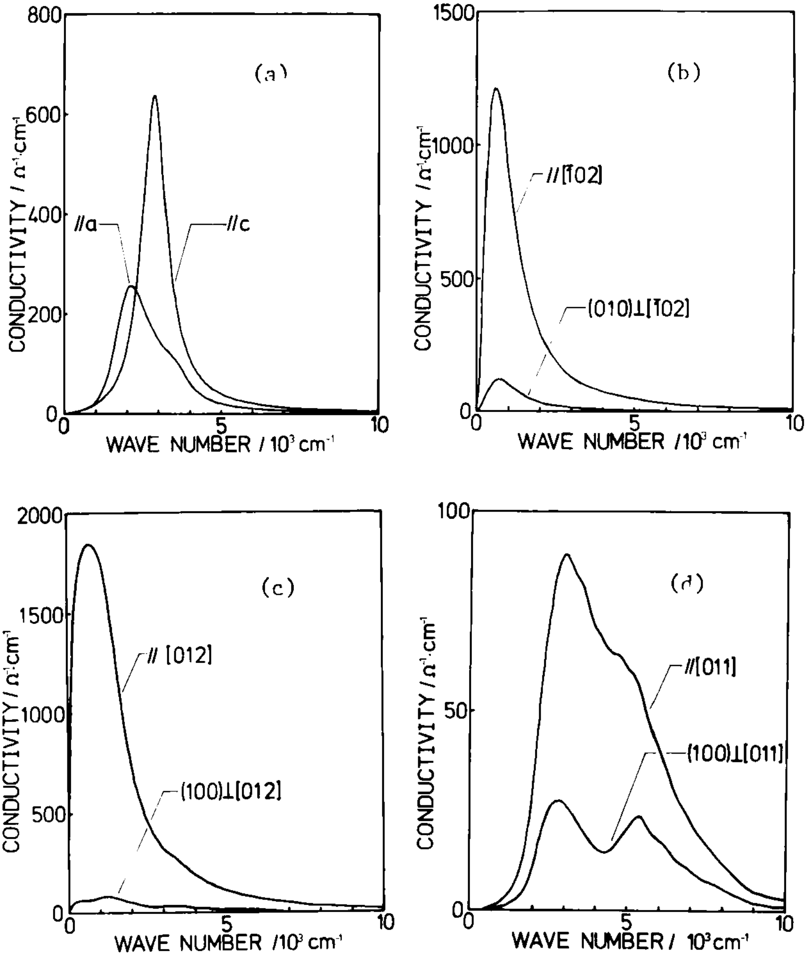


Figure 6 Conductivity spectra calculated from band structure:

(a) β-(BEDT-TTF)$_2$·PF$_6$,
(b) (BEDT-TTF)$_2$·ClO$_4$·(C$_2$H$_3$Cl$_3$)$_{0.5}$
(c) (BEDT-TTF)$_3$·(ClO$_4$)$_2$
(d) β-(BEDT-TTF)$_2$·I$_3$

$(TMTSF)_2X$ salts. This difference seems to come out from the situation that the band structures of BEDT-TTF salts have more or less two-dimensional character because of the strong intermolecular S-S interaction between BEDT-TTF stacks.

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