Spin glass state in the mixed system (Co\(_{1-x}\)Fe\(_x\))\(_2\)(OH)\(_3\)Cl on deformed pyrochlore lattice

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Abstract

Magnetic coupling in a new geometrically frustrated system (Co\(_{1-x}\)Fe\(_x\))\(_2\)(OH)\(_3\)Cl is investigated using magnetic susceptibility and \(\mu\)-SR study. In contrast to the partial ferromagnetic state in Co\(_2\)(OH)\(_3\)Cl, Fe\(_2\)(OH)\(_3\)Cl is shown to undergo an antiferromagnetic transition below \(T < T_N = 9.0\) K although the two compounds have similar crystal structure. Meanwhile, the partially substituted (Co\(_{1-x}\)Fe\(_x\))\(_2\)(OH)\(_3\)Cl series are realized, wherein ferromagnetic interaction prevails for low Fe concentration and antiferromagnetic prevails for high Fe concentration. In special, analysis of the AC magnetic susceptibility and ZF-\(\mu\)-SR for the \(x = 0.5\) sample suggest that (Co\(_{1-x}\)Fe\(_x\))\(_2\)(OH)\(_3\)Cl has both the features of a conventional random spin glass and geometrically frustrated spin glass. It is also the first spin glass material in the geometrically frustrated material series \(M_2\)(OH)\(_3\)X.

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1. Introduction

Geometrically frustrated magnetic materials show exotic magnetic properties due to their lattice geometry. In recent years, we found unconventional magnetic transitions in a mineral compound clinoatacamite Cu\(_2\)(OH)\(_3\)Cl [1], wherein we further observed the coexistence of long-range antiferromagnetic order and spin fluctuation [2]. It is the first example of the \(S = 1/2\) (Cu\(^{2+}\)) Heisenberg quantum spin on a pyrochlore lattice and the mother compound for the “perfect kagome lattice” ZnCu\(_3\)Cl\(_2\)(OH)\(_6\) exhibiting spin liquid behaviour [3].

We further found that in another compound Co\(_2\)(OH)\(_3\)Cl with the Co\(^{2+}\) magnetic ion, a partial FM order coexists with spin fluctuation below \(T_C = 10.5\) K, [4]. The partial FM order is similar to the field-induced “kagome ice” state in pyrochlore Dy\(_2\)Ti\(_2\)O\(_7\), i.e., it is a zero-field kagome ice which is
thought to be induced by the distorted pyrochlore structure.

Further, we have found that the Co$_2$(OH)$_3$Cl can be partially substituted by a different magnetic ion of Fe$^{2+}$ to result in a controlled series of (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl. The present work reports a study of the spin-spin interactions in the (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl series using magnetic measurements and the microscopic study of muon spin rotation/relaxation ($\mu$SR). Possible new phase transitions as well as the evolution of magnetic interactions in the (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl are explored to help us understand better the magnetic coupling in the Co system.

2. Experimental

Polycrystalline samples of (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl with $x = 0.1, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9,$ and 1, respectively, were prepared by a hydrothermal synthesis method at around 200°C for several hours. All samples were inspected using the high-resolution synchrotron powder x-ray diffraction performed at BL02B2, SPring-8 (Japan). The DC and AC susceptibility measurements were performed using a commercial SQUID magnetometer. Muon spin rotation/relaxation ($\mu$SR) experiments were carried out at m20, TRIUMF (Canada) using a positive surface muon beam.

3. Results and discussion

The (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl samples were successfully synthesized in single phase as is demonstrated by the x-ray diffraction patterns shown in Fig. 1. All (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl compounds for $x = 0$ to 1 crystallize in the same rhombohedral structure in space group $R\bar{3}m$ (Fig. 2). The lattice parameters of the $x = 1$ compound Fe$_2$(OH)$_3$Cl were refined to $a = 6.9401(6)$ Å and $c = 14.7267(0)$ Å, respectively, which are slightly larger as compared to the $a = 6.8370(4)$ Å and $c = 14.4965(2)$ Å in Co$_2$(OH)$_3$Cl. The monotonous change for all diffraction peaks in Fig. 1 with increasing $x$ implies a random substitution.

The temperature dependence of the DC magnetic susceptibility at $H = 100$ Oe under zero field-cooling (ZFC) and field-cooled (FC) conditions for typical samples are shown in Fig. 3(a). In contrast to the ferromagnetic Co$_2$(OH)$_3$Cl (ref. 4), the $x = 1$ compound Fe$_2$(OH)$_3$Cl showed an antiferromagnetic transition below $T < T_N = 9.0$ K. All other compounds of $x = 0.1, 0.3, 0.4, 0.5, 0.7$ and 0.8 showed spin-glass-like behaviours with different freezing temperatures.

Fig. 1 X-ray diffraction patterns for the (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl series with $x = 0, 0.1, 0.3, 0.4, 0.5, 0.7, 0.8,$ and 1, respectively.

Fig. 2 Crystal structure for (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl which is featured by alternatively stacked layers of the kagomé and triangular lattice planes along the $c$-axis.

For $x = 0.5$ a typical spin-glass behaviour is seen with saturated magnetization below around 5 K under field-cooling. The magnetization curves in Fig. 3(a) suggest that in the samples with $x < 0.5$ ferromagnetic interaction prevails and for $x > 0.5$ it turns into antiferromagnetic. The magnetic state in (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl for $x < 0.5$ and $x > 0.5$ can be interpreted as spin glass co-existing with
ferromagnetic or antiferromagnetic clusters, respectively. A plot of the transition temperatures with the ratio $x$ is given in Fig. 3(b), which depicts the phase diagram in the (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl system.

The AC susceptibilities for the $x = 0.5$ show a cusp feature characteristic of a spin glass (Fig. 4), and the freezing temperature $T_f$ shifted to higher temperature with increasing frequency. The frequency dependency, quantified by $p = \Delta T_f / T_f \Delta[\log f_0] = 0.035$, is close to the values of some typical spin-glasses. Further we performed the conventional dynamical scaling analysis. The observation time $\tau$ is expressed by $\tau_{SG} = [(T_f - T_g)/T_g]^{-z\nu}$, wherein $T_g$ is the freezing temperature in the low frequency limit, $\tau_0$ is the spin-flipping time, and the product exponent $z\nu$ is called the dynamical exponent [8]. In the $x = 0.5$ CoFe$_2$(OH)$_3$Cl, we obtained $T_g = 4.5$ K, $\tau_0 = 4.2 \times 10^{-11}$ sec, and $z\nu = 10.8$ (the inset plot in Fig. 4). This short spin-flipping time $\tau_0$ is typical of a spin glass.

However, the dynamical exponent $z\nu$ is extraordinarily large as compared to the conventional spin glass CuMn ($z\nu = 5.5$). It is also much larger than the geometrically frustrated spin glass Y$_2$Mo$_2$O$_7$ [$z\nu = 7.7$ in ref. 9]. For the study of the spin dynamics, we further carried out the ZF-$\mu$SR for the sample of $x = 0.5$ (Fig. 5). The relaxation function was fitted by

$$a_{SG}(t) = a_0 \left[ \frac{1}{3} e^{-2/3\nu t} + \frac{2}{3} (1 - a_0 t) e^{-\mu t} \right]$$

for quasi-static local field at $T < T_g$,

$$a_{SG}(t) = a_0 \exp(-\lambda_d t)^{1/2}$$

for rapidly fluctuating magnetic moments at $T > T_g$ [8], and

$$a(t) = a_0 \exp(-\lambda_d t)$$

for $T > 30$K, respectively.

Here, $a_0$ is the full asymmetry of the incident muon spins at time zero, $\nu$ is the inverse average spin-correlation time. Reflecting the fluctuations of local field, $a_0$ is average amplitude of static random local field at muon site, and $\lambda_d$ is dynamic muon spin depolarization rate. The fitted results are shown in Fig. 6. In a spin glass, the dynamic depolarization...
rate increase rapidly when $T_g$ is approached from higher temperature. According to the dynamical scaling, the critical relaxation time can be fitted by

$$
\tau_c = \tau_0 \left[ \frac{T}{T - T_g} \right]^n
$$

where $n = 2.5$. The dynamic muon spin depolarization rate $\lambda_d$ is in good agreement to $[T / (T - T_g)]^n$ with $n = 2.5$, which is very close to the $n = 2.6$ value for the conventional spin glass of 3% CuMn [10].

4. Conclusion

In summary, we have successfully synthesized a new mixed system $(\text{Co}_{1-x}\text{Fe}_x)\text{Cl}_3\text{OH}$ in the new geometrically frustrated series of $M_2\text{OH}_3X$. The magnetic coupling can be controlled by adjusting the ratio of ferromagnetic Co ions versus antiferromagnetic Fe ions on the deformed pyrochlore lattice. In special, analysis of the AC magnetic susceptibility and ZF-$\mu$SR for the $x = 0.5$ sample suggest that $(\text{Co}_{1-x}\text{Fe}_x)\text{Cl}_3\text{OH}$ has both the features of a conventional random spin glass and geometrically frustrated spin glass. It is also the first spin glass system in the new geometric frustration material series $M_2\text{OH}_3X$.

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