RESEARCH ACTIVITIES IV
Department of Molecular Assemblies

IV-A Spectroscopic Study of Charge Carriers in Organic Conductors

The low-frequency reflectivity of an organic conductor provides us with a wealth of information on the nature of charge carriers. For instance, the anisotropy of a band structure, bandwidth, effect of electron-electron correlation, and electron-molecular vibration (*e-mv*) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. We are investigating the polarized reflection spectra of various organic conductors in the spectral region of 50–33000 cm^{-1} and in the temperature range of 6–300 K. Usually the molecular vibrations (local phonons) are screened by strong electronic transition by charge carriers. Therefore, few local phonon bands are detected in the reflection spectrum. In this sense, the Raman spectroscopy is a complementary method to reflection spectroscopy for understanding molecular vibrations in a metallic state. Since some molecules have charge-sensitive vibrational modes, the Raman spectroscopic method is a powerful tool to detect the site-charge distribution (oxidation state of molecule). We are investigating the charge ordering (CO) phenomena in organic conductors using the technique of infrared and Raman spectroscopy. In the organic charge-transfer salts, CO is originated from the localization of the charge carriers. Since the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, CO will be widely found through the phase transition. The charge ordering was first found in inorganic narrow-band systems such as copper, manganese, and vanadium oxides. Recently, CO has been found in several organic conductors, and the electronic phase diagrams of typical organic conductors are re-examined taking CO into account. The CO state is drawing attention, since CO is theoretically considered as being related to the pairing mechanism in superconductivity. The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by an inhomogeneous charge distribution. Our goal is the complete understanding of the CO phase transition through the interpretation of the vibrational spectra, and the drawing of a *P-T* phase diagram.

IV-A-1 Charge-Ordering Transition in Two Crystal Modifications of θ-(BEDT-TTF)$_2$TlZn(SCN)$_4$ Studied by Vibrational Spectroscopy

SUZUKI, Kenji[1]**; YAMAMOTO, Kaoru; YAKUSHI, Kyuya**
(*[1]GUAS)*

[*Phys. Rev. B* submitted]

We are systematically investigating the phase diagram of θ-(BEDT-TTF)$_2$MM'(SCN)$_4$ (M = Tl, Rb, Cs; M' = Zn, Co). Subsequently to the thorough study of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, we investigated the phase transitions of the orthorhombic and monoclinic modifications of θ-(BEDT-TTF)$_2$TlZn(SCN)$_4$ by the method of infrared and Raman spectroscopy with aid of electrical resistivity and x-diffraction experiments. Both modifications showed the phase transitions, which were accompanied by resistivity jumps, structural changes, and charge separation. The temperature dependence of vibrational spectra of orthorhombic salt showed abrupt peak splitting at around 240 K. Below this temperature, the polarization dependence of the infrared and Raman bands of the orthorhombic modification agreed with that of the low-temperature phase of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, which had been elucidated to have a horizontal-type charge-ordering pattern (Figure 1a). The monoclinic salt also showed a resistivity jump at around 165 K. Below this temperature, the polarization dependence of infrared and Raman spectra and the pattern of the satellite peaks in x-ray diffraction were very different from those of orthorhombic modification. Analyzing these results, we concluded that the pattern of the charge order was a diagonal stripe (Figure 1b). The spectral change at the phase transition was rather gradual compared with that of orthorhombic modification. The precursory change was observed in the Raman spectrum above 165 K. This precursor was interpreted as the fluctuation of the site-charge density, namely, the charge carriers move incoherently.

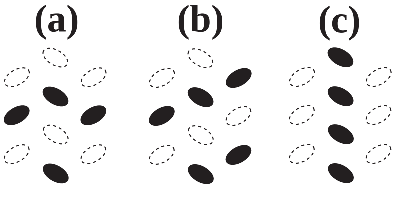

Figure 1. Schematic view of charge-ordered state in θ-type BEDT-TTF sals: (a) horizontal stripe, (b) diagonal stripe, and (c) vertical stripe. The ovals represent the arrangement of the BEDT-TTF molecules in a conducting layer. Above the phase transition temperature, the average charge (+0.5*e*/molecule) is homogeneously distributed at each site, whereas the charges are localized at the sites drawn by solid oval below the phase transition temperature.

IV-A-2 Dynamical Charge Localization in θ-(BEDT-TTF)$_2$MM'(SCN)$_4$ [M = Cs, Rb, Tl, M' = Zn,Co]

SUZUKI, Kenji[1]**; YAMAMOTO, Kaoru;**

YAKUSHI, Kyuya
([1]GUAS)

The high-temperature phase of θ-(BEDT-TTF)$_2$-MM'(SCN)$_4$ [M = Cs, Rb, Tl, M'=Zn, Co] (hereafter abbreviated as MM') exhibits an unusually broad Raman band. Although this phase is regarded as a metallic state, the temperature derivative of resistivity has a small negative value. The low-temperature phase has been characterized as a charge-ordered state, namely, the localized charge is ordered with a structural distortion. However, the nature of the high-temperature phase is not well understood. We found that the line shape of the Raman band of the charge-sensitive mode at room temperature changed systematically against the bandwidth. Figure 1a shows the line shapes of the Raman band of the charge-sensitive mode of CsZn, RbZn, and TlZn. As the high-pressure narrows the bandwidth in the θ-type BEDT-TTF salts, the various spectra are arranged in the descending sequence of bandwidth from the top to the bottom. In this spectral region, there are two charge-sensitive modes ν_2 and ν_3. We have experimentally and theoretically elucidated that ν_2 splits into two and the highest-frequency ν_3 among the split modes keeps the position, when the charge localization occurs. As shown in Figure 1a, the ν_2 band is broadened and split into two (shown by arrows), when the bandwidth is narrowed. We speculated that the systematic change of the line shape of the Raman band was ascribed to the hopping rate of the localized charge between the adjacent BEDT-TTF molecules. Figure 1b is the simulation of the linewidth based on the two-site motional-narrowing model. The agreement with the experimental results strongly suggests that the charge carrier in the high-temperature phase is not in a coherent state but is incoherently hopping between the adjacent sites in the time scale of a few ps. This state is regarded as a dynamically localized state of charge carrier. This interpretation is consistent with the non-metallic nature of the electrical resistivity.

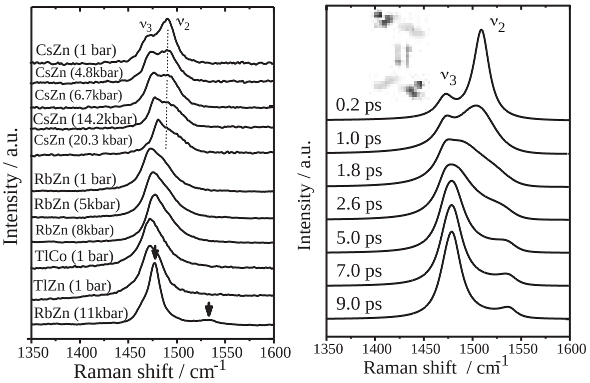

Figure 1. (a) Systematic change of the lineshape of the Raman band (λ_{ex} = 515 nm) of the title compounds at room temperature. The spectra are arranged in a descending order of bandwidth. (b) Raman spectra simulated by using a two-site motional-narrowing model. The time on each spectrum shows the hopping rate between the adjacent sites.

IV-A-3 Activation of Strong Overtone in the IR Spectrum of a Charge-Ordered Organic Conductor

YAMAMOTO, Kaoru; YAKUSHI, Kyuya

The infrared spectrum of charge ordered θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ exhibits a number of additional signals that are not present above the phase-transition temperature. The example of the additional signals is displayed by solid triangles of Figure 1a. Although the bandwidths of the activated signals seem to be of vibrational transitions, their frequencies are out of the characteristic range of ordinary vibrations. To understand the origin of these bands, we calculated the vibrational transition moment using a molecular dimer containing a single radical electron that is distributed asymmetrically as $M^{\rho+}–M^{(1-\rho)+}$. The vibrational transition moment is expressed by the series of the vibronic correction terms. Because the strongest newly activated signal (*ca.* 2750 cm^{-1}) is positioned around the twofold frequency of C=C stretching signal, we performed the numerical calculation including up to the second-order correction. We calculated the ratios of the oscillator strength of two overtones and one combination-tone to the vibronic fundamental. Figure 1b plots the ratios against the ionicity (ρ) at one site. This plot qualitatively explains that the overtones and combination tone are noticeable only when large charge disproportionation (ρ > 0.8) takes place.

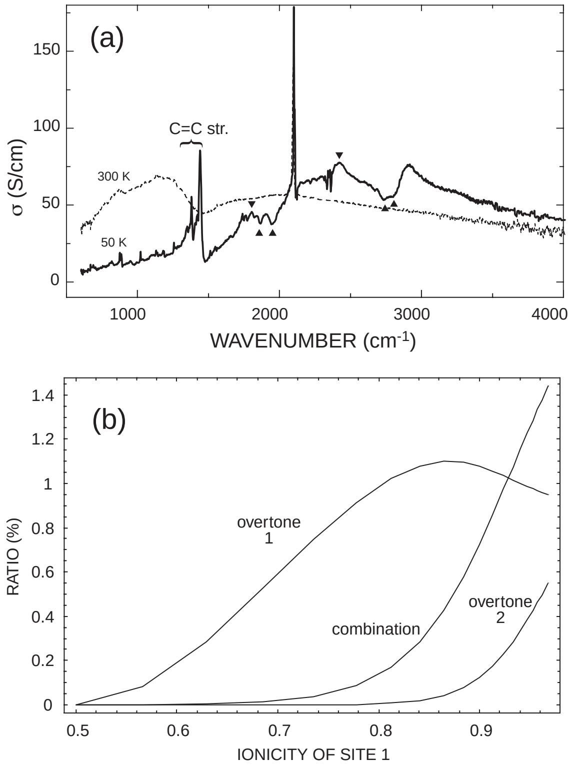

Figure 1. (a) Optical conductivity spectrum of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ above (300 K) and below (50 K) the phase transition temperature. The solid triangles show the vibronic overtones and combination tones. (b) Intensity ratios of overtones and combination tones to the fundamentals are plotted against the site charge (ρ).

IV-A-4 Charge Ordered State in θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$

YAMAMOTO, Takashi; YAKUSHI, Kyuya; SHIMIZU, Hiroyasu[1]; SAITO, Gunzi[1]
([1]Kyoto Univ.)

θ-type BEDT-TTF salts are systematically studied according to the dihedral angle (φ_d) defined from BEDT-TTF molecules in adjacent BEDT-TTF stacks. In the temperature dependence of electrical resistivity, a metal-insulator transition is observed for the most of θ-salts. With increasing φ_d, the transition temperature increases. This phenomenon can be interpreted from the narrow bandwidth due to the small transfer integral. Theoretical studies predict that these compounds fall down to the charge ordered state since Coulomb repulsions play an important role for such a narrow band system. Among numerous θ-salts, which has been synthesized so far, θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$ has the largest φ_d (~ 132°). We measured the temperature dependence of Raman spectra below 300 K, and analysed two kinds of C=C stretching modes abbreviated as ν_2 and ν_3. The ν_3 mode exhibited a factor group splitting with decreasing temperature. We were able to apply the factor group analysis exactly the same as those for θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$. This result implied that the system fell down to the horizontally charge-ordered state. Interestingly, the ν_2 mode showed a peak splitting even at 300 K, which is higher than the transition temperature in the resistivity measurement (~ 220 K). This result suggests that the charges are already dynamically localized and the localized charges are incoherently hopping between the adjacent sites at room temperature. We estimated the site charge (ρ) from the peak positions of ν_2. The estimated values were ~ $+0.8_5$ and ~ $+0.1_5$, which were found to be independent of φ_d. Among the four ν_3 modes, the ν_{3D} mode was observed in the lowest energy through an *e-mv* interaction. The peak position of this mode showed a blue shift with the increase of φ_d. This result was explained by the decrease of the transfer integrals along the *a* direction.

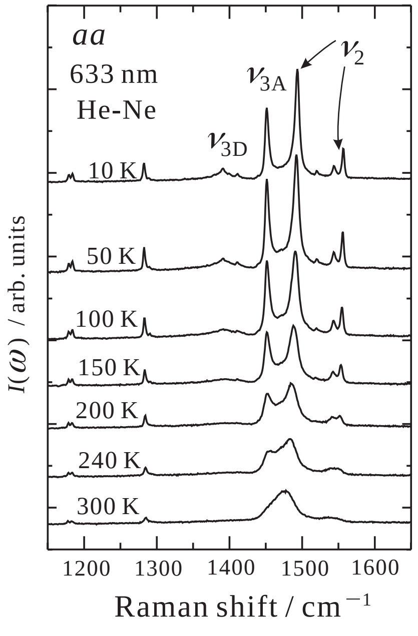

Figure 1. Temperature dependence of the Raman spectrum of θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$.

IV-A-5 Direct Evidence for the Inhomogeneous Charge Distributions and Charge Re-Distribution in β”-(ET)$_3$(ReO$_4$)$_2$

YAMAMOTO, Takashi; URUICHI, Mikio; YAKUSHI, Kyuya; YAMAURA, Jun-ichi[1]; TAJIMA, Hiroyuki[1]
([1]Univ. Tokyo)

The charge disproportionation in organic CT salt is drawing an attention since theoretical studies suggest the relation between charge fluctuation and pairing mechanism in superconductivity. An insulator-superconductor transition is observed for the several β”-type BEDT-TTF salts under the hydrostatic pressure or the ambient pressure. However, a few experimental studies were presented for the charge disproportionation in the insulating phase of BEDT-TTF salts. We measured the infrared and Raman spectra of β”-(BEDT-TTF)$_3$(ReO$_4$)$_2$ below 300 K. We analysed three kinds of C=C stretching modes abbreviated as ν_2, ν_{27} and ν_3. The ν_{27} mode shows triple peaks below 80 K, while ν_{27} exhibits a doublet above 81 K. The phase-transition temperature detected from the vibrational spectra agreed with those determined from the reflectivity and EPR experiments. In the low-temperature phase, the ν_2 mode was also observed as triple peaks. The site charges (ρ) estimated from the frequencies of ν_2 for non-equivalent BEDT-TTF were +0.2, $+0.8_5$ and $+0.9_5$. A mutual exclusion rule between the infrared and Raman spectra was broken for the three ν_3 modes. These results lead to the conclusion that an inversion center is lost below 80 K. This is in agreement with the result of the X-ray structural analysis solved at 22 K. The observed pattern of site charges in the unit cell was reproduced from the mean-field approximation of a Hubbard model. In the high temperature phase, the ν_2 mode was observed as doublets. The estimated ρ are $+0.7_3$ and $+0.5_3$. A mutual exclusion rule was found in the three ν_3 modes. These results imply that an inversion centre is kept above 81 K. This is also in agreement with the result from the X-ray structural analysis solved at 100 K. This inhomogeneous charge distribution above 81 K was reproduced from the mean-field calculation of the Hubbard model with a weak on-site Coulomb energy, where electron and hole pockets still exist in the semi-metallic band. The molecular arrangement slightly changed in this charge-ordering phase transition. This structural change brought about a re-distribution of the localized charge. It is interesting to note that the re-distribution of the charge accompanies the re-distribution of the transfer integrals.

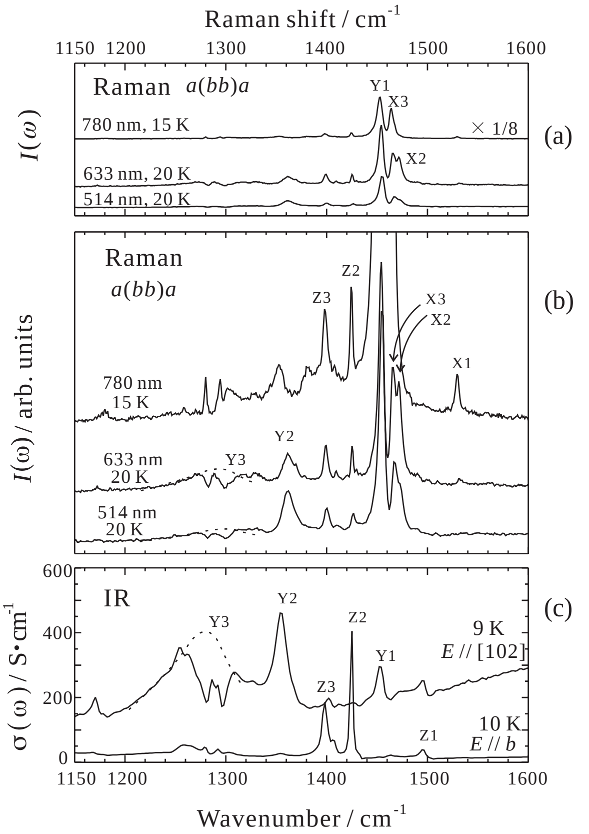

Figure 1. (a) and (b) Raman spectra at the lowest temperature we measured. X, Y and W correspond to the ν_2, ν_3 and ν_{27} modes. (c) Optical conductivity (IR) spectra. Z denotes the ν_{27} mode.

IV-A-6 Inhomogeneous Charge Distributions and Isotope Effect in β”-(BEDT-TTF)$_4$M(CN)$_4$H$_2$O (M = Ni, Pd, Pt) Group

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

The charge disproportionation in organic CT salt is drawing attention since theoretical studies suggest the relation between charge fluctuation and pairing mechanism in superconductivity. Various studies have been concentrated on the θ-type BEDT-TTF salts. However, few studies have been presented for β”-type BEDT-TTF salts, although this family has a rich variety of electrical properties including superconductivity. The title compounds are 3/4-filled β”-salts. For M = Pd and Pt, superconductivities are observed under the hydrostatic pressures. No superconductivity is observed for M = Ni salt. However, resistivity curves for three compounds exhibit insulating behaviours under the ambient pressure below ~ 100 K. We studied temperature dependence of vibrational spectra under the ambient pressure. We analysed three C=C stretching modes abbreviated as ν_2, ν_{27} and ν_3. For M = Ni and Pd, ν_2 and ν_{27} have broad linewidth around 300 K. With decreasing temperature down to 10 K, both modes show peak splitting. This observation leads to an separation of charges. The separated site charges (ρ) are ~ +0.3 and ~ +0.7. Since more than two ν_3 modes are observed in the Raman spectra, the space group is changed from $P\bar{1}$ to $P1$ at low temperature. For M = Pt, ν_2 keeps a broad linewidth down to 10 K, but ν_{27} exhibits a peak splitting at 10 K. We also observed Raman spectra for the deuterium substituted M = Pt salt, where all the hydrogen atoms in BEDT-TTF were substituted by deuterium. Interestingly, the spectral shape becomes similar to that of M = Ni salt rather than that of M = Pt salt. Such a drastic isotope effect is firstly observed in β”-salts. Our results demonstrated that M = Pt salt was located at the region close to the phase boundary that separates the insulator, metal, and superconductor phases.

IV-A-7 Dynamical Fluctuation of Site-Charge Density in Metallic β”-(BEDT-TTF)(TCNQ)

URUICHI, Mikio; YAKUSHI, Kyuya; YAMAMOTO, Hiroshi[1]; KATO, Reizo[1]
([1]*RIKEN*)

Charge disproportionation (CD) and charge ordering (CO) in organic conductors originate from the localization of charge carriers. CO has been investigated in the insulating states of several charge-transfer salts. We present dynamically fluctuating CD in the metal-like state of the title compound, which are investigated by means of infrared and Raman spectroscopy. β”-(BEDT-TTF)(TCNQ) newly synthesized by Yamamoto *et al.* consists of a segregated stack structure, where TCNQ and BEDT-TTF separately form uniform chains.[1),2)] This compound is metallic with three resistance anomalies at 175 K, 80 K, and 20 K. We measured the polarized Raman and infrared spectra. First we estimated the charge-transfer degree as 0.5 using the C=C stretching mode (ν_4) of TCNQ. All of the Raman bands of TCNQ are independent of temperature. However, the C=C stretching modes (ν_2 and ν_3) of BEDT-TTF show clear splitting, and the low-frequency component of ν_3 exhibits a broad vibronic feature. This finding indicates that the holes of BEDT-TTF are nearly localized, and thus CD arises near the room temperature. We theoretically investigated the frequency shift and Raman intensity of ν_2 and ν_3 using an asymmetric dimer model, and verified that this observation is consistent with the generation of CD. Very interestingly, the split bands of ν_2 merge into a single broad band, and the broad band is sharpened on lowering temperature. The same phenomenon is found in the infrared-active C=C stretching mode ν_{27} as shown in Figure 1. This temperature dependence is well reproduced by motional narrowing model. This finding implies that the holes in BEDT-TTF chain change the nature at low temperature.

References

1) H. M. Yamamoto, M. Hagiwara and R. Kato, *Synth. Met.* **133-134**, 449 (2003).
2) H. M. Yamamoto, N. Tajima, M. Hagiwara, R. Kato and J.-I. Yamaura, *Synth. Met.* **135-136**, 623–624 (2003).

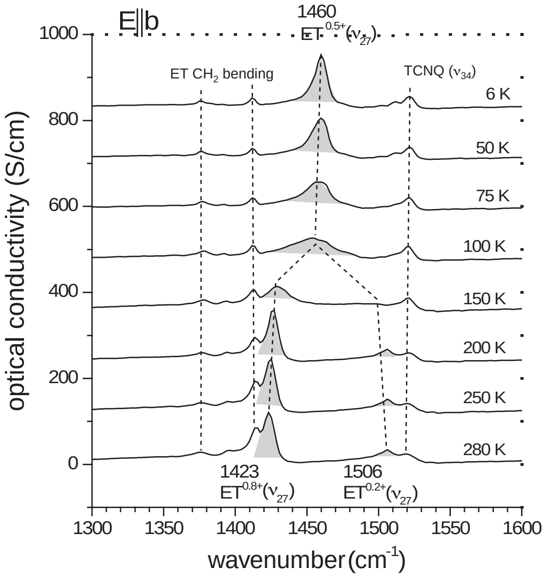

Figure 1. Temperature dependence of the infrared-active C=C stretching mode ν_{27}. The split bands merged at 100 K. This behavior was interpreted based on the motional narrowing model.

IV-A-8 Novel Type of $2k_F$ Bond-Charge-Density Wave in Quasi-One Dimensional 3/4 Filled $(EDO\text{-}TTF)_2X$ ($X = PF_6$ and AsF_6)

DROZDOVA, Olga; YAKUSHI, Kyuya; YAMAMOTO, Kaoru; OTA, Akira[1]; YAMOCHI, Hideki[1]; SAITO, Gunzi[1]
([1]Kyoto Univ.)

[*Phys. Rev. B* submitted]

Recently, charge ordering (CO) in organic charge transfer solids (CTS) has received considerable interest. In quasi-1D 1/4-filled organic CTS, a large on-site (U) and inter-site (V) Coulomb repulsion would cause, intuitively, the alternating (Wigner type) pattern of charge distribution '1010' corresponding to a $4k_F$ CDW. For V smaller than some critical $V_c \sim 2t$ (t being the intra-stack transfer integral) the '0110' ground state ($2k_F$ BCDW-I, Chart 1) can be found, while further small V would lead to $2k_F$ BCDW-II. Whereas $2k_F$ BCDW-I was found experimentally in some 1:2 TCNQ salts, $2k_F$ BCDW-II was characterized for the first time in $(EDO\text{-}TTF)_2X$ ($X = PF_6$ and AsF_6) below T_{MI} (268 K in PF_6 and 280 K in AsF_6). The stacking-axis optical conductivity spectrum at 300 K is consistent with the weak $4k_F$ BOW accompanied by *e-mv* coupling (Figure 1a). Below T_{MI} the spectrum is dominated by two charge transfer bands CT_1 and CT_2 corresponding to the electronic transition from the ground state (mainly, |0110>) to the first (|1100> (55%) and |1010> (41%)) and third (mainly, |0200>) excited states, respectively. The fact that CT_2 holds a large fraction of the total spectral weight in the nominally 1/4 filled $(EDO\text{-}TTF)_2X$ ($X = PF_6$ and AsF_6) is unique to $2k_F$ BCDW-II state and can be explained by a cooperation of large site charge difference and the type of BOW where the largest transfer integral connects two charge-rich sites. From the vibrational analysis of three charge-sensitive C=C stretching modes of EDO-TTF, the site charges below T_{MI} were estimated as +0.04 and +0.96. Besides, there is evidence for strong *e-mv* coupling of the out-of-phase mode of vibration of the central pair of molecules to CT_2, in both infrared and Raman spectra. A kind of relationship between the molecular charge, molecular deformation, and intermolecular π-π overlap is thought to play a role in stabilizing the $2k_F$ BCDW-II state.

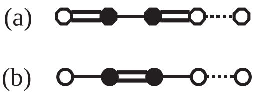

Figure 1. $2k_F$ BCDW-I (a) and $2k_F$ BCDW-II (b). Black and white circles represent charge-rich and charge-poor sites, respectively. The double, single and dotted lines denote the bond strength in descending order.

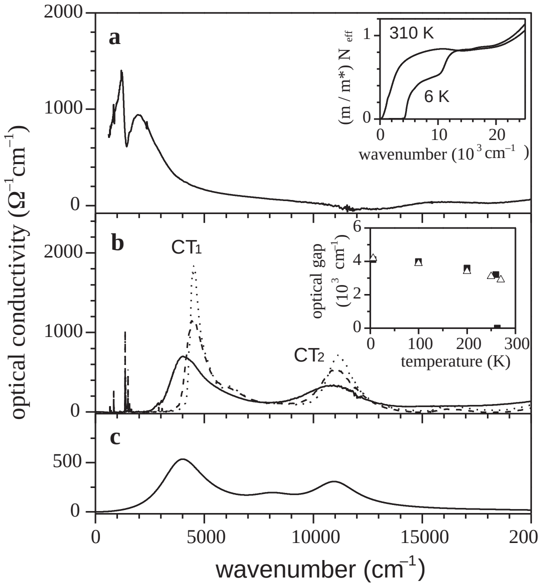

Figure 2. Stacking-axis optical conductivity spectra of $(EDO\text{-}TTF)_2PF_6$: (a) at 310 K; (b) at 270 K (solid line), 100 K (dashed line), and 6 K (dotted line); (c) spectrum calculated for a symmetric tetramer. Inset in (a) illustrates the sum rule calculation; inset in (b) the temperature dependence of the optical gap.

IV-A-9 Raman Spectra of $(Me_2\text{-}DCNQI)_2Cu_xLi_{1-x}$ ($0 \le x \le 1$)—Evidence for Charge Separation at Room Temperature in a One-Dimensional Conductor Having a Quarter-Filled Band

YAMAMOTO, Takashi[1]; TAJIMA, Hiroyuki[1]; KATO, Reizo[2]; URUICHI, Mikio; YAKUSHI, Kyuya
([1]Univ. Tokyo; [2]RIKEN)

[*J. Phys. Soc. Jpn.* **71**, 1956–1964 (2002)]

In the title alloys, the charge density on Me_2-DCNQI is expected to be varied as a function of x. These alloys are classified into three groups within $0 \le x \le 1$. For $x > 0.29$, the alloy is classified into three-dimensional metal down to the liquid helium temperature. For $x \le 0.14$, a (metal-)insulator-insulator transition is observed in the resistivity measurement, and the system falls down to a non-magnetic insulator below 60 K. For $0.14 < x \leq 0.29$, the system keeps a paramagnetic behaviour down to the liquid helium temperature, although a metal-insulator transition is observed in the resistivity measurement. Both groups ($x \leq 0.29$) are one-dimensional conductors. Observed physical properties for $x \leq 0.29$ around room temperature are interpreted in two different ways. One is a lattice dimerization through electron-phonon interaction, and another is the charge separation through Coulomb repulsion(s). Although the optical conductivity spectrum supports the latter, no direct evidence has been obtained. Raman spectroscopy is a powerful tool to evaluate the charge density on organic molecules. We have measured the Raman spectra of $(Me_2\text{-DCNQI})_2Cu_xLi_{1-x}$ ($0 \leq x \leq 1$) at room temperature, 200 K, 100 K and 5 K. The Raman band assigned to the a_g ν_{R8} fundamental mode (outer-ring C=N stretching) downshifts with an increase of x and exhibits a remarkable split for $0 \leq x \leq 0.29$. This frequency shift is attributable to the change of a charge density on a Me_2-DCNQI molecule. From the split of the ν_{R8} Raman band, it is concluded that charge disproportion occurs in $(Me_2\text{-DCNQI})_2Cu_xLi_{1-x}$ ($x \leq 0.29$) even at room temperature, where the system exhibits a metallic behaviour.

IV-A-10 Vanadyl Phthalocyanine as a High-Pressure Sensor

SUZUKI, Kenji[1]; YAMAMOTO, Kaoru; YAKUSHI, Kyuya
([1]GUAS)

The ruby fluorescence is a useful pressure sensor, which is commonly used in transparent high-pressure cell, such as diamond and sapphire anvil cells. Since this fluorescence is located at around 694 nm, it appears at around 1400 cm^{-1} in a Raman spectrum when HeNe laser (632.8 nm) is used as an exciting light. Since the strong fluorescence is close to the frequency of the C=C stretching mode, it disturbs the measurement of the Raman bands, even if the focused HeNe laser is not directly irradiated to the ruby. In order to avoid this problem, we looked for some vibrational modes of vanadyl phthalocyanine as a pressure sensor, and examined the pressure dependence of these Raman bands. Among the strong Raman bands of vanadyl phthalocyanine, the breathing mode of macrocycle at around 835 cm^{-1} showed a large blue shift upon applying high pressure. On the other hand, the C–H bending mode at around 1002 cm^{-1} showed no shift at all. Therefore, the frequency difference $\Delta\omega$ between the CH stretching and breathing modes was used as a scale to measure the pressure. Since both modes showed similar temperature dependence, the frequency difference was independent of temperature as shown in Figure 1. We proposed the equation to relate $\Delta\omega$ to P, which was shown in the inset of Figure 1.

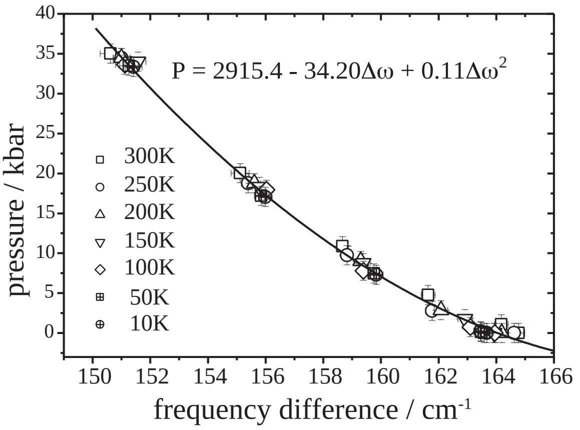

Figure 1. Pressure dependence of the frequency difference $\Delta\omega$ between the C–H bending mode (~ 1002 cm^{-1}) and the breathing mode of macrocycle (~ 835 cm^{-1}) in the Raman spectrum at various temperatures.

IV-A-11 Charge Ordering in the κ-Phase BEDT-TTF Salts with $Co(CN)_6$ and $Fe(CN)_6$ Anions Studied by Infrared and Raman Spectroscopy

SWIETLIK, Roman[1]; LAPINSKI, Andrzej[2]; OUAHAB, Lahcene[3]; YAKUSHI, Kyuya
([1]IMS and IMP, Poland; [2]IMP, Poland; [3]LCSIM-CNRS, France)

[*C. R. Acad. Sci. (Paris) Chimie* **3/6**, 395–403 (2003)]

We studied the temperature dependence of the Raman scattering spectra of two semiconducting isostructural charge-transfer salts κ-$[Et_4N](BEDT\text{-}TTF)_4M(CN)_6\cdot 3H_2O$ (M = Co^{III}, Fe^{III}) within the region of C=C stretching vibrations (1200–1700 cm^{-1}). Moreover, polarized reflectance spectra (600 to 10000 cm^{-1}) of the Co^{III} salt were recorded as a function of temperature and compared with previous infrared studies of the Fe^{III} salt. Both salts undergo a phase transition at T = 150 K related to a charge ordering inside the conducting BEDT-TTF layers. Due to the charge ordering new vibrational bands corresponding to BEDT-TTF^{+1} cations are recorded both in Raman and infrared spectra. Infrared electronic bands also experience strong modifications at 150 K: a new energy gap is formed and a new charge-transfer band in the near-infrared region is observed. The most important difference is that the charge redistribution in Fe^{III} salt is developed gradually below about 240 K, whereas in Co^{III} salt this is an abrupt process related to the phase transition at 150 K.