

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

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High-field magnetization and neutron diffraction measurements were performed on the one-dimensional compound $\text{Ca}_3\text{CoRhO}_6$. 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, $\text{Ca}_3\text{CoRhO}_6$, ferrimagnetic structure, partially disordered antiferromagnetic state

We have recently reported the synthesis, crystal structure and magnetic properties of $\text{Ca}_3\text{CoRhO}_6$,¹⁾ which belongs to $A'_3\text{ABO}_6$ -type compounds ($A' = \text{Ca, Sr, Ba}$; $A = \text{Cu, Ni, Zn, } \dots$; $B = \text{Ir, Pt, Ru, } \dots$) with the K_4CdCl_6 structure.²⁾ The structure of $\text{Ca}_3\text{CoRhO}_6$ 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, $\text{Ca}_3\text{CoRhO}_6$ 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. $\text{Ca}_3\text{CoRhO}_6$ 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.¹⁾ It should be noted in the case of $\text{Ca}_3\text{CoRhO}_6$ 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 $\text{Ca}_3\text{CoRhO}_6$ ¹⁾ (see the inset of Fig. 5) is very complex and similar to those of isostructural $\text{Sr}_3\text{NiIrO}_6$ ³⁾ and $\text{Ca}_3\text{CoIrO}_6$ ⁴⁾ [1] the values of M/H depend on H below T_1 (90 K for $\text{Ca}_3\text{CoRhO}_6$, 70 K for $\text{Sr}_3\text{NiIrO}_6$, 80 K for $\text{Ca}_3\text{CoIrO}_6$), and [2] there is a sharp

drop at T_2 reaching nearly zero (35 K for $\text{Ca}_3\text{CoRhO}_6$, 21 K for $\text{Sr}_3\text{NiIrO}_6$, 32 K for $\text{Ca}_3\text{CoIrO}_6$) 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 $\text{Sr}_3\text{NiIrO}_6$ is ascribed to a transition to the spin singlet state in the ZFC process.³⁾ Their neutron diffraction measurements at 10 K and 30 K for $\text{Sr}_3\text{NiIrO}_6$ indicate neither a structural change nor additional Bragg peaks, suggesting the absence of a magnetic superstructure. As for $\text{Ca}_3\text{CoIrO}_6$, the magnetic susceptibility has been reported only by Kageyama *et al.*⁴⁾ 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 $\text{Ca}_3\text{CoRhO}_6$. 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 $\text{Ca}_3\text{CoRhO}_6$ 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

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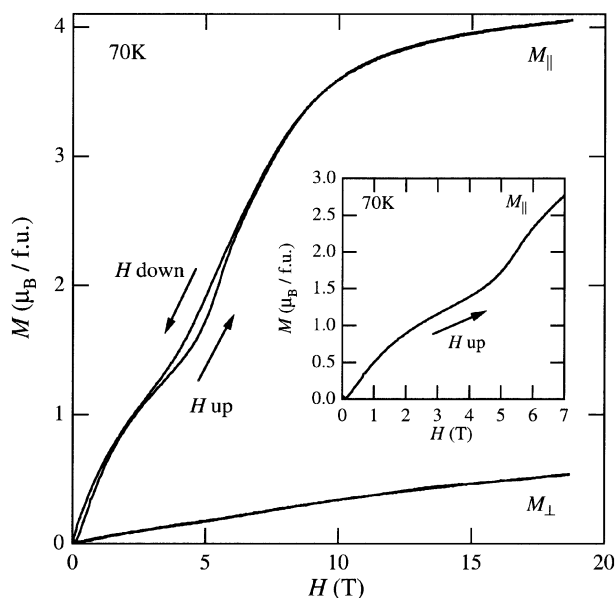


Fig. 1. Magnetization curves of $\text{Ca}_3\text{CoRhO}_6$ at 70 K in pulsed magnetic fields up to 18.7 T. The arrows along the curves indicate the directions of the field sweeps. The inset represents the low-field region in the magnetization curve for $H \parallel c$.

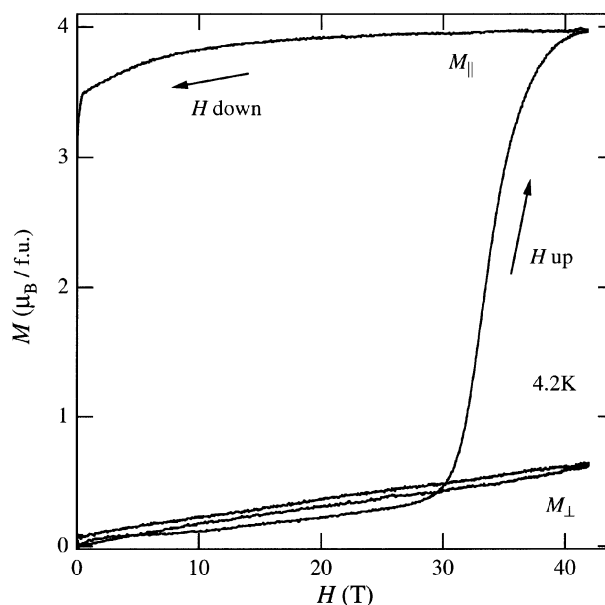


Fig. 2. Magnetization curves of $\text{Ca}_3\text{CoRhO}_6$ at 4.2 K in pulsed magnetic fields up to 42 T. The arrows along the curves indicate the directions of the field sweeps.

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 $(\Delta H/\Delta t) = 3.1 \text{ T/ms}$ 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 \AA . The data were collected in the 2θ 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 $4.05 \mu_{\text{B}}/\text{f.u.}$, eight times as large as that of M_{\perp} at 18.7 T, $0.53 \mu_{\text{B}}/\text{f.u.}$. 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 $4 \mu_{\text{B}}/\text{f.u.}$ at 15 T as seen in the inset of Fig. 1. The value of the magnetization at 4 T is $1.39 \mu_{\text{B}}/\text{f.u.}$, 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 mag-

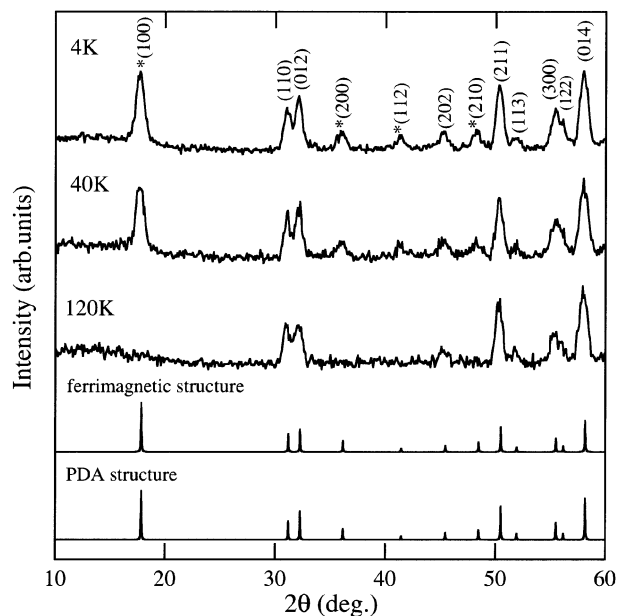


Fig. 3. Neutron powder diffraction patterns of $\text{Ca}_3\text{CoRhO}_6$ observed at 4 K, 40 K, and 120 K and the calculated neutron powder diffraction patterns for ferrimagnetic and PDA (F-PDA) structures on the assumption that Co and Rh have the magnetic moments of $3 \mu_{\text{B}}/\text{f.u.}$ and $1 \mu_{\text{B}}/\text{f.u.}$, respectively. Indexing of the observed peaks is based on the chemical unit cell. The additional magnetic peaks are marked by asterisks.

netic fields up to 42 T at 4.2 K below T_2 . M_{\perp} increases linearly, reaching $0.64 \mu_{\text{B}}/\text{f.u.}$ 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 $4 \mu_{\text{B}}/\text{f.u.}$, 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

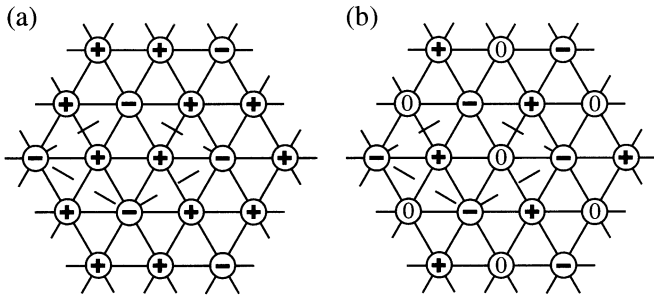


Fig. 4. Schematic illustration of (a) ferrimagnetic structure and (b) partially disordered antiferromagnetic structure projected on the c plane. Plus and minus signs indicate the directions of the moments in the ferromagnetic Ising chains. Zero(0) represents either + or - at random.

field due to spin freezing. This hard process agrees well with the spin glass behavior seen in M/H below T_2 .¹⁾

The powder neutron diffraction patterns of $\text{Ca}_3\text{CoRhO}_6$ measured at 4 K, 40 K, and 120 K 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 4 K and 40 K, 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 10 K. This is the first time the existence of magnetic ordering has been confirmed among $\text{Ca}_3\text{CoRhO}_6$, $\text{Sr}_3\text{NiIrO}_6$, and $\text{Ca}_3\text{CoIrO}_6$. It also indicates that $\text{Sr}_3\text{NiIrO}_6$ and $\text{Ca}_3\text{CoRhO}_6$ have different magnetic structures, although the temperature dependence of M/H of $\text{Sr}_3\text{NiIrO}_6$ is similar to that of $\text{Ca}_3\text{CoRhO}_6$.

The four magnetic peaks may be explained in term of a ferrimagnetic structure by the comparison between the powder neutron diffraction patterns at 4 K and 40 K 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 $3\mu_B/\text{f.u.}$ and $1\mu_B/\text{f.u.}$, respectively. This assumption is based on the saturation magnetization, $4\mu_B/\text{f.u.}$ and the bond valence calculation.¹⁾ The ferrimagnetic structure projected on the c plane is illustrated in Fig. 4(a). All the moments are aligned along [001] and ferromagnetic coupling dominates within the chains. These ferromagnetic Ising chains are ordered ferrimagnetically in the c plane. This ferrimagnetic structure is the same as the magnetic structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ at low temperatures,⁶⁾ consistent with the $1/3$ plateau observed at 70 K in M_{\parallel} , 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_{0T} , at $H = 2$ T for ZFC, I_{2T-ZFC} , and at $H = 2$ T for FC, I_{2T-FC} . The temperature dependence of I_{0T} exhibits no anomaly at T_2 . We estimated the long-range ordering temperature, T_N by fitting I_{0T} between 50 K and 85 K to the following formula,

$$I_{0T} = A(1 - T/T_N)^\beta + I_0,$$

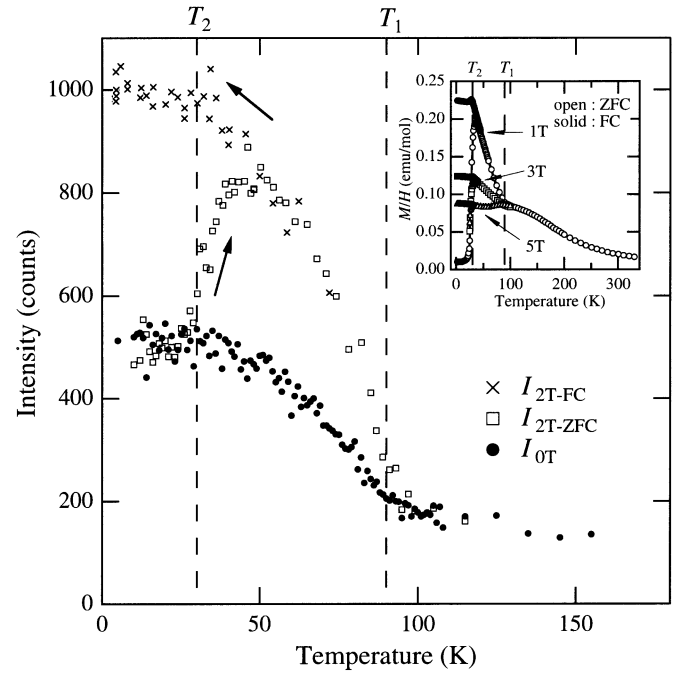


Fig. 5. Temperature dependences of peak intensity of (100) reflection. Solid circles denote I_{0T} , open squares I_{2T-ZFC} , and crosses I_{2T-FC} . The inset shows the temperature dependences of the magnetic susceptibilities M/H of $\text{Ca}_3\text{CoRhO}_6$ measured at $H = 1, 3,$ and 5 T.

where A is the coefficient of the temperature dependent term, β 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_{2T-ZFC} exhibits unusual temperature dependence for a simple ferrimagnet. Although the values of I_{2T-ZFC} are the same as those of I_{0T} below 30 K, I_{2T-ZFC} increases sharply at 30 K on heating. Note that the abrupt increases of I_{2T-ZFC} and the susceptibilities M/H for ZFC occur at about the same temperature. The values of I_{2T-ZFC} above 50 K are about twice as large as those of I_{0T} . The T_N estimated from I_{2T-ZFC} by the above-mentioned method is 90.8 ± 3.1 K, consistent with the T_N estimated from I_{0T} . One can see the difference between I_{2T-ZFC} and I_{2T-FC} below 40 K.

One explanation for the origin of the increase in I_{2T-ZFC} at 30 K 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_{2T-ZFC} at 30 K implies anomalously large volume of spin glass regions inconsistent with the Ising spin nature of $\text{Ca}_3\text{CoRhO}_6$, although the possibility of this case cannot be ruled out.

Here we propose the following model that can explain the increase at 30 K in I_{2T-ZFC} more suitably. Below 90 K, the ferromagnetic spin chains in $\text{Ca}_3\text{CoRhO}_6$ are partially ordered antiferromagnetically. In other words, the partially disordered antiferromagnetic (PDA) state is realized below 90 K. In the PDA state as illustrated in Fig. 4(b), $2/3$ of the ferromagnetic Ising chains order antiferromagnetically with each other and the remaining

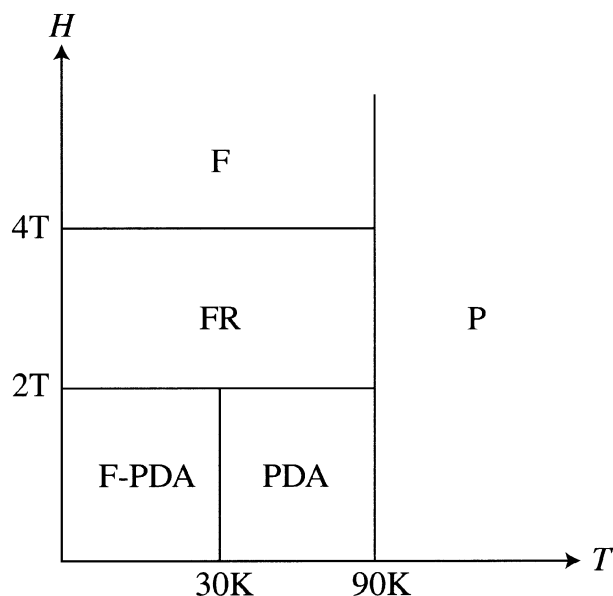


Fig. 6. Schematic magnetic phase diagram for T and H . P, the paramagnetic state; F, the ferromagnetic state; FR, the ferrimagnetic state; PDA, the partially disordered antiferromagnetic state; F-PDA, the frozen PDA state.

$1/3$ 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 ferromagnetic 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 $\text{Ca}_3\text{CoRhO}_6$ 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 approximation⁷⁾ and Monte Carlo simulation⁸⁾ 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 struc-

ture. 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 $I_{2T\text{-ZFC}}$ 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 $I_{2T\text{-ZFC}}$ is the same as I_{0T} 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 $I_{2T\text{-ZFC}}$. 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 $\text{Ca}_3\text{CoRhO}_6$ 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 $\text{Ca}_3\text{CoRhO}_6$, of which the incoherent chains freeze randomly below 30 K.

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