1H-NMR study of $S = 1/2$ frustrated antiferromagnet $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ varying from kagomé ($x = 1$) to pyrochlore ($x = 0$)

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Abstract. 1H-NMR and magnetic susceptibility $\chi(T)$ are measured on $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ ($0 \leq x \leq 1$), whose end member at $x = 0$ is a distorted pyrochlore- and $x = 1$ is a kagomé-lattice spin frustrated antiferromagnet. For $x = 0$ compound, NMR spectra broaden abruptly at $T_N = 18$ K, and a spin - lattice relaxation rate shows large divergent behavior at $T_C = 6$ K. These anomalies indicate an onset of magnetic order at $T_N$ and $T_C$. For $x = 1$ compound, no magnetic order is observed, which is consistent with the previously reported result. Determined values of $T_N$ and $T_C$ from anomalies in NMR and $\chi(T)$ results are summarized in a detailed $x$-$T$ phase diagram.

1. Introduction

Geometrically frustrated magnetic systems provide us intriguing issues such as a spin liquid ground state. The magnetic properties of $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ ($0 \leq x \leq 1$) attracts much interest recently. $\text{Cu}_4(\text{OH})_6\text{Cl}_2$ ($x = 0$) is a 3D distorted pyrochlore lattice antiferromagnet and successive magnetic phase transitions at $T_N = 18$ K and $T_C = 6.4$ and 6.2 K are reported [1]. On the other hand, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ ($x = 1$) is proposed as an ideal 2D kagomé antiferromagnet with $S = 1/2$ and no long-range magnetic ordering is observed down to about 50 mK in spite of large Weiss temperature [2, 3]. As increasing Zn concentration $x$, crystal structure changes from monoclinic ($x < 0.33 ; P2_1/n$) to rhombohedral ($R3m ; x > 0.33$) at around $x_c = 0.33$ and non-magnetic Zn$^{2+}$ ions are believed to replace apical Cu$^{2+}$ ions between kagomé layers. Thus, continuous crossover from 3D pyrochlore to 2D kagomé frustrated systems can be studied by changing $x$ of $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$. Lee and his coworker [4] measured elastic and inelastic neutron scattering on $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ and, based on the experimental observations, proposed the magnetic phase diagram as a function of $x$ and temperature. They found the VBS (valence bond solid) state is realized in the intermediate phase for $x = 0$ compound. The spin structure of the low temperature phase below about 7 K is found to be collinear one. As increasing $x$ from 0, the VBS state collapse at around $x = 0.3$, and a spin glass phase appears for $x = 0.5-0.7$. $\mu$SR study for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ found that a transition from partly frozen ground state to dynamical one occurred around $x = 0.5$ [5]. The phase diagram of this system is very interesting and worthwhile to study. NMR method is microscopic and dynamical probe and thus suitable for the study of the magnetic ordering of this system.
We synthesized powder samples of $\text{Zn}_x\text{Cu}_{4-x} (\text{OH})_6\text{Cl}_2$ and carried out magnetic susceptibility and $^1$H-NMR measurements to investigate the change of the magnetic state against Zn concentration.

2. Experimental details

Powder samples of $\text{Zn}_x\text{Cu}_{4-x} (\text{OH})_6\text{Cl}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.66, 0.8$ and $1$) are synthesized using a hydrothermal reaction method following a procedure described in literature [2]. Quality of the sample is checked by powder X-ray diffraction. All measurements are carried out using the powder sample. Magnetic susceptibility $\chi(T)$ is measured using a SQUID magnetometer in the temperature range 2 - 300 K. $^1$H-NMR spectra and spin-lattice relaxation time $T_1$ were measured using a pulsed-spin echo method down to about 0.5 K. $T_1$ data are mainly taken at center position of the NMR spectra.

3. Results and Discussion

Magnetic susceptibility curves of $\text{Zn}_x\text{Cu}_{4-x} (\text{OH})_6\text{Cl}_2$ ($0 \leq x \leq 1$) measured at 100 Oe are shown in Fig. 1.

Figure 1. $\chi$ data of $\text{Zn}_x\text{Cu}_{4-x} (\text{OH})_6\text{Cl}_2$ measured at 100 Oe are plotted as a function of $x$ and temperature. FC and ZFC magnetizations are indicated by solid and open circles, respectively. Inset shows magnetization for $x=0.8$ and 1.

For the samples with $x = 0 - 0.8$, field-cooled (FC) and zero-field-cooled (ZFC) magnetizations behave differently below about 6 K, which is considered as a fingerprint of a weak-ferromagnetic or a spin-glass order. Negative remnants of ZFC magnetizations, seen for $x \leq 0.9$ samples, are often observed in weak-ferromagnets [6]. Even for $x=0.9$ compound, FC and ZFC magnetizations take different value below 6 K. The difference between FC and ZFC magnetization below order temperature decreases as increasing $x$. For $x=1$ compound, namely the kagomé compound, ZFC and FC magnetizations take same value down to the lowest temperature of 2 K and no magnetic anomaly appears, being consistent with the reported result. The order temperature $T_C$ determined from $\chi$ data are plotted as a function of $x$ in Fig. 5.

NMR spectra of $x=0$ compound broaden abruptly below about $T_N =18$ K as shown in an inset of Fig. 2. Since the spectra below $T_N$ do not take simple form, we calculated a second-moment (or variance) of the spectrum to estimate a line width. The calculated results of the
Figure 2. Temperature dependence of the first and second moments of $^1$H-NMR spectra of Cu$_4$(OH)$_6$Cl$_2$ are plotted in open and solid circles, respectively. Inset shows $^1$H-NMR spectra at several temperatures. Sharp peak observed at around 1.06 T is a signal of $^{19}$F in PTFE tape.

Figure 3. Temperature dependence of the first and second moments of $^1$H-NMR spectra of ZnCu$_3$(OH)$_6$Cl$_2$ are plotted in open and solid circles, respectively. Inset shows $^1$H-NMR spectra at several temperatures. Sharp peak observed at around 1.06 T is a signal of $^{19}$F in PTFE tape.

second-moment and first moment are plotted in Fig. 2. The second moment increases rapidly at 18 K which suggests an appearance of an internal field at $^1$H sites due to the occurrence of the magnetic order. It is noticeable that the magnetic order at 18 K reveals itself in the distinct anomaly of NMR spectra but does not appears in the magnetic susceptibility. The second moment also increases at around $T_C = 6$ K where the anomaly of the magnetic susceptibility is detected. On the contrary to the $x = 0$ result, the second moment of $x = 1$ compound increases monotonically without any distinct anomaly as shown in Fig. 3, and is found to be proportional to $\chi(T)$ data. The broadening of the $x = 1$ spectra is thus inhomogeneous broadening induced by a bulk magnetic susceptibility.

Figure 4 shows temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of $x=0-1$ compounds measured under magnetic field of nearly 1 T. $T_1^{-1}$ of $x = 0$ compound shows large divergent behavior at 6 K where the $\chi$ also has the anomaly. Below this temperature $T_1^{-1}$ is found to be proportional to $T^3$, which could be explained in a framework of a magnon relaxation mechanism. At around 18 K where large enhancement of the spectra width is observed, $T_1^{-1}$ begins to increase but no divergence is observed. As increasing Zn concentration $x$, the divergence at $T_C$ diminishes rapidly and only small hump-like anomalies at 6 and 17 K are observed for $x = 0.3$ compound. In $x = 0.5$ compound, the hump anomaly is taken place by a small change of a slope of $T_1^{-1}$ at around 5 K. For $x = 1$ compound, $T_1^{-1}$ decreases monotonically as decreasing temperature and no anomaly is observed down to the lowest temperature and no spin gap is observed. These results are consistent with the reported ones [7].

In Fig. 5, the magnetic ordering temperatures determined from $\chi$ and NMR results are plotted as a function of $x$. In NMR, $T_N$ and $T_C$ are mainly determined from the second moment and $T_1^{-1}$, respectively. Besides our results, ordering temperatures obtained from neutron scattering[4] are also plotted in Fig. 5. As described in Introduction, the crystal structure changes from monoclinic to rhombohedral at $x_c = 0.33$. An evolution of the magnetic phase against $x$ corresponds exactly to the structural change. Below $x_c$, the magnetic order occurs successively at $T_N$ and $T_C$, while $T_N$ vanishes and only $T_C$ survives above $x_c$. It is noteworthy that $T_C$ changes little as increasing $x$ in rhombohedral phase above $x_c$ but no magnetic order
occurs at $x=1$. In the geometrically frustrated magnet, it is believed that very small amount of non-magnetic impurities will induce magnetic order such as spin glass transition. In fact, a spin glass transition of a typical kagomé compound SrCr$_{9-x}$Ga$_3$xO$_{19}$, in which Cr$^{3+}$ ions ($S = 3/2$) form kagomé plane but several percent of Cr$^{3+}$ ions are inevitably substituted by non-magnetic Ga$^{3+}$ ions, was discussed in terms of the randomness in the kagomé plane [8, 9, 10]. In $x = 1$ compound, although Cu/Zn substitution of 5 - 10 % in the kagomé plane is reported [4, 11], magnetic state remains paramagnet. A relation between the structural disorder and the magnetic phase in ZnCu$_3$(OH)$_6$Cl$_2$ is an open question and the $x$-$T$ phase diagram obtained in this study might be helpful to understand it.

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Figure 4. Temperature and Zn concentration dependences of $T_{1^{-1}}$ measured under applied field of about 1 T.

Figure 5. $T_N$ and $T_C$ determined from $\chi(T)$ and NMR are plotted against $x$. Data obtained from neutron[4] and $\mu$SR[5] are plotted for reference.