IV-B Magnetic Resonance Studies for Molecular-Based Conductors

Magnetic resonance measurements are powerful investigations to understand the fundamental electronic properties, because they are microscopic and also dynamical measurements. Molecular based conductors are one of the extensively studied materials. The development of the understanding of the electronic phases of these materials enables us systematic investigations of low-dimensional highly correlated electrons systems. Competition of the electronic phases in molecular based conductors has attracted much attention. The investigations of such electronic phases by means of magnetic resonance measurements are important to understand the unsolved fundamental problems in the field of solid state physics.

In this project, we performed the multi-frequency ESR (X-, Q- and W-bands), and broad-line NMR measurements for molecular based conductors to understand the electron spin dynamics in the low temperature electronic phases.

IV-B-1 Competition Electronic States of $(TMTTF)_2MF_6$: ESR Investigations

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ESR measurements were performed to investigate the low-temperature electronic states of $(TMTTF)_2MF_6$ (M = P, As, Sb and their mixed alloys). The temperature dependence of the ESR linewidth, ΔH_{pp}, of AsF_6 does not change its anisotropy at around T_{sp}. On the other hand, PF_6 and some P-AsF_6 alloys show changes of the ΔH_{pp} anisotropy at around T_{sp}, suggesting reconstruction of electronic charges. We propose the possible charge ordering configuration in the vicinity of the low temperature ground states from the ESR point of view.

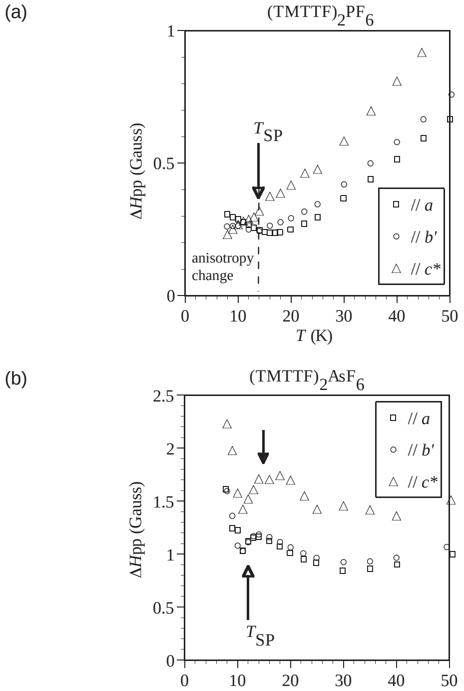

Figure 1. (a)–(b) Temperature dependence of the linewidth, ΔH_{pp}, for (a) PF_6 and (b) AsF_6 in the vicinity of the sP transitions.

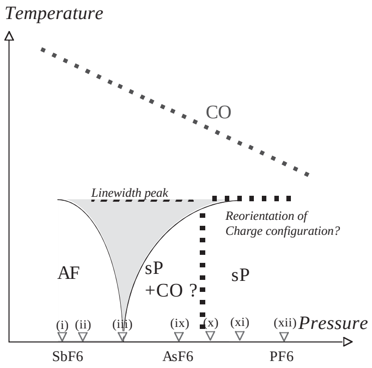

Figure 2. Schematic diagram of the possible electronic phases with the compositions (chemical pressures) for the MF_6 and their alloys deduced by the ESR results; (i)SbF_6, (ii) $(AsF_6)_{0.2}(SbF_6)_{0.8}$, (iii) $(AsF_6)_{0.5}(SbF_6)_{0.5}$, (ix) AsF_6, (x) $(PF_6)_{0.3}(AsF_6)_{0.7}$ (xi) $(PF_6)_{0.6}(AsF_6)_{0.4}$ and (xii) PF_6.

IV-B-2 ESR Study on Low-Dimensional Antiferromagnet α-$(BEDT\text{-}TTF)_2PF_6$ and ζ-$(BEDT\text{-}TTF)_2PF_6(THF)$

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ESR measurements were carried out for α-$(BEDT\text{-}TTF)_2PF_6$ and ζ-$(BEDT\text{-}TTF)_2PF_6(THF)$. The temperature dependences of the spin susceptibility of the two salts are very similar to each other and seem to behave as typical paramagnetic insulators with low-dimensional antiferromagnetic interaction. The absolute values of the macroscopic antiferromagnetic interaction, J/k_B, are also very close. However, there are obvious differences in their ground states and microscopic behaviours. ζ-$(BEDT\text{-}TTF)_2PF_6(THF)$ undergoes an antiferromagnetic transition at around 5 K, while α-$(BEDT\text{-}TTF)_2PF_6$ shows no long-range magnetic ordering down to 2 K. The temperature dependent behaviours of the ESR linewidth, ΔH_{pp}, are quite different: The ΔH_{pp} of ζ-$(BEDT\text{-}TTF)_2PF_6(THF)$ is almost temperature independent in the paramagnetic region and shows an abrupt increase below about 30 K, while the ΔH_{pp} of α-$(BEDT\text{-}TTF)_2PF_6$ gradually decreases as the temperature decreases. The low temperature electronic states of these salts are discussed from the microscopic point of view.

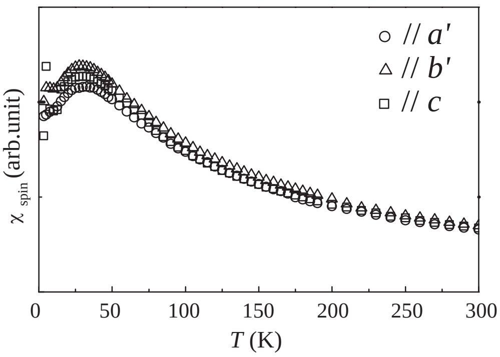

Figure 1. Temperature dependence of the spin susceptibility of α-(BEDT-TTF)$_2$PF$_6$. The exchange interaction, J/k_B, is about 27 K evaluated from the Bonner-Fisher model. This behavior is in good agreement with the static susceptibility measured by SQUID.

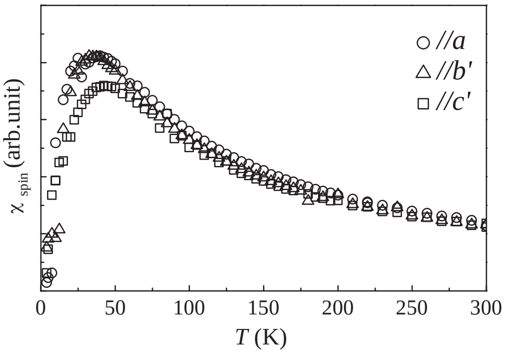

Figure 2. Temperature dependences of the spin susceptibility of ζ-(BEDT-TTF)$_2$PF$_6$(THF). The exchange interaction, J/k_B, is about 25 K.

IV-B-3 Multi-Frequency ESR Measurements for (TMTTF)$_2$*X*

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TMTTF family salts are now attracted attention by the recent progress of the charge ordering (CO) investigations. Recently, we proposed the possible charge ordering configurations for each of (TMTTF)$_2X$ salts according to the difference of the ESR linewidth anisotropy at low temperatures. The CO configurations of (TMTTF)$_2X$ are roughly divided into three groups, and this classification is consistent with the results determined by other measurements. However the origin of the charge ordering phenomena is not clarified, and the quantitative understanding of the ESR linewidth is not succeeded so far. So we performed multi-frequency (X- [10 GHz], Q- [30 GHz], and W-bands [100 GHz]) ESR measurements for one of typical TMTTF salts, (TMTTF)$_2$SbF$_6$, which shows the charge ordering transition at 154 K. The ESR linewidth determined by the W-band measurement is obviously larger than that by X-band below the charge ordering transition. We discuss the low temperature electron spin dynamics from the ESR point of view.

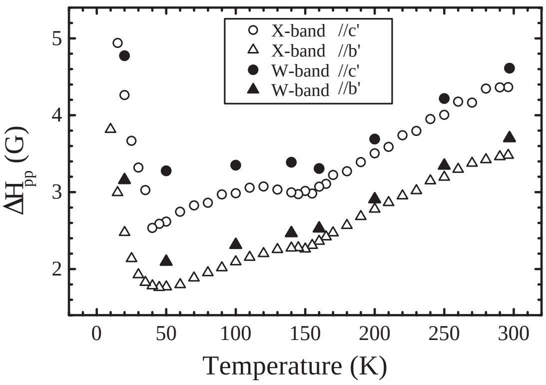

Figure 1. Temperature dependence of the ESR width, ΔH_{pp}, of (TMTTF)$_2$SbF$_6$ determined by X- (open symbols) and W-bands (solid symbols).

IV-B-4 Correlation between Molecular and Spin Structures of (TMTTF)$_2$*X*

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The *g*-values of organic conductors are determined by the *g*-tensor of the radicals and their configuration. So the *g*-values of the crystal generally do not change with temperature. According our recent detailed ESR measurement, the *g*-values of the several TMTTF salts shows significant change with temperature, although these salts do not indicate structural changes. In order to understand the anomalous *g*-shift, we performed molecular orbital calculation with the Gaussian03, and estimated the *g*-values by the GIAO method. According to the calculation results, we found that the deformation of the TMTTF molecules along the molecular long axis cause a *g*-shift toward to an uni-axial symmetry. We can explain the anomalous *g*-shift observed if we assume the shrink of the TMTTF molecules along the molecular long-axis as the temperature decreases. Further structural investigation such as low-temperature X-ray measurements are now going on.

IV-B-5 Dynamical Charge Disproportionation in Metallic State in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$

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Results of ^{13}C-NMR experiments on charge ordering in non-dimerized BEDT-TTF salts are discussed. It has been experimentally confirmed in θ-(ET)$_2$RbZn(SCN)$_4$ that charge disproportionation already develops well above the metal-insulator transition temperature while no long-range charge order is stabilized. Dynamics of the charge fluctuations has been determined in this salt and compared with the situations in α-(ET)$_2$I$_3$. This result seems to require a serious reconsideration of the transport properties in the metallic state.

IV-B-6 Charge Disproportionation in the Metallic States of α-(BEDT-TTF)$_2$I$_3$

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[*J. Phys. IV France* **114**, 399–400 (2004)]

^{13}C-NMR measurements have been carried out on the quasi two-dimensional organic conductor, α-(BEDT-TTF)$_2$I$_3$. We measured the angular dependence of ^{13}C-NMR spectrum at several temperatures above metal-insulator transition temperature, 135 K (= T_{MI}). We found that charge (spin) disproportionation already exists in the metallic state and gradually develops as temperature approaches to T_{MI}.