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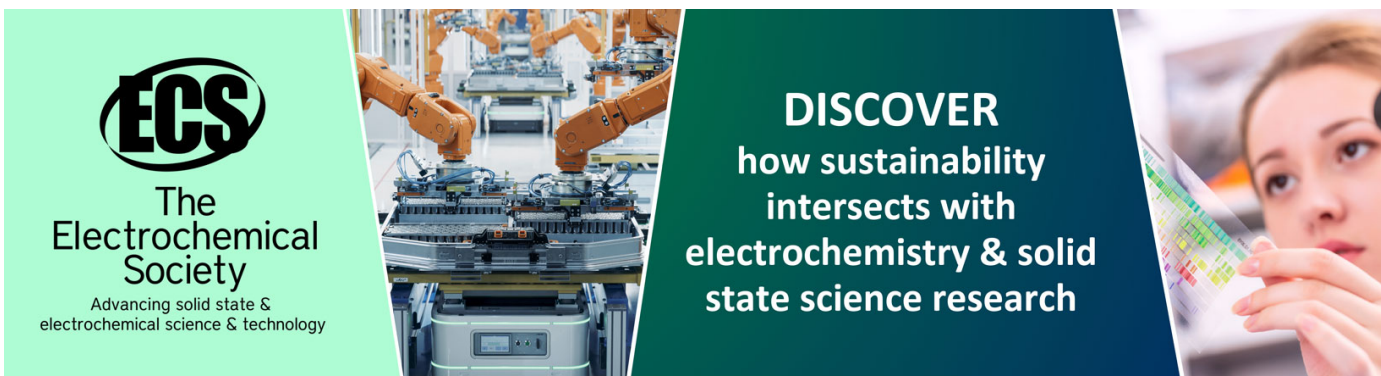
## An exotic ordered phase in the pyrochlore-like antiferromagnet $\text{Ni}_2(\text{OH})_3\text{Cl}$ studied by NMR

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# An exotic ordered phase in the pyrochlore-like antiferromagnet $\text{Ni}_2(\text{OH})_3\text{Cl}$ studied by NMR

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**Abstract.** We investigated a three-dimensional frustrated 3d-electron magnet on a pyrochlore-like lattice  $\text{Ni}_2(\text{OH})_3\text{Cl}$  with  $s = 1$  by means of  $^1\text{H}$ -NMR measurements. Previous specific heat measurements reported that this material shows a phase transition at 4.0 K and also has an anomaly at around 20 K. Our  $^1\text{H}$ -NMR measurement in 0.73 T has demonstrated that both the spin-lattice relaxation rates  $T_1^{-1}$  and the spectra show clear evidences of a magnetic long-range ordering below 4.0 K. However, they do not show any anomalies at 20 K. By contrast the width of the  $^1\text{H}$ -NMR spectra in 4.3 T starts to deviate from linearity to the magnetization below 20 K, which suggests that the magnetic anisotropy is induced by the magnetic field. In addition,  $T_1^{-1}$  starts to decrease below 20 K, which indicates the suppression of spin fluctuation. We discuss the unusual spin state below 20K.

## 1. Introduction

The pyrochlore lattice is one of the most fascinating stages of three-dimensional geometrical frustration. Magnets on the pyrochlore lattice raise many interesting topics. Neither classical nor quantum Heisenberg antiferromagnets with nearest-neighbour interaction on the pyrochlore lattice have any magnetic ordering, and spin liquid states emerge [1, 2]. Our interest is rather in the novel ordering state induced by the additional perturbative interactions. For instance, it is predicted that further neighbouring exchange interactions will produce a spin nematic state or an unusual state with an ordered spin Fourier component and fluctuating phase degree of freedom [3, 4]. Biquadratic exchange interactions induce the spin nematic state and vector multipolar state [5]. Another perturbation such as anisotropies, lattice deformations or external magnetic field can also lead to novel magnetic ordered states.

The 3d electron compound  $\text{Ni}_2(\text{OH})_3\text{Cl}$  is a Heisenberg antiferromagnet on a pyrochlore-like lattice, where the magnetic ions  $\text{Ni}^{2+}$  with spin  $s = 1$  are located on the vertices of distorted tetrahedra. Magnetic susceptibility and neutron scattering measurements have been reported to show an antiferromagnetic ordering at 4.0 K, however the Weiss temperature is 19 K, which indicates the existence of ferromagnetic interactions [6, 7]. Thus, it is considered that this material has both antiferromagnetic and ferromagnetic interactions. Specific heat measurements performed on this material have revealed a successive phase transition at 20 and 4.0 K [8]. A large peak of the specific heat at 4.0 K in zero field shifts to lower temperatures and diminishes when the magnetic field is increased. The peak almost vanishes in 3 T [8]. The other transition at 20 K was observed as a kink in

the temperature dependence of the specific heat, whose anomaly is smaller than that at 4.0 K in zero magnetic field. A large broad peak of the specific heat was observed at 20 K in a field of 3 T, in contrast to the diminution of the peak at 4.0 K. No obvious anomaly was observed around 20 K by magnetic susceptibility and neutron scattering measurements in zero or nonzero magnetic fields. The nature of the intermediate phase of this frustrated magnet remains open question.

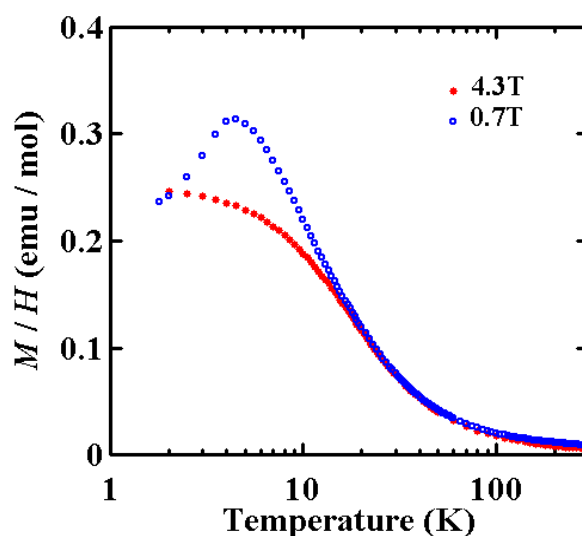
We performed magnetization and  $^1\text{H}$ -NMR measurements on  $\text{Ni}_2(\text{OH})_3\text{Cl}$  in order to reveal the nature of the intermediate phase from a microscopic view point.

## 2. Experimental Methods

A powder sample of  $\text{Ni}_2(\text{OH})_3\text{Cl}$  was prepared by hydrothermal reactions [7].  $^1\text{H}$ -NMR measurements were conducted at frequencies of 31.0 and 178.9 MHz, whose resonance fields are about 0.73 and 4.3 T, respectively, by a coherent pulsed NMR method from 1.5 to 300 K. The NMR spectra were obtained from the integrated intensities of spin echo signals measured by sweeping the magnetic field at a fixed frequency. The spin-lattice relaxation rates  $T_1^{-1}$  were determined from the recovery of the integrated spin-echo intensity  $M(t)$  after a time delay  $t$  from saturation comb pulses. The magnetization measurements were performed by a SQUID magnetometer between 1.7 and 300 K in a magnetic field of 0.73 and 4.3 T.

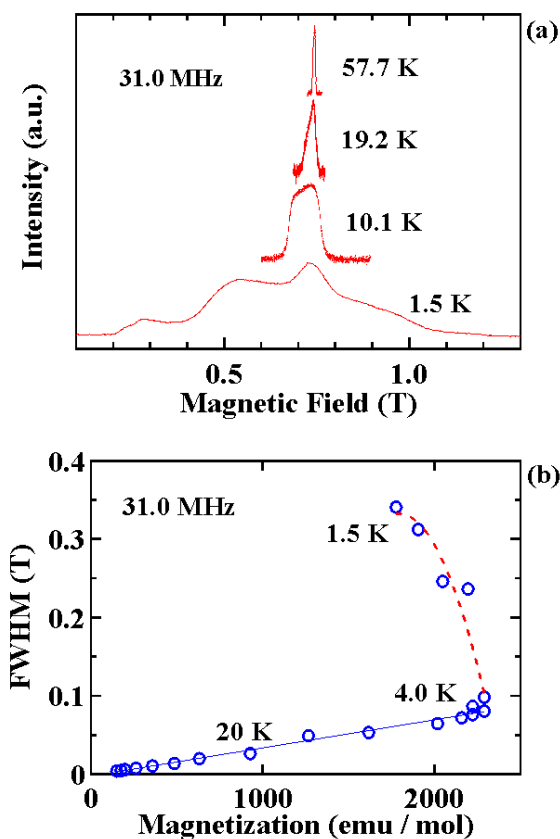
## 3. Results and Discussion

Figure 1 shows the temperature dependence of the magnetization divided by the external field  $M/H$ , obtained in 0.73 and 4.3 T. These magnetic fields correspond to the 31.0 and 178.9 MHz of the resonant frequencies used in our  $^1\text{H}$ -NMR experiment. The values  $M/H$  in both magnetic fields increase with decreasing temperature in the paramagnetic phase. The peak of  $M/H$  at 4.0 K in 0.73 T indicates the antiferromagnetic transition, while the value in 4.3 T increases monotonically over the entire temperature region, and no antiferromagnetic ordering is observed down to 2.0 K. It is thought that antiferromagnetic ordering is suppressed in 4.3 T, which is consistent with the specific heat measurements. Meanwhile, there is no anomaly near 20 K in the temperature dependence of the magnetization, in contrast to the specific heat measurement results, which show an anomaly around 20 K in 3 T [8].

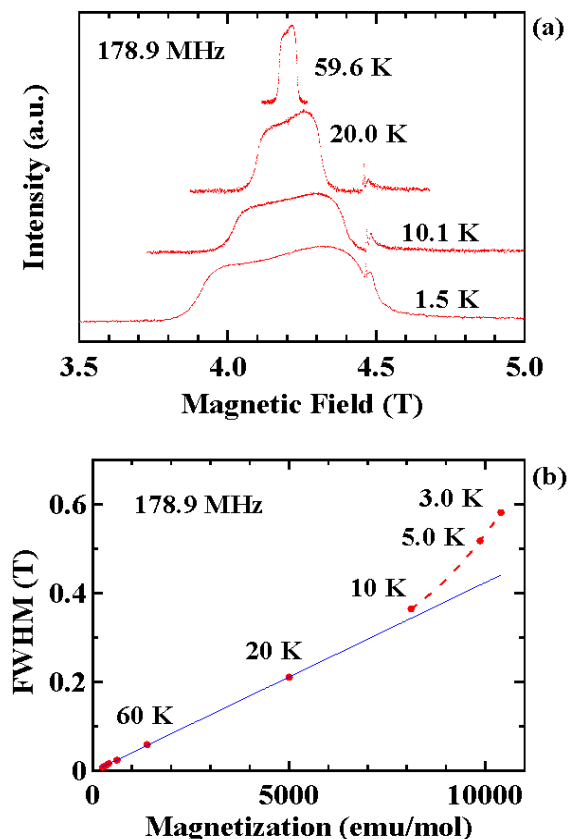


**Figure 1.** Temperature dependence of  $M/H$ , measured under the fields of 0.73 and 4.3 T.

Figure 2(a) shows the temperature variation of the  $^1\text{H}$ -NMR spectra of  $\text{Ni}_2(\text{OH})_3\text{Cl}$  at 31.0 MHz. Peaks of  $^1\text{H}$  resonance in the paramagnetic phase were observed around 0.73 T for 31.0 MHz. The spectra above 4.0 K have asymmetric profiles characteristic of powder patterns, which are caused by the anisotropic hyperfine interaction that is dipolar tensor. For the powder sample, the angles between grains in the sample and the external magnetic field distribute randomly. This random distribution of the angle causes the width of the spectra, because the internal fields at  $^1\text{H}$  sites produced by  $\text{Ni}^{2+}$  moments varies with the angle owing to the anisotropy of the dipolar interaction. We estimated the width as the full width at half maximum (FWHM) of the  $^1\text{H}$ -NMR spectra. The width increases gradually as the temperature decreases down to 4.0 K. It should be noted that this linewidth is proportional to the macroscopic magnetization in usual paramagnets where field-induced magnetic moments are homogeneous and parallel to the applied field. This proportionality is clearly seen above 4 K in figure 2(b), which is the plot of the width as a function of the macroscopic magnetization measured in a field of 0.73 T. If a conventional magnetic ordering occurs, the additional large broadening of the NMR spectra is observed as the additional internal fields at  $^1\text{H}$  sites. Actually, below 4.0 K the width increases steeply and the shape of the spectra changes into a pattern with three steps, which indicates the emergence of the large internal field due to the conventional magnetic ordering. On the other hand, no additional broadening is observed around 20 K, which indicates there is no conventional ordering at 20 K.



**Figure 2.** (a) Temperature variation of  $^1\text{H}$ -NMR spectra at 31.0 MHz. (b) FWHM vs. magnetization plot. Magnetization is measured in 0.73 T.



**Figure 3.** (a) Temperature variation of  $^1\text{H}$ -NMR spectra at 178.9 MHz. (b) FWHM vs. magnetization plot. Magnetization is measured in 4.3 T.

Figure 3(a) shows that the width of the spectra at 178.9 MHz gradually increases with decreasing temperature, while the shape of the spectra remains almost the same down to 1.5 K. The sharp peaks at 4.5 T are due to the resonance of  $^{19}\text{F}$  nuclei contained in the Teflon coating of the resonance coil. It seems that magnetic long-range ordering does not occur down to 1.5 K in this magnetic field. However, a noticeable change appears in the width of the spectra. The width FWHM at 178.9 MHz is shown as a function of magnetization in 4.3 T in figure 3(b). The width of the spectra starts to deviate gradually from linearity to the magnetization below 20 K. This deviation shows the additional broadening of the spectra with no obvious change in the shape of the spectra. As the hyperfine interaction has no temperature dependence, this additional broadening indicates that field-induced magnetic moments become anisotropic or inhomogeneous below 20 K.

Figure 4 shows the temperature dependence of the  $^1\text{H}$  spin-lattice relaxation rates  $T_1^{-1}$ , which were measured at 31.0 and 178.9 MHz. All the recoveries of the nuclear magnetization at 31.0 MHz are fitted by double-exponential functions

$$\frac{M(\infty) - M(t)}{M(\infty)} = A \exp\left(-\frac{t}{T_1}\right) + (1 - A) \exp\left(-\frac{t}{T_{1L}}\right), \quad (1)$$

where  $M(\infty)$  is the nuclear magnetization at thermal equilibrium and  $M(t)$  is the recovered nuclear magnetization after a time delay  $t$  from the saturation pulses. Single-exponential recoveries that correspond to  $A = 1$  were observed above 20 K, and the longer relaxation time  $T_{1L}$  appeared below around 20 K. The rate  $T_1^{-1}$  increases with decreasing temperature down to 4.0 K for 31.0 MHz. The temperature dependence of  $T_1^{-1}$  is expected to be proportional to  $\chi T$ , where  $\chi$  is magnetic susceptibility and  $T$  is temperature, when spins fluctuate randomly without spin correlation in the paramagnetic phase. The temperature dependence of  $\chi T$  is shown by a solid curve in figure 4. The experimental data of  $T_1^{-1}$  agrees well down to 40 K with the curve calculated using the experimental susceptibility, but deviates below this temperature, which indicates that spin correlations with  $q \neq 0$  develop below 40 K.

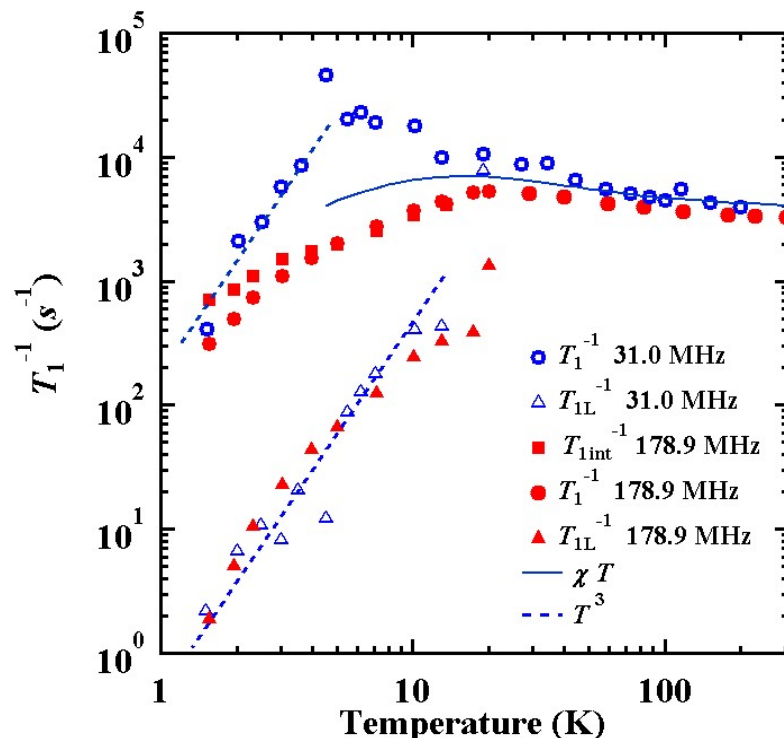


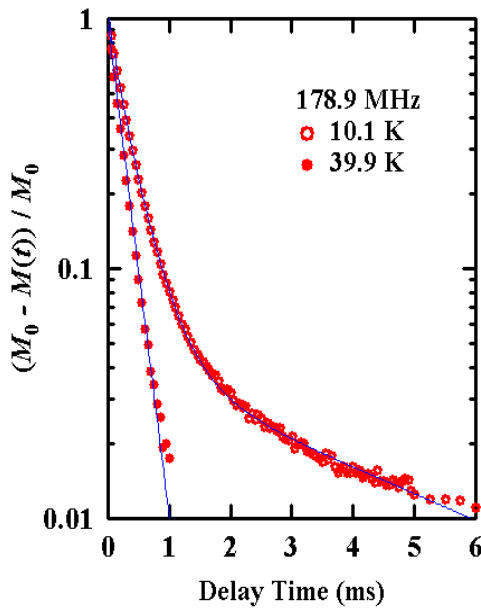
Figure 4. The temperature dependence of the spin lattice relaxation rate  $T_1^{-1}$ .

Then the rate  $T_1^{-1}$  exhibits a sharp peak at 4.0 K, which clearly indicates the phase transition to the long-range ordering. The rate decreases sharply with decreasing temperature proportionally to  $T^{-3}$  below 4.0 K. It should be noted that no anomaly was observed in the temperature dependence of  $T_1^{-1}$  around the higher transition temperature of 20 K. Meanwhile, the relaxation rate  $T_{1L}^{-1}$  has the temperature dependence proportional to  $T^{-3}$ . However, we are not yet certain whether the  $T_{1L}$  component is intrinsic, because the value of the coefficient (1-A) is only about 0.1, which might be due to impurities. We need to examine the sample dependence of the  $T_{1L}$  component.

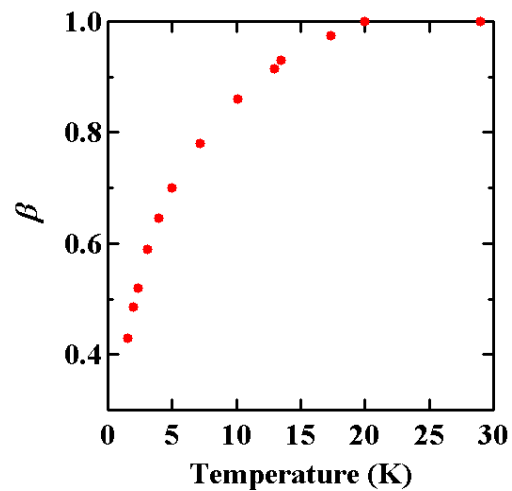
The recovery curves at 178.9 MHz in the higher field of 4.3 T could be fitted by a single-exponential function above 20 K as well as those at 31.0 MHz, as shown in figure 5. On the other hand, another characteristic behavior at 178.9 MHz was observed below about 20 K. Relaxation curves below 20 K deviate from the single-exponential decay as shown in figure 5, and could be fitted by the following stretched exponential function:

$$\frac{M(\infty) - M(t)}{M(\infty)} = B \exp \left[ - \left( \frac{t}{T_1} \right)^\beta \right] + (1 - B) \exp \left( - \frac{t}{T_{1L}} \right). \quad (2)$$

This behavior was not seen at 31.0 MHz, while the slow relaxation component  $T_{1L}$  was also observed below 20 K at 178.9 MHz as well as at 31.0 MHz, and the relaxation rate  $T_{1L}^{-1}$  is almost the same as that of 31.0 MHz. The stretching coefficient  $\beta$  denotes the degree of inhomogeneity of the spin system, while the nuclear magnetization in the homogeneous system relaxes exponentially with  $\beta=1$ . The temperature dependence of  $\beta$  is shown in figure 6. The value  $\beta$  decreases as temperature decreases below 20 K, which indicates the growth of the inhomogeneity with decreasing temperature. The magnetic field of 4.3 T gives rise to some inhomogeneity in the material. The rate  $T_1^{-1}$  in the high-temperature phase increases as temperature decreases, and starts to decrease gradually around 20 K. This temperature dependence is essentially the same as the alternative estimation of relaxation rate  $T_{1int}^{-1}$ , which is obtained from the initial decay of the relaxation curves. The difference between  $T_1^{-1}$  and  $T_{1int}^{-1}$ , which indicates an inhomogeneity of the system, becomes clear in low temperatures. The



**Figure 5.** Nuclear magnetization recoveries at 10.1 and 39.9 K for 178.9 MHz.



**Figure 6.** The temperature dependence of  $\beta$  below 30 K, observed at 178.9 MHz (4.3 T).

decreases of  $T_1^{-1}$  and  $T_{1\text{int}}^{-1}$  with lowering temperature below 20 K suggest that the spin fluctuation is suppressed by the magnetic field below this temperature. This result may correspond to the results of specific heat measurements, in which the large broad peak around 20 K was observed in 3 T [8].

No obvious anomaly like critical phenomenon observed in a conventional magnetic ordering is observed around 20 K in our NMR experiment. The temperature dependences of the spectra and  $T_1^{-1}$  between 4.0 K and 20 K are quite paramagnetic-like in the low field of 0.73 T. However, we observed the appearance of an additional broadening in the  $^1\text{H}$ -NMR spectra and the suppression of spin fluctuation in the high field of 4.3 T. These unusual behaviors may be closely related to the transition at 20 K, which was observed as a large broad peak of specific heat measurement in 3 T [8].

We comment on the nematic state which has been proposed theoretically [3, 4, 9]. The simplest order parameter of the spin quadrupolar moment among nematic orderings can be expressed as

$$Q_{\mu\mu'} = \frac{1}{2} \langle S^\mu S^{\mu'} + S^{\mu'} S^\mu \rangle - \frac{1}{3} S(S+1) \delta_{\mu\mu'}, \quad (3)$$

where  $\mu$  is the spin index. This spin quadrupolar moment, which denotes the anisotropy of spin fluctuation, has a finite value in the spin nematic ordered state and exhibits anisotropic spin susceptibility. This anisotropic susceptibility is compatible with our observation that the NMR spectra show the additional broadening below 20 K. The anisotropic spin fluctuation in nematic states can also cause the inhomogeneity observed in the distribution of  $T_1^{-1}$ . The rate  $T_1^{-1}$  depends on the angle between a grain and the applied field directions in such a case, since the rate reflects the transverse component of the fluctuating local fields with respect to the applied field.

The unusual behaviors, however, can be explained also by other scenarios. For example, the  $\text{Ni}^{2+}$  ions have more or less inherent anisotropic susceptibility like single-ionic anisotropy. Moreover, the  $\text{Ni}^{2+}$  ions have two different crystallographical sites. Both of these can also cause the additional broadening, which indicates the anisotropy or inhomogeneity in the spin system.

Further study is required to elucidate the spin state of the frustrated magnet on the pyrochlore lattice  $\text{Ni}_2\text{OH}_3\text{Cl}$ .

### Acknowledgements

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