High-Field Magnetization and $^1$H-NMR Study of the Dimer Compound CoSeO$_3$·2H$_2$O

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Abstract. We report magnetic properties of a dimer compound CoSeO$_3$·2H$_2$O whose anisotropy is expected to be large. We have performed susceptibility measurements, high field magnetization measurements up to 60 T below 4.2 K and $^1$H-NMR experiment in an applied field of 1 T on this compound. A multi-step magnetization with hysteresis was observed. NMR spectra broadened suddenly below about 6 K, suggesting an occurrence of a magnetic order. The nature of the magnetic transition is assumed to be the first order, since distinct divergent behavior was not observed in the spin-lattice relaxation rate and a coexistence of spectra was detected around the transition temperature.

1. Introduction
Spin dimer system in a magnetic field produces exotic quantum phases like magnetic plateau or BEC of magnons [1]. Supersolid state of magnon is expected to emerge if large magnetic anisotropy is added to the spin dimer system [2]. Many spin dimer compounds studied so far are based on isotropic Cu$^{2+}$ ions whose intrinsic anisotropies are small [3–6]. Cobalt(II) hydrated selenite CoSeO$_3$·2H$_2$O consists of dimeric Co$^{2+}$ ions [7, 8] whose anisotropy is generally supposed to be large. This compound crystallizes in the monoclinic $P2_1/n$ space group. Edge-sharing Co$_2$O$_{10}$ dimeric octahedra are linked by SeO$_3$ in three dimensions. Coordination of a Co$^{2+}$ ion are elongated nearly along the crystallographic c-axis.

In order to scrutinize magnetic properties of this spin dimer compound, we have performed susceptibility, high-field magnetization and $^1$H-NMR measurements. The powder sample of CoSeO$_3$·2H$_2$O was synthesized according to the literature [7, 8] and checked by X-ray diffraction. The susceptibility was measured by a SQUID magnetometer in a temperature range between 2 and 300 K and in the field range up to 7 T. The high-field magnetization was measured at ISSP, University of Tokyo in pulsed fields up to 60 T with a pulse duration of 6 ms at 4.2 K and 1.3 K. NMR experiments were performed at University of Fukui with an operating frequency of 42.6 MHz and with a superconducting magnet. We used a conventional pulsed NMR method.

2. Experimental results and discussions
Figure 1 shows a temperature dependence of the susceptibility $\chi$ of CoSeO$_3$·2H$_2$O under an applied field of 0.01 T. The susceptibility had a broad maximum around 11 K, which is almost
the same as the reported one [8]. Weiss temperature is estimated to be $\theta = -22$ K from fitting Curie-Weiss law to our data above 150 K. It is found here that there was a jump-like anomaly at 6.5 K, since the temperature derivative of $\chi$ shows a divergent behavior as shown in Fig. 1(b) and that the susceptibility became nearly constant below about 3 K. There were no differences between field cooled and zero-field cooled data.

The results of the magnetization measurement and its field derivative ($dM/dH$) are shown in Figs. 2 and 3, respectively. A clear hysteresis was found in the magnetization curve. We confirmed the existence of this hysteresis from measurements under static fields up to 7 T with SQUID magnetometer. For a typical antiferromagnetically (AF) ordered spin system with Ising-like anisotropy, the magnetization suddenly increases due to a spin-flop transition at a certain field and then grows up linearly toward its saturation value. However, CoSeO$_3$·2H$_2$O showed multi-step magnetization accompanied by several jumps. Such a complicated behavior infers effects of interdimer interactions. As shown in Fig. 1(c), the susceptibility $M/H$ at 7 T deviated from those at lower fields below about 15 K, which shows the change of the ground state.

**Figure 1.** (a) Temperature dependence of the susceptibility $\chi$ for a powder sample of CoSeO$_3$·2H$_2$O under the applied field of 0.01 T. (b) Temperature derivative of $\chi$ data shown in the panel (a). (c) Low temperature susceptibilities measured under the field of 0.01 T (solid circle), 1 T (open square) and 7 T (open triangle).

**Figure 2.** The magnetization $M$ as a function of the externally applied field $H$ observed at 4.2 K and 1.3 K. The data at 4.2 K is shifted by 0.5 $\mu_B$/f.u. The inset shows the magnetization curve in the pulsed magnetic field of 14.5 T.

**Figure 3.** The field derivative of the magnetization at 1.3 K. Solid (black) and dotted (red) lines show the data for raising and lowering field, respectively.
NMR spectra were recorded by sweeping the external field while measuring the spin-echo intensity. Obtained $^1$H-NMR spectra above 6 K and below 5 K are shown in Figs. 4 and 5, respectively. At high temperatures, the spectrum had an asymmetric line shape which is associated with a powder pattern due to dipolar hyperfine fields from paramagnetic magnetic moments on cobalt ions. Below about 30 K, the spectrum became broader with decreasing temperature, and a single line remained at the central position below about 8 K. At further lower temperatures below 6 K, we obtained a strongly broadened shape with square shoulders which is known as the AF ordered powder pattern [9].

Here, let us try to reproduce the low temperature spectrum by calculation. We tentatively put a magnetic moment on each Co$^{2+}$ ion ($S = 3/2$) with the magnitude 3 $\mu_B$ directed parallel or antiparallel to the crystallographic c-axis. Then, for each of four crystallographically inequivalent proton sites, we calculated the dipolar field made by Co$^{2+}$ ions within 15 Å distance. As shown in Fig. 5, the calculated spectrum reproduces fairly well the experimental result in spite of such a simple assumption of the spin structure.

It should be pointed out that the positions of the shoulders of low temperature spectra were independent of the temperature. Further, the intensity ratio of the remaining central peak to the AF powder pattern gradually decreased with decreasing temperature. Such a coexistence of the spectrum is a sign of the first order transition. Recalling that the anomaly of the susceptibility was observed at 6.5 K, we consider that AF order occurs at this temperature.

Temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of $^1$H is shown in Fig. 6. $T_1^{-1}$ was measured at peak position of the spectrum above 5 K, and off peak position by $\sim$0.02 T below 4.3 K in order to avoid the effect of the central sharp peak. We observed a few distinct values of $T_1^{-1}$ in a single relaxation measurement, according to the following procedure: A set of the values of $T_1^{-1}$ was obtained by fitting the relaxation data to $I(t)/I(\infty) = \sum A_i \exp(-t/T_{1i})$, where $t$ is the delay time from the end of comb pulses to the beginning of $\pi/2$-$\pi$ pulses, $I(t)$ is the echo intensity for a delay time $t$, and $A_i$ is the intensity ratio for $i$-th relaxation rate $T_{1i}^{-1}$. Such a multi-$T_1$ relaxation is probably because inequivalent proton sites have different values of $T_1$. We show here the data of the biggest and the second biggest relaxation rates. Below 4.3 K, $T_1^{-1}$ decreased quite steeply with decreasing temperature. The power-law dependence of $T_1^{-1} \sim T^9$ or $T^{11}$ usually suggests the occurrence of a long-range order, though it is beyond the aim of this paper to discuss the origin of this power and the site dependence. Around the

![Figure 4. $^1$H-NMR spectra above 6 K obtained with operating frequency 42.6 MHz.](image-url)

![Figure 5. $^1$H-NMR spectra below 5 K. $^{19}$F-NMR signal appeared because it was contained in a sample holder. The thin (red) line shows the calculated spectrum (see the text).](image-url)
transition temperature $\sim 7$ K, we obtained only one value of $T_1^{-1}$ which was just linked to the second biggest $T_1^{-1}$ for higher temperatures (open square in Fig. 6). It was impossible to determine the other $T_1$'s due to their small intensity. This may be because of short relaxation time and/or because NMR spectrum of the corresponding proton site is strongly broadened. As a result, the second biggest $T_1^{-1}$ (open square) was observed down to at least 5 K without a remarkable anomaly. Thus, no divergent behavior of $T_1^{-1}$ of this site was found near the transition temperature of $\sim 7$ K. Therefore, we believe that the results of $T_1^{-1}$ support the proposal of the occurrence of the first order transition. The continuation between the data at higher and lower temperatures than 4.3 K is unclear at present.

3. Summary

In summary, we found, from $^1$H-NMR measurement of CoSeO$_3$·2H$_2$O under 1 T, the clear evidence of an antiferromagnetic order at around 6 K, which probably corresponds to a jump-like anomaly of the susceptibility at 6.5 K. The nature of this magnetic transition suggested to be the first order. Unfortunately, a supersolid state of magnon does not appear, but an AF ordered state does in this compound. High-field magnetization showed the multi-step curve which can not be explained by a simple spin-flop transition, suggesting effects of interdimer interactions. In order to discuss in detail, the information of anisotropy (by ESR experiment etc.) is necessary. We are also planning to measure with a field-oriented sample.

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