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 ferroelectric property. To detect CO states, we employ infrared and Raman spectroscopy. Some molecules have charge-sensitive intramolecular vibrational modes, the frequency of which shifts proportional to 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 of molecular charge. The goal of this study is (1) the understanding of the unusual electronic state of the conducting phase 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 Examination of the Charge-Sensitive Vibrational Modes in ET Molecule

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[*J. Phys. Chem. B* **109**, 15226 (2005)]

We re-investigated the two C=C stretching modes of the five-member rings of ET [ET = bis(ethylenedithio) tetrathiafulvalene], namely, ν_2 (in-phase mode) and ν_{27} (out-of-phase mode). The frequency of the ν_{27} mode of ET^+ was corrected to be ~1400 cm^{-1}, which was identified from the polarized infrared reflectance spectra of $(ET)(ClO_4)$, $(ET)(AuBr_2Cl_2)$ and the deuterium- or ^{13}C-substituted compounds of $(ET)(AuBr_2Cl_2)$. It was clarified from DFT calculations that the frequency of the ν_{27} mode of the flat ET^0 molecule was significantly different from that of the boat-shaped ET^0 molecule. We obtained the linear relationship between the frequency and the charge on the molecule, ρ, for the flat ET molecule, which was shown to be $\nu_{27}(\rho) = 1398 + 140(1–\rho)$ cm^{-1}. The frequency shift due to oxidation is remarkably larger than reported in previous studies. The fractional charges of several ET salts in a charge-ordered state can be successfully estimated by applying this relationship. Therefore, the ν_{27} mode is an efficient probe to detect ρ in the charge-transfer salts of ET. Similarly, the linear relationship for the ν_2 mode was obtained as $\nu_2(\rho) = 1447 + 120(1–\rho)$. This relationship was successfully applied to the charge-poor molecule of θ-type ET salts in the charge-ordered state, but could not be applied to the charge-rich molecule. This discrepancy was semi-quantitatively explained by the hybridization between the ν_2 and ν_3 modes.

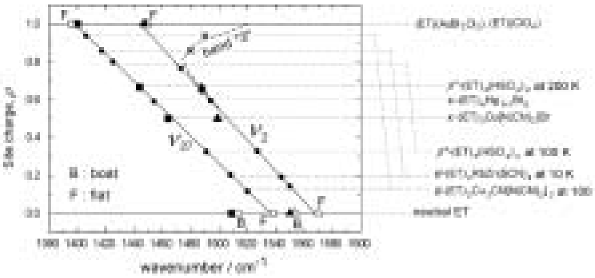

Figure 1. Frequencies of the ν_{27} and ν_2 modes plotted as a function of the charge, ρ, on the ET molecule. Solid squares and solid triangles denote the experimental data, and open squares and open triangles denote the calculation data. The straight lines show the linear relationships between the frequencies and ρ, deduced from least-squares fitting. The ρ value of the ET salts is inversely estimated from the linear relation and the data points thus obtained are indicated by solid circles. The broken line shows the ρ dependence of the band "3", and × denotes the frequencies of the *A*-symmetry mode of the θ-type ET salts.

IV-A-2 Infrared and Raman Studies of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$: Comparison with the Frozen State of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$

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[*J. Phys. Soc. Jpn.* **74**, 2631–2639 (2005)]

We present the optical conductivity and Raman spectra of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$. The vibrational and vibronic bands in the 1200–1600 cm^{-1} region was assigned with the aid of the ^{13}C-substituted compound. The nearly uniform charge distribution was found in a whole temperature range from 300 K to 6 K. However, the space group symmetry *I222* is locally broken already at room temperature. The broken symmetry suggests the resemblance to the high-temperature phase and frozen state of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, which consists of short-range ordered charge-ordering domains. The amplitude in the charge-ordering domain of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ is extremely small in a whole temperature range. At room temperature, hydrostatic pressure narrows the bandwidth of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ to enlarge the amplitude in short-ranged ordered domains. The long-range ordered charge ordering in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ was found at 10 K under the hydrostatic pressure of 2.5 GPa.

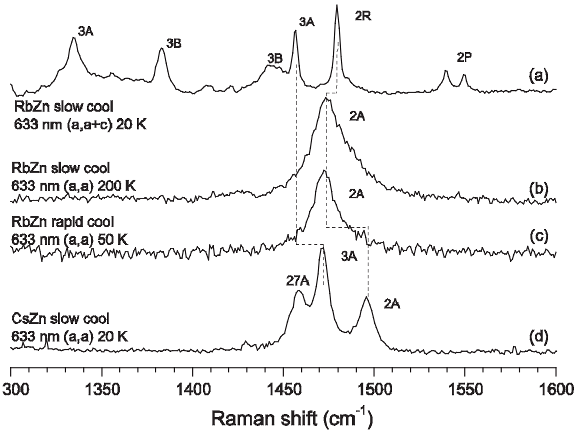

Figure 1. Comparison of the Raman spectra excited by 633 nm laser of slowly cooled RbZn measured at (a) 20 K (below T_{CO}) and (b) 200 K (above T_{CO}), (c) rapidly cooled RbZn measured at 50 K, and (d) slowly cooled CsZn measured at 20 K. ν_{2P} and ν_{2R} denote the ν_2 modes at charge-poor (ρ = 0.2) site and charge-rich (ρ = 0.8) site, respectively.

IV-A-3 Robust Superconducting State in the Low-Quasiparticle-Density Organic Metals β”-(BEDT-TTF)$_4$[(H$_3$O)*M*(C$_2$O$_4$)$_3$]·*Y*: Superconductivity due to Proximity to a Charge-Ordered State

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[*Phys. Rev. B* **72**, 014543 (13 pages) (2005)]

We report magneto-transport measurements on the quasi-two-dimensional charge-transfer salts β”-(BEDT-TTF)$_4$[(H$_3$O)*M*(C$_2$O$_4$)$_3$]·*Y*, with *Y* = C_6H_5NO and C_6H_5CN using magnetic fields of up to 45 T and temperature down to 0.5 K. A surprisingly robust superconducting state with an in-plane upper critical field $B_{c2||} \approx 33$ T, comparable to the highest critical field of any BEDT-TTF superconductor, and critical temperature $T_c \approx 7$ K is observed when M = Ga and $Y = C_6H_5NO_2$. The presence of magnetic *M* ions reduces the in-plane upper critical field to ≈18 T for M = Cr and $Y = C_6H_5NO_2$ and M = Fe and $Y = C_6H_5CN$. Prominent superconducting salts posses Fermi surfaces with one or two small quasi-two-dimensional pockets, their total area comprising ≤6% of the room-temperature Brillouin zone; the quasiparticle effective masses were found to be enhanced when the ion *M* was magnetic (Fe or Cr). The low effective masses and quasiparticle densities, and the systematic variation of the properties of the β”-(BEDT-TTF)$_4$[(H$_3$O)*M*(C$_2$O$_4$)$_3$]·*Y* salts with unit-cell volume points to the possibility of a superconducting ground state with a charge-fluctuation-mediated superconductivity mechanism such as that proposed by Merino and McKenzie [*Phys. Rev. Lett.* **87**, 237002 (2001)] rather than the spin-fluctuation mechanism appropriate for the κ-(BEDT-TTF)$_2$X salts.

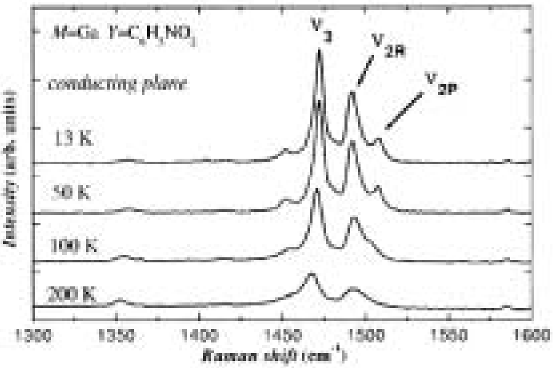

Figure 1. Raman spectra of β”-(BEDT-TTF)$_4$[(H$_3$O)Ga (C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$ taken at fixed temperature in the range 13 ≤ T ≤ 200 K. Note that the charge-sensitive ν_2 band shows a clear splitting, which suggests the CO state below 50 K in this compound.

IV-A-4 Influence of the Cooling Rate on Low-Temperature Raman and Infrared-Reflection Spectra of Partially Deuterated κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Br

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[*Synth. Met.* **149**, 13–18 (2005)]

Raman and infrared-reflection spectra of κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Br and its deuterated and partially deuterated analogues were measured at temperatures between 5 and 300 K and cooling rates from 1 to 20 K/min. It was found that, in partially deuterated samples, the interdimer electron-molecular vibration splitting of ν_3 mode in Raman spectra, and linewidths of some phonon peaks both in Raman and infrared spectra depend on the cooling rate. These observations were explained by disorder-related effects.

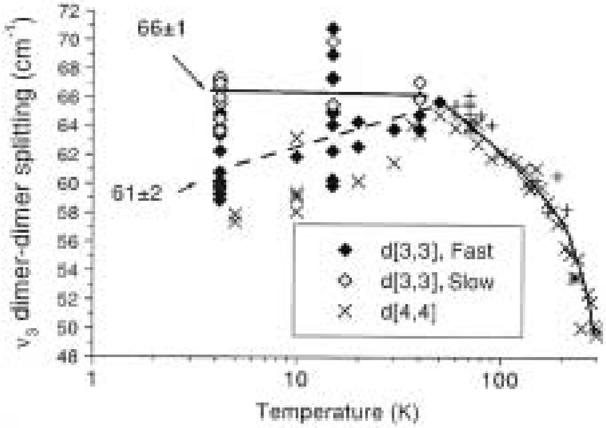

Figure 1. Temperature dependence of the dimer-dimer EMV (electron-molecular vibration) splitting of ν_3 for d(3,3) after "slow" cooling (◇), "fast" cooling (◆), and above 50 K (crosses, +). The results for d(4,4) are also shown (crosses, ×). Lines are guide to the eye.

IV-A-5 Optical Second Harmonic Generation in a Charge-Ordered Organic Conductor α-(BEDT-TTF)$_2$I$_3$

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Charge ordering (CO) in highly correlated CT complexes induces large modulation in the charge distribution. Since the modulation causes strong local polarization, it is suggested that such a polar state may show special features in dielectric properties, as ionic crystals do. In the present study, we investigated the nonlinear optical property of the title compound by means of the observation of second-harmonic generation (SHG). Near-IR ultra-short laser pulses were irradiated to a filmy single crystal as the excitation light, and the generated SH signal was detected in a transmission geometry.

It is known that this compound transforms from a semiconductor to an insulator at T_{CO} (135 K) due to CO. As shown in (Figure 1), the SH signal emerges below T_{CO}, indicating that the inversion symmetry, existing at high temperatures, is broken by the spontaneous polarization induced by CO below T_{CO}. The prominent feature of the highly correlated system is in the competition of several electronic phases. Therefore, understanding of the mechanism of CO and then finding the way to connect it with the optical nonlinearity discovered here are important to explore the potential application of the correlated materials as a unique nonlinear optical media.

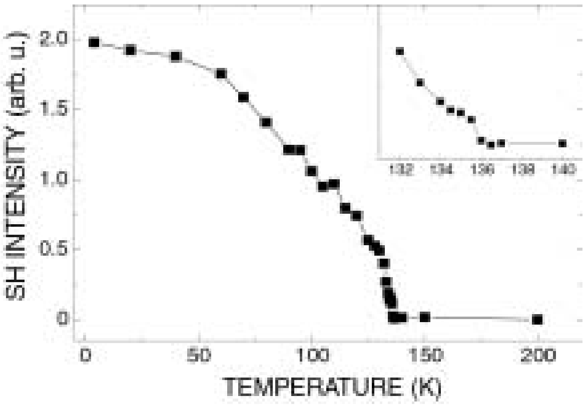

Figure 1. Temperature dependence of the intensity of second harmonic light from α-(BEDT-TTF)$_2$I$_3$. Inset shows the close-up of the data around T_{CO}.

IV-A-6 Correlation between Structural Instabilities and Raman Shift and Width in β-(ET)$_2$I$_3$ and κ-(ET)$_2$Cu[N(CN)$_2$]I

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Motivation of this study is to test the temperature dependence (Raman shift and width) of some selected intramolecular vibrations under the influence of both structural and electronic anomalies, in order to find a sensitive and reliable method to distinguish the nature clearly between such anomalies. For this purpose, we measured simultaneously the C=C modes of the ET molecule (ν_2 and ν_3, these are sensitive to ET geometry and local charge, as well as transfer integral), and CN mode of the polymeric anion (sensitive to structural effects only). Here we report the results obtained on the titled compounds because of possibility to directly compare the data with the published low-temperature structural studies.

(a) **β-(ET)$_2$I$_3$**: Anomalies in the Raman shift of ν_2 were found at 100 and 170 K, where superstructures are known to appear.1) No abnormality was observed in the Raman shift of ν_3 nor in the line width of the modes of ν_2 and ν_3.

(b) **κ-(ET)$_2$Cu[N(CN)$_2$]I**: Discontinuous jumps in the Raman shift (clear deviations from T^2 behavior) of both ν_2 and ν_3 (A_g), as well as ν(CN) were found at 155 and 220 K. These are characteristic temperatures where $0.5c^*$ and $0.38c^*$ superstructures are formed.2) In addition, a rapid increase in Raman shift of ν_2 was observed below 45 K. On the other hand, ν_2 (B_{2g}) showed approximately linear temperature dependence of an opposite sign, with a change of slope at 50 K. Further studies of κ-(ET)$_2$X compounds will be performed and compared with other physical properties.

References

1) T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, Springer 1998, and references therein.
2) M. A. Tanatar, V. S. Yefanov, S. Kagoshima, E. Ohmichi, T. Osada, N. D. Kushch and E. B. Yagubskii, *Phys. Rev. Lett.* submitted.

IV-A-7 Inhomogeneous Charge Distribution in (EDO-TTF)$_2$X (X = ReO$_4$ and GaCl$_4$)

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Recently synthesized organic conductors (EDO-TTF)$_2$X (where X = ReO$_4$ and GaCl$_4$) have quasi-one-dimensional (Q1D) crystal structure formed by two differently packed columns (A and B) of EDO-TTF alternated with chains of inorganic anion. Each column involves non-equivalent EDO-TTF molecules A1, A2, B1, and B2. The infrared spectra showed a phase transition at T^* = 125 K, where the Drude contribution disappeared, an optical gap opened, and a strong vibronic bands emerged. On the other hand, the Raman spectra were insensitive to T^*, and showed no essential change in the whole temperature region 300–4.2 K. The Raman-active C=C stretching vibrations of EDO-TTF, sensitive to the molecular charge, were split into several components (Figure 1). These were interpreted as an inhomogeneous charge distribution on the four sites in the unit cell. From the Raman shift frequencies, the respective site charge differences were found as A1 – A2 = 0.25*e*, and B1 – B2 = 0.1*e*. Charge localization was suggested as a driving force of the phase transition at 125 K.

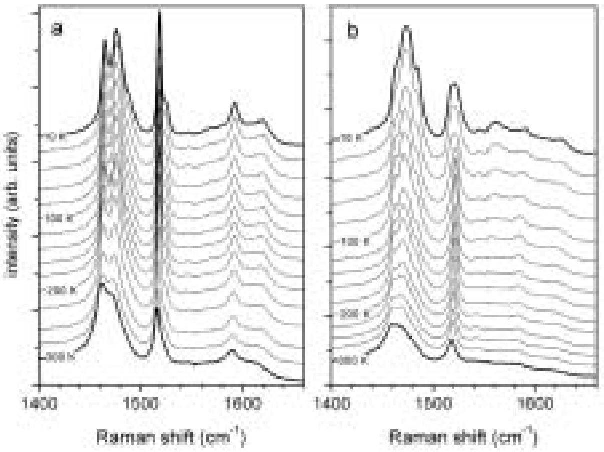

Figure 1. Temperature dependence of the Raman spectra of (a) (EDO-TTF)$_2$ReO$_4$ and (b) (EDO-TTF)$_2$GaCl$_4$.

IV-A-8 Re-Examination of the Site Charge Difference in TEA(TCNQ)$_2$

DROZDOVA, Olga; YAKUSHI, Kyuya

In 1/4-filled organic charge transfer salts (CTS) the charge ordered (CO) state is classified into 4k_F(0101) and 2k_F(0110) waves. The latter is further divided into 2k_F BCDW-I (○ ·· ○ = ● — ● = ○ ·· ○) and 2k_F BCDW-II (○ ·· ○ — ● = ● — ○ ·· ○), where the open circle has the charge of (1–Δ*q*)/2 and that at the solid circle has the charge of (1+Δ*q*)/2. We have recently analyzed the 2k_F BCDW-II state in (EDO-TTF)$_2$X (X = PF$_6$, AsF$_6$).[1)] TEA(TCNQ)$_2$ is regarded as a typical representative compound for 2k_F BCDW-I based on the x-ray crystal structure analysis. We analyzed the site charge distribution using vibrational analysis and determined Δ*q*. The Raman-active (gerade) modes of TCNQ were perturbed by *emv* coupling. Therefore we employed the IR-active (ungerade) modes. Cs$_2$(TCNQ)$_3$ compound was used as a reference. The results obtained at 300 K and 6 K are summarized in the Table 1.

Table 1. Estimation of the difference in site charge, Δ*q*.

TCNQ Mode	shift (per 1*e*) Δν cm^{-1}	Cs$_2$TCNQ$_3$		TEA(TCNQ)$_2$			
				300 K		6 K	
		obs. Δν cm^{-1}	charge difference Δ*q*	Δν cm^{-1}	Δ*q*	Δν cm^{-1}	Δ*q*
$b_{2u}\nu_{34}$ C=C	36	30	0.83	18	0.50	20	0.56
$b_{2u}\nu_{33}$ C≡N	75	50	0.67	44	0.59	47	0.63
$b_{1u}\nu_{19}$ C≡N	47	44	0.94	34	0.72	37	0.79
averaged site charge			0.78		0.61		0.66

Reference

1) O. Drozdova, K. Yakushi, K. Yamamoto, A. Ota, H. Yamochi, G. Saito, H. Tashiro and D. B. Tanner, *Phys. Rev. B* **70**, 075107 (2004).

IV-A-9 Spectroscopic Evidence for the Monovalent-to-Divalent Phase Transition of Biferrocenium (F$_1$TCNQ)$_3$

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([1]Toho Univ.)

[*J. Low Temp. Phys.* submitted]

The ionic crystal D$^+$A$_3^-$ (D = dineopentylbiferrocene and A = F$_1$TCNQ) undergoes a first-order phase transition, in which second ionization occurs to form a doubly ionized state, D^{2+}A$_3^{2-}$.[1)] As shown in the left panel of Figure 1, we found a dramatic change in the optical transition in the near-infrared region. This optical transition is interpreted as the charge-transfer excitation within the F$_1$TCNQ trimer. We simulated the optical transition employing a trimer model. First, the transfer integral and site energy within the F$_1$TCNQ trimer, A^{3-}, were estimated to reproduce the spectrum (oscillator strength and peak position) of 290 K. The site energy is introduced to take effectively the intra- and inter-trimer Coulomb interaction energy into account. Using the parameters thus obtained, the spectrum of A$_3^{2-}$ is simulated. As shown in the right panel of Figure 1, the change of this optical transition is quantitatively reproduced by the trimer model, in which the valence of the trimer changes from A$_3^-$ to A$_3^{2-}$. This result strongly supports the valence change character of this phase transition.

Reference

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).

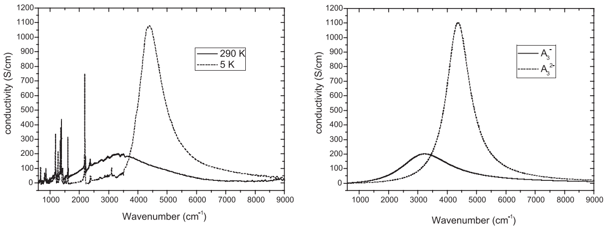

Figure 1. Optical conductivity spectra at 290 K and 5 K (left panel), and the Simulation based on a trimer model (right panel).

IV-A-10 Phase Separation in the Monovalent-to-Divalent Phase Transition of Biferrocenium-$(F_1TCNQ)_3$

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 gradually occurs in a wide temperature range from 160 K to 100 K. X-ray diffraction experiments showed that the Bragg spots consist of pairs of spots between 160 K and 100 K. One set is assigned to the unit cell of high-temperature phase and another is assigned to the low-temperature phase. On decreasing temperature, the intensities of the spots of high-temperature phase decreased and those of low-temperature phase increased. This observation is strong evidence for the phase separation in the temperature range of 160 K–100 K.

The Raman spectrum above 160 K also showed a big change below 100 K. When the laser is focused on the area of 2 μm diameter, the Raman spectrum shows position dependence: Only the monovalent peak (1446 cm^{-1}) is found in some area, while the divalent peak (1431 cm^{-1}) is found in other area, and both peaks are observed at the boundary of the two areas. The thickness of the boundary is estimated to be ~10–15 μm. In this boundary, the intensity ratio of the monovalent and divalent peaks changes gradually. The boundary area is so thick that may involve monovalent and divalent domains smaller than 2 μm. We mapped the 100 μm × 200 μm area at the phase-separation temperature. In this area, we observed only macroscopic domains, the size of which changes depending on the temperature.

The Raman spectrum and X-ray diffraction experiments described above showed that macroscopic domains of the monovalent and divalent phases coexist between 160 K and 100 K and the volume fraction of the two phases continuously changes in this phase-separation temperature region.

Reference

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).