Optical Studies of Charge Ordering in Organic Conductors

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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 localized states, and thus various organic charge-transfer compounds show metal–insulator phase transition. Recently, charge-ordered (CO) state originated from Coulomb interaction is widely found in organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. The CO state attracts much attention, first because charge-mediated superconductivity is theoretically predicted in superconducting compounds neighbored on CO phase, second because some compounds in CO phase show ferroelectricity through the crystallization of conduction electrons, third because the narrow-band compounds have a poorly understood intermediate state between metallic and CO states. We have investigated the CO state and metallic state near CO employing infrared and Raman, and reflection spectroscopy.

1. Charge Order–Disorder Phase Transition in α'-(BEDT-TTF)$_2$IBr$_2$[1)]

Among a variety of organic conductors, the α-type BEDT-TTF salts shows rich properties such as charge order, superconductivity, zero-gap state, persistent photoconductivity, photo-induced phase transition, and non-linear optical response. Although α'-(BEDT-TTF)$_2$IBr$_2$ is not isostructural to α-type BEDT-TTF salts, it has a herringbone molecular arrangement similar to α-type BEDT-TTF salts. This compound shows an insulator-insulator phase transition differently from conventional metal-insulator transition. According to the x-ray diffraction study, no distinct structural change was reported at phase transition temperature. We elucidated the mechanism of this phase transition.

Kinetic energy arising from hopping process is directly correlated with bandwidth. To compare the bandwidth with other α-type BEDT-TTF salts, the kinetic energy was esti-
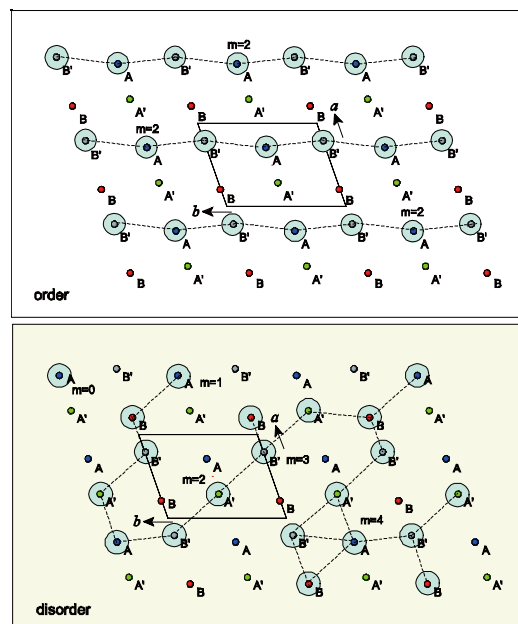
Figure 1. Snapshot of order (top) and disorder (bottom) model. The blue circles denote holes (charge-rich sites). The dashed lines denote the inter-site Coulomb interaction. In ordered state, every charge-rich site is surrounded by two charge-rich sites ($m = 2$), whereas in disordered state various configurations ($m = 0, ..., 6$).are accessible as shown in the above figures.

mated from integration of optical conductivity in the far-infrared and infrared region. It was found that the kinetic energy of α'-(BEDT-TTF)$_2$IBr$_2$ is much smaller than other α-type BEDT-TTF) salts, and therefore the bandwidth is narrowest among the α-type BEDT-TTF salts.

The investigation of infrared and Raman spectra of α'-(BEDT-TTF)$_2$IBr$_2$ with the aid of ^{13}C-substituted compound showed clear evidence that the low-temperature high-resistivity phase is a charge-ordered state. The horizontal stripe of charge order is most stable, but dislocation can be easily generated

because a diagonal stripe is energetically very close to the horizontal stripe.

It was found from infrared and Raman spectra that the electrons are localized even in the high-temperature (HT) phase. In HT phase, however, inter-site hopping rate significantly increases, symmetry changes from $P1$ to $P\bar{1}$, diagnostic vibronic mode which reflects order parameter vanishes, and the density of state near Fermi energy appears. All of these observations indicate that the HT phase is a dynamically disordered state. Therefore, this insulator-to-insulator transition is regarded as an order-disorder phase transition of localized charge. This localized electronic state in the whole temperature range is ascribed to the very narrow bandwidth.

Based on this picture, we proposed a simple electronic model using point charge approximation neglecting all transfer integrals. In this model, the energy states can be calculated from the electrostatic inter-site Coulomb energy (see Figure 2). Using this model, the energy states of charge-rich sites (holes) are calculated for ordered and disordered states. The estimation of the activation energies in low-temperature and high-temperature phase, resistivity jump can be qualitatively explained. The optical gap in low-temperature phase and the increase of optical weight in the gap region in high-temperature phase also is well explained by this model. The magnetic susceptibility is also consistent with this localized model.

Hydrostaic pressure suppresses the order-disorder transition temperature down to 100 K at 1.2 GPa, above which the phase transition changes the character such as a metal-insulator transition. The Raman spectrum was measured up to 2.3 GPa at various temperatures. The Raman spectrum also changes spectral features above 1.6 GPa. The author presents a pressure-temperature phase diagram using the spectral characteristic feature and electrical resistivity. The order-disorder transition extends up to 1.3 GP, above which metal-insulator transition appears. The insulating states above 1.3 GPa is a dimer-Mott state or density-wave state.

2. Direct Observation of Ferroelectric Domains Created by the Wigner Crystallisation of Electrons in an Organic Conductor[2]

In an effort to materialize a novel class of ferroelectrics, the possibility of pure-electronic mechanisms of spontaneous polarization, draws recent attention.[3] We have proposed in the previous study that an organic superconductor α-(BEDT-TTF)$_2$I$_3$ could be a promising candidate of a compound corresponding to the above picture.[4] In the present study, we examined to reveal the ferroelectric domains created in the organic complex by means of second-harmonic (SH) generation interferometry.

The ferroelectric transition in the compound is driven by Wigner crystallization of valence electrons. Since the charge ordering forms a pattern which is incompatible with the centric crystal symmetry underlying the valence charges. The domains created by such a transition that breaks centric symmetry, 180°
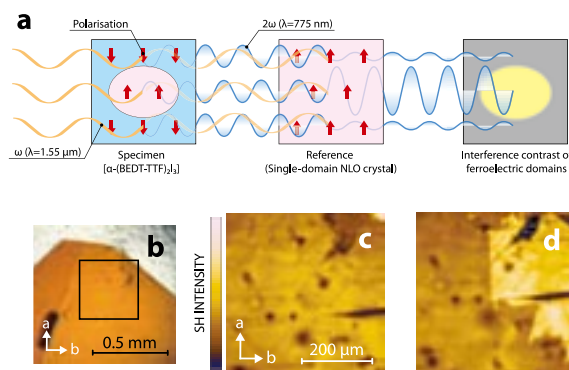
Figure 2. (a) Propagations of the excitation and SH light waves in the SH interferometry. (b) Transmission microscope image of a thin single crystal of α-(BEDT-TTF)$_2$I$_3$ used for the SH interference measurement. (c) and (d) show the SH contrast images measured from the rectangular region in (b) masured at above (140 K) and lower (50 K) temperature than the transition point (135 K), respectively.

polar domains, in which different domains have opposite polarizations, should be formed.

The SH intereferometry enables us to observe 180° polar domains that cannot be observed by a conventional microscope. Figure 1(a) illustrates the trajectory of the SH light waves in the interferometry. As shown in this sketch, the phase of SH wave generated from a domain is reversed from that of different domains of opposite polarization. On the SH beam generated by the specimen, harmonic beam produced by a single-domain nonlinear-optical crystal is overlaid as reference wave. The two beams interfere constructively or destructively depending on the phase difference, resulting in the SH contrast of domain structure.

Figure 1(b) shows the microscope image of the crystal used for the domain observations. Figures 1(c) and 1(d) show the SH images observed from the rectangular region in 1(b) at above (140 K) and lower (50 K) temperature than the transition point (T_{CO} = 135 K), respectively. The SH image showed the drastic change from 1(c) to (d); the image was split into bright and dark regions representing the formation of polar domains.

The growth of macroscopic domains manifests that the polar state forms as a stable bulk phase in the complex, materializing the feasibility of the electronic mechanism of ferroelectric polarization. The visualization of domain structures is important as the first step for understanding the nature of the ferroelectric compounds. Furthermore, the ability of discerning different polarizations can be utilized as a means of non-destructive readout of information in memory applications of the compound.

References

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