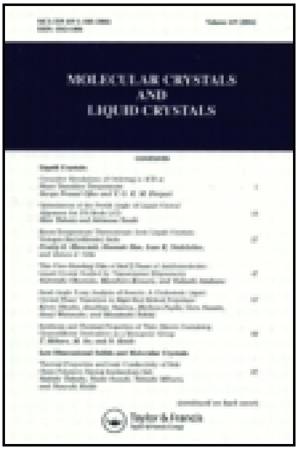

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CHARGE ORDER IN θ-(BDT-TTP) 2 Cu(NCS) 2

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θ-(BDT-TTP)$_2$Cu(NCS)$_2$ (BDT-TTP=2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathia-pentalene) is a highly correlated organic conductor with a quasi-two-dimensional electronic structure. This compound undergoes a second-order phase transition at 250 K. Below the phase transition temperature, the optical gap significantly broadens. From the analysis of the Raman spectrum, we found that the phase transition was accompanied by a disproportionation of charge. The separated charge forms a vertical stripe along the b-axis, and the b-axis is likely to be doubled at 5 K.

Keywords: charge ordering; organic conductor; BDT-TTP; Raman scattering; reflectivity

INTRODUCTION

In highly correlated organic conductors, the role of the inter-site Coulomb interaction has recently attracted attention [1, 2, 3]. Owing to the strong inter-site Coulomb interaction, the charge localization and ordering has been experimentally suggested for several organic conductors. In the quasi-one-dimensional conductor (DI-DCNQI)$_2$Ag, the two equivalently charged molecules in a unit cell are separated into charge-rich and -poor molecules at 220 K [2, 4]. In the case of quasi-two-dimensional organic conductors, the charge ordering is found by NMR in the low-temperature phase of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ [5]. Recently, Seo published a theoretical study on the charge ordering in BEDT-TTF salts using a mean field theory [6]. Among the highly conductive BDT-TTP based organic metals [7, 8, 9], θ-(BDT-TTP)$_2$Cu(NCS)$_2$ is an exceptionally non-metallic compound. In this crystal, the molecules are arranged like a herringbone without dimerized structure. This compound shows a second-order phase transition at 250 K, which was accompanied by a dramatic change in the reflection and Raman spectra [10]. In this article, we show spectroscopic evidence for the disproportionation of charge and ordered pattern of the localized charge in θ-(BDT-TTP)$_2$Cu(NCS)$_2$.

BAND STRUCTURE AND REFLECTION SPECTRUM

θ-(BDT-TTP)$_2$Cu(NCS)$_2$ belongs to the monoclinic system with space group Cc [11]. The unit cell contains two conducting layers separated by the counter anion. Each conducting layer involves two BDT-TTP molecules connected by a glide-plane. The four molecules in the unit cell are therefore crystallographically equivalent. Based on the molecular arrangement in the conducting layer, the two-dimensional tight-binding band is yielded by the following equation:

$$E(k_b, k_c) = 2t_b \cos(k_b b) \pm \sqrt{2(1 + \cos(k_c c))(t_{p1}^2 + t_{p2}^2 + 2t_{p1}t_{p2}\cos(k_b b))}. \tag{1}$$

Equation (1) produces a closed Fermi surface under the restriction $|t_b| < |t_{p1}| \approx |t_{p2}|$, where t_b is the transfer integrals along the b-axis and t_{p1} and t_{p2} are those between the molecules related by a glide plane [See Figure 4]. The band calculation requires a metallic state for this compound. However, the resistivity shows non-metallic behavior in a whole temperature range, which suggests a strong correlation in this compound. Below the second-order phase transition at 250 K, the charge gap increases from 17 meV to 100 meV.

Figure 1 shows the temperature dependence of the optical conductivity. The optical conductivity has a spectral weight also in the b-polarization. This indicates that θ-(BDT-TTP)$_2$Cu(NCS)$_2$ is a quasi-two-dimensional system. The strong polarization along the c-axis is consistent with the relation between the transfer integrals $|t_b| < |t_{p1}|, |t_{p2}|$. A continuous and drastic change is observed in the conductivity spectrum with the decrease of temperature. Below the phase transition temperature (250 K), the low-frequency spectral weight is lost in both directions. This spectral change is consistent with the broadening of the charge gap observed in the resistivity experiment.

DISPROPORTIONATION OF CHARGE

Figure 2 shows the temperature-dependent (c,c) Raman spectrum excited by the 633 nm laser in the region of the C=C stretching modes. When the

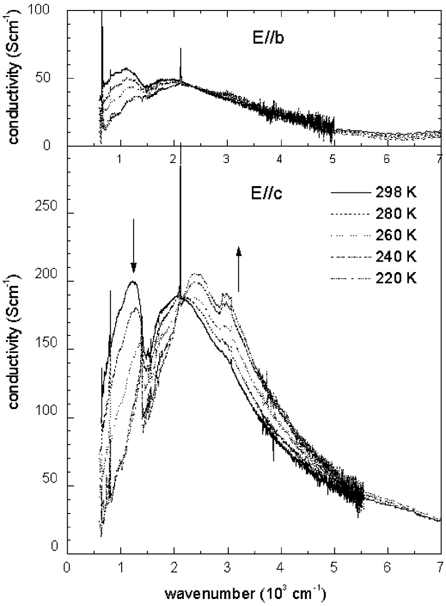

FIGURE 1 Temperature dependence of the optical conductivity spectra.

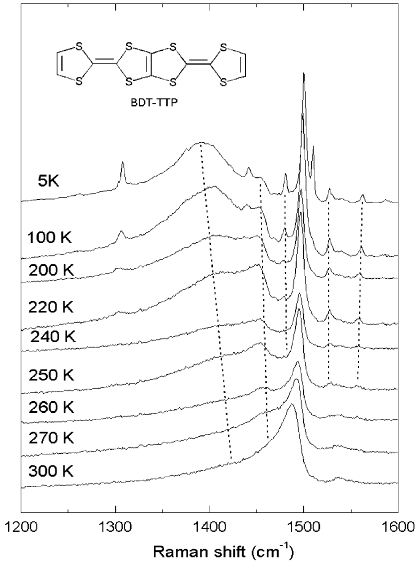

FIGURE 2 Temperature dependence of the (*c*,*c*+*b*) Raman spectrum in the region of C=C stretching modes.

temperature is lowered, the Raman spectrum shows a dramatic change. The broad band at 1486 cm^{-1} sharpens continuously along with a remarkable high-frequency shift. At 5 K, this band reaches at 1500 cm^{-1}. There appear strong and weak broad bands at 1391 cm^{-1} and 1457 cm^{-1}, respectively. In addition, the other five sharp peaks appear at 1440, 1480, 1509, 1526, and 1560 cm^{-1}. The spectral change is continuous from room temperature to 5 K, but drastic around 250 K. This change is consistent with the second order phase transition. Figure 3 shows the (c,c), (c,b), and (b,b) spectra excited by 633 nm, the (c,c) spectrum excited by 515 nm, and the spectra of (BDT-TTP)$_2$SbF$_6$ and BDT-TTP excited by 633 nm. As shown in Figure 3, BDT-TTP exhibits three strong Raman bands in this region, which are associated with the three kinds of non-equivalent C=C bonds: inner ring C=C, bridging C=C, and outer ring C=C [see the inset of Figure 2] [10].

Let us consider the factor group analysis of this compound under the space group of Cc. Since the unit layer contains two molecules, every intra-molecular vibrational mode is twofold degenerate if the inter-molecular charge-transfer interaction is weak enough. In the factor group of C$_s$, the vibrational modes are classified into the crystal modes with an A$'$ and A$''$ symmetry. The A$'$ mode corresponds to the in-phase molecular vibration,

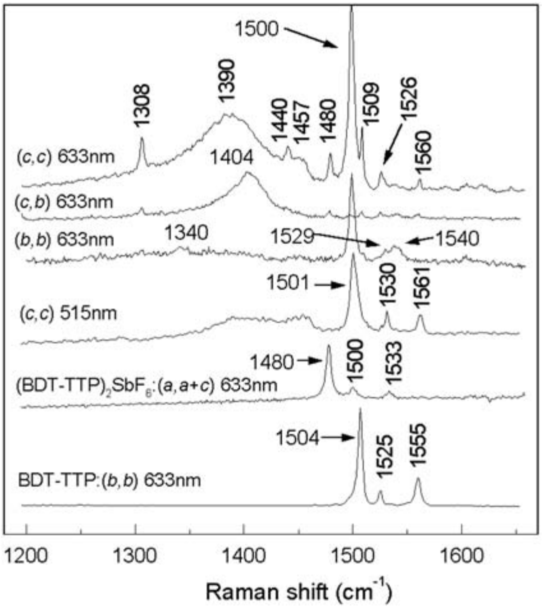

FIGURE 3 Comparison of the Raman spectra.

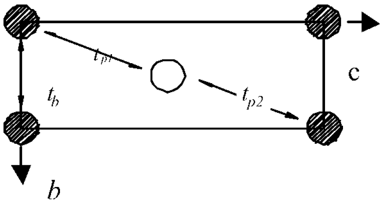

FIGURE 4 Ordering pattern. Hatched circles denote the charge-rich molecules.

where the molecules connected by the glide plane vibrate in phase with each other. On the other hand, in the A″ mode, the molecules related by symmetry vibrate out of phase. In the latter case, the electron-molecular-vibration (*emv*) interaction works strongly through the charge transfer between the molecules in the unit cell, and thus the coupled vibration modulates the electric dipole and polarizability of the unit cell[12]. As is well known in the infrared spectrum of organic conductors, the A″ mode shifts to the low-frequency side depending upon the coupling constant and broadens the linewidth. The appearance of many Raman bands at 5 K suggests the splitting of the degenerate modes through an *emv* interaction. The A′ mode is allowed in (*a,a*), (*b,b*), (*c,c*), and (*a,c*) polarizations, whereas the A″ mode is allowed in (*a,b*) and (*b,c*) polarizations. A comparison between the (*c,c*) and (*c,b*) spectra shows that this selection rule is broken for 1480, 1509, 1526, and 1560 bands. Furthermore, the broad bands appear in the (*cc*) polarization. These results indicate that the glide-plane symmetry is broken at 5 K. If the unit-cell size is preserved, the observable Raman band is at most six because the molecule has three Raman active C=C stretching modes. Since nine bands are found in the 1320—1580 cm^{-1} region of the (*cc*) spectrum, we conclude that the unit cell is doubled without preserving the glide-plane symmetry. As a whole, we observe seven sharp bands and five broad bands including the other bands found in the (*a,a*) and (*b,b*) spectra.

When we compare the Raman spectrum of this compound with that of $(\mathrm{BDT\text{-}TTP})_2\mathrm{SbF}_6$, which has the same average charge as BDT-TTP, the 1560 cm^{-1} band is higher in frequency than the highest band at 1533 cm^{-1} of $(\mathrm{BDT\text{-}TTP})_2\mathrm{SbF}_6$. Since the *emv* interaction always shifts the coupled mode to the low-frequency side, the doubling of the unit cell and lowering of the symmetry cannot explain this band. However, the high-frequency shift can be reasonably explained by the charge disproportionation such as $(\mathrm{BDT\text{-}TTP}^{0.5+})_2 \rightarrow \mathrm{BDT\text{-}TTP}^{\delta+} + \mathrm{BDT\text{-}TTP}^{(1-\delta)+}$ because the frequencies of the C=C stretching modes are sensitive to the charge on BDT-TTP. When the spectrum is measured by 515 nm light, three sharp bands and two broad bands are enhanced and the other bands are suppressed as shown in

Figure 3. It is difficult to explain this excitation-light dependence by means of the structural change. The characteristic feature can also be explained by the charge disproportionation if we consider that the lowest singlet state of BDT-TTP is found at $19–24 \times 10^3\,\mathrm{cm}^{-1}$ in the solution spectrum. Based on these two reasons, we conclude that the molecule with an average charge of +0.5 shows a disproportionation to a charge-rich (BDT-$\mathrm{TTP}^{(1-\delta)+}$) and charge-poor (BDT-$\mathrm{TTP}^{\delta+}$) species at 5 K.

CHARGE ORDERING AND UNIT-CELL DOUBLING

Optical Conductivity

According to Seo's theory, the separated charge is ordered in three different ways, such as vertical, horizontal, and diagonal stripes, depending upon the parameters, U, V, and t. Recently, Tajima et al. calculated the optical conductivity by means of a mean field approximation and interpreted the optical spectra of θ-(BEDT-TTF)$_2$MM$'$(SCN)$_4$ (MM$'$ = CsZn, RbCo, RbZn) [13]. Their conclusion is as follows: If the charge-ordering pattern is horizontal, the mid-infrared optical absorption consists of three electronic bands, whereas it consists of a single band if the ordering pattern is vertical. In θ-(BDT-TTP)$_2$Cu(NCS)$_2$, the low-temperature optical conductivity in the infrared region appears to be a single peak as shown in (Figure 1). If we follow Tajima's proposal, the localized charge forms a *vertical stripe* along the b-axis after the phase transition. This model is consistent with the breakdown of the glide-plane symmetry.

Magnetic Properties

If the localized charge forms horizontal or diagonal stripes, the magnetic susceptibility is suppressed by the direct antiferromagnetic interaction through the transfer integrals t_{p1} and t_{p2}. On the other hand, the antiferromagnetic interaction will be weak, if the charge forms a vertical stripe because the direct antiferromagnetic interaction along the b-axis is produced by the small transfer integral t_b. The magnetic susceptibility in the 25–300 K region follows the Curie-Weiss law with C = 0.154 emu K/mol and $\theta = -29\,\mathrm{K}$. The effective magnetic moment is calculated to be $\mu_{\mathrm{eff}} = 1.1\mu_{\mathrm{B}}$ from the Curie constant. Below 25 K, the susceptibility deviates from the Curie-Weiss law and tends to saturate at 4.5 K and steeply increases again below 3 K owing to the crystal defect. The spin susceptibility measured by ESR shows a peak at 7–8 K and sharply decreases below 5 K. The spin susceptibility in the 5–100 K region is well fitted by the Boner-Fisher model with J = 8 K. Such a weak exchange interaction between the separated charges strongly supports the vertical stripe.

The sharp decrease of the spin susceptibility at 5 K suggests a magnetic phase transition to a non-magnetic state. The plausible candidate for this phase transition is the spin-Peierls transition. If this is the case, the *b*-axis is probably doubled at this temperature. We have discussed about the unit-cell doubling, when we interpret the 5 K Raman spectrum. The doubling of unit cell seems to occur locally above the temperature of this magnetic phase transition. Among the 12 Raman active bands, the 5 bands already appear at 250–240 K. This result suggests the scenario that the charge disproportionation first occurs at 250 K, then the fluctuation of the *b*-axis distortion begins to occurs below 100 K, and the *b*-axis local distortion is three dimensionally ordered at 5 K.

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