RESEARCH ACTIVITIES IV
Department of Molecular Assemblies

IV-A Optical Study of Charge Ordering States in Organic Conductors

In the organic charge-transfer salts, the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, mainly because the interatomic distances between the neighboring molecules are much longer than the bond length within the molecule. Therefore, charge ordering (CO) originated from the localization of the charge carriers is widely found in organic conductors through the phase transition. Recently, CO has been found in several organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. The CO state is drawing attention, 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 expected to be electronic, third because the narrow-band compounds have an unusual intermediate state between metallic and CO state. To detect CO states, we employ infrared and Raman spectroscopy. Some molecules have charge-sensitive intramolecular vibrational modes, the frequency of which shifts depending upon the molecular charge (oxidation state of molecule). The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by an inhomogeneous distribution with large amplitude. The goal of this study is (1) the understanding of the intermediate state above the CO phase transition, (2) the investigation of the optical properties related to the ferroelectric CO phase, and (3) the characterization of the insulating electronic state near the superconducting phase.

IV-A-1 Charge Ordering State of β''-$(ET)_3(HSO_4)_2$ and β''-$(ET)_3(ClO_4)_2$ by Temperature-Dependent Infrared and Raman Spectroscopy

YAMAMOTO, Takashi; URUICHI, Mikio;
YAKUSHI, Kyuya; KAWAMOTO, Atsushi[1]
(*[1]Hokkaido Univ.*)

We present the temperature-dependent infrared and Raman spectra of β''-$(ET)_3X_2$ (X = HSO$_4$ and ClO$_4$; ET = Bis-ethylenedithio-tetrathiafulvalene) compounds which undergo a metal-insulator transition. The infrared-active ν_{27} mode discontinuously split into two bands at the metal–insulator transition temperature of 127 K in the X = HSO$_4$ salt, whereas, the corresponding mode continuously changed across the metal–insulator transition temperature of ~170 K in the X = ClO$_4$ salt. In both compounds, the charge-sensitive ν_{27} mode split into two in the insulating phase. This drastic spectral change indicates that the metal–insulator transition originated in the charge ordering. Employing the frequencies of the split ν_{27} bands, the site charges are estimated to be $+0.3_4$ and $+0.8_1$ for X = HSO$_4$ and $+0.3_6$ and $+0.8_1$ for X = ClO$_4$. We also estimated the site charges using the Raman-active ν_2 mode and obtained consistent results. Examining the selection rule of the ν_3 mode, we reached the conclusion that the unit cell with space group $P1$ has a pseudo-inversion center in the charge-ordered phase. Based on the symmetry, we propose a charge-ordering pattern for the X = HSO$_4$ and X = ClO$_4$ salts, which is quite different from that of the X = ReO$_4$ salt reported previously. We qualitatively discuss the differences in the charge-ordering pattern considering the anisotropic inter-site Coulomb interaction.
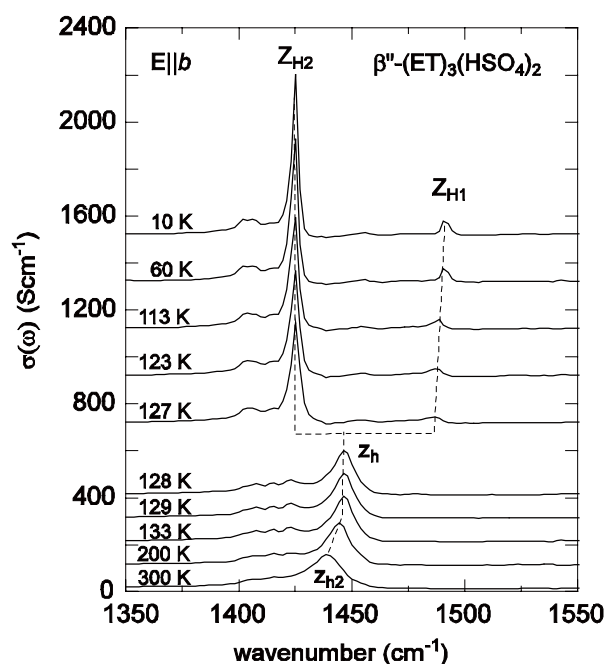

Figure 1. Temperature dependence of the conductivity spectra obtained through Kramers-Kronig transformations of the b-polarized reflectance spectra of β''-$(ET)_3(HSO_4)_2$. The infrared-active bands, z_h is the out-of-phase mode of the ring C=C stretching in highly conductive phase. The bands, denoted by Z_{H1} and Z_{H2} are respectively the ring C=C stretching modes of charge-poor and charge-rich molecules of β''-$(ET)_3(HSO_4)_2$.

IV-A-2 Infrared and Raman Studies of the Charge-Ordering Phase Transition at ~170 K in the Quarter-Filled Organic Conductor, β''-(ET)(TCNQ)

URUICHI, Mikio; YAKUSHI, Kyuya; YAMAMOTO, Hiroshi M.[1]; KATO, Reizo[1]
(*[1]RIKEN and JST/CREST*)

We present the optical conductivity, infrared- and Raman-active charge-sensitive phonon modes, and the x-ray diffraction superlattice spots of β''-(ET)(TCNQ) [ET = bis(ethylenedithio) tetrathiafulvalene, TCNQ = 7,7,8,8-tetracyanoquino-dimethane], which is characterized as a quarter-filled narrow band system. Above ~170 K, we found weak superlattice spots and splitting of the C=C and C–S stretching modes of ET. These results indicate the charge-ordering state in the ET layer. As the temperature is decreased, the superlattice spots abruptly disappeared at ~170 K and the split modes continuously merged into a single band below ~170 K. Concomitantly, the spectral weight of the optical conductivity ascribed to the ET layer significantly shifts toward lower energy. Through the analyses of these experimental results, we propose the view that the incoherent conducting electron in the ET layer shows a crossover behavior into a coherent Fermi liquid state below the structural phase transition at ~170 K.
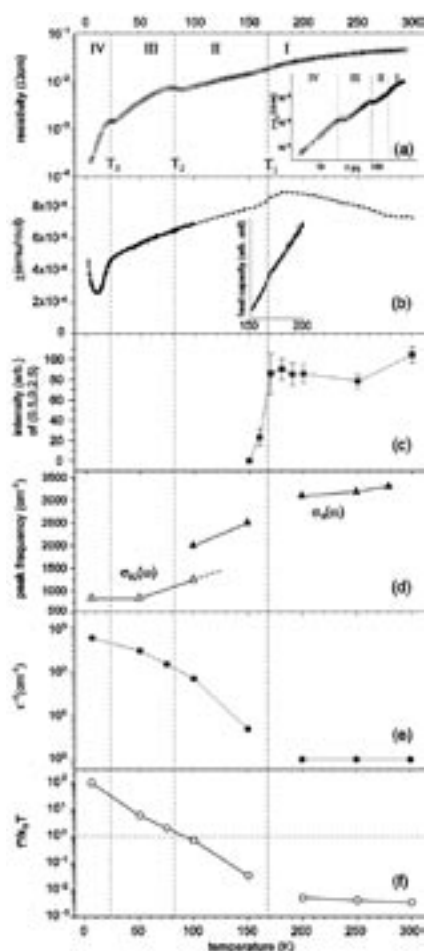

Figure 1. Comparison of (a) the dc resistivity, (b) the magnetic susceptibility and heat capacity (inset), (c) the intensity of the superlattice (1/2, 0, 21/2), (d) peak frequency in the optical conductivity of ET layer, (e) the intersite hopping rate in the ET layer, (f) the ratio of effective transfer energy to temperature.

IV-A-3 Unusual Intermediate State between Metallic and Charge-Ordered States in θ-Type ET Salts

TAKAHASHI, Toshihiro[1]; NOGAMI, Yoshio[2]; YAKUSHI, Kyuya
(*[1]Gakushuin Univ.; [2]Okayama Univ.*)

The Raman spectrum of narrow-band θ-type ET salts in highly conducting phase exhibit a single broad band as shown in Figure 1(c). This Raman band was assigned to the ν_2 mode based on the isotope shift of the ^{13}C-substituted compound. If the high-temperature phase is a metal, the ν_2 mode should appear between the ν_{2P} and ν_{2R} bands which are shown in Figure 1(a). However, the broad ν_2 band above T_{CO} is located at the ν_{2R} band. In addition, the ν_{2P} mode, the counterpart of ν_{2R}, is found in the highly conducting phase of the monoclinic TlZn salt (See Figure 1(b)). These spectra were quite different from the spectrum (Figure 1(d)) of metallic θ-(ET)$_2$I$_3$, in which the ν_2 mode nearly located at the center of ν_{2P} and ν_{2R} modes. The spectra of the narrow-band compounds in high-temperature phase rather resemble the spectrum (Figure 1(a)) of charge-ordered state. Therefore, the charges in high-temperature phase are nearly localized and hop to neighbor site slowly less than 10^{11} Hz (~1 meV). This hopping rate is much slower than the motion of the charge carriers of organic metal. The high-temperature phase of narrow-band θ-type ET salts is considered as an intermediate state between metallic and CO states.
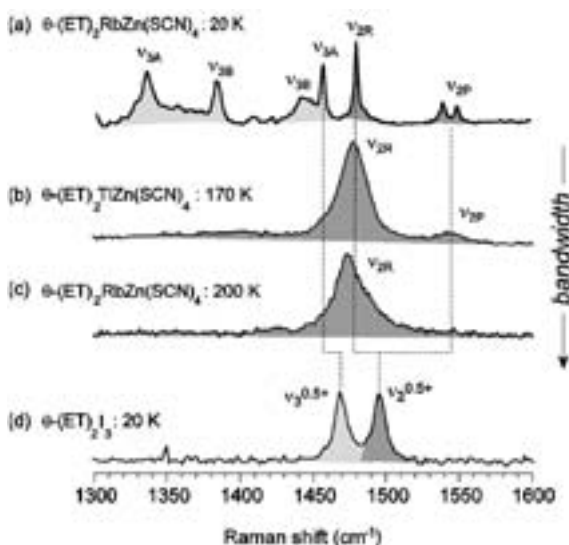

Figure 1. Comparison of the ν_2 and ν_3 bands of (a) the CO phase of RbZn, high-temperature phases of (b) TlZn, (c) RbZn, and (e) I$_3$ salts. Note that the ν_2 mode in high-temperature phase of (b) and (c) is already split.

IV-A-4 Photo-Gatable Second Harmonic Generation in Ferroelectric Organic Conductor with Strongly Correlated Electrons

YAMAMOTO, Kaoru; IWAI, Shinichiro[1,2]; BOYKO, Sergiy[3]; KASHIWAZAKI, Akimitsu[1]; HIRAMATSU, Fukiko[1]; OKABE, Chie; NISHI, Nobuyuki; YAKUSHI, Kyuya
(*[1]Tohoku Univ.; [2]JST/PREST; [3]Univ. Ontario*)

Ferroelectricity is characterised by the spontaneous polarisation, which shows dramatic temperature- and electric-field responses. By means of optical second-harmonic generation (SHG) measurement, we demonstrated that a two-dimensional organic metal α-(ET)$_2$I$_3$ [ET: bis(ethylenedithio)tetrathiafulvalene] undergoes ferroelectric transformation associated with Wigner-crystal like charge ordering (CO). It was found that the nonlinear electric susceptibility of the compound in the ferroelectric state was much greater than that of a nonlinear optical crystal β-BaB$_2$O$_4$ (BBO), suggesting the generation of macroscopic polarisation as in ferroelectrics. In terms of controlling the electronically induced FE polarisation, the photo-response of the macroscopic polarisation to femtosecond laser pulse was investigated. Pump-probe SHG measurement showed that the polarisation was sharply suppressed by the photo-excitation. More noteworthy is the fact that the suppressed polarisation instantaneously recovered in the time scale of 10 ps. The photo-gatable optical nonlinearity based on the electron FE might be applied as a unique medium that functions as a fast optical switch in future all-optical devices.

IV-A-5 Evaluation of Charge Transfer Degree in the Bis(ethylenethio) Tetrathiafulvalene Salts by Raman Spectroscopy

KOWALSKA, Aneta[1]; WOJCIECHOWSKI, Roman[1]; ULANSKI, Jacek[1]; MAS-TORRENT, Marta[2]; LAUKHINA, Elena[2]; ROVIRA, Concepcio[2]; YAKUSHI, Kyuya
(*[1]Univ. Lodz; [2]Inst. Ciencia Mater. Barcelona*)

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Raman spectroscopy studies for a series of charge-transfer salts based on the bis(ethylenethio)tetrathiafulvalene (BET-TTF) were carried out in order to analyze the charge distribution on the donor molecules in the unit cell of crystals. With the help of the density functional theory calculations for BET-TTF^0 and BET-TTF$^+$ molecules it was shown that the Raman spectroscopy can be applied to determine the stoichiometry in the BET-TTF salts. For salts exhibiting increase of the resistivity below *ca.* 100 K, the Raman spectra at variable temperature indicate that this behavior is not related to the charge disproportionation phenomenon.

IV-A-6 Installation of a Cryostat to the Far-Infrared Spectrometer and the Transmission Measurement of α-(BEDT-TTF)$_2$I$_3$

YAKUSHI, Kyuya; YAMAMOTO, Kaoru;

NAKANO, Chikako

The measurement of the reflectivity or transmittance in the far-infrared region of organic conductors has been conducted for very restricted materials, owing to the difficulty of the growth of a large single crystal of several mm. The optical conductivity in the far-infrared region provides the information of the electronic state near Fermi energy. For example, the incoherent conducting state is expected to give a non-Drude type optical conductivity, whereas the coherent state provides a well-defined Drude type conductivity. The absorption spectrum of insulating compounds provides the information of the low-frequency local phonons and lattice phonons, which are sometimes closely related to the mechanism of phase transition. We have installed a top-loading type of cryostat, Oxford Optistat CF, to the far-infrared spectrometer, Bruker IFS-66v, whose sample and optics chamber can be evacuated to avoid the strong absorption of water vapor. We introduced a XY stage to fix the bottom of the cryostat to adjust the sample position. Z position can be adjusted using a sample rod controlled by a micrometer. Figure 1 shows the polarized transmittance spectrum of α-(BEDT-TTF)$_2$I$_3$ of 2 mm × 2 mm. As shown in this figure, the optical gap appears abruptly at 136 K. Although this phase transition is of first order, the evolution of the gap was observed. This observation is consistent with the evolution of the SHG (second harmonic generation) signal below the phase transition temperature.
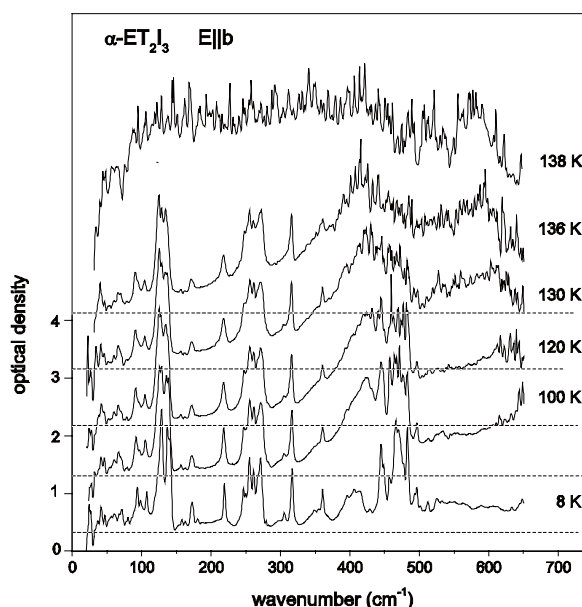

Figure 1. Temperature dependence of the *E//b* polarized transmittance of the single crystal of α-(BEDT-TTF)$_2$I$_3$. Note that the evolution of the gap is observed.

IV-A-7 Mechanism of the Phase Separation in the Monovalent-to-Divalent Phase Transition of Biferrocenium-(F$_1$TCNQ)$_3$

URUICHI, Mikio; YAKUSHI, Kyuya; MOCHIDA, Tomoyuki[1]
(*[1]Toho Univ.*)

The ionic crystal $D^+A_3^-$ (D = dineopentylbiferrocene and A = F_1TCNQ) undergoes a first-order phase transition, in which second ionization occurs to form a doubly ionized state, $D^{2+}A_3^{2-}$.[1] This monovalent-to-divalent phase transition continuously occurs in a wide temperature range from 160 K to 100 K. X-ray diffraction and Raman spectroscopy showed that the macroscopic domains of monovalent and divalent phases coexist in this temperature range.[2] We investigated this unusual phase transition and elucidated the mechanism of the phase separation based on the general understanding of the first-order phase transition. According to the theory of first-order phase transition, the free-energy *vs.* order parameter has an energy barrier E_B between the two phases (monovalent and divalent phases). (See Figure 1) If E_B is smaller than the phase transition temperature kT ($T \sim$ 100–160 K), one of the domains can be thermally activated. Therefore, the continuous phase change accompanied by the phase separation can be well explained. Interestingly, the behavior of the first-order phase transition changes from hysteretic behavior to continuous behavior on decreasing the ratio kT/E_B as shown in Figure 1. We speculate that the small energy barrier arises from the mechanism of this phase transition that the Madelung energy gain is the driving force.

References
1) T. Mochida, K. Takazawa, M. Takahashi, M. Takeda, Y. Nishio, M. Sato, K. Kajita, H. Mori, M. M. Matsushita and T. Sugawara, *J. Phys. Soc. Jpn.* **74**, 2214 (2005).
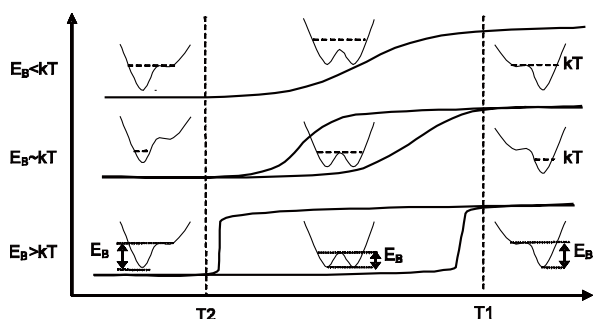2) M. Uruichi, K. Yakushi and T. Mochida, *J. Low Temp. Phys.* in press.

Figure 1. The behavior of first-order phase transition is classified by the ratio between the energy barrier E_B and the phase transition temperature kT. Abscissa is temperature and ordinate is the physical quantity that changes through a phase transition.