Long-time variation of magnetic structure in multistep metamagnets \( \text{Ca}_3(\text{Co-M})\text{O}_6 \)

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Abstract. A long-time variation of magnetic structure has been observed in a geometrically frustrated magnet \( \text{Ca}_3\text{Co}_2\text{O}_6 \). In order to clarify that the long-time variation in this material does not originate in randomness due to impurities, magnetization measurements have been made on single crystals of diluted compounds \( \text{Ca}_3(\text{Co-M})\text{O}_6 \) (\( M = \text{Ga, Mg and Al} \)). The long-time variations of the magnetization were detected in these compounds and characteristics of the time variation behavior were not much modified by the introduction of disorder produced by the substitution of non-magnetic atoms. These results show that the long-time variation of the magnetic structure in \( \text{Ca}_3\text{Co}_2\text{O}_6 \) is not caused by randomness or imperfections.

1. Introduction
In spin-glass systems, long-time variations of magnetic properties have been regarded as a characteristic behavior due to the multi-valley structure of the free energy which comes from random magnetic interactions [1]. Therefore, in a system without randomness, we have not expected to observe long-time variation of magnetic properties. However, a long-time variation of magnetic structure has been detected in \( \text{CeIr}_3\text{Si}_2 \) which has no randomness or imperfections [2, 3]. This compound shows successive magnetic transitions and multi-step metamagnetic transitions in low magnetic field, which indicate the presence of frustrating magnetic interactions. We examined several compounds which show those magnetic transitions and found a long-time variation of magnetic structure in \( \text{Ca}_3\text{Co}_2\text{O}_6 \) and several rare-earth intermetallic compounds [4-6]. We think that the long-time variation of magnetic structure in these materials is caused by the competing magnetic interactions.

\( \text{Ca}_3\text{Co}_2\text{O}_6 \) crystallizes in a hexagonal structure [7]. It consists of Co chains along the \( c \)-axis and these chains are arranged in a triangular lattice in the \( c \)-plane. This material exhibits two magnetic transitions at \( T_{c1} = 25 \text{ K} \) and \( T_{c2} = 13 \text{ K} \) and 5-step metamagnetic transitions below 7 T at 1.9 K [8].

In neutron scattering measurements, we found that the magnetic Bragg peak observed at \((1, 0, \delta)\) immediately after cooled below \( T_{c1} \) moved towards \( \delta = 0 \) with time. We determined that the magnetic moments of Co atoms form a series \(+++\cdots+++/−−\cdots−−/++++\cdots+++\) along a Co chain where + and − mean the moment direction parallel and antiparallel to the \( c \) direction, respectively. Therefore, the shift of the peak position with time corresponds to an increase of the ferromagnetically coupled length of the Co chain.

In order to clarify that the long-time variation of magnetic structure in this material does not originate in randomness due to impurities or defects, we have investigated the time variation of...
the magnetization of Ca$_3$(Co-M)$_2$O$_6$ (M=Ga, Mg and Al).

2. Experimental procedure
A single crystal of Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ was prepared by the flux method [9]. The size of the crystal is $\sim$0.5 mm $\times$ $\sim$0.5 mm $\times$ $\sim$3 mm with the longest direction parallel to the c-axis. The lattice parameters at room temperature are $a$=9.094 Å and $c$=10.441 Å (hexagonal unit cell). The concentration of Ga was determined by Electron Probe Micro Analyzer.

Magnetization measurements were made using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design model MPMS). A magnetic field was applied parallel to the c-axis. The temperature variation of magnetization was measured with zero-field-cooled (ZFC) and field-cooled (FC) processes at a field of $B$=5 mT. Magnetization processes was measured at $T$=1.9 K with increasing and decreasing magnetic field of up to $B$=5.5 T. The time variations of magnetization were measured after the sample was cooled to various target temperatures from $T$=30 K ($T>T_c$) at $B$=5 mT. A typical time needed to reach the target temperature was $\sim$7 min. Then the magnetization was repeatedly measured as a function of time $t$. Specific heat measurements were made using a Quantum Design PPMS. The same measurements were made on single crystals of the Mg-doped and the Al-doped compounds.

3. Results and Discussion
Figure 1 (a) shows the temperature variation of magnetization of Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ measured with $B$=5 mT along the c-axis. Solid and open symbols are the data measured in the ZFC and FC processes, respectively. The ZFC curve shows a sudden increase at $T_{c1}$=23 K with decreasing $T$ and it shows peaks at $T_{c2}$=13 K and $T_{c3}$=8 K. In the FC process, an increase in magnetization at $T_{c1}$ was observed, but peaks at $T_{c2}$ and $T_{c3}$ were not observed. The transition temperatures $T_{c1}$ and $T_{c2}$ are close to those of Ca$_3$Co$_2$O$_6$. The behaviors at $T_{c1}$ and $T_{c2}$ are also similar to those of Ca$_3$Co$_2$O$_6$. However, the magnetization value is about 1/5 of that of Ca$_3$Co$_2$O$_6$ and a peak at $T_{c3}$ was not observed in Ca$_3$Co$_2$O$_6$.

![Figure 1](image1.png)

Figure 1. (a) Temperature variation of magnetization of Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ measured with $B$=5 mT applied along the c-axis. Solid and open symbols are the data measured in the zero-field-cooled and field-cooled processes, respectively. (b) Magnetization processes of Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ measured at $T$=1.9 K. Solid and open symbols are the data measured in the increasing and decreasing processes, respectively.

![Figure 2](image2.png)

Figure 2. Temperature variation of specific heat of Ca$_3$Co$_2$O$_6$ (closed circle) and Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ (open circle).
Figure 1(b) shows the magnetic field variation of the magnetization of Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ measured at $T=1.9$ K up to $B=5.5$ T. Solid and open symbols are the data measured in the increasing and decreasing processes, respectively. In this measurement, the broad metamagnetic transitions were observed. The magnetization values and critical magnetic fields are different between two processes. In the increasing process, the magnetization curve shows metamagnetic transitions at $B_{c1}=0.1$ T, $B_{c2}=1.0$ T, $B_{c3}=1.8$ T and $B_{c4}=3.6$ T. In the decreasing process, metamagnetic transitions were observed at $B'_{c1}=0.1$ T and $B'_{c2}=0.8$ T. The metamagnetic transitions are much broader than those observed in Ca$_3$Co$_2$O$_6$. The saturation magnetization was $\sim 4 \mu_B$ per formula unit, which is smaller than that of Ca$_3$Co$_2$O$_6$.

Figure 2 shows the temperature variation of the specific heat of Ca$_3$Co$_2$O$_6$ and Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$. These curves show sharp peaks at 24.4 K and 22.6 K. These temperatures are close to the magnetic transition temperature $T_{c1}$ observed in the temperature variation of magnetization. Moreover, the shapes of the peaks of two curves are quite similar. These results show that Ga atoms are substituted uniformly into the Co positions.

Figure 3 shows the time variation of magnetization Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ measured with FC process at $B=5$ mT. The time variation behavior systematically changes with temperature. At $T=2$, 5 and 7 K, the magnetization ($M$) decreases with time ($t$) up to $t \sim 1000$ min. At 8.5 K, $M$ increases with $t$ and changes the curvature at $\sim 400$ min. Above 10 K, $M$ monotonically increases with $t$. These time variation behavior of magnetization is quite similar to that of Ca$_3$Co$_2$O$_6$. In order to investigate the detail of the time variation behavior, for $T \geq 8$ K, we fit the data by a sum of two exponential functions as

$$M(t) = M_0 + \Delta M_{MF} \exp(-t/t^*_{MF}) + \Delta M_{MS} \exp(-t/t^*_{MS}),$$  \hspace{1cm} (1)
Table 1. Activation energies $E_{aMF}/k_B$ and $E_{aMS}/k_B$ of Ca$_3$Co$_2$O$_6$ and Ca$_3$(Co-M)$_2$O$_6$.

|                | $E_{aMF}/k_B$ (K) | $E_{aMS}/k_B$ (K) |
|----------------|------------------|------------------|
| Ca$_3$Co$_2$O$_6$ | 90±8             | 48±7             |
| Ca$_3$(Co$_{0.986}$Ga$_{0.014}$)$_2$O$_6$ | 137±3           | 76±7             |
| Ca$_3$(Co$_{0.985}$Mg$_{0.015}$)$_2$O$_6$ | 120±8           | 63±5             |
| Ca$_3$(Co$_{0.996}$Al$_{0.004}$)$_2$O$_6$ | 90±7             | 49±5             |

which is the same function used in the case of Ca$_3$Co$_2$O$_6$ in ref. 4. In this equation, $t^{*}_{MF}$ and $t^{*}_{MS}$ mean the fast and slow components of the characteristic times for the time variation in $M$. The Mg-doped and the Al-doped samples also showed similar time variation of $M$ and we fitted the data by the same function.

Figure 4 shows the Arrhenius plot ($\log(1/t^*)$ vs $1/T$ plot) of the two characteristic times $t^{*}_{MF}$ and $t^{*}_{MS}$. Below $T_c2$ (i.e., $1/T>0.08$ K$^{-1}$) two characteristic times follow the Arrhenius law as shown by the straight lines. The value and the temperature dependence of $t^{*}_{MF}$ and $t^{*}_{MS}$ are nearly same to those of Ca$_3$Co$_2$O$_6$. Table 1 shows the activation energies $E_{aMF}$ and $E_{aMS}$ for the fast and slow components of the time variation of $M$ for all samples observed in the present measurements. The activation energies for Ca$_3$(Co-M)$_2$O$_6$ are not largely modified from those of Ca$_3$Co$_2$O$_6$.

To summarize, we investigated the long-time variation of the magnetization of Ca$_3$(Co-M)$_2$O$_6$ (M=Ga, Mg and Al). Characteristics of the time variation behavior were not much modified by the disorder produced by the substitution of non-magnetic atoms. These results show that the long-time variation of the magnetic structure in Ca$_3$Co$_2$O$_6$ is not caused by randomness or imperfections.

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