μSR study of the stabilization mechanism of antiferromagnetic state in molecular π-d system λ-(BEDT-STF)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$

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In some molecular conductors, the coexistence of strongly correlated π electrons and localized $3d$ spins is realized by introducing magnetic molecules, such as $FeCl_4^-$ and $FeBr_4^-$, as anion molecules. Such coexistent systems are known as π-d systems. In π-d systems, the magnetic interactions between strongly correlated π electrons and localized $3d$ spins (π-d interaction) give rise to interesting magnetic and conducting properties.

λ-(BEDT-STF)$_2$FeCl$_4$, where BEDT-STF denotes bis(ethylenedithio)dithiadiselenafulvalene, exhibits an antiferromagnetic ordering at 16 K.[1,2] In the alloy compound of λ-(BEDT-STF)$_2$Fe$_{0.2}$Ga$_{0.8}$Cl$_4$, an antiferromagnetic ordering is observed at 8 K. In contrast, λ-(BEDT-STF)$_2$GaCl$_4$ shows no magnetic ordering down to 300 mK. These results indicate that the introduction of π-d interaction stabilizes the antiferromagnetic ground state. However, the stabilization mechanism has not yet been demonstrated. This study aims to clarify the stabilization mechanism of the antiferromagnetic ground state induced by π-d interaction.

In this study, we performed zero field (ZF) μSR measurements below 10 K and longitudinal field (LF) μSR measurements at base temperature and 10 K for λ-(BEDT-STF)$_2$Fe$_{0.1}$Ga$_{0.9}$Cl$_4$ (Fe-0.1) and λ-(BEDT-STF)$_2$Fe$_{0.05}$Ga$_{0.95}$Cl$_4$ (Fe-0.05), respectively.

Figure 1 shows the temperature dependence of the ZF time spectra of Fe-0.1 and Fe-0.05. In this analysis, we fitted the time spectra by the following functions.

$$A(t) = A_0\exp(-\lambda_0 t) + G_{\mathrm{KT}}(t) + A_{\mathrm{bg}}, \quad (1)$$

$$A(t) = A_1\exp(-\lambda_1 t) + A_2\cos(\omega t + \phi)\exp(-\lambda_2 t) + A_{\mathrm{bg}}, \quad (2)$$

$$A(t) = A_3\exp(-\lambda_3 t) + A_4\exp(-\lambda_4 t) + A_{\mathrm{bg}}. \quad (3)$$

Here, A_i and λ_i denote the initial asymmetries and relaxation rates, respectively. A_{bg} is the background contribution derived from the muons stopped in the sample holder. $G_{\mathrm{KT}}(t)$ is the Kubo-Toyabe function. ω and ϕ are the precession frequency and phase of muon spin precession, respectively. The time spectra measured at high temperatures were fitted using Eq. (1), and those of Fe-0.1 and Fe-0.05 measured below 7 K were fitted using Eqs. (2) and (3), respectively.

We confirmed that the shape of the ZF time spectra of Fe-0.1 changes below 7 K, suggesting that an antiferromagnetic transition occurs around 7 K. In contrast, no clear change was observed in the shape of the ZF time spectra down to 1.5 K for Fe-0.05. As complementary experiments, we performed ^{13}C NMR measurements for λ-(BEDT-STF)$_2$Fe$_{0.05}$Ga$_{0.95}$Cl$_4$ and confirmed that no peak was observed in the temperature dependence of the spin-lattice relaxation rate ($1/T_1$) down to 4 K. These suggest that T_{N} of Fe-0.05 is lower than 4 K or does not exist and antiferromagnetic ordering is drastically stabilized in the small Fe content region below $x = 0.1$. These results are consistent with theoretical studies suggesting that the antiferromagnetic ground state is stabilized even for small π-d interactions.[3] However, our results indicate that there exists a phase boundary between the no- and antiferromagnetic-ordered states in the low Fe content region between $x = 0$ and 0.1, which is different from the theoretical prediction. Detailed analysis regarding the development of internal fields from the results of μSR time spectra and comparison with the results of theoretical studies are in progress.

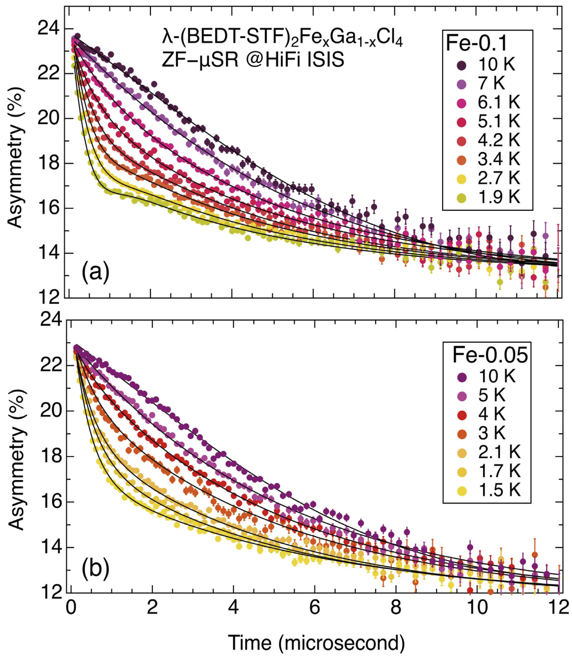

Fig. 1. Temperature dependence of the ZF time spectra of (a) Fe-0.1 and (b) Fe-0.05.

References

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