Optical Studies of Charge Ordering in Organic Conductors

Department of Materials Molecular Science
Division of Electronic Properties

YAKUSHI, Kyuya	Professor
YAMAMOTO, Kaoru	Assistant Professor
URUICHI, Mikio	Technical Associate
KOWALSKA, Aneta	JSPS Post-Doctoral Fellow
NAKANO, Chikako	Research Fellow
TANAKA, Masayuki	Graduate Student
YUE, Yue	Graduate Student
TADA, Nao	Secretary

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 of the charge carriers 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 new type of pairing mechanism for superconductivity is theoretically predicted, second because some compounds in a CO phase shows ferroelectricity, the origin of which is attributable to the electronic displacement, third because the narrow-band compounds have an inhomogeneous intermediate state between metallic and CO states. We employ infrared and Raman spectroscopy to study the CO state, since the infrared and Raman spectra change dramatically at the CO phase-transition temperature.

1. Two-Phase Coexistence in the Monovalent–Divalent Phase Transition of Dineopentylbiferrocene-Fluorotetracyano Qinodimethane, (npBifc-(F_1TCNQ)$_3$)1)

The Gibbs rule implies that two-phase coexistence is possible at a single temperature point in a single-component system. However, the-phase coexistence has been reported in some temperature interval near the phase transition temperature, for example, in the neutral-ionic phase transition of TTF-CA (tetrathiafulvalene-chloranil), in the orientational ordering phase transition of C_{60}, in the spin-crossover temperature range of [Fe(2-pic)$_3$]Cl$_2$·MeOH (2-pic: 2-picolylamine), and in the diffuse phase transition of relaxor ferroelectrics such as PMN (PbMg$_{1/3}$Nb$_{2/3}$O$_3$). Two mesoscopic phases are observed in a very narrow temperature interval of TTF-CA and C_{60}, in which the phase transformation occurs abruptly. On the other hand, microscopic domains are suggested in a wide temperature interval in [Fe(2-pic)$_3$]Cl$_2$·MeOH and PMN, in which the phase transformation occurs gradually in a broad temperature interval.

Dineopentylbiferrocene-fluorotetracyanoquinodimethane, ((npBifc)$^{n+}$(F_1TCNQ)$_3$$^{n-}$), undergoes a monovalent (n = 1)- to-divalent (n = 2) phase transition. The phase-transition behavior was studied using the magnetization, χT, which showed a continuous increase in the temperature interval of ~60 K from 160 to 100 K. Mochida *et al*. suggested the coexistence of LT and HT phases to explain the continuous transformation. If a domain structure causes the continuous phase transformation, the domain size seems to be microscopic like spin-crossover compounds and relaxor ferroelectrics. Contrary to this expectation, we found macroscopic domains in the temperature interval of gradual phase transformation. In this temperature interval, we found that the Bragg peaks split into two groups which correspond to the monovalent and divalent phases.

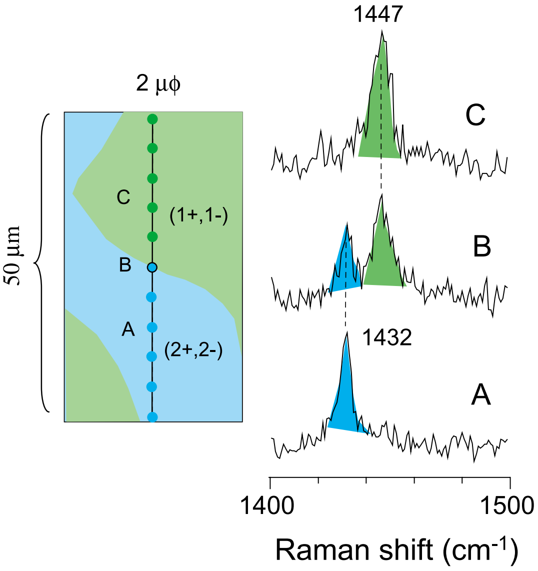

Figure 1. Position dependence of the Raman spectrum at 120 K. The Raman band at 1447 cm^{-1} appears in a monovalent (n = 1) state, whereas the 1432 cm^{-1} band appears in a divalent (n = 2) state. We have measured 11 points with the laser spot of of 2 μm diameter. In the region A, only the 1432 cm^{-1} band is observed, whereas in other region C, 1447 cm^{-1} band is observed. At the boundary B, both are observed.

Below 100 K, the Bragg peaks of monovalent phase are completely replaced by the Bragg peaks of divalent phase. In addition, we found a strong position dependence of the Raman spectrum (See Figure 1). Both experiments show that the macroscopic domains of monovalent and divalent phases coexist in the transition temperature region. This finding is unique, because two *macroscopic domains* stably exist in a *wide* temperature interval near the gradual phase transformation. We consider that the large volume contraction ($\Delta V/V \sim 0.03$) at ~130 K is related to the stableness of the macroscopic coexistent domains. We examined a simple Landau-Ginzburg model including volumetric strain. According to this model, a stable coexistent state is obtained near the transition temperature region, and the coexistent temperature range increases as the elastic compliance and/or the volumetric strain is large. However, this model is very preliminary, and more realistic theory is necessary to fully understand the stable coexistent state.

2. Infrared and Raman Study of the Charge-Ordered State in the Vicinity of the Superconducting State in a Organic Conductor β-(*meso*-DMBEDT-TTF)$_2$PF$_6$[2)]

The competition between charge ordering and superconductivity has been attracting attention, because in systems in which such competition occurs, charge fluctuation possibly contributes to the superconductivity pairing mechanism. Such competition can be depicted in an electronic phase diagram. From this viewpoint, the insulating charge-ordered (CO) phase in the vicinity of the superconducting phase has been studied in both organic and inorganic compounds.

β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ is possibly the typical compound, in which CO is competing with SC to be a ground state. We present spectroscopic evidence for the charge ordering in β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ below ~70 K. The infrared and Raman spectra abruptly changed at ~70 K, and the amplitude of charge order was estimated to be 0.5 from the splitting of the infrared-active C=C stretching mode. The coexistence of the high-temperature and low-temperature signals was observed in a narrow temperature range (~4 K) at the phase transition temperature. The pressure and temperature phase diagram was obtained in the vicinity of the superconducting phase. The checkerboard-type charge-order (CCO) phase is not adjacent to the superconducting phase, but the short-range ordered charge-ordering (SRO) phase is next to the superconducting (SC) phase. The coexistent region significantly expands under the hydrostatic pressure. In the coexistent region, the crystal is inhomogeneous not only in macroscopic scale but also in mesoscopic scale.

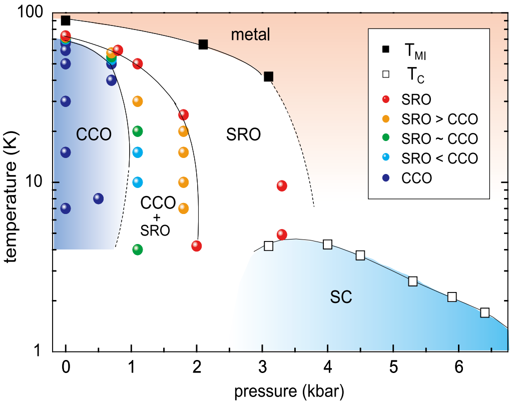

Figure 2. Pressure and temperature phase diagram. CCO and SRO respectively denote the checker-board type charge-order phase and short-range ordered fluctuating charge-order phase. CCO+SRO denotes the coexisting phase.

3. Charge Ordered State and Frustration of the Site-Charges in (ET)$_3$Te$_2$I$_6$ and (BETS)$_2$Te$_2$I$_6$[3)]

The θ-type ET salt is most extensively studied for the charge-ordering (CO) phase transition. As the crystal lattice is uniform with herringbone structure, several electronic configurations are frustrating above the phase transition. The low-temperature horizontal CO is stabilized by the structural transformation, that is, electron-lattice interaction as well as Coulomb interaction takes part in the phase transition. To examine the role of Coulomb interaction, we have studied (ET)$_5$Te$_2$I$_6$ and (BETS)$_5$Te$_2$I$_6$ [ET = bis(ethylenedithio) tetrathiafulvalene and BETS = bis(ethylenedithio) tetraselenafulvalene], whose organic layer takes the non-uniform lattice with a herringbone structure. We have studied x-ray structural analysis, temperature dependence of vibrational spectra and temperature dependence of electrical resistivity under the uniaxial strain for (ET)$_5$Te$_2$I$_6$ and (BETS)$_5$Te$_2$I$_6$. In the low-temperature insulating phase for each salt, a charge sensitive mode, ν_2, exhibits a peak splitting, and a vibronic ν_3 mode shows the factor group splitting. This observation confirms the charge ordered state. The distribution of the site charges is determined from the factor group analysis of the vibronic ν_3 mode, and the site charge takes an inner distribution. This result is in agreement with that suggested from the x-ray crystal structure analysis of the ET-salt. In the high temperature conducting phase, the vibronic ν_3 mode is smeared out whereas the frequencies of the two charge sensitive modes are almost unchanged in the whole temperature range. We have proposed the model that the highly conducting state is ascribed to the frustration between the inner distribution in the insulating state and the other charge distribution, which contributes to reducing the inter-site Coulomb interaction along the stacking and diagonal directions, respectively. Our conjecture is supported from the temperature dependence of the electrical resistivity under the uni-axial strain.

References

1) M. Uruichi, Y. Yue, K. Yakushi and T. Mochida, submitted.
2) M. Tanaka, K. Yamamoto, M. Uruichi, T. Yamamoto, K. Yakushi, S. Kimura and H. Mori, submitted.
3) T. Yamamoto, J. Eda, A. Nakao, R. Kato and K. Yakushi, *Phys. Rev. B* **75**, 205132 (18 pages) (2007).