

RESEARCH ACTIVITIES IV

Department of Molecular Assemblies

IV-A Spectroscopic Study of Organic Conductors

The reflectivity of an organic conductor provides us with a wealth of information on the electronic structure. For instance, the anisotropy of a band structure, band width, 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. Raman spectroscopy is a complementary method to reflection spectroscopy for understanding molecular vibrations (local phonons). We are investigating the charge ordering (CO) or charge disproportionation phenomena in organic conductors using the technique of vibrational spectroscopy. The charge ordering was found in inorganic narrow-band systems such as copper, manganese, and vanadium oxides. Recently, a charge-ordered ground state has been found in several organic conductors. The Raman and infrared spectra change dramatically at the CO phase transition temperature. Our goal is the complete understanding of the CO phase transition through the interpretation of the vibrational spectra.

IV-A-1 Charge Disproportionation of θ -(BEDT-TTF) $_2$ RbZn(SCN) $_4$ Studied by Raman Spectroscopy

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[*Synth. Met.* in press]

Charge-transfer radical salt θ -(BEDT-TTF) $_2$ RbZn(SCN) $_4$ undergoes a metal-to-insulator (MI) transition with a structural change as the temperature is slowly lowered. In the present study, the electronic structure has been investigated by Raman spectroscopy. The observed Raman spectrum around the characteristic frequency of C=C stretching shows noticeable variation accompanying the MI transition. The spectrum of the insulating phase provides multiple C=C stretching modes, though a BEDT-TTF molecule has only two Raman active modes relating to C=C stretching. The multiple peaks can be assigned in a systematic way based on the 2D tetramer model, in which the symmetry of the combination modes and charge disproportionation among four BEDT-TTF molecules are taken into consideration. The resultant assignment indicates the local arrangement of the charge forms a stripe pattern perpendicular to the molecular stacks.

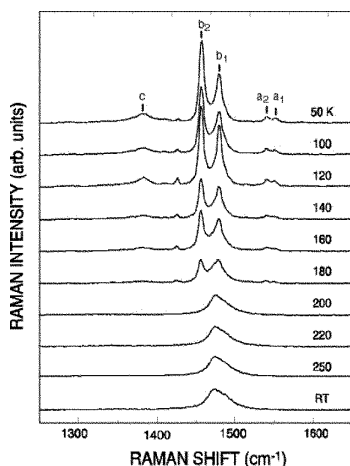


Figure 1. Temperature dependence of the Raman spectrum of θ -(BEDT-TTF) $_2$ RbZn(SCN) $_4$ observed on (101) surface.

IV-A-2 Isotope Shift and Charge Susceptibility of C=C Related Normal Modes of BEDT-TTF Molecule

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We have been developing a method to apply vibrational spectroscopy to the investigation of the spatial charge distribution formed in two-dimensional charge ordering systems. One of the most troublesome problems to the end is in the difficulty in the spectral assignment, owing to the charge-dependent reconstruction of normal modes formed by the combination of vibrations of several chemical bonds. The decisive method to assign the spectrum is the inquiry of the isotope shift. Its interpretation requires thorough knowledge on the relation among the normal mode reconstruction, degree of ionization, and isotope replacement. In the present study, we have investigated the characteristics of the normal modes relating to the C=C bonds of BEDT-TTF by measuring the isotope shift of the Raman and infrared reflectance spectra. It has been recognized as an established argument that the relevant two symmetric C=C modes are constructed from the combinations of two types of C=C bonds, *i.e.*, the ring and central C=C vibrations, in the neutral BEDT-TTF, and the two vibrations are completely separated to form the distinct normal modes in the monocationic state. However, the present study indicates that BEDT-TTF in a nearly monocationic state provides the normal modes based on the combinations of the two C=C stretching modes. It turns out that the replacement of the carbon atoms of the central C=C bond by ¹³C results in the complete separation of the two types of modes in the relevant normal modes of the nearly monocationic BEDT-TTF.

IV-A-3 Raman-Active C=C Stretching Vibrations of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br

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κ -(BEDT-TTF)₂X salts are the most extensively investigated charge-transfer salts including Raman and IR spectra. Nevertheless some principal and strong lines in their Raman spectra are not unambiguously assigned yet. We measured the resonant Raman spectra of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, κ -(BEDT-TTF)₂Cu(CNS)₂, and their several isotopic analogues in the region of C=C stretching vibrations with various combinations of polarizations. There exists a big (~ 50 cm⁻¹) factor group splitting for the ν_3 mode, which is assigned mainly to the stretching of the central C=C bond in a BEDT-TTF molecule. The splitting is ascribed to the inter-dimer e - mv interaction inside a conducting layer. The Raman-active e - mv coupled ν_3 mode appears in the $b(a,c)b$ spectrum with a broad linewidth, low-frequency shift, and a characteristic temperature dependence. The temperature dependence of the frequency this mode is very different from that of the infrared-active intra-dimer e - mv coupled ν_3 mode. An analogous splitting is found for ν_2 of ¹³C(2) compound (see Figure 1, bottom). However in a ¹²C(2) crystal, ν_2 and ν_3 provide additional splittings that cannot be explained by a simple factor group analysis. We suppose that a crystal symmetry changes through the C¹²-C¹³ substitution. These unusual results are still puzzling for us.

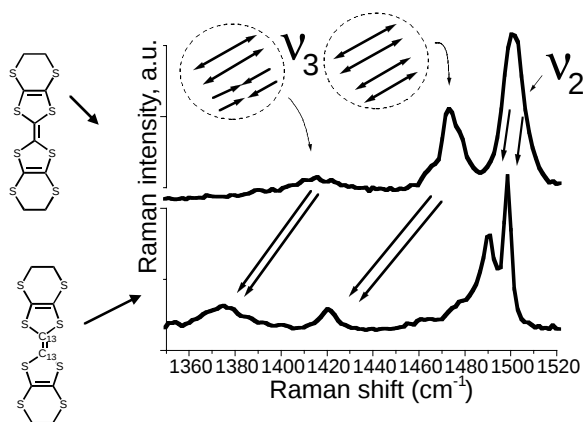


Figure 1. Raman spectra of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (top) and κ -(¹³C(2)-BEDT-TTF)₂Cu[N(CN)₂]Br (bottom). In the latter, the two central carbon atoms in the BEDT-TTF molecule are replaced by ¹³C. As a result ν_3 mode is shifted to low-frequency side. Laser polarisation is parallel to the c -axis.

IV-A-4 An Influence of the Cooling Rate to the Raman and IR Spectra of Partially Deuterated κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

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The set of progressively deuterated isotopic analogues of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br lies on the

border between a metal and insulator in the phase diagram of κ -type BEDT-TTF salts. It is known that the cooling rate from 80 K to 50 K influences the volume fraction of the metallic and antiferromagnetic domains in the crystal.

We examined the cooling rate dependence in the Raman and IR spectra of d[0,0], d[2,2], d[3,3], and d[4,4] single crystals, where the numbers denote the deuterium numbers in each ethylene group of BEDT-TTF. In d[0,0], d[4,4] crystals, no cooling rate dependence was found. On the other hand, in d[2,2], d[3,3], we found a cooling rate dependence for (1) factor group splitting of the ν_3 mode, (2) resonance enhancement of the ν_3 intensity, and (3) linewidths of some phonons both in the Raman and infrared spectra. Probably, all these phenomena are associated with the inhomogeneous metal-antiferromagnet domain structure.

Unlike d[3,3], the crystal d[2,2] shows a big sample dependence. The cooling rate was equally important in the 50–150 K range, although the cooling rate in the 50–80 K range was reported to be much more effective to the dc conductivity than that in 80–150 K. For the C=C stretching modes, we found no annealing effect that has been regarded to influence the dc conductivity. Besides, we found no cooling-rate dependence in the optical conductivity at least above 100 cm⁻¹.

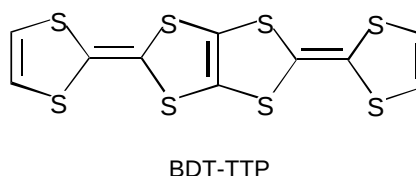
IV-A-5 Spectroscopic Evidence for the Charge Disproportionation in a Two-Dimensional Organic Conductor, θ -(BDT-TTP)₂Cu(NCS)₂

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[Phys. Rev. B in press]

We present spectroscopic evidence for the charge disproportionation in the crystal of θ -(BDT-TTP)₂Cu(NCS)₂. θ -(BDT-TTP)₂Cu(NCS)₂ is a highly correlated organic conductor with a quasi-two-dimensional electronic structure. In the electrical resistance of this compound, we found a second-order like phase transition at 250 K. Below this phase transition temperature, the optical absorption in the mid-infrared region exhibits a broadening of the energy gap. The Raman active C=C stretching modes ν_2 , ν_3 , and ν_4 , which are sensitive to the charge on BDT-TTP, split into seven sharp bands and four broad bands. Using the resonance effect, the sharp bands were classified into two groups. At 5 K these groups are reasonably assigned to the charge-poor and charge-rich BDT-TTP molecules. This is direct evidence for the charge disproportionation accompanying the phase transition.



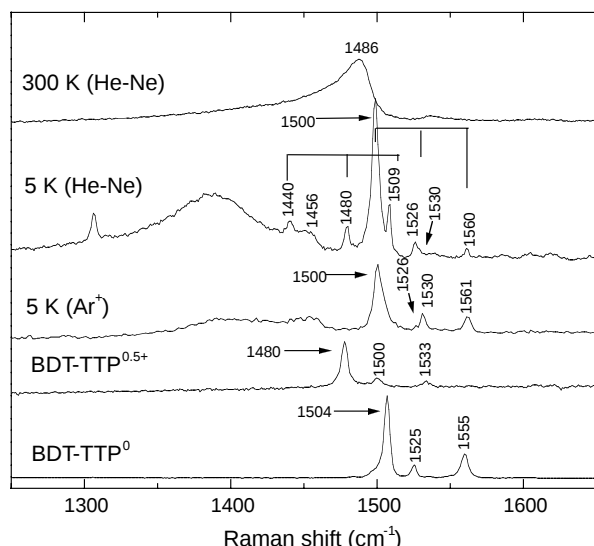


Figure 1. The Raman spectra of the C=C stretching region at 300 K and 5 K in the θ -(BDT-TTP) $_2$ Cu(NCS) $_2$ crystal, below which the room-temperature spectra of (BDT-TTP) $_2$ AsF $_6$ and BDT-TTP crystals are displayed. The sharp bands at 5 K is classified into two groups as shown in this figure.

IV-A-6 ESR Properties of a Quasi-Two-Dimensional Organic Conductor, θ -(BDT-TTP) $_2$ -Cu(NCS) $_2$

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As shown in IV-A-5, θ -(BDT-TTP) $_2$ Cu(NCS) $_2$ undergoes a phase transition accompanying the charge disproportionation. To investigate the magnetic properties, particularly below the phase transition temperature (T_p), we conducted the angular dependence of the g value at 8.5 K around the three crystallographic axes and the temperature dependence of the intensity, g value, and linewidth. The principal axes obtained from the angular dependencies along the a^* , c - and b -axes agreed within 11° with those calculated from the principal axes of the molecule. The principal g values are 2.0026, 2.0046, and 2.0130, which requires the principal g values of the molecule as 2.0129, 2.0053, and 2.0022 along the long, short, and normal axes. This means that the hole is located on the both sides of herring bone.

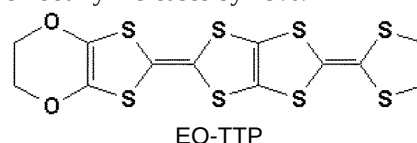
On lowering temperature, the linewidth rapidly decreases from 70 G (300 K) to 10 G (200 K) and levels off below 200 K. We consider that this temperature dependence of the linewidth is associated with the second-order phase transition at 250 K. Below 200 K, the spin susceptibility approximately follows a Bonner-Fisher behavior with $J \sim 8$ K down to ~ 5 K. Below 5.2 K a sudden drop is observed for the ESR intensity. We consider this behavior as a magnetic phase transition to a non-magnetic state.

IV-A-7 Infrared Spectroscopic Study of the Band Structure of (EO-TTP) $_2$ AsF $_6$

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Ethylenedioxy substituted BDT-TTP (EO-TTP) produced a number of organic metals with tetrahedral and octahedral anions.¹⁾ (EO-TTP) $_2$ AsF $_6$ has β -type donor array and shows metallic conductivity down to 1.5 K. Polarized IR reflectance spectra on the conductive (010) plane display well-defined plasma edges along ($E||a$) and ($E||c$) directions suggesting two-dimensional (2D) while highly anisotropic band structure. We have experimentally estimated intra- (t_a) and inter-stack (t_c) transfer integrals as -0.229 and 0.047 eV, respectively. These transfer integrals yield Fermi surface open in k_C direction while strongly warped. On the contrary, theoretical calculation ($t_{a1} = -0.269$, $t_{a2} = -0.252$, $t_c = 0.091$ eV) largely overestimates t_c and gives closed Fermi surface, similar to what was found earlier in (BDT-TTP) $_2$ X (X = SbF $_6$, AsF $_6$) compounds.²⁾ On lowering temperature down to 13 K, t_a smoothly increases by $\sim 9\%$.



References

- 1) Y. Misaki, K. Tanaka, M. Taniguchi, T. Yamabe, T. Kawamoto and T. Mori, *Chem. Lett.* 1249 (1999).
- 2) J. Ouyang, K. Yakushi, Y. Misaki and K. Tanaka, *J. Phys. Soc. Jpn.* 67, 3191 (1998).

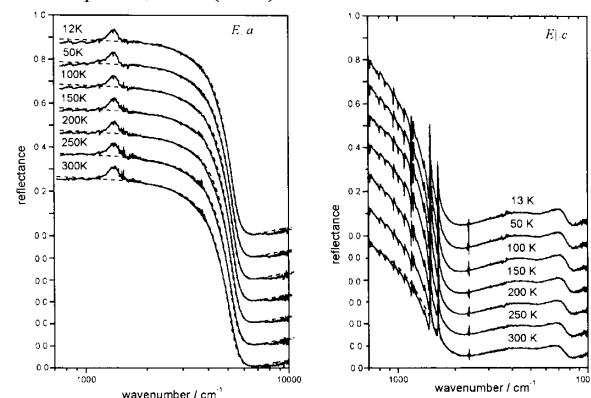


Figure 1. Temperature dependence of IR reflectivity of (EO-TTP) $_2$ AsF $_6$ along a - and c -axes. Solid line, experiment; dashed line, Drude-Lorentz model.

IV-A-8 Optical Properties and Metal-Insulator Transitions in Organic Metals (BEDT-ATD) $_2$ X-(solvent) (X = PF $_6$, AsF $_6$, BF $_4$; solvent = THF, DHF, DO)

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We present the polarized reflection spectra of (BEDT-ATD) $_2$ X(solvent) (X = AsF $_6$, PF $_6$, BF $_4$; solvent = THF, DHF, DO), where THF is tetrahydrofuran, DHF 2,5-dihydrofuran, and DO 1,3-dioxolane. BEDT-ATD $^+$

has an intra-molecular excitation in a very low-energy region (4000–5000 cm^{-1}). These isostructural compounds are characterized as strongly correlated quasi-1D metals. The optical spectra in all these compounds suggest that the screw-axis symmetry is broken below the metal-insulator transition temperature. This broken symmetry is confirmed by the X-ray diffraction experiment in $(\text{BEDT-ATD})_2\text{BF}_4(\text{THF})$ and $(\text{BEDT-ATD})_2\text{PF}_6(\text{DHF})$. The low-temperature structure has the $4k_F$ -modulated lattice (dimerized

structure). The magnetic susceptibility also supports this $4k_F$ modulation. We present the low-temperature crystal structures of $(\text{BEDT-ATD})_2\text{BF}_4(\text{THF})$ and $(\text{BEDT-ATD})_2\text{PF}_6(\text{DHF})$. BF_4^- and THF are fully ordered in $(\text{BEDT-ATD})_2\text{BF}_4(\text{THF})$ and DHF is almost ordered in $(\text{BEDT-ATD})_2\text{PF}_6(\text{DHF})$. The vibronic modes are observed in the reflection spectra of all these compounds even above the metal-insulator transition temperature, which suggests that the screw-axis symmetry is locally broken.

IV-B Solid State Properties of Organic Conductors with π -d Interaction

Some phthalocyanine molecules contain unpaired d-electrons in the conjugated π -electron system. Due to this nature, the itinerant π -electrons coexist with localized unpaired d-electrons in solid phthalocyanine salts, in which a one-dimensional double-chain system (metal and ligand chain) is formed. Furthermore these chains make up wide (π -band) and narrow (d-band) one-dimensional bands. The energy of the narrow band is close to the Fermi energy of the wide band. The phthalocyanine conductor is thus a two-chain and two-band system. The electronic structure of phthalocyanine conductors is analogous to that of the f-electron system, in which a narrow f-band coexists with a wide s-band and they are hybridized near the Fermi level. To understand the electronic structure of this two-band system, we are investigating the charge-transfer salts of NiPc and CoPc and their mixed crystals.

IV-B-1 Magnetic Exchange Interactions in Quasi-One-Dimensional Organic Alloy of $\text{Co}_{0.01}\text{Ni}_{0.99}\text{Pc}(\text{AsF}_6)_{0.5}$

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[Phys. Rev. B in press]

We have continued to study the ESR properties of $\text{Co}_x\text{Ni}_{1-x}\text{Pc}(\text{AsF}_6)_{0.5}$ to obtain the magnitude of the magnetic exchange interaction between local spins of Co^{2+} ions and itinerant spins of Pc-ligands. Subsequently to the finding of the hyperfine structure in a insulating phase of $\text{Co}_{0.01}\text{Ni}_{0.99}\text{Pc}(\text{AsF}_6)_{0.5}$ below 30 K, we analyzed the temperature dependence of the g value and linewidth in a metallic phase. In this phase, the d- and π -spins are coupled by the exchange interaction. This coupling brings about a bottle-neck state in the spin-relaxation process and yields a single Lorentzian line shape for the ESR signal. We used a molecular field approximation which has been used to interpret the ESR line shape of a dilute alloy. Based on the simulation of the temperature dependence of the g value and line shape, we obtained the exchange interaction as $J = 0.013 \pm 0.002$ eV) and the density of states at Fermi level as $D_F = 3.8 \pm 0.2$ eV^{-1} . From these parameters, we can roughly estimate the Kondo temperature as $T_k \sim 10^{-5}$ K. This means that the exchange interaction between d- and π -spins are extremely small.

IV-B-2 Pressure Dependence of Resistivity in Quasi-One-Dimensional Conductor $\text{CoPc}(\text{AsF}_6)_{0.5}$

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At ambient pressure, $\text{CoPc}(\text{AsF}_6)_{0.5}$ shows a broad resistivity minimum at room temperature, which is exceptional among the metallic phthalocyanine conductors. The crystal is so sensitive to temperature that it shows multiple resistivity jumps below 200 K. High pressure suppressed the resistivity jump and allowed us for the first time to conduct the resistance-vs.-temperature measurement. As shown in the figure, a metallic phase expands to lower temperature when we increase the pressure. This pressure dependence is different from the analogous compound $\text{NiPc}(\text{AsF}_6)_{0.5}$, in which a metal-insulator transition temperature increased from 40 K to room temperature upon increasing pressure. A hump was found at 75 K at 0.3 GPa, which shifted to high-temperature side upon increasing pressure. Finally, under 0.9 GPa, $\text{CoPc}(\text{AsF}_6)_{0.5}$ became metallic down to 100 K.

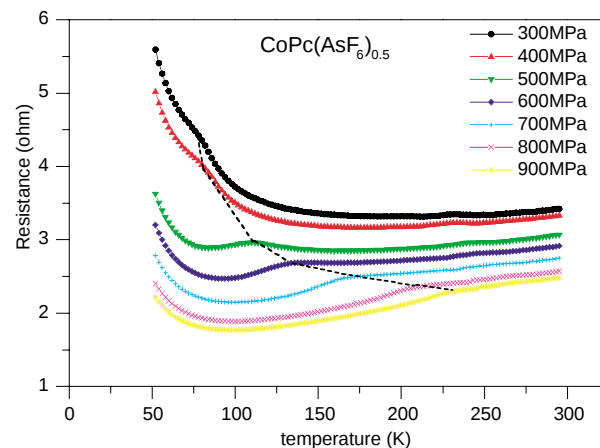
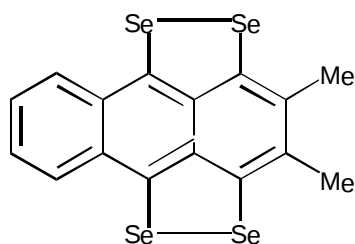


Figure 1. Temperature dependence of the resistance of $\text{CoPc}(\text{AsF}_6)_{0.5}$

IV-B-3 Antiferromagnetic Phase Transition of DMTSA-FeCl₄

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We found isostructural charge-transfer salts of DMTSA which involves magnetic and non-magnetic counter anions, (DMTSA)FeCl₄ and (DMTSA)GeCl₄. Both compounds are semiconductors, room-temperature resistivities being $3 \times 10^1 \Omega\text{cm}$ for the FeCl₄ salt and $2 \times 10^2 \Omega\text{cm}$ for the GeCl₄ salt. We found from the magnetic susceptibility of the oriented crystals that the former compound showed an antiferromagnetic phase transition at 12.0 K. DMTSA and FeCl₄ forms an mixed stacked structure, which is often found in an ionic crystal. The network of a magnetic interaction seems to be formed by the Se-Se and Se-Cl and Cl-Cl interactions. The heat capacity shows an anomaly near the phase transition temperature. By comparing with the heat capacity of (DMTSA)GeCl₄, the contribution of lattice phonons were subtracted. The magnetic heat capacity ranges from 25 K to < 2 K, which suggests a low-dimensional magnetic interaction. The entropy change during this phase transition was close to $R \ln 6$. This result means that the magnetic moment of Fe²⁺ ($S = 5/2$) mainly contributes to the antiferromagnetic ordering.



DMTSA