

# Studies of Charge-Order State in Organic Conductors

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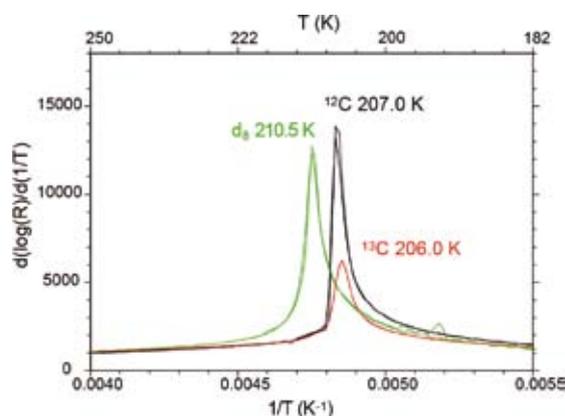
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In organic conductors, kinetic energy is comparable with on-site and inter-site Coulomb energy. Due to this reason, many organic conductors are located in a boundary area between metallic and insulating states, and thus various organic charge-transfer compounds show metal–insulator phase transition. Recently, charge-ordered (CO) state originated from interelectron Coulomb interaction is widely found in organic conductors. The CO state attracts attention, first because charge-fluctuation-mediated superconductivity is theoretically predicted in superconducting compounds neighbored on CO phase, second because some compounds in CO phase show ferroelectricity. The macroscopic polarization in this ferroelectric transition is recognized not as the result of ionic displacements, but as the result of coherent integration of electronic polarizations induced by the CO transition. We have investigated the CO state and metallic state near CO employing infrared and Raman spectroscopy and SHG microscopy.

## 1. Hydrogen Isotope Effect on the Charge-Ordering Phase Transition in $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub>

$\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> has a layered structure with two-dimensional interaction within the layer. In a variety of organic conductors,  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> is one of the most narrow-bandwidth compounds. Because of the narrow-bandwidth, the charge carriers of this compound is localized, and thus  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> is an insulator in a whole temperature range from 350 K to 4.2 K. This insulating compound shows successive phase transitions at 207 K, ~160 K, and ~30 K. The resistivity jump at 207 K is regarded as an order-disorder phase transition of localized holes.<sup>1)</sup> Below ~160 K, macroscopic polarization evolves, suggesting a ferroelectric phase transition. Finally this compound undergoes a first order magnetic phase transition at ~30 K. Our goal is to understand the mechanism of this successive phase transition. In this section, we focus on the hydrogen isotope effect on the order-disorder phase transition at 207 K.



**Figure 1.** Comparison of the derivatives of electrical resistivity of  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub>, deuterium-substituted compound,  $\alpha'$ -(d<sub>8</sub>-BEDT-TTF)<sub>2</sub>IBr<sub>2</sub>, and <sup>13</sup>C-substituted compound,  $\alpha'$ -(<sup>13</sup>C-BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> where <sup>13</sup>C is substituted at the central C=C bond of BEDT-TTF.  $\alpha'$ -(d<sub>8</sub>-BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> shows a significant isotope effect on the order-disorder phase transition.

Figure 1 shows the derivative of the electrical resistance,  $d(\log R)/d(1/T)$ , where the peak temperature corresponds to the phase transition temperature,  $T_C$ . As shown in this figure,  $T_C$  of  $\alpha'$ -(d<sub>8</sub>-BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> shows a high-temperature shift of 3–4 K. The unit cell volume of  $\alpha'$ -(d<sub>8</sub>-BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> shrinks by about 0.4% compared with that of  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub>. The volume change can be regarded as the result of chemical pressure. If we assume that the chemical pressure pushes up  $T_C$ , the isotope shift means  $dT_C/dP > 0$ . However, this assumption is opposite to the experimentally obtained pressure dependence of  $T_C$ ,  $dT_C/dP < 0$ .<sup>1)</sup> Therefore, the isotope effect cannot be attributed to the effect of chemical pressure. We therefore propose a small polaron model, in which the effective transfer integral is reduced as  $\tilde{t} = t \exp(-S)$ , where  $S = (E_b/\hbar\omega_0) \coth(\hbar\omega_0/2kT)$  is a vibrational overlap factor (Huang-Rhys factor). The deuterium substitution may soften the optical phonon mode  $\omega_0$ , and increases  $S$ . This effect reduces the effective transfer integral, and thus the

bandwidth. The decrease of bandwidth is regarded as the application of negative pressure. Combined with the relationship,  $dT_c/dP < 0$ , this small polaron model can qualitatively explain the isotope effect on the phase transition. We speculate that the librational modes around the short axis and the axis perpendicular to the molecular plane work most effectively as the optical phonon  $\omega_0$ .

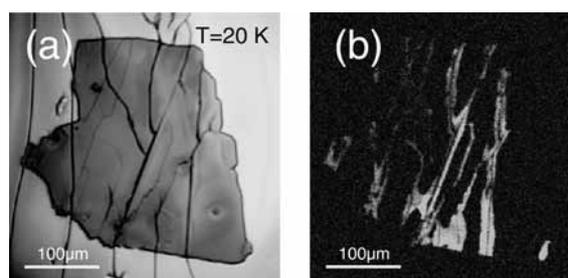
## 2. Inhomogeneous Ferroelectric Polarization in $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> Revealed by Second-Harmonic Generation Microscopy<sup>2)</sup>

As an effort to expand the material family of unconventional class of ferroelectrics, we focused in the present study on  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub>, which is another BEDT-TTF complex with trihalide anions similar to  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. As expected from the similarity in the crystal structure, we have confirmed that the complex shows charge ordering at low temperatures<sup>1)</sup> in a separate study. The result of SHG measurements indeed verified that the complex also showed SHG in a charge-ordered phase, though the transition features of the complex turned out to be substantially different from those of the triiodide complex.

One of the interesting features is an inhomogeneous generation of SH signal from a single crystal, revealed by mapping measurement of SHG. The spatially resolved observation was performed for a filmy singly crystal ( $t = ca. 3 \mu\text{m}$ ) in transmission geometry using a homemade scanning laser microscope equipped with an Er-doped fiber laser ( $\lambda = 1.55 \mu\text{m}$ , pulse duration: 100 fs, repetition: 20 MHz). The laser beam was focused by an objective lens into a spot ( $\phi = ca. 20 \mu\text{m}$ ) on the  $ab$ -plane of the crystal with an excitation power density of less than  $ca. 500 \text{ W/cm}^2$ . To efficiently dissipate the heat at the spot, the crystal was embedded in polymer resin, afterwards sandwiched by a pair of two sapphire slides, then cooled by a liquid He flowing cryostat.

Figure 2 shows the comparison of the transmission and SHG images of the single crystal. As shown by the crack observed in the transmission image [Figure 2(a)], the crystal was cleaved together with the polymer matrix when cooled. As is displayed in Figure 2(b), the SHG image shows uneven distribution of the nonlinear optical signal; the signal was emanated from limited regions near the cracks and the edges of the crystal, whereas other regions far from cracks are almost completely dark.

Note that the SHG signal is generated not only from the very end of the crystal edges at the crack, but regions with a



**Figure 2.** (a) Transmission image of a single crystal of  $\alpha'$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> embedded in polymer resin, and (b) its SH image measured at 20 K. The SHG intensity in (b) is in proportional to the brightness.

macroscopic width. This clearly indicates that the activation of SHG is not caused by the surface effect at the crack, but should be a manifestation of the breakdown of centrosymmetry in the bulk region. The uneven signal distribution is presumably attributed to inhomogeneous pressure distribution associated with the crack in polymer matrix generating at low temperatures; the matrix adhering to a sapphire plate should feel a stretching force (since the thermal expansion coefficient of the polymer is larger than sapphire), whereas the region near the crack would be free from the stretching force. Hence, the region near the crack, emanating the SHG light, seems to represent the ambient pressure property of the bulk state.

The coexistence of the dark region in the image would be noteworthy. This indicates that the generation of the ferroelectric polarization is suppressed presumably by a small negative pressure, suggesting that a non-polar phase exists near the ferroelectric CO phase in the phase diagram. One may notice that the bright and dark regions are divided by clear boundaries, which fact implies that these two phases would be separated by a first-order transition.

The appearance of the distinct phases strongly suggests that there would be several stable arrangements for the charge order as realized for the spin system with geometrical frustration. To understand the intriguing features of the ferroelectric transition in this compound, precise crystal geometry at low temperatures as well as the SHG data measured without application of mechanical stress is necessary.

### References

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### Award

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