Spin dynamics in 3d electron pyrochlore-like systems

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Abstract.
\textsuperscript{1}H NMR measurements of 3d electron three-dimensional frustrated systems, Co\textsubscript{2}(OH)\textsubscript{3}Cl with $s = 3/2$ and Cu\textsubscript{2}(OH)\textsubscript{3}Cl with $s = 1/2$ have been performed. The relaxation rates $T^{-1}_1$ of both compounds suggest the development of spin correlations at much higher temperatures compared with the magnetic transition temperatures. The temperature dependence of $T^{-1}_1$ below 6 K of both compounds indicates the magnetic ordering and the existence of magnon excitations. The estimated magnon energy gaps are 13 K and 27 K for Cu\textsubscript{2}(OH)\textsubscript{3}Cl and Co\textsubscript{2}(OH)\textsubscript{3}Cl, respectively, which are consistent with the inelastic neutron experiments. The intermediate phase between $T_{N1} = 18.1$ K and $T_{N2} = 6.4$ K for Cu\textsubscript{2}(OH)\textsubscript{3}Cl shows the conflicting behaviors which are the coexistence of the freezing of the moments and the paramagnetic spin dynamics. The partial freezing and the time scale of spin dynamics should be crucial to understand these frustrated systems.

1. Introduction
Three-dimensional frustrated systems attract much attention recently. Magnetic moments in the pyrochlore systems form a network of corner-sharing tetrahedrons. So far the pyrochlore systems composed of rare earth ions have been intensively studied as they are good examples of three dimensional frustration. The dominant interactions between magnetic moments in rare earth pyrochlore systems are long range dipolar interactions in most cases. Here we present NMR studies of 3d electron pyrochlore-like systems, Co\textsubscript{2}(OH)\textsubscript{3}Cl with $s = 3/2$ and Cu\textsubscript{2}(OH)\textsubscript{3}Cl with $s = 1/2$. In these systems, the magnetic interactions are ascribed to the short range superexchange-type.

The crystal structure of Co\textsubscript{2}(OH)\textsubscript{3}Cl is trigonal R\textsubscript{3}m and contains slightly distorted corner sharing tetrahedrons. One can regard the structure as the alternating stack of triangular-lattice planes and Kagome-lattice planes composed of magnetic atoms along the $\langle 111 \rangle$ direction. It is reported for Co\textsubscript{2}(OH)\textsubscript{3}Cl that below $T_N = 10.5$ K only the Co\textsuperscript{2+} spins on the triangular-lattice plane order ferromagnetically and the Co\textsuperscript{2+} spins on the Kagome-lattice plane remain to be disordered. This partially ordered state is regarded as a Kagome ice state in zero magnetic field, as the residual entropy is consistent with the expected value for the Kagome ice state. Zheng et al. proposed that the kagome ice state is stable in Co\textsubscript{2}(OH)\textsubscript{3}Cl without magnetic field because of the slight distortion of the tetrahedrons [1].

Another compound Cu\textsubscript{2}(OH)\textsubscript{3}Cl is monoclinic P2\textsubscript{1}/n and contains slightly distorted corner sharing tetrahedrons too. The triangular lattice and the Kagome lattice in Cu\textsubscript{2}(OH)\textsubscript{3}Cl are also slightly distorted [2]. The compound Cu\textsubscript{2}(OH)\textsubscript{3}Cl shows the successive phase transitions.
at 18.1 K, 6.4 K and 6.2 K [3]. Recently it was claimed from the inelastic neutron scattering measurements that there exist the valence bond liquid (VBL) state above \( T_{N_1} \) = 18 K, the valence bond solid (VBS) state between \( T_{N_1} \) and \( T_{N_2} \) = 6 K and the VBS state + collinear Neel order below \( T_{N_2} \) [4]. This novel explanation interests many researchers, however, the explanation seems to be not convincing. In order to investigate spin dynamics of both compounds, we have performed \(^1\)H NMR measurements.

2. Experimental Procedures

Magnetization measurements were performed by SQUID magnetometer between 2 K and 300 K. \(^1\)H NMR measurements of the powder samples were performed by a coherent pulsed spectrometer. Spin echo spectra were measured by the fast Fourier transformation of the spin echo signals or by the field sweep. The relaxation rates \( T_{1}^{-1} \) were determined from the recovery of the spin echo signals after the comb pulses for the saturation.

3. Results and Discussions

Figure 1 shows the temperature dependence of the \(^1\)H spin-lattice relaxation rates \( T_{1}^{-1} \) of Cu2(OH)3Cl and Co2(OH)3Cl. The rates for both compounds increase with decreasing temperature below 300 K. Usually the temperature dependence of \( T_{1}^{-1} \) for the antiferromagnets at higher temperatures in the paramagnetic region can be described as \( T_{1}^{-1} \propto \chi T \), where \( \chi \) is magnetic susceptibility and \( T \) is temperature [5]. The dashed lines in Fig. 1 show \( \chi T \) curves which are normalized to fit \( T_{1}^{-1} \) at 300 K. The substantial deviation between \( \chi T \) curve and the data of \( T_{1}^{-1} \) suggests the development of spin correlations at much higher temperatures compared with the magnetic transition temperatures in these compounds. The increase of \( T_{1}^{-1} \) has already started from 300 K. We estimated that the hyperfine coupling between a \(^1\)H nuclear spin and Co\(^{2+}\) spins in Co2(OH)3Cl is 1.2 kOe/\( \mu_B \) from the relation between the width of NMR spectra and the susceptibility. Using the hyperfine coupling and the exchange frequency, \( T_{1}^{-1} \) at high temperature limit can be estimated to be about 8000 s\(^{-1}\). The experimental value of \( T_{1}^{-1} \) at 300 K is the same order as the estimated value. This estimation also demonstrate that the development of the spin correlation has already started from the room temperature.

The relaxation rate \( T_{1}^{-1} \) of Co2(OH)3Cl continues to increase down to 20 K. NMR signals were not observed between 20 K and 7 K because of the extremely large spin-spin relaxation rates and spin-lattice relaxation rates. The divergent behavior of the relaxation rates demonstrates that the critical slowing down of the spin fluctuations occurs around the transition temperature of 10.5 K.

On the other hand, \( T_{1}^{-1} \) of Cu2(OH)3Cl is almost constant between 100 K and 6 K although there is a magnetic transition at \( T_{N_1} \) = 18.1 K. The prominent anomaly was not observed in the relaxation rate and the recovery curves at \( T_{N_1} \).

Figure 2 shows the temperature variation of \(^1\)H-NMR spectra for Cu2(OH)3Cl. The spectra above 40 K were acquired by the FFT-NMR with a constant magnetic field and those below 40 K were acquired by the field sweep with a constant frequency. The spectra above \( T_{N_1} \) are very sharp and the width increase gradually with decreasing temperature. The spectra below \( T_{N_1} \) are significantly broad and the width is roughly 0.1 T. The large broadening demonstrates the appearance of the static internal field below \( T_{N_1} \) at \(^1\)H sites. This large internal field suggests that Cu\(^{2+}\) spins order or freeze magnetically below \( T_{N_1} \), which conflicts with a singlet state like VBS. \( \mu_S \)SR measurements also observed the internal field below \( T_{N_1} \) [2]. It is surprising that no clear anomaly is observed in the relaxation rate at \( T_{N_1} \) in spite of the noticeable broadening of the spectra. The structure of the spectra below \( T_{N_2} \) were remarkably different from those above \( T_{N_2} \) but the width is almost the same. This suggests that the magnetic structure changes at \( T_{N_2} \).
Figure 1. Temperature dependence of the $^1$H spin relaxation rates $T_1^{-1}$ of Cu$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Cl. The dashed lines show $\chi T$ curves.

Figure 2. $^1$H-NMR spectra for Cu$_2$(OH)$_3$Cl. The spectra above 40 K were obtained by the FFT-NMR and those below 40 K were obtained by the field sweep at 64.16 MHz.

The development of large internal field at $^1$H sites were observed below $T_{N_1} = 18$ K by our NMR spectra. On the other hand, the susceptibility and specific heat indicate only a slight anomaly and the entropy change is extremely small (0.05 Rln2) at $T_{N_1}$. Furthermore $T_1^{-1}$ has no prominent anomaly at $T_{N_1}$. These results may suggest a partial freezing of Cu spins at $T_{N_1}$ although the magnetic structure is unknown. The singlet state like VBS is not plausible. However, the nature of the intermediate phase is still controversial because $T_1^{-1}$ is still constant below $T_{N_1}$.

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The rates $T_1^{-1}$ below 6 K of both compounds show the steep decrease with decreasing temperature. The steep temperature dependence of $T_1^{-1}$ indicates the magnetic ordering and the existence of magnon excitations. The rate $T_1^{-1}$ of Co$_2$(OH)$_3$Cl decreases more rapidly than that of Cu$_2$(OH)$_3$Cl. We tried to fit the experimental results with the theory of the two magnon process of nuclear spin relaxation. The rate $T_1^{-1}$ is expresses under a long wave approximation as [5],[6],[7],

$$ T_1^{-1} \propto \frac{1}{(T_m^2 - T_0^2)^3} T^5 \int_0^{T_m/T} x^2 - \left( \frac{T_0}{T} \right)^2 \{ x^2 + \left( \frac{T_m}{T} \right)^2 \} e^{x} \left( e^x - 1 \right)^2 dx, \tag{1} $$

where $T_0$ is an energy gap and $T_m$ is the maximum energy of a dispersion curve of magnons.

Figure 3 shows the low temperature part of $T_1^{-1}$ and lines are the theoretical curves. The rates $T_1^{-1}$ are well reproduced with energy gaps of 13 K and 27 K with small dispersions for Cu$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Cl, respectively. These results indicate that there is an almost dispersionless excitation at finite energy in magnetically ordered state in both compounds. Here we note that the low energy excitation in Cu$_2$(OH)$_3$Cl observed by the inelastic neutron scattering is dispersionless at 1.3 meV [4], which is compatible with our result. The dispersionless excitation can be ascribed to the spin wave excitations in the Neel state of Kagome-lattice plane. In the case of Co$_2$(OH)$_3$Cl, only Co spins on the triangular-lattice plane order ferromagnetically.
Thus the observed excitation may not be related with the Kagome lattice but the three dimensional tetrahedron structure.

![Figure 3](image_url) **Figure 3.** The low temperature part of $T^{-1}$ of both compounds and the solid line and the dotted line are the theoretical curves.

Recent specific heat measurements have revealed the absence of nuclear Zeeman contribution even at low temperatures down to 0.1 K [8]. This means there is no internal field, which is discrepant with our NMR and μSR measurements [2]. On the other hand, μSR measurements showed that there is a slow spin fluctuation of the long range ordered part in Cu$_2$(OH)$_3$Cl below $T_{N_2}$. Also inelastic neutron scattering measurements showed another excitation spectra around zero energy below $T_{N_2}$ [4]. These results suggests that the slow dynamics is a key point to understand the ordered state below $T_{N_2}$.

In summary, we have performed $^1$H NMR measurements of Cu$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Cl. We found the large internal field below 18 K, which is not consistent with the non-magnetic VBS state. Furthermore the spin wave excitations observed by relaxation rates below 6 K demonstrate the existence of long range magnetic ordering. Therefore our experimental results are not consistent with VBS or VBL state proposed by the inelastic neutron scattering experiments. The discrepancy between NMR, μSR and specific heat suggests the long range ordered moments fluctuate with a time scale which is faster than that of specific heat measurement but is slower than those of NMR and μSR measurements.

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