Optical Studies of Charge Ordering in Organic Conductors

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In many organic charge-transfer salts, the electronic state of charge carriers is located at the boundary between localized and delocalized states. Recently the charge ordering (CO) originated from the localization due to Coulomb interaction is widely found in organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. We are interested in the CO state, first because a CO phase is neighbored on a superconducting phase, wherein a charge-mediated superconductivity is theoretically predicted, second because some compounds in a CO phase shows ferroelectricity, the origin of which is attributable to the electron displacement, third because the narrow-band compounds have an inhomogeneous intermediate state between metallic and CO states, which is not well understood. We employ infrared and Raman spectroscopy to study the CO state.

1. Strong Optical Nonlinearity and Its Ultrafast Response Associated with Electron Ferroelectricity in an Organic Conductor[1)]

We yielded an experimental evidence for spontaneous generation of electric polarization in an organic conductor α-$(ET)_2I_3$ [ET: bis(ethylenedithio)tetrathiafulvalene] by measuring optical second-harmonic generation (SHG), and discussed an electron-associated mechanism of the ferroelectric polarization based on the observation of ultrafast photo-modulation of the SHG.

This compound belongs to a series of radical-cationic complex with strongly correlated electrons. On account of D_2A chemical stoichiometry (D: donor, A: monovalent anion), donor molecules (ET) of the class of compounds receive one-half of positive charge from counterions ($2D + A \rightarrow 2D^{0.5+} + A^-$). It has been manifested however that some complexes including α-$(ET)_2I_3$ lost the mixed valency due to charge disproportionation ($2D^{0.5+} \rightarrow D^+ + D^0$) driven by repulsive Coulomb interactions between charges (Wigner crystallization).

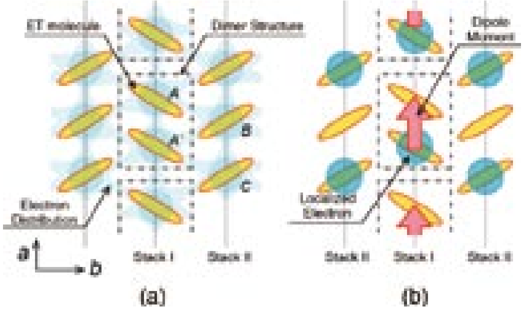

Figure 1. Schematic views of the arrangement of ETs and electrons. (a) In the metallic phase ($T > T_{CO}$), electrons are delocalized, and thus each ET has +0.5e. (b) In the charge ordered insulator phase ($T < T_{CO}$), charges are localized on some ETs. Because of finite alternation in Stack I, dipole moments between *A* and *A'* (solid arrows) survives in the unit cell.

The crystal of α-$(ET)_2I_3$ contains four ETs in the triclinic $P\bar{1}$ unit cell [Figure 1(a)]. There are two crystallographically independent stacks of ETs along the *a* axis; Stack I is a weakly dimerized chain composed of crystallographically equivalent ETs (labeled by *A* and *A'*), and Stack II is a uniform chain composed of *B* and *C*. According to an expected pattern of charge ordering, charges, which are delocalized in the metallic phase [Figure 1(a)], are localized to form such a pattern as illustrated in Figure 1(b) by the charge ordering. Since the equivalence between *A* and *A'* is broken in this pattern, the unit cell should possess a finite electrical dipole moment.

For most materials, electrical fields of those dipoles are cancelled out by the formation of an antiparallel dipole pair. However, we discovered that this complex exhibits SHG signal when it undergoes a metal-to-insulator transition due to charge ordering, manifesting that the transition is ferroelectric one, *i. e.*, local dipole moments are ordered in a polar arrangement to generate macroscopic polarization.

To examine the dynamic properties of the permanent polarization, we performed femtosecond pump-and-probe measurements of SHG; a crystal of the complex in ferroelectric state (T = 100 K) was stimulated by a pumping pulse, then induced variation of SHG was recorded with a probing pulse. Figure 2 shows the evolution of the photoinduced variation of SHG observed. The profile demonstrates the very fast photoresponse of the permanent polarization. The SHG signal instantly loses a large part of its intensity on pumping with the femtosecond pulse. Afterwards, it recovers to its original magnitude in the picosecond regime.

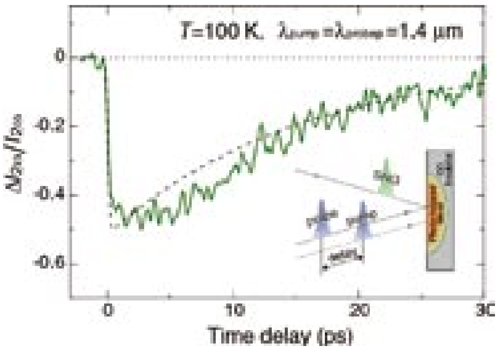

Figure 2. Photoinduced variation of SHG intensity as a function of the delay time between pump ($E \| b$, 100 μJ/cm^2) and probe ($E \| a$, 5 μJ/cm^2) pulses. The sample temperature was 100 K. The dashed line shows the fitted curve of single exponential decay (τ = 15 ps). The inset illustrates the pulse sequence of the time-resolved measurements.

Polarization in conventional ferroelectrics is attributed to a lattice modulation, such as polar displacement of ions, whereas one can hardly explain such fast photo-response of SHG with such a crystal lattice modulation. The substantially fast response illustrates that the ferroelectric polarization is modulated via a pure electronic process. It would be sure that the polarization is essentially attributed to the displacement of electrons due to the charge ordering.

Such electron-associated ferroelectrics are being recognized as a distinct class of the polar dielectrics. We believe that fast response of the polarization to external perturbations is one important characteristic of the new ferroelectrics, which may help to solve the problem in applying the controllable polarization to optoelectronic devices.

2. Inhomogeneous Site Charges at the Boundary between the Insulating, Superconducting, and Metallic Phases of β”-Type bis-ethylenedithio-tetrathiafulvalene Molecular Charge-Transfer Salts[2)]

β”-type ET salt involves rich superconducting compounds with the absence of strong dimerization. This family is possibly the good candidate for the charge-mediated superconducting transition, which is predicted by Merion and McKenzie. Some compounds in this family exhibits superconducting transition from an insulating ($d\rho/dT < 0$) state. We examined time-averaged charges on ET molecules around the phase boundary between the insulating, superconducting, and metal phases of β”-type ET salts with one hole per two molecules and two holes per three molecules by means of vibrational spectroscopy. We found that around the phase boundary, the site charges are neither those expected for a well-developed charge-ordered sate nor a uniform metallic state. The charge distribution is slightly inhomogeneous just above the insulator-superconductor phase transition temperature. We analyzed the distribution of the site charges from the viewpoint of the alternation of the strongest intersite Coulomb interaction along the stacking direction. The degenerate energy of several charge-ordered configuration generates a uniform state, the closeness in the energy of several charge-ordering configuration mostly contributes to the slight inhomogeneous distribution, and a large difference in their energy levels contributes to the charge ordered state. Our observation indicates that the instability due to the closeness in the energy of several configurations correlates with the insulator-superconductor transition in nondimerized or weakly dimerized molecular conductors.

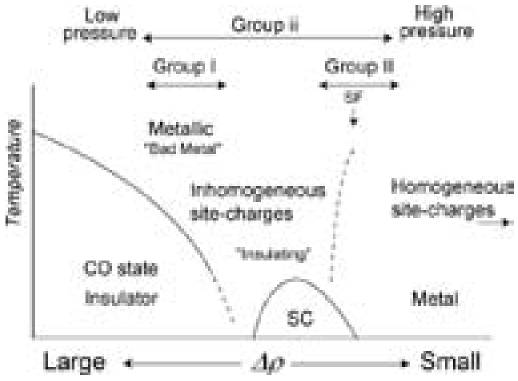

Figure 3. Schematic phase diagram of the β”-type ET salts plotted against the amplitude (Δρ) of charge density wave. “SF” denotes β”-$(ET)_2SF_5CH_2CF_2SO_3$. The superconducting phase appears when $\Delta\rho \neq 0$.

References

1) K. Yamamoto, *et al., J. Phys. Soc. Jpn.* **77**, 074709 (2008).
2) T. Yamamoto, *et al., Phys. Rev. B* **77**, 205120 (2008).

Award

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