High-Field Magnetization and Neutron Diffraction Studies of One-Dimensional Compound Ca$_3$CoRhO$_6$

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High-field magnetization and neutron diffraction measurements were performed on the one-dimensional compound Ca$_3$CoRhO$_6$. The long-range ordered state was first observed below 90 K. A plateau at 1/3 of the saturation magnetization was observed in the magnetization curve at 70 K, indicating ferrimagnetic alignment of the ferromagnetic Ising chains. We also observed a large hysteresis originating from a spin freezing of ferromagnetic chains in the magnetization curve at 4.2 K. Based on the results of high-field magnetization and neutron diffraction measurements, a possible magnetic structure is discussed in terms of the spin frustration on the triangular lattice.

KEYWORDS: one-dimensional magnetic chain, triangular lattice, Ising spin system, frustration, Ca$_3$CoRhO$_6$, ferrimagnetic structure, partially disordered antiferromagnetic state

We have recently reported the synthesis, crystal structure and magnetic properties of Ca$_3$CoRhO$_6$, which belongs to $A'B'ABO_6$-type compounds ($A' = $ Ca, Sr, Ba; $A = $ Cu, Ni, Zn, …; $B = $ Ir, Pt, Ru, …) with the $K_ACdCl_6$ structure. The structure of Ca$_3$CoRhO$_6$ consists of one-dimensional (1-D) chains of alternating face-sharing CoO$_6$ trigonal prisms and RhO$_6$ octahedra. The chains are separated by calcium cations, forming a triangular lattice in the $c$ plane. The distance between the nearest neighbor chains is 5.313 Å, about twice as long as the intrachain spacing between Co and Rh, 2.682 Å. Therefore, Ca$_3$CoRhO$_6$ has a structural similarity to $ABX_3$-type compounds, for example, CsCoCl$_3$ and CsCuCl$_3$ in the respect that chains consisting of magnetic ions are arranged on a triangular lattice, which is expected to show interesting magnetic characteristics of a 1-D chain and/or a triangular lattice. Ca$_3$CoRhO$_6$ has the positive Weiss temperature of 150 K, suggesting that the intrachain exchange interaction is ferromagnetic and relatively strong compared with that of $ABX_3$-type compounds. It should be noted in the case of Ca$_3$CoRhO$_6$ that each chain has a different phase of the atomic sequence from three nearest-neighbor chains by 1/6 along the $c$ axis (the chain direction) and from the other three by 2/6 along the same axis.

The temperature dependence of the magnetic susceptibility $M/H$ of Ca$_3$CoRhO$_6$ (see the inset of Fig. 5) is very complex and similar to those of isostructural Sr$_3$NiIrO$_6$ and Ca$_3$CoIrO$_6$. [1] The values of $M/H$ depend on $H$ below $T_1$ (90 K for Ca$_3$CoRhO$_6$, 70 K for Sr$_3$NiIrO$_6$, 80 K for Ca$_3$CoIrO$_6$), and [2] there is a sharp drop at $T_2$ reaching nearly zero (35 K for Ca$_3$CoRhO$_6$, 21 K for Sr$_3$NiIrO$_6$, 32 K for Ca$_3$CoIrO$_6$) in zero field cooling (ZFC) measurements, and the $M/H$ does not drop in field cooling (FC) measurements. Hence, it is considered that these three compounds have similar magnetic properties which can be attributed to the 1-D chain and/or the triangular lattice and possibly the alternating arrangement of two different ions. Nyugen and Loye considered that the abrupt drop in $M/H$ of Sr$_3$NiIrO$_6$ is ascribed to a transition to the spin singlet state in the ZFC process. Their neutron diffraction measurements at 10 K and 30 K for Sr$_3$NiIrO$_6$ indicate neither a structural change nor additional Bragg peaks, suggesting the absence of a magnetic superstructure. As for Ca$_3$CoIrO$_6$, the magnetic susceptibility has been reported only by Kageyama et al. Thus still little is known about the ground states and the phase transitions of these three compounds.

In order to elucidate the above-mentioned unusual magnetic behaviors, we have performed high-field magnetization and powder neutron diffraction measurements of Ca$_3$CoRhO$_6$. The main findings are that the $M/H$ curve at 70 K shows a plateau at 1/3 of the saturation magnetization and that four magnetic Bragg reflections indicating a magnetic ordering were observed below 90 K. The polycrystalline sample of Ca$_3$CoRhO$_6$ was prepared by a solid state reaction from starting materials CaCO$_3$(99.99%), CoO(99.99%), and Rh(>99.95%). They were mixed in a stoichiometric proportion, pressed into pellets, and calcined in air at 1173 K for one day. Then the sample was heated at 1473 K in air for one week with several intermediate grindings. Field-oriented
Fig. 1. Magnetization curves of Ca$_3$CoRhO$_6$ at 70 K in pulsed magnetic fields up to 18.7 T. The arrows along the curves indicate the directions of the field sweeps. The inset represents the low-field region in the magnetization curve for $H \parallel c$.

samples for high-field magnetization measurements were prepared by solidifying the powder dispersed in epoxy resin Stycast 1226 under the magnetic field of 8 T at room temperature. X-ray diffraction measurement confirmed the alignment of the polycrystalline samples along the hexagonal $c$ axis. High-field magnetization measurements were carried out for the field-oriented samples by an induction method in a pulsed high magnetic field up to 18.7 T at 70 K and 42 T at 4.2 K. The duration of the pulsed field was 12 ms, roughly corresponding to $\frac{\Delta H}{\Delta t} = 3.1$ T/ms at 70 K, and 7.0 T/ms at 4.2 K. Powder neutron diffraction measurements were performed using the HQR diffractometer installed at JRR-3M Guide Hall in Japan Atomic Energy Research Institute. The wavelength of the incident neutrons was 2.467 Å. The data were collected in the $2\theta$ range of 10° to 60° at an interval of 0.1° in the temperature range of 4–155 K under an applied magnetic field of 0–2 T. The powder neutron diffraction patterns of two magnetic structures were calculated using Rietan.5)

In Fig. 1 we show the magnetization curves of the field-oriented samples in pulsed magnetic fields up to 18.7 T at 70 K between $T_2$ and $T_1$. There is a large difference between the magnetization for $H \parallel c$, $M_\parallel$, and that for $H \perp c$, $M_\perp$. The value of $M_\parallel$ at 18.7 T is 4.05$\mu_B$/f.u., eight times as large as that of $M_\perp$ at 18.7 T, 0.53$\mu_B$/f.u. This indicates the Ising spin nature of this system. $M_\perp$ shows linear field dependence up to 18.7 T. On the other hand, $M_\parallel$ exhibits a plateau around 4 T reaching 4$\mu_B$/f.u. at 15 T as seen in the inset of Fig. 1. The value of the magnetization at 4 T is 1.39$\mu_B$/f.u., corresponding to 1/3 of the saturation magnetization. The plateau at the value of 1/3 of the full moment implies a ferrimagnetic alignment of ferromagnetic spin chains supported by the positive Weiss temperature.1)

Figure 2 shows magnetization curves in pulsed magnetic fields up to 42 T at 4.2 K below $T_2$. $M_\parallel$ increases linearly, reaching 0.64$\mu_B$/f.u. at 42 T. Although the values of $M_\parallel$ below 28 T are about the same as those of $M_\perp$, $M_\parallel$ shows a steep increase above 28 T and reaches 4$\mu_B$/f.u., corresponding to the saturation magnetization at 70 K. A plateau is not observed in $M_\parallel$ at 4.2 K unlike that at 70 K. We can see a distinct hysteresis in $M_\parallel$, indicating a hard magnetization process against an external
The existence of magnetic ordering has been confirmed phase transition down to 10K. This is the first time diffraction does not show any indication of structural ascribed to a magnetic ordering because powder X-ray on the chemical unit cell, respectively. These peaks are 40K, indexed as (100), (200), (112), and (210) based on the saturation magnetization, 4

The powder neutron diffraction patterns of Ca$_3$CoRhO$_6$ at 4K, 40K, and 120K are shown in Fig. 3. Four additional Bragg peaks at 17.7°, 35.9°, 41.4° and 48.2° were observed in the patterns obtained at 4K and 40K, indexed as (100), (200), (112), and (210) based on the chemical unit cell, respectively. These peaks are ascribed to a magnetic ordering because powder X-ray diffraction does not show any indication of structural phase transition down to 10K. This is the first time the existence of magnetic ordering has been confirmed among Ca$_3$CoRhO$_6$, Sr$_3$NiIrO$_6$, and Ca$_3$CoIrO$_6$. It also indicates that Sr$_3$NiIrO$_6$ and Ca$_3$CoRhO$_6$ have different magnetic structures, although the temperature dependence of $M/H$ of Sr$_3$NiIrO$_6$ is similar to that of Ca$_3$CoRhO$_6$.

The four magnetic peaks may be explained in term of a ferrimagnetic structure by the comparison between the powder neutron diffraction patterns at 4K and 40K and the calculated powder neutron diffraction pattern of the ferrimagnetic structure as seen in Fig. 3. In the calculation of the diffraction pattern, Co and Rh were assumed to have the magnetic moments of 3$\mu_B$/f.u. and 1$\mu_B$/f.u., respectively. This assumption is based on the saturation magnetization, 4$\mu_B$/f.u. and the bond valence calculation.

The ferrimagnetic structure projected on the $c$ plane is illustrated in Fig. 4(a). All the moments are aligned along [001] and ferrimagnetic coupling dominates within the chains. These ferrimagnetic Ising chains are ordered ferrimagnetically in the c plane. This ferrimagnetic structure is the same as the magnetic structure of Ca$_3$Co$_2$O$_6$ at low temperatures, consistent with the 1/3 plateau observed at 70 K in $M/\mu_B$, the Ising spin nature, and the high relative intensity of the (100) magnetic reflection.

Figure 5 represents the temperature dependence of the (100) peak intensity at $H = 0$T, $I_{\text{ZFC}}$, at $H = 2$T for ZFC, $I_{\text{ZT-ZFC}}$, and at $H = 2$T for FC, $I_{\text{ZT-FC}}$. The temperature dependence of $I_{\text{ZFC}}$ exhibits no anomaly at $T_2$. We estimated the long-range ordering temperature, $T_N$ by fitting $I_{\text{ZFC}}$ between 50 K and 85 K to the following formula,

$$I_{\text{ZFC}} = A(1 - T/T_N)^\beta + I_0,$$

where $A$ is the coefficient of the temperature dependent term, $\beta$ the critical exponent, and $I_0$ the constant term. The obtained $T_N$ is 89.9 ± 2.9 K, in good agreement with $T_1$.

$I_{\text{ZT-ZFC}}$ exhibits unusual temperature dependence for a simple ferrimagnet. Although the values of $I_{\text{ZT-ZFC}}$ are the same as those of $I_{\text{ZFC}}$ below 30K, $I_{\text{ZT-ZFC}}$ increases sharply at 30K on heating. Note that the abrupt increases of $I_{\text{ZT-ZFC}}$ and the susceptibilities $M/H$ for ZFC occur at about the same temperature. The values of $I_{\text{ZT-ZFC}}$ above 50K are about twice as large as those of $I_{\text{ZFC}}$. The $T_N$ estimated from $I_{\text{ZT-ZFC}}$ by the above-mentioned method is 90.8 ± 3.1K, consistent with the $T_N$ estimated from $I_{\text{ZFC}}$. One can see the difference between $I_{\text{ZT-ZFC}}$ and $I_{\text{ZT-FC}}$ below 40K.

One explanation for the origin of the increase in $I_{\text{ZT-ZFC}}$ at 30K may be that spin glass regions between predominant ferrimagnetic regions are changed into domains of the ferrimagnetic structure by the magnetic field against the random freezing. Based on this explanation, the observed increase in $I_{\text{ZT-ZFC}}$ at 30K implies anomalously large volume of spin glass regions inconsistent with the Ising spin nature of Ca$_3$CoRhO$_6$, although the possibility of this case cannot be ruled out.

Here we propose the following model that can explain the increase at 30K in $I_{\text{ZT-ZFC}}$ more suitably. Below 90K, the ferrimagnetic spin chains in Ca$_3$CoRhO$_6$ are partially ordered antiferromagnetically. In other words, the partially disordered antiferromagnetic (PDA) state is realized below 90K. In the PDA state as illustrated in Fig. 4(b), 2/3 of the ferrimagnetic Ising chains order antiferromagnetically with each other and the remaining
1/3 are left incoherent with the other chains. The short-range ferromagnetic order is well developed even within each incoherent chain. The 1/3 incoherent ferromagnetic chain originates from the cancellation of the antiferromagnetic exchange interactions with the six nearest neighbor chains and the entropy effect. The incoherent ferromagnetic chains fluctuate by means of the propagation of the domain walls. Below 30 K, a spin freezing of the incoherent ferromagnetic chains occurs, resulting in a frozen PDA (F-PDA) state. In the F-PDA structure, 2/3 of the ferromagnetic chains order antiferromagnetically similar to the case above 30 K and the moments in the 1/3 incoherent ferromagnetic Ising chains freeze randomly due to a finite activation energy for the spin inversion in antiferromagnetic Ising chains. The randomly frozen Ising spin chains have much lower magnetic susceptibility than the fluctuating chains. This accounts for the sharp drop of the magnetic susceptibility at 30 K. We show a rough magnetic phase diagram of Ca$_3$CoRhO$_6$ in Fig. 6. The two critical fields at 2 T and 4 T in the phase diagram are roughly estimated from the magnetization curve at 70 K in $M_{\parallel}$.

It is theoretically indicated by molecular field approximation $^7$ and Monte Carlo simulation $^8$ that a PDA phase equivalent to that of our model appears in the triangular Ising lattice with an antiferromagnetic nearest neighbor interaction together with a weak ferromagnetic second neighbor interaction. GdInCu$_4$ is given as a case in which incoherent spins in a PDA state freeze at low temperatures $^9$.

We briefly examine the results mentioned above from the viewpoint of our model. The 1/3 plateau at 70 K in $M_{\parallel}$ originates from a ferromagnetic alignment of the 1/3 incoherent chains, leading to the ferrimagnetic structure. The powder neutron diffraction patterns at 4 K and 40 K can be explained qualitatively by the PDA (F-PDA) structure similar to the ferrimagnetic structure as seen in Fig. 3. It should be noted that the calculated pattern of the F-PDA structure is identical to that of the PDA structure since the randomly frozen chains do not contribute any Bragg scattering. The unusual temperature dependence of $I_{2T-ZFC}$ can be explained by a transition from the F-PDA state to the ferrimagnetic state. Although the thermodynamically stable state at $H = 2$ T below 90 K is the ferrimagnetic state as shown in Fig. 6, 2 T is not strong enough to change the F-PDA state into the ferrimagnetic state below 30 K, so that $I_{2T-ZFC}$ is the same as $I_{2T}$ below 30 K. Above 30 K, it is possible to change the system into a ferrimagnetic structure at 2 T. The magnetic structure factor of the (100) peak in the ferrimagnetic structure is larger than that in the F-PDA structure, resulting in the steep increase at 30 K in the temperature dependence of $I_{2T-ZFC}$. In order to confirm our model, specific heat, ESR, and NMR measurements are now in progress.

In conclusion, we have investigated the magnetic properties of Ca$_3$CoRhO$_6$ by high-field magnetization and powder neutron diffraction measurements. The plateau at 1/3 of the saturation magnetization was observed in the magnetization curve at 70 K, indicating a ferrimagnetic alignment of ferromagnetic spin chains. Four magnetic Bragg peaks ascribed to a magnetic ordering were observed in the powder neutron diffraction patterns below 90 K. The existence of magnetic long-range ordering has been first confirmed among three compounds which show similar temperature dependences of $M/H$. We propose a partially disordered antiferromagnetic state as a possible magnetic structure of Ca$_3$CoRhO$_6$, of which the incoherent chains freeze randomly below 30 K.

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