51V-NMR Study of Honeycomb Lattice Antiferromagnet InCu$_{2/3}$V$_{1/3}$O$_3$

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Abstract. We report here the results of 51V-NMR experiments as well as susceptibility and high-filed magnetization measurements on a spin-1/2 honeycomb lattice antiferromagnet InCu$_{2/3}$V$_{1/3}$O$_3$. The magnetization curve at 4.2 K showed no anomaly up to 54 T. A small anomaly around 38 K was found in the nuclear spin-lattice relaxation rate $T_1^{-1}$ as well as the susceptibility, while NMR spectrum was temperature independent. Further, $T_1^{-1}$ showed a broad maximum around 15 K and a tendency to be constant towards the lowest temperature of 2 K. Our results suggest that a large spin fluctuation remains until 2 K without a specific magnetic long-range ordering. Preliminary NMR results for an oriented sample are also shown.

1. Introduction

A honeycomb lattice is one of the simplest two-dimensional (2D) regular lattices. A lot of theoretical works have been devoted to classical and quantum spin systems on this lattice. However, model compounds of honeycomb lattice antiferromagnets are scarcely known to date. InCu$_{2/3}$V$_{1/3}$O$_3$ was found recently to be a model compound [1]. This compound crystallizes isotypically with InMO$_3$ (M = Mn, Ga, Fe) where M ions form a triangular lattice [2]. Nonmagnetic V$^{5+}$ and magnetic Cu$^{2+}$ ($S = 1/2$) ions share a common site with 5-fold trigonal-bipyramidal coordination of oxygen ions. As a result, Cu$^{2+}$ ions form a 2D honeycomb lattice in a crystallographic $c$-plane. The exchange coupling between Cu$^{2+}$ ions is reported to be $2J/k_B \simeq -280$ K from the susceptibility measurement [1]. Quite recently, it was reported from the neutron diffraction and the specific heat measurements that no signature of magnetic ordering was found down to 1.5 K [3], even though there is a kink of the susceptibility at 38 K. Further, they proposed that there are crystal structure domains of a typical diameter $\sim 300$ Å.

In order to investigate magnetic properties of InCu$_{2/3}$V$_{1/3}$O$_3$ at low temperatures, we have performed susceptibility, high-field magnetization and 51V-NMR measurements.

2. Experimental

We synthesized InCu$_{2/3}$V$_{1/3}$O$_3$ according to the literature [1]. The obtained powder sample was checked by X-ray diffraction. The susceptibility was measured by a SQUID magnetometer under
an applied field of 1 T. The high-field magnetization was measured at ISSP, University of Tokyo in pulsed fields up to 54 T with a pulse duration of 6 ms. NMR experiments on \( ^{51}\text{V} \) (\( I = 7/2 \)) were performed with an operating frequency of 11.72 MHz. We used a conventional pulsed NMR method. NMR spectra were recorded by sweeping the external field while measuring the spin-echo intensity. We prepared a field-oriented sample as follows: The powder sample of InCu\(_{2/3}\)V\(_{1/3}\)O\(_3\) and epoxy resin were mixed with mass ratio 1:2 and left in a magnetic field (we call it ‘alignment field’ hereafter) of 10 T at room temperature. Achievement of the orientation was demonstrated by ESR measurements in which only one ESR line was observed for the sample.

3. Experimental results and discussions

Figure 1 shows the magnetic susceptibility \( \chi(T) \) of InCu\(_{2/3}\)V\(_{1/3}\)O\(_3\) under the applied field of 1 T. \( \chi(T) \) exhibited a broad maximum around 170 K indicating low dimensionality, and a small jump at 38 K. The upturn at low temperatures may be attributed to a Curie-law contribution \( \chi_C = \frac{C_{\text{def}}}{T} \) which originates from free spins at defect sites. We tentatively put \( C_{\text{def}} = 0.001 \text{ emu-K/mol} \) (0.4 % of total spins) and obtained a corrected susceptibility \( \chi_{\text{corr}} = \chi - \chi_C \), as shown in Fig. 1. The behavior of measured \( \chi \) is qualitatively the same as the reported one [1, 3].

Figure 2 shows the magnetization curve at 4.2 K. The magnetization \( M \) grew linearly with increasing field above 15 T without anomalies and was still small even at the highest field of 54 T. According to a theoretical work [5], the saturation field is \( g\mu_B H_s = 12J/S \) for a Heisenberg honeycomb lattice antiferromagnet. We obtain \( H_s \approx 600 \text{ T} \) by putting the values of \( 2J/k_B \approx -280 \text{ K} \) and \( g = 2.16 [1] \). The rounded \( M-H \) curve in the low field region is probably due to the contribution from free spins at defect sites. If the intrinsic magnetization of this compound is linear to \( H \) in all over the relevant field region, such a free spin contribution is about 0.004 \( \mu_B \)/f.u. which is 0.6 % of the saturation magnetization 0.72 \( \mu_B /\text{f.u.} \). The slope of the assumed linear \( M-H \) curve corresponds to \( 6.7 \times 10^{-4} \text{ emu/mol} \). This value is close to \( \chi_{\text{corr}} \) at 4.2 K. Consequently, the above estimation is approximately consistent with \( \chi(T) \) data.

Figure 3 shows \( ^{51}\text{V}-\text{NMR} \) spectra of powder sample of InCu\(_{2/3}\)V\(_{1/3}\)O\(_3\) measured with an operating frequency of 11.72 MHz. The spectrum exhibited a typical powder pattern of \( I = 7/2 \).

**Figure 1.** The magnetic susceptibility \( \chi(T) \) of InCu\(_{2/3}\)V\(_{1/3}\)O\(_3\). Solid and open squares represent the data of \( \chi \) as measured and the corrected susceptibility \( \chi_{\text{corr}} = \chi - \chi_C \), respectively. The dotted line \( (\chi_C) \) shows Curie-law contribution from free spins.

**Figure 2.** High-field magnetization of InCu\(_{2/3}\)V\(_{1/3}\)O\(_3\) at 4.2 K. The dashed (red) line is drawn for guide for the eye to show linear behavior of the magnetization.
nucleus in an uniaxial electric field gradient (EFG) and was temperature independent, suggesting that the EFG is uniform in the crystal and temperature independent. The quantity $A_1$ indicated in Fig. 3 represents quadrupole interaction, which will be discussed later. It may be noteworthy that, because $^{51}$V is situated just in the center of surrounding six Cu$^{2+}$ ions, the internal field created by antiferromagnetic spin configuration must vanish at $^{51}$V site.

Temperature dependence of the nuclear spin-lattice relaxation rate $T_1^{-1}$ of $^{51}$V is shown in Fig. 4. Above 38 K, $T_1^{-1}$ was nearly proportional to $\chi T$, suggesting paramagnetic spin fluctuations. We found a sharp but weak enhancement of $T_1^{-1}$ around 38 K. Further, a broad maximum was found around 15 K, and $T_1^{-1}$ showed a tendency to be constant at low temperatures. Such a behavior hints a large fluctuation remaining even at lowest temperature of 2 K instead of a usual long-range ordering.

Here, we refer to the structural domain proposed in Ref. 3. We may not detect NMR of $^{51}$V on the domain boundary, because the number of such $^{51}$V nuclei is too small. However, it might be possible that the electron spins on the domain boundary affect spins inside the domain at low temperatures, because the spin-spin correlation develops with decreasing temperature as pointed out by quantum-Monte Carlo calculations [3]. Thus, we at present consider that the observed anomalies of $T_1^{-1}$ are possibly explained by the existence of the structural domain instead of a long-range ordering. Especially, since the domain size will become comparable to the correlation length at 15 K, collective fluctuations induced by inter-domain or inter-layer interactions may bring about the enhancement of $T_1^{-1}$.

Finally, we show a preliminary NMR result for an oriented sample. Figure 5(a) shows $^{51}$V-NMR spectra obtained for the oriented sample under the field applied parallel to the alignment field. Each resonance line for the oriented sample coincided with a shoulder of the powder spectrum. Here, let us discuss on the shift due to quadrupole interaction. Generally, the quadrupole shift of a resonance line for a transition $m \leftrightarrow m - 1$ ($m = -I + 1, -I + 2, \ldots, I$) is given by

$$\Delta \omega_Q(m \leftrightarrow m - 1) = A_1 \left( m - \frac{1}{2} \right) (3 \cos^2 \theta - 1),$$

(1)

where $\theta$ is the angle between the applied magnetic field $B_0$ and a local principal axis $z$. In eq. (1), $A_1 = \frac{3}{4(2I-1)} \frac{e^2 Q}{h}$, where $Q$ is the quadrupole moment of $^{51}$V and $eQ$ is EFG along $z$-axis.
Figure 5. (a) $^{51}$V-NMR spectrum obtained for the oriented sample under the field applied parallel to the alignment field (red bold line). The spectrum for the powder sample is also shown by a black thin line for comparison. (b) Local coordination around $^{51}$V. $\theta$ is defined as the angle between the principal axis $z$ of EFG and the applied magnetic field $B_0$.

axis, respectively [6]. The $z$-axis around $V^{5+}$ ion in this compound is parallel to crystallographic $c$-axis as shown in Fig. 5(b). $A_1$ corresponds to the splitting between shoulders of the powder spectrum as shown in Fig. 3. Then, our results require $3 \cos^2 \theta - 1 = \pm 1$, namely, $\theta = 90^\circ$ or $35^\circ$. It is natural to take $\theta = 90^\circ$ because of the crystal symmetry. Therefore, the magnetic easy plane perpendicular to $c$-axis is suggested. This agrees with the results of ESR measurements that $g_\parallel > g_\perp$ [1, 4].

4. Summary
We have performed susceptibility, high-field magnetization and $^{51}$V-NMR measurements for powder and oriented samples of InCu$_{2/3}$V$_{1/3}$O$_3$. The high-field magnetization data at 4.2 K is consistent with the susceptibility data on the basis that the sample contains free spins of less than 1 %. NMR results suggest that large fluctuation survives towards the lowest temperature of 2 K without a specific magnetic long-range ordering nor structural transitions. From comparison between observed spectra of powder and oriented samples, we suggest that $c$-plane is a magnetic easy plane. We are planning to perform further experiments with the oriented sample.

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