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In-plane quasi-isotropic organic superconductor di[bis(ethylenedithiolo) tetrathiafulvalene] bis(isothiocyanato) cuprate(I), $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$: Polarized reflectance spectra

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Polarized reflectance spectra with polarizations parallel to the crystallographic *b* and *c* axes which lie on the two-dimensional conducting planes of a new ambient-pressure organic superconductor $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ were measured over the range from 500 to 28000 cm^{-1} at room temperature. Plasma-edge-like dispersion with the minimum near 5000 cm^{-1} was observed for both polarizations. The bandwidths of the superconductor evaluated in terms of the Drude model and the tight-binding approximation were found to be 0.73 eV in the *b*-axis direction and 0.40 eV in the *c*-axis direction, thereby indicating the quasi-isotropic nature of the optical charge transport in the *bc* plane.

The synthesis of a new class of materials based on the sulfur containing organic donor bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) has opened new perspectives in the field of organic superconductivity.[1,2] We have recently found a new ambient-pressure organic superconductor $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ which has the critical temperature $T_c = 10.4$ K.[3] This material consists of two-dimensional conducting sheets of BEDT-TTF molecules with a zigzag arrangement of molecular dimers in the *bc* plane and the sheets are interleaved by sheets of $[Cu(NCS)_2]^-$ ions.[4] The conductivity in the plane is nearly isotropic, while the conductivity normal to the plane is about 600 times as small as that in the plane.[5]

Previously, we have examined the polarized reflectance spectra of the organic superconductors β-$(BEDT\text{-}TTF)_2X$ ($X = I_3$ and IBr_2) (Ref. 6) and have shown that they are optically anisotropic in the two-dimensional molecular plane, although the dc conductivity is nearly isotropic.[7] Such a discrepancy is, however, not surprising, because reflectance measurements are more strict in polarization characteristics than dc conductivity measurements. In this respect, polarized reflectance measurements are of great importance for a study of the electronic anisotropy in these organic superconductors.

In this paper, we present the polarized reflectance spectra of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ measured at room temperature and then evaluate the transport parameters in terms of the Drude model and the tight-binding approximation. From the results, it is found that the charge transport in the two-dimensional conducting sheet of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ is nearly isotropic not only in the dc conductivity but also in the optical conductivity.

Single crystals shaped like thin distorted hexagon plates were prepared by the electrochemical oxidation of BEDT-TTF in a 1,1,2-trichloroethane solution under the constant current of 1.5 μA at room temperature using potassium thiocyanate, copper(I) thiocyanate, and 18-crown-6 ether as the supporting electrolytes and platinum rods as the electrodes. The polarized reflectance spectra at nearly normal incidence were measured over the spectral range from 500 to 6000 cm^{-1} by using a Perkin-Elmer 1760 Fourier-transform infrared (FTIR) spectrometer equipped with a Spectra-Tech IR-PLAN$_{TM}$ microscope and a gold wire-grid polarizer and the range from 4000 to 28000 cm^{-1} by a homemade microspectrophotometer.[8]

The crystal of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ exhibits a significant plasma-edge-like dispersion when the incident light polarized parallel to the *b* axis is irradiated onto the (100) crystal face, as shown in Fig. 1. A similar dispersion is also observed for the light polarized parallel to the *c* axis. These results indicate that there is little electronic anisotropy in the conducting plane composed of BEDT-TTF species.

The plasma-edge-like dispersion observed in the infrared region of the reflectance spectra of organic conductors has often been analyzed in terms of the Drude model for the dielectric function:

$$\epsilon(\omega) = \epsilon_{\text{core}} - \omega_p^2/\omega(\omega + i/\tau) \ , \tag{1}$$

where ω_p is the plasma frequency, ϵ_{core} is the residual dielectric constant at high frequency, and τ is the relaxation time of carriers. The reflectance spectra in the frequency region lower than about 3000 cm^{-1} seem to deviate from Drude behavior. It has been pointed out, however, that the plasma frequency is insensitive to the detailed nature of the short-range electron-electron and electron-phonon interactions, which are responsible for the deviations from Drude behavior at low frequencies.[9] Therefore, here we have employed the Drude model to evaluate

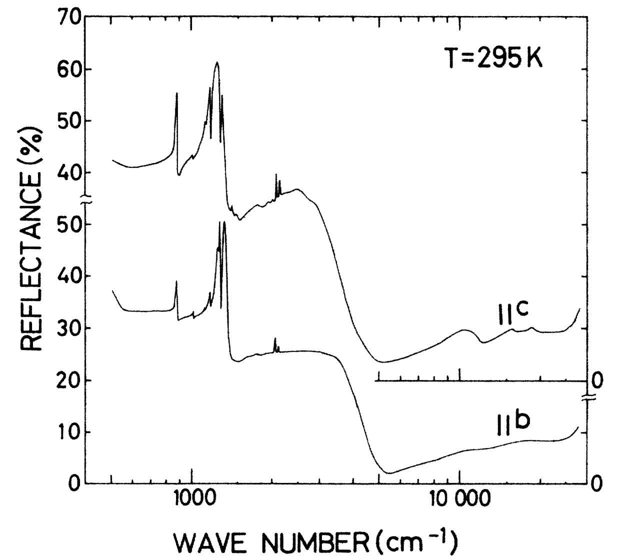

FIG. 1. Polarized reflectance spectra of the (100) crystal face of (BEDT-TTF)$_2$[Cu(NCS)$_2$] at room temperature for polarizations parallel to the b and c axes.

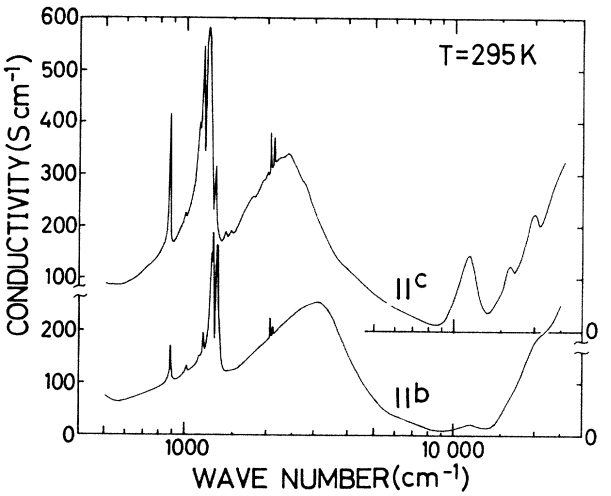

FIG. 2. Conductivity spectra of .(BEDT-TTF)$_2$[Cu(NCS)$_2$] derived by the Kramers-Kronig transformation.

ω_p, τ, and ϵ_{core}. The Drude parameters obtained for both polarizations are listed in Table I.

We now apply a simplified tight-binding band-structure model proposed by Jacobsen, Williams, and Wang[10] to estimate the anisotropy in the two-dimensional conducting plane. The transfer integrals parallel to the b and c axes, t_b and t_c, are to be considered as weighted averages of several transfer integrals in the correct band structure. From the values in Table I, we derive a quantity $(\omega_p^c/\omega_p^b)\times(d_b/d_c)=0.58$, where d_b and d_c are the molecular repeat distances 4.22 Å and 6.56 Å along the b and c axes, respectively. The ratio t_b/t_c is estimated to be 1.8 from the quantity based on the numerical results reported by Jacobsen *et al.*[10] The ratio indicates the quasi-isotropic nature of charge transport in the plane. Four times the transfer integrals obtained are $4t_b=0.73$ eV and $4t_c=0.40$ eV. These values are in reasonable agreement with the tight-binding bandwidth 0.7–0.8 eV calculated by Mori.[11] The bandwidth 0.16 eV estimated from the Pauli-type paramagnetic susceptibility[12] is, however, a few times as small as those mentioned above. Such discrepancy could result from the enhancement of the Pauli paramagnetism due to the on-site Coulomb repulsion effect.[13] The effect could also result in the deviation from the Drude behavior.

Considerably small electronic anisotropy in the conducting plane of BEDT-TTF species in (BEDT-TTF)$_2$[Cu(NCS)$_2$] is also observed in the low-frequency region of the conductivity spectra. The conductivity spectra obtained by the Kramers-Kronig transformation is shown in Fig. 2. The optical conductivity near 500 cm^{-1} in the polarization $\parallel c$ spectrum is about 90 S cm^{-1}. This value is only slightly greater than 70 S cm^{-1} obtained for the polarization $\parallel b$ spectrum. The dc conductivity parallel to the c axis (24–40 S cm^{-1}) is also slightly greater than that parallel to the b axis (14–20 S cm^{-1}).[5]

From the discussion above, it is concluded that (BEDT-TTF)$_2$[Cu(NCS)$_2$] has a very small anisotropy in the charge transport in the sheet of BEDT-TTF species not only in the dc conductivity but also in the optical conductivity. Such a small optical anisotropy is a significant feature of (BEDT-TTF)$_2$[Cu(NCS)$_2$] in contrast with the other ambient-pressure organic superconductors β-(BEDT-TTF)$_2X$ ($X=I_3$, IBr$_2$, and AuI$_2$) which show a large optical anisotropy in the conducting plane in spite of a small anisotropy in the dc conductivity.[6-8,14,15]

The difference in the magnitude of optical anisotropy would arise from the quite different molecular arrangements of BEDT-TTF species between (BEDT-TTF)$_2$[Cu(NCS)$_2$] (Ref. 4) and β-(BEDT-TTF)$_2X$.[16] The molecular dimers of BEDT-TTF in the former salt stack in a two-dimensional network in which one dimer is nearly perpendicular to the neighboring dimers as shown in Fig. 3, while the dimers in the latter salt stack face to face. Therefore, the molecular anisotropy is preserved in the

TABLE I. The transport parameters obtained from the analysis of the reflectance spectra of (BEDT-TTF)$_2$[Cu(NCS)$_2$] in the infrared region using the Drude model. $\Gamma=\tau^{-1}$, $m^*=\omega_p^2/(4\pi ne^2)$, and $n=1.19\times10^{21}$ cm^{-3}.

Polarization	$\omega p/2\pi c$ (cm^{-1})	$\Gamma/2\pi c$ (cm^{-1})	τ (10^{-15} s)	m^*/m_e	$4t$ (eV)
$\parallel b$	8380	1760	3.0	1.5	0.73
$\parallel c$	7560	2240	2.4	1.9	0.40

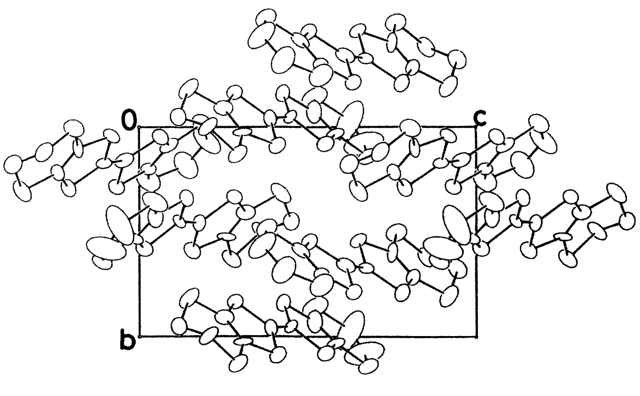

FIG. 3. Molecular arrangement of BEDT-TTF species in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ at room temperature projected onto the (100) plane. Anions are not shown.

crystals of β-$(BEDT\text{-}TTF)_2X$ but not in the crystals of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$.

The conductivity spectra for both polarizations exhibit several absorption bands as shown in Fig. 2. In the visible region, three bands are superimposed on a broad absorption band, the peak position of which would be at a higher frequency than the frequency region examined here. The bands are observed at 11 400, 16 100, and 19 900 cm^{-1} in the polarization $\parallel c$ spectrum, but they are hardly observed in the polarization $\parallel b$ spectrum. The molecular arrangement of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ projected onto the (100) plane (Fig. 3) indicates that the molecular long axis of BEDT-TTF is predominantly oriented parallel to the c-axis direction in the (100) plane. Therefore, these bands would be assigned to the intramolecular excitations of BEDT-TTF radical cation which are polarized along the long axis of the molecule. The polarized reflectance spectrum of α-$(BEDT\text{-}TTF)_2I_3$, measured with light polarization parallel to the c^* direction which is nearly parallel to the molecular long axis of BEDT-TTF, shows a strong absorption band at 9700 cm^{-1} and weak bands at 16000 and 20000 cm^{-1}.[17] This supports the above assignment.

Sharp doublet bands appearing at 2067 and 2110 cm^{-1} would be assigned to the CN stretching mode of the $[Cu(NCS)_2]^-$ anion. There are two kinds of the isothiocyanate groups in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$. One is forming an infinite chain along the b axis and the other is just a pendant in the manner of $[\text{-}Cu(NCS)\text{-}NCS\text{-}]_n$.[4] Since the CN stretching vibration of the bridging (M-NCS-M') complexes appears at the frequencies above 2100 cm^{-1} and that of the N-bonded complexes near 2050 cm^{-1},[18] the band at 2110 cm^{-1} is attributed to the CN stretching mode of the bridging isothiocyanate and the band at 2067 cm^{-1} to the N-bonded pendulous isothiocyanate.

Another sharp band near 880 cm^{-1} would be attributed to the totally symmetric C–S stretching mode of BEDT-TTF induced by the electron-molecular vibration (emv) interaction because the mode appears at 876 cm^{-1} in the Raman spectrum of BEDT-TTF.[19] The strong bands appearing in the frequency region between 1150 and 1320 cm^{-1} are probably assigned as being due to CH bending modes of the BEDT-TTF moiety, although those bands have been sometimes ascribed to the C=C stretching modes the intensity of which are enhanced by the emv interaction.[19,20] However, the latter assignments would need more elaboration, because the bands near 1500 cm^{-1} are observed in the Raman spectra of BEDT-TTF and its cation radical salts.[19,20] Further investigation of polarized reflectance spectra of deuterated $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ is indispensable and currently in progress.

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