Spin Dynamics of Novel Charge Transfer Phase Transition in Iron Mixed-Valence Complex, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = $C_2O_2S_2$, n = 3, 5) by μSR

M. Enomoto[1], N. Kida[1], I. Watanabe[2], T. Suzuki[2] and N. Kojima[1]

[1] *Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan*

[2] *Advanced Meson Science Laboratory, RIKEN Nishina Center, Wako, Saitama 351-0198, Japan*

In the case of iron mixed-valence complexes whose spin states are situated in the spin-crossover region, conjugated phenomena coupled with spin and charge are expected. In general, the Fe site coordinated by six S atoms is in the low spin state, while the Fe site coordinated by six O atoms is in the high spin state. From this viewpoint, we have investigated the magnetic properties of the iron mixed-valence complexes, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = $C_2O_2S_2$, n = 3, 5), in which not only a ferromagnetic transition but also a novel charge transfer phase transition (CTPT) with spin-transition between Fe^{II} and Fe^{III} take place. The spin states of the $[Fe^{II}Fe^{III}(dto)_3]$ layer strongly depends on the size of intercalated cation. The CTPT takes place for n = 3 and 4, while it does not take place between 4 and 300 K for n = 5. The low temperature phase with $Fe^{II}(S = 0)$ and $Fe^{III}(S = 5/2)$ causes the ferromagnetic transition at T_C = 7 K for n = 3, while the high temperature phase with $Fe^{II}(S = 2)$ and $Fe^{III}(S = 1/2)$ gives one at 19.5 K for n = 5, respectively. Muon spin relaxation (μSR) measurement is one of the most powerful probe for the investigation of the dynamical process of CTPT. In this presentation, we report the measurements of the relaxation process of μSR for the ferromagnetic transition of n = 3 and 5 and the CTPT of n = 3.

As shown in Fig. 1, the depolarization rates of the zero-field μSR exhibit peaks at 15 and 22 K for n = 3 and 5, respectively. These strong enhancements are due to the critical slowing down of the fluctuations of Fe spins toward the ferromagnetic transition. Moreover, an anomalous enhancement with thermal hysteresis in the depolarization rate is observed between 60 and 140 K for n = 3, while there is no peak around that temperature region for n = 5. The temperature range of the anomalous enhancement of the depolarization rate for n = 3 corresponds to that of the hysteresis loop in the magnetic susceptibility as shown in the inset of Fig. 1. Moreover, the longitudinal field dependence of the depolarization rate gives a detailed information on the dynamic properties of the electron-transfer. Judging from the analysis of the field dependence of time spectrum, the anomalous enhancement in the zero-field μSR was concluded to be due to the oscillation of electron-transfer between the Fe^{II} and Fe^{III} sites caused by the CTPT [1].

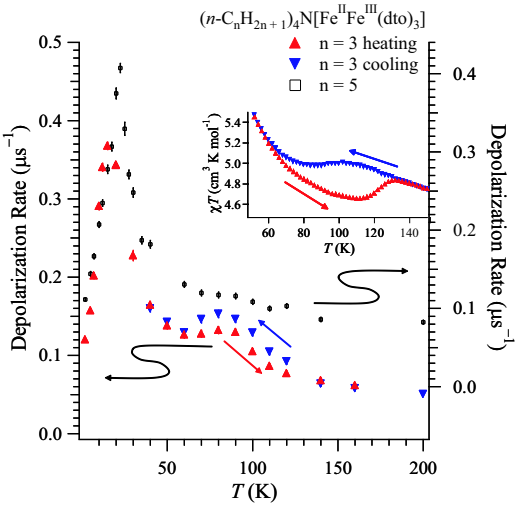

Fig. 1 Temperature dependences of the dynamic muon-spin depolarization rate.

[1] (a) N. Kida, et al., *Phys. Rev.* **B 77** (2007) 144427., (b) N. Kojima, et al., *RIKEN Accel.Prog. Rep.*, **40** (2007) v.