IV-C Microscopic Investigation of Molecular-Based Conductors

One of the most remarkable features of molecular-based conductors is taking various electronic phases. Especially, the competition of the ground states is one of the crucial problems of them. Although detailed electronic structure of them are not clear so far, these curious behaviors are believed to be originated from their characteristic natures; highly electronic correlation.

To clarify the low temperature electronic states, we performed the static susceptibility, EPR, ^{1}H- and ^{13}C-NMR measurements for molecular based conductors.

IV-C-1 Low-Temperature Electronic States in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$: Competition of Different Ground States

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[*Synth. Met.* **103**, 1898 (1999)]

Magnetic properties of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ were studied. The compounds of this family are expected to be 2D-metals with a quarter-filled band. However the title salt undergoes a M-I transition around 190 K. The mechanism of the M-I transition and the low-temperature electronic states of the θ-type are not known. To clarify the electronic states of the low-temperature non-metallic phase and the mechanism of the M-I transition, we performed SQUID, EPR, ^{1}H- and ^{13}C-NMR measurements.

The low temperature behavior of the spin susceptibility, χ_{spin}, was found to depend on the cooling speed around 190 K. The EPR linewidth, ΔH_{pp}, analyses show that a phase transition exists around 190 K, and that the electronic state realized by the rapid-cooling is a meta-stable state. In the case of slow-cooling, the electron spin concentration exponentially decreases through the formation of spin-gap, and only residual spins concern the NMR relaxation. In the case of rapid-cooling, a large enhancement of the NMR-T_1^{-1} was observed below 90 K where the χ_{spin} shows an abrupt increase. These facts suggest that the NMR relaxation is caused by dilute local magnetic moments. The quenched state may be understood as a new-type charge localization. A small amount of chemical doping caused pronounced influence on the electronic states. The sensitivity to impurities suggests that this spin-singlet state may be a low-dimensional phenomenon. The EPR relaxation rate measurements show a spin-gap even in the doped system.

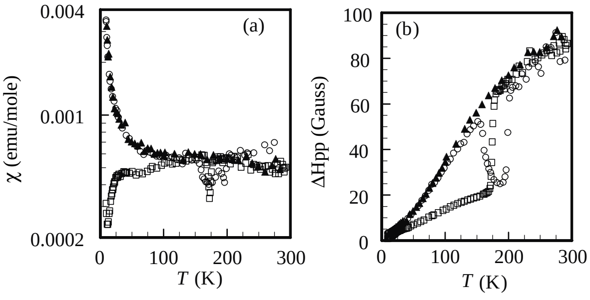

Figure 1. Temperature dependence of the (a) χ_{spin}, and (b) ΔH_{pp} along the *a*-axis (slow-cooling (open square), rapid-cooling (open circle) and the MT 5% doped salt (solid triangle)).

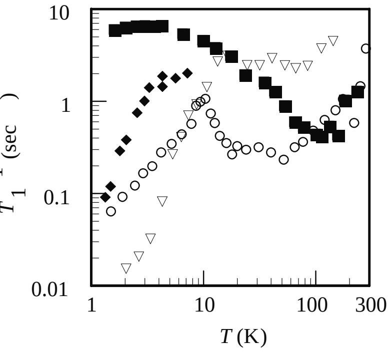

Figure 2. Temperature dependence of the NMR-T_1^{-1} under slow-cooling (^{1}H-T_1^{-1} (circle), ^{13}C-T_1^{-1} (triangle)) and rapid-cooling (^{1}H-T_1^{-1} (square), ^{13}C-T_1^{-1} (diamond)).

IV-C-2 Magnetic Properties of a New Two-Chain Organic Conductor: (CPDT-STF)-TCNQ

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[*Synth. Met.* **103**, 1900 (1999)]

(CPDT-STF)-TCNQ is a new organic conductor based on TCNQ and CPDT-STF where CPDT-STF is one of selenium-containing analogs of DT-TTF. Although the resistivity shows a metallic behavior down to 0.5 K, the spin susceptibility, χ_{spin}, is Curie-like at low temperatures. The purpose of the present study is to clarify the origin of the paramagnetic moments from microscopic points of view. Between 50 K and 300 K, the *g*-values gradually change with temperature. This indicates that the relative contributions to χ_{spin} of the CPDT-STF and TCNQ stacks are significantly temperature dependent. The decomposition of the χ_{spin} of (CPDT-STF)-TCNQ into the contributions of CPDT-STF, χ_D, and TCNQ, χ_A, was performed. The χ_A shows Curie-like behavior up to at least 200 K, indicating the existence of local moments on the TCNQ stacks. The spin concentration determined from the Curie constant is about 0.17 per formula unit assuming $S = 1/2$. On the other hand, the χ_D is almost temperature independent, suggesting a Pauli paramagnetism on the CPDT-TTF layers. It is quite natural that the metallic conduction is attributed to the itinerant electron on the CPDT-STF.

The nature of the local moments on TCNQ is now an open question. The spin concentration is different from the case of (BEDT-TTF)-TCNQ, where one spin per TCNQ dimer is localized. Experiments to address this problem are in progress.

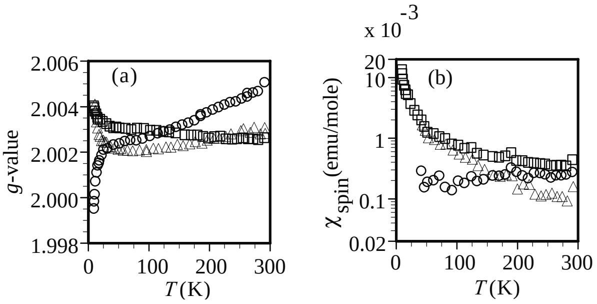

Figure 1. (a) Temperature dependence of the g-values (//a* (square), //b* (circle), //c*(triangle)). (b) Temperature dependence of the total $\chi_{\rm spin}$ (square), and separate contributions of CPDT-STF (circle), TCNQ (triangle)).

IV-C-3 ESR and NMR Investigation of β'-R_4Z-[Pd(dmit)$_2$]$_2$

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[*Synth. Met.* **103**, 2142 (1999)]

β-type Pd(dmit)$_2$ salts and related salts show non-metallic behavior at ambient pressure. They undergo an antiferromagnetic transition, and that the paramagnetic states at ambient pressure should be considered as a Mott-Hubbard insulator. However, several problems remain unsolved; ^{1}H-NMR investigations showed the antiferromagnetic states possesses a small local magnetization. The local magnetizations and transition temperatures, $T_{\rm N}$, are different between the Pd(dmit)$_2$ and the selenium-containing analogs Pd(dmise)$_2$ based salts. The main aim of this study is to clarify the anti-ferromagnetic states by systematic investigations of Pd(dmit)$_2$ salts. Figure 1 shows the temperature dependence of the EPR parameters of the Et$_2$Me$_2$P salts. The abrupt decrease of the $\chi_{\rm spin}$ and the divergence of the $\Delta H_{\rm pp}$ around 18 K obviously show the existence of the magnetic order. The observed g-tensor cannot be explained by that of single Pd(dmit)$_2$ molecule. We believe that this is due to the strong dimer structure of the Pd(dmit)$_2$ based organic conductors. The $T_{\rm N}$ and the amplitude of antiferromagnetic local moments determined by ^{1}H-NMR shows a close correlation with the cation size. The $T_{\rm N}$ seems to decrease as the inter-dimer interaction within stacks decreases. The Et$_2$Me$_2$-Sb salt, of which the inter-dimer interactions within stacks is comparable to those between stacks, shows no antiferromagnetic order down to 7 K. The detailed analysis is now going on.

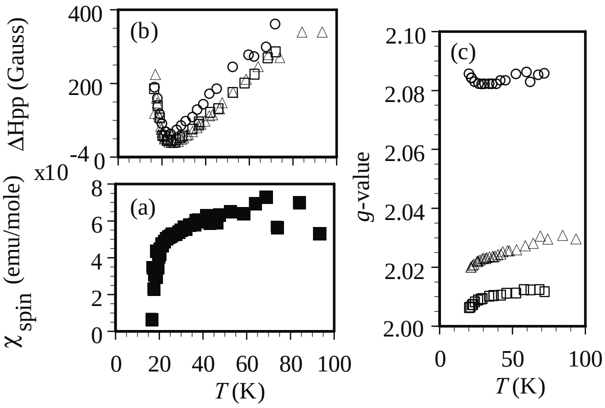

Figure 1. Temperature dependence of (a) the spin susceptibility, $\chi_{\rm spin}$, determined by EPR intensity, (b) the EPR linewidth, $\Delta H_{\rm pp}$, and (c) the g values (//a* (square), //b* (circle), //c* (triangle)).

IV-C-4 New Type Charge Localization in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$

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[*J. Phys. Soc. Jpn.* submitted]

^{1}H-NMR, EPR and static magnetic susceptibility measurements have been performed on an organic conductor, θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$. The ^{1}H-NMR-T_1^{-1} and the spin susceptibility exhibit anomalous enhancements at low temperatures. Around 20 K, where the spin susceptibility shows a minimum, the principal axes of the EPR g-tensor changed their directions, keeping the principal values constant. It indicates a possible change of the electronic nature. The low-temperature electronic state is discussed.

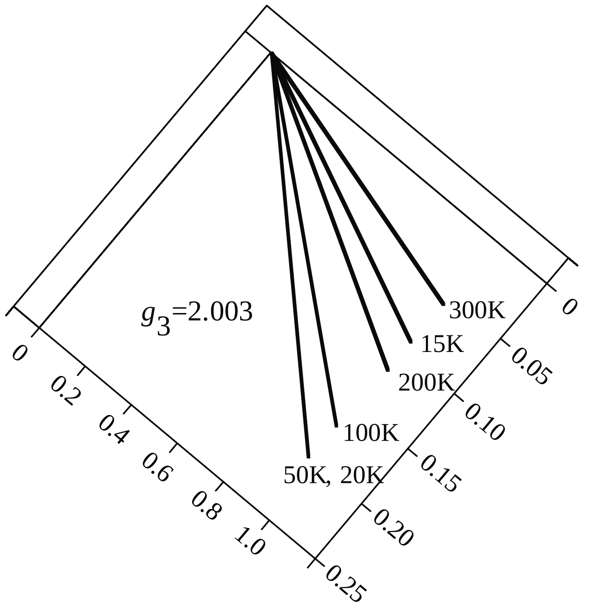

Figure 1. Temperature dependence of the direction of the principal axes of the g-tensor; magnificated the scale for g_3 (top of view) at typical temperatures.

IV-D Thermodynamic Study of Organic Conductors

In order to get reliable information on the electron density of states and entropy distribution around various types of phase transitions, specific heat studies are inevitable. In this project, we aim at constructing several types of calorimeters available at low-temperatures and under magnetic fields and performing systematic investigation on organic materials from a thermodynamic viewpoint.

IV-D-1 Electronic Ground States of (BEDT-TTF)$_2$X System Studied by Specific Heat Measurements

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[*Synrh. Met.* **103**, 1903 (1999)]

The 2:1 organic salts, (BEDT-TTF)$_2$X, give a variety of electronic phases such as metallic, superconductive, spin/charge density wave and antiferromagnetic insulating phases, etc. due to the variation of the molecular arrangement in the donor layers. The efforts to inquire into the origin and the peculiar features of the electronic structure of these phases have been widely made in these days, since they provide numerous interesting information of the condensed matter physics related to low-dimensional, low carriers and strongly correlated systems. Systematic studies to get an overall picture on the relationship between donor arrangement and the electronic ground states produced by π-electrons is now being performed from both experimental and theoretical viewpoints. In this study, we compare the low-temperature specific heat behavior of several 2:1 salts consist of BEDT-TTF molecules in order to get a systematic understanding of these π-electron systems from the thermodynamic viewpoint. Figures 1 and 2 show typical specific heat curves of metallic salts and Mott insulating salts, respectively. Although one can find finite γ term in the metallic samples, the Mott insulating salts does not have any electronic contribution in C_p/T vs T^2 curves at low-temperatures due to formation of charge-gap by the electron correlation effect.

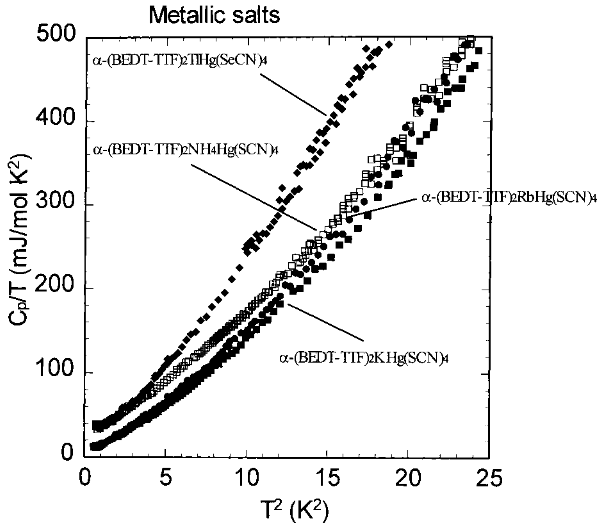

Figure 1. C_p/T vs T^2 plot of several metallic salts of (BEDT-TTF)$_2$X.

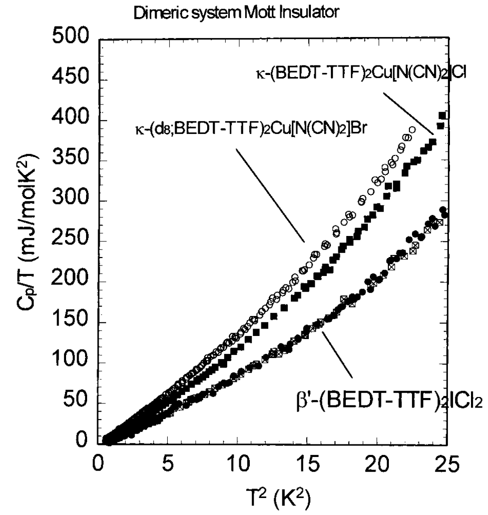

Figure 2. C_p/T vs T^2 plot of Mott insulating salts of (BEDT-TTF)$_2$X.

IV-D-2 Thermodynamic Investigation of the Electronic States of Deuterated κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Br

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[*Phys. Rev. B* **60**, 4263 (1999)]

The low-temperature specific heat of the deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br situated in the critical region of the Mott transition in the κ-(BEDT-TTF)$_2$X systems was measured after different cooling processes, which are known to affect the superconducting volume fraction from the resistivity and the magnetic susceptibility measurements. Temperature and magnetic field dependences of the electronic specific heat do not show distinct variation by changing cooling rate from 0.07 K/min to 50 K/min and under magnetic field up to 6 T. We show in Figure 1 the low-temperature data obtained by a dilution refrigerator cooled down with the rates of 0.07 K/min, 0.8 K/min and 1.7 K/min from room temperature down to 4.2 K. The electronic specific heat coefficient, γ is found to be 0–1 mJ/molK^2 in all three curves and this values are much smaller than those of bulk superconducting materials of hydrogenated X = Cu[N(CN)$_2$]Br and Cu(NCS)$_2$.

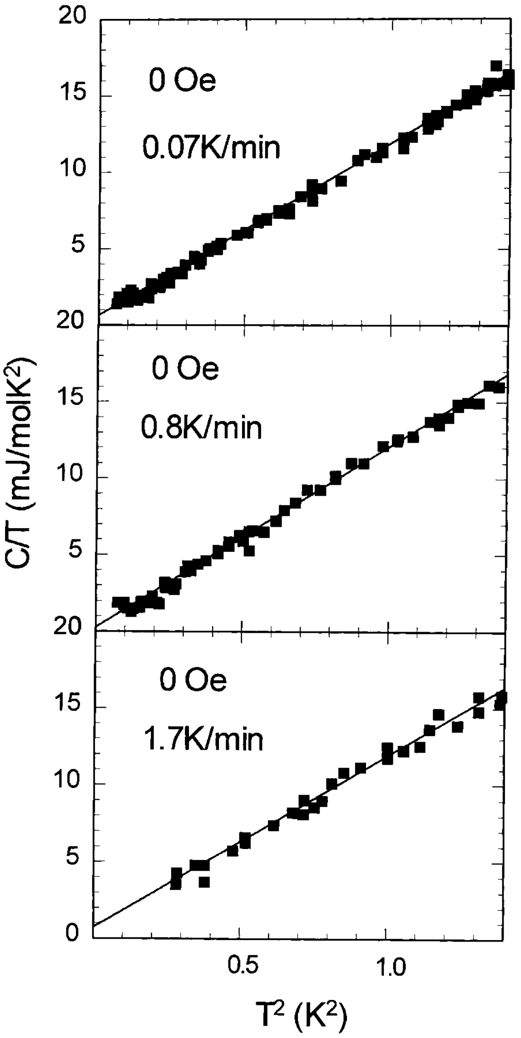

Figure 1. Low-temperature specific heat curves of κ-(d_8;BEDT-TTF)$_2$Cu[N(CN)$_2$]Br cooled down at different rates of 0.07, 0.8, and 1.7 K/min.

IV-D-3 Electronic Specific Heat at the Boundary Region of Mott Transition in Two-Dimensional Electronic System of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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The electronic specific heat studies of partially deuterated single crystals of organic conductors κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br which are situated across the critical boundary of band-width control type of Mott transition in two dimension are performed at low-temperatures below 3 K and under magnetic fields up to 10 T. In order to see the variation of normal-state electronic density of states near the transition, we had gradually access to the M-I boundary with the progressive dueteration of BEDT-TTF molecules and found that the electron density of states or effective mass in the metallic states diminishes towards the Mott boundary. This is in fine contrast to the case of V_2O_3, where the Brinkmann and Rice's prediction of electron mass enhancement occurs in the critical region. This result is marked a basis for the future study of electronic feature related to the unconventional superconductivity and also on the universality and variation of the Mott transition in two dimensional systems.