Magnetic ground state of Cu₆O₈MCl (M = Y, Pb) with a caged structure

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Cu₆O₈MCl (M=cation) compound has a Cu₆O₈ cage which forms a three-dimensional Cu-O network by connecting their faces in its crystal structure ¹. The formal Cu valence in the Cu₆O₈ cage is +2.15 for M = Pb⁴⁺ and +2.33 for M = Y³⁺, suggesting the existence of Cu⁺(3d⁹), Cu²⁺(3d⁸) with S = 1/2 spin, and Cu³⁺(3d⁷) ². If there is partial existence of S = 1/2 spins on the Cu site in the Cu₆O₈ cage, the static magnetic ordered state is expected in the square-lattice and the dynamical spin fluctuation in the triangular-lattice i.e., the magnetic competition state is expected in the magnetic ground state of Cu₆O₈MCl. To elucidate the detailed physical properties of Cu₆O₈MCl, we focused on clarifying the magnetic ground states of Cu₆O₈PbCl, which is the semiconducting material, and compared the observed data with the based material of Cu₆O₈YCl, which is the metallic compound with paramagnetic behavior.

μSR experiments were performed at the RIKEN-RAL Muon facility at the Rutherford-Appleton Laboratory, UK. Fig. 1 shows the zero field (ZF) μSR spectra of Cu₆O₈MCl (M=Y, Pb) at various temperatures. With the decrease in the temperature, the initial asymmetry of Cu₆O₈PbCl rapidly decreased below 20 K (Fig. 1(b)). On the other hand, clear decreasing behavior of the initial asymmetry was not observed in the ZF-μSR spectra of Cu₆O₈YCl down to 0.3 K, indicating that there is no magnetic ordered state in this system (Fig. 1(a)). The ZF-μSR spectra in Fig. 1 were analyzed using the following function,

\[ P(t) = A \exp(-\Delta t) G_{K}(\Delta t) + A_{B} \]  

where \( A \) is the initial asymmetry at \( t = 0 \), \( \Delta \) is relaxation ratio of the muon spin, and \( A_{B} \) is the background signal. \( G_{K}(\Delta t) \) is the static Kubo-Toyabe function with a half-width of \( \Delta \), describing the distribution of the nuclear-dipole field at the muon site ³. Results of the best-fit of eq. 1 are indicated by the solid line in Fig. 1, and the observed adjusted parameters \( A, \Delta, \lambda \) of Cu₆O₈MCl (M=Y, Pb) as functions of temperature are shown in Fig. 2. \( A \) (\( \alpha \)-relaxing) of Cu₆O₈YCl slightly decreases with the decrease in the temperature (Fig. 2), whereas \( \Delta \) and \( \lambda \) of Cu₆O₈YCl are almost constant, being temperature independent. These facts indicate that there is no change of spin dynamic and long range magnetic ordered state in Cu₆O₈YCl, which is a metallic compound with paramagnetic behavior. For Cu₆O₈PbCl, the temperature dependence of \( \alpha \)-relaxing, \( \lambda \), and \( \Delta \) change below 20 K, indicating the change in the magnetic spin state (Fig. 2). However, clear precession signal is not confirmed in the ZF-μSR spectra below 20 K. The Cu₆O₈ cage has a square-lattice and triangular-lattice on its surface, and the Cu sites in the Cu₆O₈ cage are occupied by various valences of Cu⁺, Cu²⁺, and Cu³⁺ ². These conditions encumber the formation of the completely static magnetic ordered state in Cu₆O₈PbCl. The observed behavior of ZF-μSR spectra and Fig. 2 data of Cu₆O₈PbCl indicate the growth of the short-range magnetic interaction between \( S = 1/2 \) spins below 20 K. Consequently, the magnetic ground state of Cu₆O₈PbCl does not have a static long range magnetic ordered state such as an antiferromagnetic state in high-\( T_{c} \) cuprate. There is possibility that the short range interaction of Cu₆O₈PbCl forms the spin glass state below 20 K like under-doping material in high-\( T_{c} \) cuprate. The magnetic ground state of Cu₆O₈MCl compound depends on the valence state of the M site ion.

References