

1H-NMR study of the idle-spin magnet Cu$_3$(OH)$_4$SO$_4$

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Abstract. 1H-NMR study of a spin-$1/2$ triple-chain system Cu$_3$(OH)$_4$SO$_4$, in which the realization of an ‘idle-spin’ state has been suggested recently from neutron experiments, were carried out in the temperature range down to 1.4 K. In the experiments under about 1 T, we found a clear anomaly of the nuclear magnetic relaxation rate and drastic change of the spectrum at around $T_N = 5.4$ K. NMR spectrum below $T_N$ has a characteristic shape of an antiferromagnetic ordered state. This low-temperature spectrum is consistently reproduced by the calculation of local fields at proton sites on the basis of the idle-spin state. Further, $T_N$ decreased as the applied field is increased up to 6.9 T.

1. Introduction

Cu$_3$(OH)$_4$SO$_4$, called as antlerite of natural mineral name, attracts much interest because neutron experiments suggested the possibility of an ‘idle-spin’ state. In this compound, Cu$^{2+}$ carrying spin-$1/2$ forms a triple-chains structure with triangles as shown in the inset of Fig. 1(a). A magnetic transition at $T_N = 5$ K is observed by the susceptibility and the specific heat measurements [1, 2]. Vilminot et al. reported from powder neutron diffraction at 1.4 K that the magnetic moments of the copper ions belonging to outer chains (indicated as Cu2 in the inset of Fig. 1) are oriented with ferromagnetic order inside a chain and antiferromagnetic order between the two outer chains, while no long-range magnetic order is observed along the central chain (Cu1) [1]. This unusual magnetic behavior is referred to as an idle-spin state. We can expect the frustration effect to play an important role to this behavior. While the realization of the idle-spin state is reported for several compounds [3–7], Cu$_3$(OH)$_4$SO$_4$ is, to our knowledge, the first quantum spin system between idle-spin compounds. One may consider the possibility of a singlet ground state for Cu1 sites. However, exchange interaction between Cu1 sites is crystallographically identical. Further, distances between neighboring copper ions are in the range 3 – 3.27 Å [1]. Thus, we believe that the interaction between Cu1 ions is not much stronger than others.

In order to study static and dynamic magnetic properties of Cu$_3$(OH)$_4$SO$_4$, we have performed 1H-NMR measurements with the powder sample of this compound in the temperature range down to 1.4 K. The sample was confirmed by X-ray diffraction and magnetic susceptibility measurements. We used a conventional pulsed NMR method. A spectrum was obtained by recording the spin-echo intensity while sweeping the magnetic field.
Figure 1. $^1$H-NMR spectra at various temperatures with operating frequency of (a) 42.5 MHz and (b) 291 MHz. The sharp peak at about 1.0 T probably comes from insulator of a wire which is accidentally placed near the detection coil. The inset of (a) shows the schematic draw of a triple chains of Cu$^{2+}$ (spin 1/2) in Cu$_3$(OH)$_4$SO$_4$.

Figure 2. Temperature dependence of the nuclear spin-lattice relaxation rate $T_1^{-1}$ for 42.5, 239 and 291 MHz.

2. Experimental results

Figure 1 shows $^1$H-spectra obtained with operating frequencies of 42.5 MHz and 291 MHz. From the results of 42.5 MHz, it is clearly suggested that the system undergoes a magnetic phase transition at around 5.4 K which is close to $T_N$ at zero field. The spin-echo intensity was lost around 5.4 K, mainly because the spin-spin relaxation time $T_2$ became very short. The obtained spectrum for 42.5 MHz below this temperature was strongly broadened, and at lowest temperature it showed a characteristic shape composed of rectangles. Such a shape is known
as a power pattern of an antiferromagnetically (AF) ordered state. At higher temperatures for both frequencies, the spectrum shows an asymmetric shape with a peak at higher field, which is a power pattern of a paramagnetic state. We will discuss the shape of these spectra in the next section.

Figure 2 shows temperature dependence of the nuclear spin-lattice relaxation rate $T_1^{-1}$ of $^1$H for 42.5, 239 and 291 MHz. As shown, a sharp peak was observed for each magnetic field. Such a peak generally corresponds to a phase transition accompanying critical slowing down. Below the peak, $T_1^{-1}$ decreases steeply with decreasing temperature (third to fifth power of the temperature), suggesting that the low temperature phase is a three dimensionally ordered phase. So, we use $T_N$ also to call the transition temperature under the magnetic field, from now on. As shown, $T_N$ decreases with increasing field. $T_N$ for 291 MHz (under the applied field of $\sim 6.9$ T) is suggested to be 3.4 $\pm$ 0.2 K, although the spectrum does not change drastically around this temperature.

3. Discussions

In order to consider the spin arrangement at lower temperatures, we tried to reproduce the spectrum obtained for 42.5 MHz by calculation. Let us pick up spectra at 26 K for paramagnetic phase and at 1.4 K for ordered phase to fit calculated spectra. We calculated for two types of spin configurations for the ordered phase: One is the idle-spin state as stated above which is suggested originally in ref. 1. Here, we put Cu1 to be completely nonmagnetic for simplicity. The other is, as proposed in ref. 2, with AF ordered Cu2 moments which is the same as the first one, while Cu1 moments are ordered ferromagnetically along the chain but directed randomly between the chains with 1 $\mu_B$. We call the former as idle-spin model and the latter as random order model, respectively. The latter is introduced in order to explain both results of neutron experiments and specific heat measurements [2].

We calculated a dipolar field made at each of three proton sites by electron spins within the distance 24 Å from the proton, on the basis of the point-dipole model. In the calculation for random order model, we generated 8000 patterns of spin arrangement and took distribution of the shift for them. For the other models, analytical forms are known well to produce the power pattern. In Fig. 3, calculated results are compared with experimentally obtained spectra.

As shown in Fig. 3(b), the calculated spectrum for the random order model has a round peak at zero shift and nearly symmetric to it, being qualitatively different from the experimental
result. It is contrast markedly that the calculation for the idle-spin model agrees fairly well with the experimental result. This calculated shape is distorted slightly, because the resonance magnetic field at each proton is yielded by a vector sum of external and internal fields [8]. It should be noted that one may be able to reproduce the low temperature spectrum from other AF ordered spin arrangements instead of the idle-spin model, because the experimental results only suggest the AF ordered spin configuration. However, the random order model or any others with randomness will not account for our experimental results.

We note here that, for all calculation, each magnetic moment on copper was reduced by 8 % which was transferred to neighboring oxygens. Therefore, we took into account not only copper sites but also oxygen sites with small magnetic moments. It was found that, when all of the spin density is put on the copper site, the calculated spectrum for the paramagnetic phase becomes too sharp. So, we assumed that the spin density distributes also on oxygens. The reduction of 8 % was selected to reproduce well the spectra for both the paramagnetic and the ordered low-temperature phases.

4. Summary
In summary, $^1$H-NMR study of a spin-1/2 triple-chain system Cu$_3$(OH)$_4$SO$_4$ has been carried out in the temperature range down to 1.4 K and in the field range up to 6.9 T. In the experiments under about 1 T, we found a clear anomaly of the nuclear magnetic relaxation rate and drastic change of the spectrum at around $T_N = 5.4$ K, which is near to the ordering temperature 5 K suggested from the specific heat measurements. Further, $T_N$ decreased as the applied field is increased up to 6.9 T.

The obtained NMR spectra under the field of about 1 T showed typical powder patterns above and below $T_N$. Both paramagnetic and ordered spectra are reproduced well by calculations of the internal field at proton sites on the basis of the point-dipole model. In particular, we found that the idle-spin model (or AF ordered state) is preferable to the random order model in order to explain the low-temperature spectrum. The real spin structure for low temperature phase is still open problem.

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