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Temperature Dependence of the Reflectance Spectra of the Single Crystals of Bis(ethylenedithio)tetrathiafulvalenium Salts. α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ and α-(BEDT-TTF)$_2$I$_3$

Kyuya YAKUSHI,* Hirohisa KANBARA, Hiroyuki TAJIMA, Haruo KURODA, Gunzi SAITO,† and Takehiko MORI††
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113
†Institute for Solid State Physics, the University of Tokyo, Roppongi, Tokyo 106
††Institute for Molecular Science, Okazaki, Aichi 444
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Polarized reflectance spectra were measured on the single crystals of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ and α-(BEDT-TTF)$_2$I$_3$. The optical spectra of these materials were interpreted on the basis of a simple semimetallic band model, and the anisotropic character of the intermolecular interaction in these crystals was quantitatively examined by analyzing the observed spectra. The observed temperature dependence of reflectance spectrum reflects the change of the electronic structure accompanying the metal-insulator phase transition, and is consistent with our interpretation of the spectra.

In the charge-transfer salts of BEDT-TTF(bis(ethylenedithio)tetrathiafulvalene), the Peierls instability is expected to be suppressed by the introduction of a relatively strong interchain interaction through sulfur atoms.[1,2] In fact studies on the crystal structures of BEDT-TTF salts revealed a presence of the two-dimensional network of short S-S contacts.[3] The optical experiment on (BEDT-TTF)$_4$(ClO$_4$)$_2$(TCE)$_{1.0}$ proved that a strong charge-transfer interaction between donor molecules takes place through these S-S contacts.[4] Some of the trihalide salts of BEDT-TTF remain metallic down to low temperature and exhibit a superconducting transition at ambient pressure.[5-8] However. a large majority of BEDT-TTF salts undergo a metal-insulator transition at low temperature. The nature of this metal-insulator transition has not been well characterized so far. α-(BEDT-TTF)$_3$(ReO$_4$)$_2$[9,10] and α-(BEDT-TTF)$_2$I$_3$[11-13] belong to this kind of BEDT-TTF salt, showing the metal-insulator transition at 88 and 135 K, respectively. The phase transitions of these materials have been studied by means of the electrical[9,11] and magnetic[10,12,13] experiments. These experiments are sensitive to a small change near a Fermi surface, whereas the optical experiment probes the overall band structure. Furthermore, the optical experiment is a powerful tool to inspect the effect of an electron-electron correlation. We have conducted a systematic study on the metallic BEDT-TTF salts and analyzed the optical spectra on the basis of a simple one-electron band model.[14-18] In this paper we present the experimental results of the temperature dependence of the reflectance spectra of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ and α-(BEDT-TTF)$_2$I$_3$, and discuss the change of the electronic structure accompanying the metal-insulator phase transition.

Experimental

Single crystals of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ and α-(BEDT-TTF)$_2$I$_3$ were prepared by using an electrochemical method from the tetrahydrofuran and benzonitrile solutions, respectively. The dimensions of the crystal used in this experiment were 1×2 mm^2 for α-(BEDT-TTF)$_2$I$_3$ and 1.5×1.5 mm^2 for α-(BEDT-TTF)$_2$I$_3$. Polarized reflectance spectra were measured from 720 cm^{-1} to 25000 cm^{-1} by using the two types of microspectrophotometers, the one for the visible and near-infrared regions and the other for the infrared region, both of which were designed in our laboratory (Department of Chemistry, the University of Tokyo) to measure the reflectivity of a tiny crystal.[13,19] A polarized reflectance spectrum was measured for the two polarization directions parallel to the optical axes projected onto the crystal face. These axes were searched by using the light of 3330 cm^{-1}, because the dispersion of reflectivity around this wavenumber was strongest in the spectral region concerned with the present experiment. The optical axes are mutually perpendicular and give the maximum and minimum reflectivities. The crystallographic axes which correspond to these directions were identified by means of X-ray diffraction. As cryostats to cool the sample crystal, Oxford CF104A was used for the infrared spectrometer and CTi SPECTRIM^{tm} for the visible spectrometer. The sample crystal was fixed with vacuum grease on a Si single crystal plate, the surface of which was painted by carbon paint to remove a stray light, and was transferred from one cryostat to another. The Si plate was glued with silver paint onto the goniometer head which was fixed to the cold stage of the cryostat. A thermocouple, Au(Fe)/Chromel, was attached near the sample on the goniometer head. The electrical resistivity of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ were measured along the c-axis by using a low-frequency four-probe method. The electrical contacts to the 10 μm gold wires were made by carbon paint.

Results and Discussion

α-(BEDT-TTF)$_3$(ReO$_4$)$_2$. The crystal of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ belongs to the monoclinic system, six BEDT-TTF molecules being contained in the unit cell.[20] Figure 1 shows the polarized reflectance spectrum measured on the (010) crystal face, the arrangement of BEDT-TTF molecules in one of the two crystallographically equivalent molecular sheets being also shown there. The maximum dispersion was found for the light polarization parallel to the [102] axis. This axis coincides with the direction of the maximum overlap integral between the neighboring

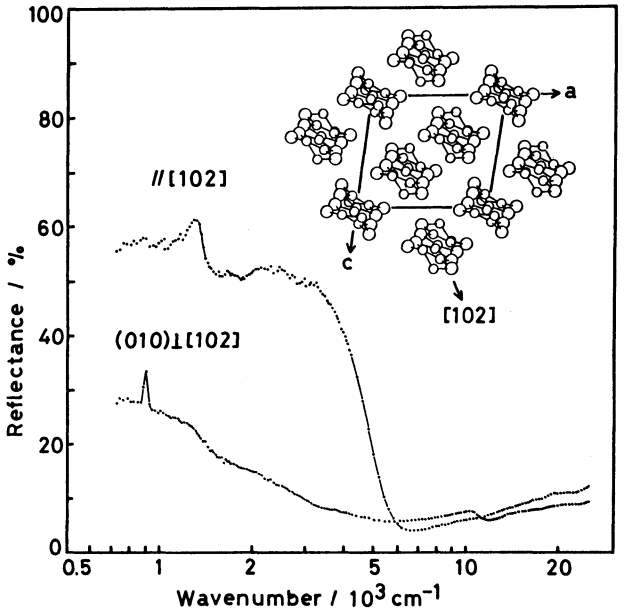

Fig. 1. Reflectance spectrum of α-(BEDT-TTF)$_3$-(ReO$_4$)$_2$. The inset shows the crystal structure viewed nearly along the long axis of BEDT-TTF molecule.

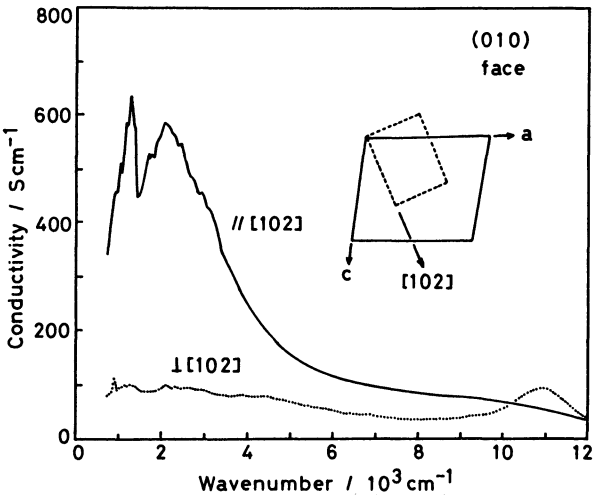

Fig. 2. Conductivity spectrum of α-(BEDT-TTF)$_3$-(ReO$_4$)$_2$. The inset shows the relation between the unit cell (solid line) and the reduced cell (dotted line).

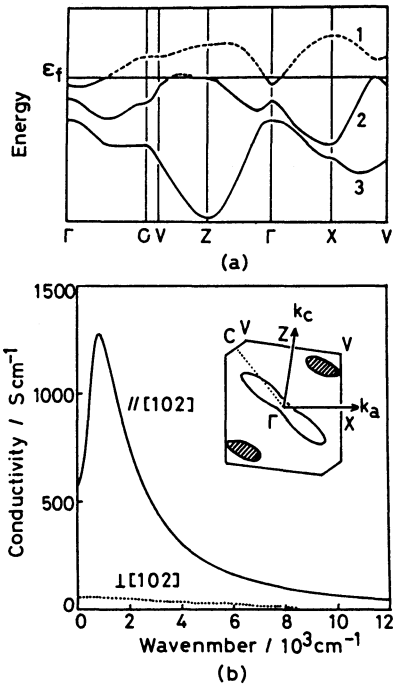

Fig. 3. (a) Band structure of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$. (b) Conductivity spectrum of α-(BEDT-TTF)$_3$-(ReO$_4$)$_2$ calculated by assuming the point charge approximation. The inset shows the names of special points and the Fermi surface in the Brillouin zone.

BEDT-TTF molecules. Therefore, this material is essentially composed of the molecular chains along the [102] axis, although the molecules are stacking along the [$\bar{1}$01] axis. However, a weak dispersion was also observed in the low-wavenumber region of the ⊥[102] spectrum. This dispersion clearly indicates the existence of a significant magnitude of interchain interaction. Figure 2 shows the optical conductivity spectrum obtained through the Kramers-Kronig transformation of the reflectance spectrum illustrated in Fig. 1. The integrated intensity of the electronic transition in the infrared region is related to the magnitude of the intermolecular interaction along the polarization direction. In order to obtain a quantitative measure for the anisotropy of the intermolecular interaction, we calculated the average transfer integrals in the hypothetical reduced unit cell drawn in the inset of Fig. 2. The method of calculation is the same as the one used by Jacobsen in the analysis of β-(BEDT-TTF)$_2$I$_3$.[21] We calculated the plasma frequency by the following equation,

$$\omega_p{}^2 = 8\int_0^{10\times10^3\,\mathrm{cm}^{-1}} \sigma(\omega)\,\mathrm{d}\omega$$

and obtained $\omega_{p//}$=9.5×10^3 cm^{-1} and $\omega_{p\perp}$=4.8×10^3 cm^{-1}. Then, the transfer integrals were calculated to be $t_{//}$=0.10 eV and $t_\perp$=0.07 eV by using $d_{//}$=6.0 Å (//[102]) and $d_\perp$=4.4 Å (⊥[102]). The ratio, $t_{//}/t_\perp$=1.4, is much smaller than the corresponding value, 10, found for (TMTSF)$_2$PF$_6$.[22] This fact indicates the strong two dimensionality of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$.

The conductivity spectrum of the //[102] polarization exhibits a broad peak around 2000 cm^{-1} and a sharp peak at 1250 cm^{-1}. The feature that the conductivity falls down at low wavenumber showing a peak around 2000 cm^{-1} is not dependent on the method of extrapolation of the reflectivity which has to be assumed in the Kramers-Kronig transformation. This spectral shape inevitably comes from the low reflectivity in the low-wavenumber region. The presence of the peak is also supported by the comparison with the DC electrical conductivity which corresponds to the

optical conductivity at zero wavenumber. The DC conductivity measured at room temperature along the c-axis is about 20 $S\,cm^{-1}$, which is much smaller than the maximum conductivity, 600 $\Omega^{-1}cm^{-1}$ at 2000 cm^{-1}. The observed shape of the conductivity spectrum is significantly different from that predicted from a Drude model. For organic conductors, the deviation from the Drude-like line shape in conductivity spectrum has been often interpreted as the one associated with a strong Coulomb interaction between conduction electrons. This kind of interpretation was given for the spectrum of $(TMTTF)_2X$ salts.[23,24] If this is the case, the optical transition across a Hubbard gap or equivalently the charge-transfer transition between the BEDT-TTF cations should be observed around 5×10^3 cm^{-1} [25] in the //[102] spectrum, since two of the three BEDT-TTF molecules are formally cations, and in this situation the probability for the neighboring BEDT-TTF molecules to be the cation state is quite large. In fact, the corresponding charge-transfer band was observed in the case of the radical salts of TTF halides[26] which have a similar situation. However, we could not find any dispersion corresponding to the charge-transfer between neighboring cations in the near infrared region of the //[102] spectrum. Therefore, we adopted another standpoint, that is to consider the effect of the interband transition on the basis of one-electron model. For example, the optical spectrum of graphite is considerably deviated from a Drude model due to the presence of the interband transition

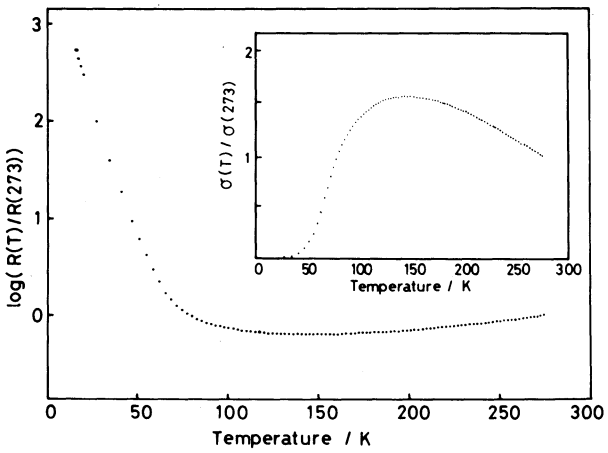

Fig. 4. Temperature dependence of the electrical resistivity and conductivity (inset) of α-(BEDT-TTF)$_3$(ReO_4)$_2$.

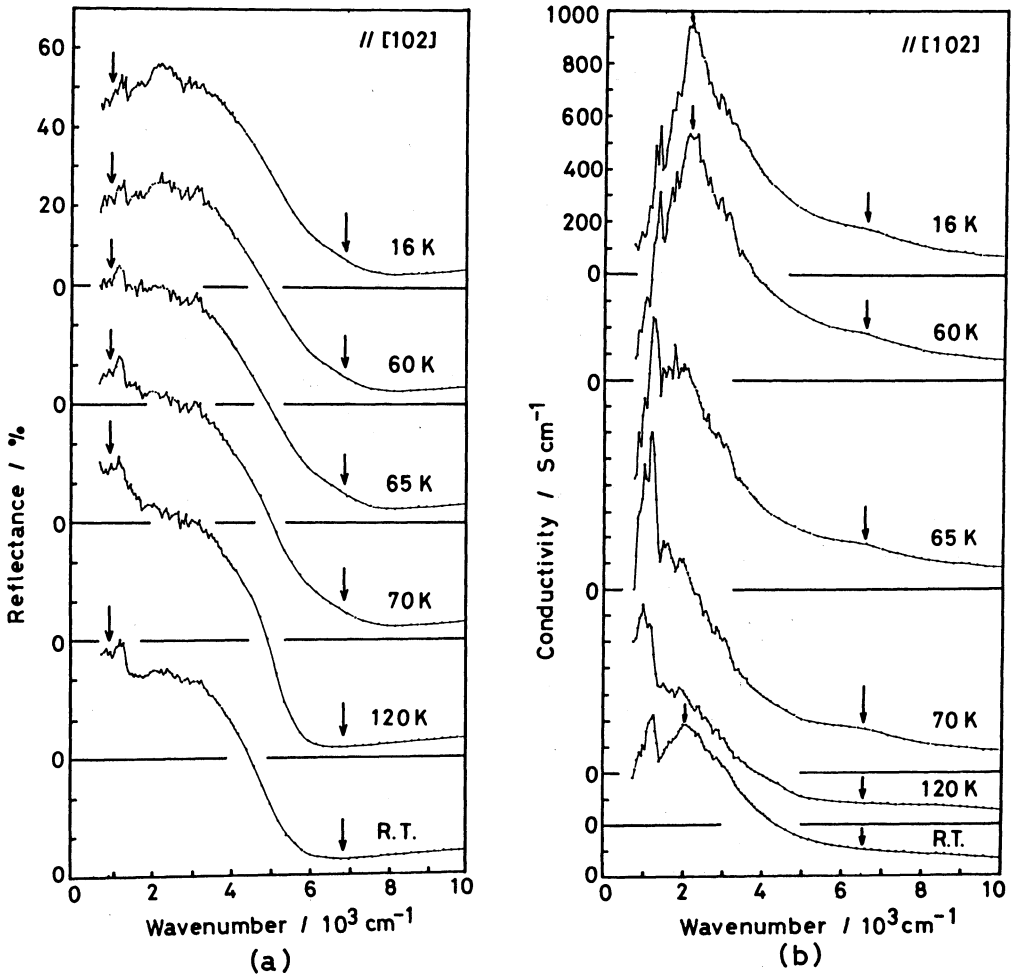

Fig. 5. Temperature dependence of (a) reflectance spectrum and (b) conductivity spectrum of α-(BEDT-TTF)$_3$(ReO_4)$_2$.

near the plasma edge.[27] To examine the effect of the interband transition we calculated the two-dimensional band structure in the (010) plane using the tight binding approximation within the framework of the extended Huckel method. The π-band produced from the HOMO's of BEDT-TTF splits into three, among which the lower two bands were nearly filled as shown in Fig. 3a, since the two-dimensional unit cell contains three BEDT-TTF molecules and two of them is oxidized. Therefore, this material is predicted to have a semimetallic small Fermi surface. Figure 3b shows the conductivity spectrum calculated by the point charge approximation on the basis of this band structure.[16] This spectrum contains the contribution of the intraband transition associated with the conduction electrons at the small Fermi surface, and the contribution of the interband transition from the bands 2 and 3 to the band 1. The agreement with the observed spectrum shown in Fig. 2 is qualitatively good.

Parkin et al. found a metal-insulator transition in the experiment on the electrical resistivity of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$: The resistivity showed a shallow minimum at about 150 K and steeply increased at about 115 K.[9] On the other hand, Carneiro et al. reported a gentle phase transition at about 88 K in the ESR expriment.[10] Our result of the electrical resistivity measured along the c-axis was illustrated in Fig. 4. The shallow minimum appeared at almost the same temperature as that of Parkin et al., but this sample showed a steeper slope at about 85 K. No hysteresis was observed in the cooling and heating cycle. This metal-insulator transition is very gentle and is similar to the temperature dependence of the magnetic susceptibility. Figure 5a shows the temperature dependence of the //[102] reflectance spectrum. On lowering temperature, salient changes were observed typically around 900 and 6800 cm^{-1} as shown by arrows in Fig. 5a. Let us first discuss the change observed in the low-wavenumber region. The temperature dependence of the reflectivity at 900 cm^{-1} were plotted in Fig. 6a. A gentle but remarkable change of reflectivity takes place around the phase-transition temperature. The increase of the reflectivity from room temperature to 120 K is probably related to the increase of the relaxation time of the conduction electrons, and the decrease below 70 K corresponds to the disappearance of the conduction electrons probably due to the some structural change. The temperature dependence of the optical conductivity spectra were shown in Fig. 5b. The peak of the interband transition shifts to the low-wavenumber side on lowering the temperature from room temperature to 120 K, then shifts to the high wavenumber side from 70 K to 60 K, and remains at the same position below 60 K down to 16 K. The reason for the gradual shift of the interband transition below 70 K is not clear at present. Since the peak position of the interband transition at 16 K is almost the same as that of room temperature spectrum, we consider that the metal-insulator transition brings about a minor change to the overall structure of the energy band, although it gradually introduces a small band gap at low temperature. In contrast to the temperature dependence of reflectivity around 900 cm^{-1}, the reflectivity change at 6800 cm^{-1} abruptly increases on going

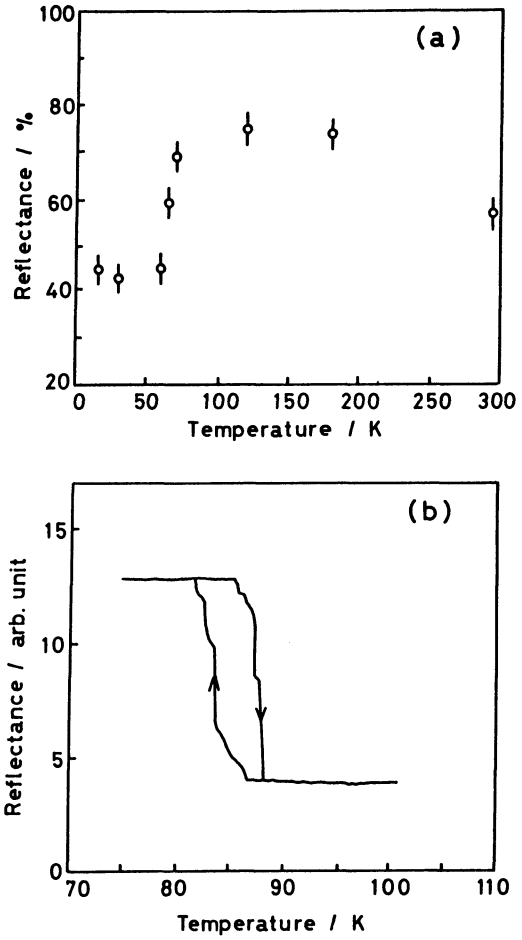

Fig. 6. Temperature dependence of the reflectivity of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ at (a) 900 cm^{-1} and (b) 6800 cm^{-1}.

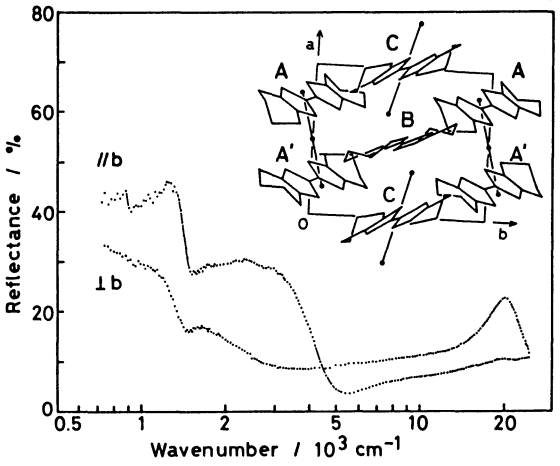

Fig. 7. Reflectance spectrum of α-(BEDT-TTF)$_2$I$_3$. The inset shows the crystal structure projected onto the (001) plane.

from the metallic phase to the semiconductive phase, as shown in Fig. 5a. The details of the temperature dependence were examined at 6000 cm^{-1} by changing the sample temperature at the rate of 2° min^{-1}. The results are shown in Fig. 6b, which clearly indicates the abrupt reflectivity change around the phase transition temperature reported by Carneiro et al. The increase of the reflectivity is reflected on appearance of a hump at about 6500 cm^{-1} in the conductivity spectrum as shown in Fig. 5b. This new hump may be associated with the transition from the band 3 to the band 1 which is introduced by a small structural change on the phase transition. Another possible assignment is that this weak hump corresponds to the charge-transfer band between BEDT-TTF^+ which appears as the result of the reduction of the screening effect in the semiconductive phase.

α-(BEDT-TTF)$_2$I$_3$. The crystal of α-(BEDT-TTF)$_2$I$_3$ belongs to triclinic system and the unit cell contains four BEDT-TTF molecules as shown in Fig. 7.[10] The structure is composed of two crystallographically independent stacks along the a-axis. However, the maximum reflectivity at 3330 cm^{-1} was found in the polarization direction parallel to the b-axis. Figure 7 shows the polarized reflectance spectra measured on the (001) crystal face. The reflectivity and the anisotropy of the reflectance spectrum are much smaller

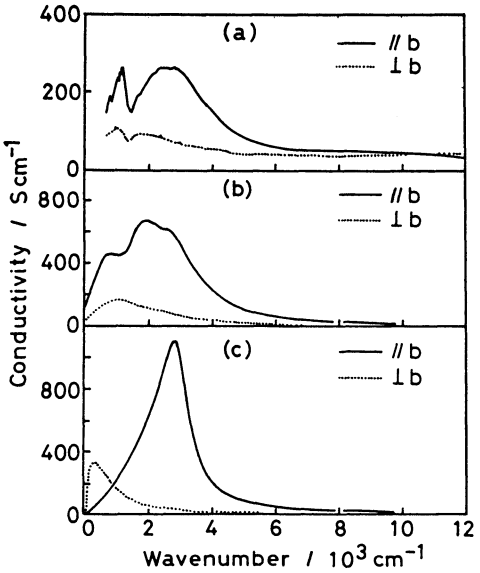

Fig. 8. Conductivity spectrum of α-(BEDT-TTF)$_2$I$_3$. (a) The observed spectrum (b) calculated spectrum based on the two-dimensional model (c) calculated spectrum based on the one-dimensional model.

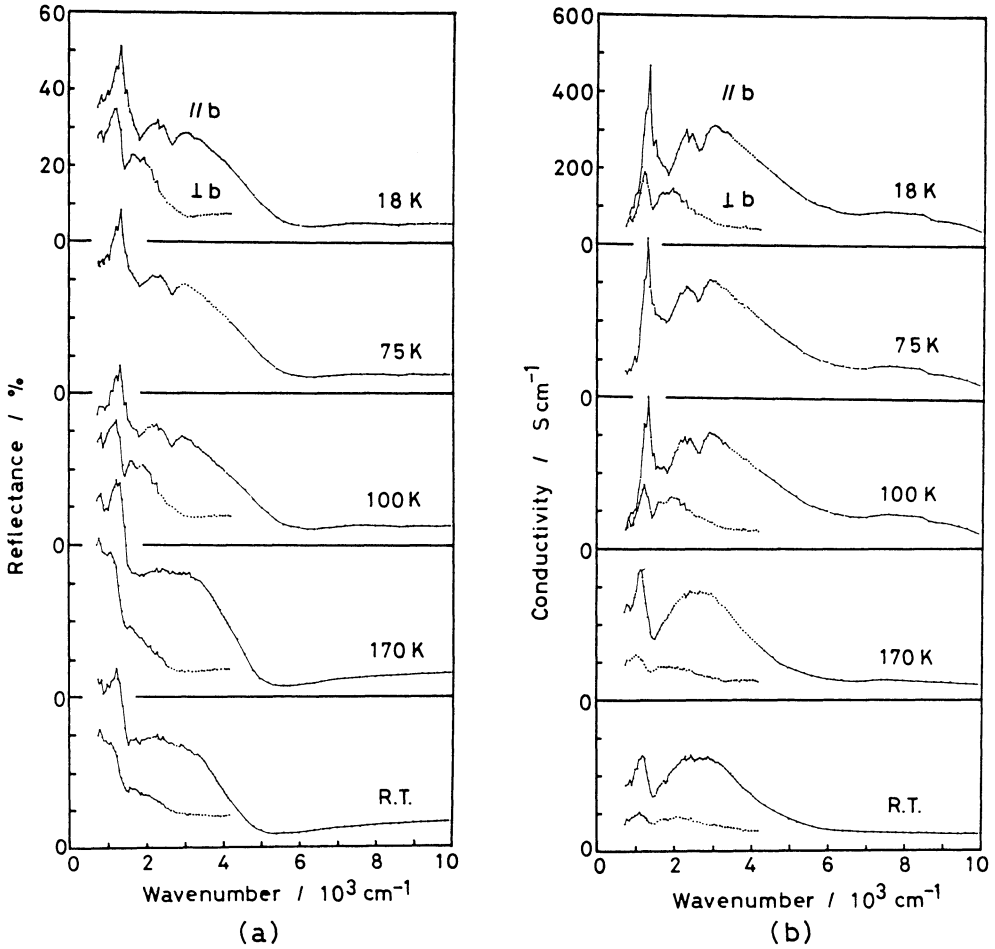

Fig. 9. Temperature dependence of (a) reflectance spectrum and (b) conductivity spectrum of α-(BEDT-TTF)$_2$I$_3$.

than those of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$. The conductivity spectrum was shown in Fig. 8a. The average transfer integrals obtained by the same method mentioned in the previous section were $t_{//}$=0.07 eV and $t_{\perp}$=0.06 eV, the ratio being 1.2, where we used the anisotropic plasma frequencies $\omega_{p//}$=6.5×10^3 cm^{-1} and $\omega_{p\perp}$=4.6×10^3 cm^{-1} and the reduced unit cell parameters, $d_{//}$=5.4 Å (//b) and $d_{\perp}$=4.6 Å ($\perp$b). The small anisotropy of transfer integrals is in accord with the almost isotropic electrical resistivity.[10] We calculated the conductivity spectra of the intraband and interband transitions based on the semi-metallic band structure reported by Mori et al.[28] The calculated result shown in Fig. 8b coincides qualitatively with the observed spectra: The transition probability for the //b polarization is larger than that for the $\perp$b polarization, and the //b transition appears at the higher wavenumber region than the $\perp$b transition. According to the overlap integral calculated by Mori et al., the largest two integrals which are those between C and A′ and between A′and B are markedly larger as compared with the remaining integrals. If we neglect the latters, the electronic structure becomes one-dimensional along the zigzag chain through C-A′-B-A-C. The conductivity spectra calculated by this model are shown in Fig. 8c. We wish to emphasize that the interchain interaction is quite important to reproduce the line shape of the observed spectrumm.

α-(BEDT-TTF)$_2$I$_3$ is metallic at room temperature and exhibits a metal-insulator transition at 135 K, according to the experiment of the electrical resistivity.[10] It was also reported that the intensity and the line width of ESR signal suddenly decreased at about 135 K.[11,12] The study by X-ray diffraction elucidated the structural change that the inversion symmetry, which exists in the high-temperature phase, is lost in the low-temperature phase.[29] The change of the infrared spectrum also indicated the symmetry breaking at low temperature.[30] All these experiment suggest that the phase change is of the first order. Figures 9a and 9b show the temperature dependence of the reflectance spectrum and the conductivity spectrum. The spectra at different temperatures in the metallic phase are essentially the same with each other, and those in the semiconductive phase are also the same with each other. To examine the temperature dependence in detail, we conducted the same experiment as that we have done on α-(BEDT-TTF)$_3$(ReO$_4$)$_2$, at the wavenumber of 5600 cm^{-1}. The reflectivity change took place abruptly and no hysteresis was observed as shown in Fig. 10. These optical results are consistent with the results of other experiments. The remarkable features found for the spectrum of the semiconductive phase are (1) the decrease of the reflectivity and therefore the decrease of the conductivity in the low-wavenumber region, (2) the splitting (2350 and 2950 cm^{-1}) of the broad interband transition at 2600 cm^{-1}, and (3) the increase of the reflectivity around the tail of the interband transition at about 5000 cm^{-1}. The first one corresponds to the disappearance of the conduction electrons. The second and the third are probably related to a small change of the band structure arising from the slight structural change. Incidentally, it is worth to be noted that the spectral change observed at 5000 cm^{-1} on α-(BEDT-TTF)$_2$I$_3$ is very much similar to that observed for the semiconductive phase of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$.

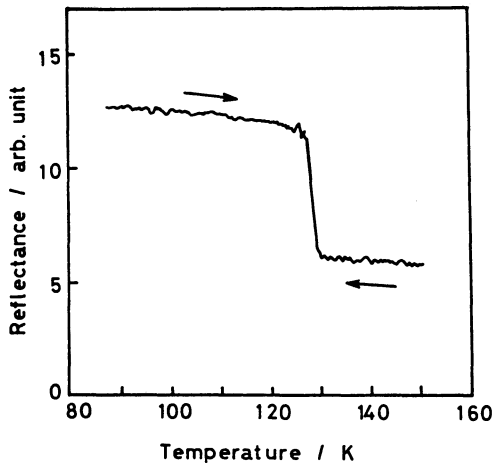

Fig. 10. Temperature dependence of the reflectivity of α-(BEDT-TTF)$_2$I$_3$ at 5600 cm^{-1}.

Summary and Conclusion

The anisotropic character of intermolecular interaction was examined by determining the average transfer integrals from the observed reflectance data. We conclude that the two-dimensional interaction of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$ is weaker than that of α-(BEDT-TTF)$_2$I$_3$ but significantly stronger than that of Bechgaard salts. The observed electronic transition of the BEDT-TTF salts in the infrared region was interpreted to be an overlap between the strong interband transition and the weak intraband transition. We found two common features on the temperature dependence of the reflectance spectra of the two salts. The one is the decrease of the reflectance at low wavenumber on lowering temperature in the semiconductive phase due to the decrease of the density of conduction electrons, the other is the appearance of a new hump at high-wavenumber region. A curious phenomenon was found in the temperature dependence of the hump of α-(BEDT-TTF)$_3$(ReO$_4$)$_2$: This hump appeared abruptly near the phase transition temperature although the phase transition takes place rather gradually. Finally it should be noted that the optical conductivity spectra did not change drastically between the metallic and semiconductive phases. This fact further support that the electronic transition of the infrared region is attributable mainly to the interband transition.

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