

Antiferromagnetic ordering of λ -(BEST)₂FeCl₄ observed by μ SR measurement

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In the organic conductor λ -(BETS)₂FeCl₄ (see Fig. 1 for BETS), there is a significant strong exchange interaction between the 3d electrons of Fe ions, and π electrons of BETS molecules, *i.e.*, π -d interaction. This results in exotic properties such as a field-induced superconductivity¹⁾ and a metal-insulator transition with antiferromagnetic (AF) ordering, where 3d electrons are paramagnetic even below the AF transition temperature indicated by the heat capacity measurement.²⁾ To understand these phenomena, a deep understanding of the π -d interaction mechanism is required. As a clue to this, the magnetism of λ -(STF)₂FeCl₄ has been recently evaluated. As shown in Fig. 1, the STF molecule is a molecule in which part of the selenium in the BETS molecule is replaced by sulphur. Magnetisation, NMR, and Mössbauer measurements showed that λ -(STF)₂FeCl₄ exhibits AF ordering at 16 K, where both 3d and π electrons are ordered, whereas further development of the internal magnetic field owing to the polarized magnetisation of the 3d spins was observed below 8 K.³⁻⁵⁾ In addition, μ SR measurements demonstrated that the slow precession signals due to the AF order of π -electrons and the fast precession signals due to the polarization of 3d spins appear from different temperatures. The magnetic properties that appeared when the BETS molecule was replaced by the STF molecule are thought to be caused by changes in the π -d and d-d interactions. Therefore, to evaluate the relationship between the molecular substitution and the change in the π -d interaction, we focused on the substitution from BETS to BEST molecules (see Fig. 1 for BEST). Because the electron density of the outer chalcogen atoms is small, the expansion of the orbitals by the substitution from S to Se is expected to cause steric hindrance and reduce the π -d interaction.

According to the reported magnetisation measurement of λ -(BEST)₂FeCl₄, it exhibits paramagnetic behaviour down to 4 K.⁶⁾ However, because the observed spin susceptibility is dominated by 3d spins, the magnetism of π spins is almost concealed. To reveal the magnetic order of the 3d and π electrons, a microscopic measurement that can sensitively detect the internal field is necessary.

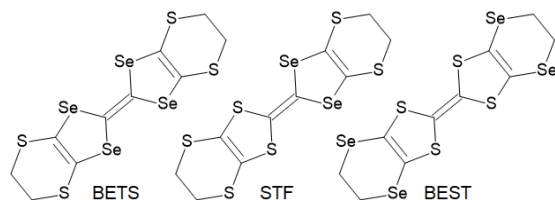


Fig. 1. Structures of donor molecules.

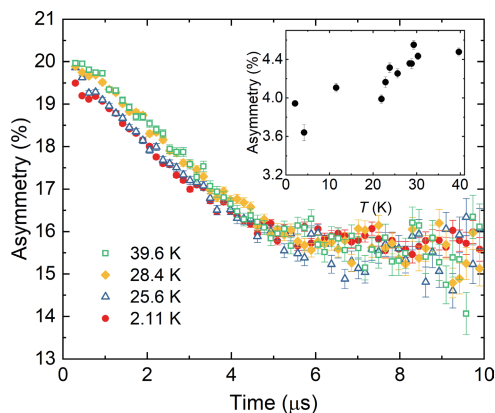


Fig. 2. Zero-field μ SR time spectra of λ -(BEST)₂FeCl₄. Inset: temperature dependence of initial asymmetry.

For this purpose, we performed μ SR measurements on λ -(BEST)₂FeCl₄.

Figure 2 shows the μ SR time spectra at several temperatures. We observed that the initial asymmetry changes abruptly between 28.4 K and 25.6 K. The time spectra $A(t)$ are fitted by the stretched exponential function, $A(t) = A \exp[-(\lambda t)^\beta] + A_{bg}$, where A and A_{bg} are the asymmetries due to the muons stopped inside the sample and at the sample holder, λ is the relaxation rate, and β is the stretched exponent, respectively. From this analysis, we deduced that the initial asymmetry A indeed decreases below ~ 30 K, as shown in the inset of Fig. 2, although its transition temperature is not clear. Because the AF order of π spin was also observed in λ -(BEST)₂GaCl₄ consisting of nonmagnetic Ga ions, the change in the initial asymmetry observed in λ -(BEST)₂FeCl₄ can be understood by the AF order. In fact, the disappearance of the paramagnetic EPR signal was observed at 25 K in recent ESR measurements, suggesting an AF transition.

Compared to λ -(STF)₂FeCl₄, it is interesting to know whether the fast precession signal due to the polarization of 3d spins is observed or not. Within our experimental error, no significant spectral change was observed from 25.6 K to 2.11 K, suggesting that only the π spins are magnetically ordered. In λ -(BETS)₂FeCl₄, unlike λ -(BEST)₂GaCl₄, the anisotropy of the magnetic susceptibility was observed with AF transition. Therefore, we confirmed that the magnetic state of λ -(BEST)₂GaCl₄ is different from that of λ -(BETS)₂FeCl₄ and λ -(STF)₂FeCl₄. These results provide important clues for the mechanism of π -d interaction.

References

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