Magnetic properties of layered compounds
LnCoAsO ($Ln = \text{lanthanoids}$) with itinerant-electron ferromagnetism

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Abstract. We synthesized polycrystalline samples of layered compounds $LnCoAsO$ ($Ln = \text{La - Gd}$) and measured magnetization of the samples, especially, in the cases of $Ln = \text{Nd, Sm}$ and Gd, which show ferromagnetic-antiferromagnetic transitions (FAFT). From the results of magnetic measurements, we successfully draw the magnetic phase diagrams of these compounds. We showed that the FAFT temperatures $T_N$ at various magnetic fields in the cases of $Ln = \text{Nd}$ and Sm well scale to the de Gennes factors of the trivalent ions of Nd and Sm, showing that the Ruderman-Kittel-Kasuya-Yoshida interaction is the origin of the FAFT in these compounds. We also draw the total magnetic phase diagram of $LnCoAsO$ ($Ln = \text{La - Gd}$).

1. Introduction
Recent discoveries of superconductivity with high superconducting transition temperature up to 55 K in doped $LnFeAsO$ [1, 2] and in the related compounds[3, 4, 5, 6] have aroused much interest. On the other hand of tremendous number of studies on the Fe-based superconductors, the number of studies on Co-based compounds such as $LnCoAsO$ have been increasing recently. Among them, LaCo$PnO$ ($Pn = F, As$) has been still basic and important since they are suitable to a study on electronic natures of Co$Pn$ planes. LaCoAsO and LaCoPO were reported to show a ferromagnetic ordering below the Curie temperature ($T_C$) equal to about 50 and 60 K, respectively [7, 8, 9]. Magnetic properties of these two compounds can be almost understood within a framework of the ferromagnetic spin-fluctuation theory, and two-dimensional nature of spin fluctuations has also been pointed out [9].

As reported by both Zimmer and Quebe, lanthanum in LaCo$PnO$ can be substituted by other lanthanoid elements [10, 11]. The $4f$-electrons of $Ln^{3+}$ with a localized character interact with itinerant electrons of Co through the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction. As a result, a magnetic structure of ferromagnetically ordered moments of Co is forced to change in the low-temperature region. Especially, in the cases of $Ln = \text{Nd, Sm and Gd}$, a ferromagnetic-antiferromagnetic transition (FAFT) was observed below $T_C$ [12, 13, 14, 15, 16]. Recently, we studied the magnetic property of SmCoAsO and showed its detailed magnetic phase diagram [16]. It should be interesting to compare the magnetic phase diagrams of NdCoAsO, SmCoAsO, and GdCoAsO with each other, since it gives a hint for the detailed mechanism of FAFTs in those compounds.
In this report, we showed detailed results of magnetic measurements on polycrystalline samples of \(\text{LnCoAsO (Ln = Nd, Sm and Gd)}\). From the results of measurements, we draw the magnetic phase diagrams of these three compounds and compared the curvatures of the FAFT line.

2. Experiments
For the synthesis of polycrystalline samples of \(\text{LnCoAsO}\), we used powders of \(\text{Ln (Nd, Sm and Gd)}\) (purity: 99.9%), As (99.99%) and CoO (99.99 %) as starting materials. Powders of \(\text{Ln}\) and As were first mixed and sealed in an evacuated silica tube. The sealed tube was carefully fired in a furnace at 550°C for 5 h and then at 800°C for 12 h. The obtained powder of \(\text{LnAs}\) was mixed with powder of CoO to a stoichiometric ratio and was ground well in hexane to avoid oxidation. The pelletized mixture of \(\text{LnAs}\) and CoO was sealed in an evacuated silica tube and fired at 1000°C for 12 h.

We measured powder X-ray diffractions (XRDs) of the obtained samples and confirmed them to be in a single phase of \(\text{LnCoAsO}\) with the space group of \(P4/nmm\). We estimated lattice parameters from the powder XRD patterns and confirmed to be the same with the previous report[11]. The detailed XRD results can be seen in our previous report[12]. Magnetization (\(M\)) of the obtained samples was measured as a function of temperature (\(T\)) and magnetic field (\(H\)) by using a superconducting quantum interference device magnetometer installed in Research Center for Low Temperature and Materials Sciences, Kyoto University up to 55 kOe.
3. Results and Discussions

Figure 1 shows $T$ dependence of $M/H$ of (a) NdCoAsO, (b) SmCoAsO and (c) GdCoAsO measured at $H = 1$ kOe. In the high-$T$ region, $M$ of all the samples showed a Curie-Weiss like increase with decreasing $T$, while in the low-$T$ region $M$ of NdCoAsO and SmCoAsO showed an abrupt decrease around 15 and 40 K, respectively. In the case of GdCoAsO, $M$ showed a kink at about 75 K and showed a broad peak around 30 K. We have reported in the previous paper that these compounds show a ferromagnetic transition at about 75 K and an FAFT at the low-$T$ region[12]. Especially, in the case of GdCoAsO both the ferromagnetic transition and the FAFT simultaneously occur at about 75 K. We have pointed out that because the FAFT temperature ($T_N$) well scales to the de Gennes factor of $Ln^{3+}$ ions the FAFT corresponds to an antiferromagnetic ordering of magnetic moments of 4$f$-electrons of $Ln^{3+}$ ions and ferromagnetic ordered magnetic moments of 3$d$-electrons of Co through the RKKY interaction[12]. In the case of GdCoAsO, according to the value of the de Gennes factor, the FAFT must occur around 150 K. However, in such a high-$T$ region, magnetic moments of Co do not order. Therefore, $T_N$ of GdCoAsO is suppressed to 75 K where magnetic moments of Co ions ferromagnetically order.

To study the magnetic phase diagram of these compounds in detail, we precisely measured magnetization around $T_N$. Figure 2 shows $T$ dependence of $M$ of (a) NdCoAsO, (b) SmCoAsO and (c) GdCoAsO between 5 and 60 K at $H = 1 \sim 9$ kOe with every 1 kOe, 10 $\sim$ 20 kOe with every 2.5 kOe and 25 $\sim$ 55 kOe with every 5 kOe. The $T_N$ decreased with the increase of $H$ in the cases of NdCoAsO and SmCoAsO. In the case of GdCoAsO, the kink temperature which also indicates $T_N$ decreased with the increase of $H$. In both cases of NdCoAsO and GdCoAsO, $T_N$
is completely suppressed to zero within 55 kOe, while in the case of SmCoAsO higher magnetic field is needed to suppress \( T_N \) to zero.

Figure 3 shows \( H \) dependence of \( M \) at \( T = 5 \sim 60 \) K with every 5 K. With increasing \( H \), jumps of \( M \) indicating the magnetic field induced FAFT were observed in all the samples below \( T_N \). Since the magnetic moments of 4\( f \)-electrons of Sm\(^{3+}\) is much smaller than those of other two lanthanoids, the FAFT is much clearer than in the cases of other two compounds. We measured \( M \) of SmCoAsO at 4.2 K up to 650 kOe (65 T) using a pulsed magnet and at various \( T \) up to 140 kOe (14 T) using a 14 T superconducting magnet, and successfully draw the magnetic phase diagram\[16\]. Those data will appear in the magnetic phase diagram later. From the results of \( T \) dependence of \( M \) of each sample, we successfully draw the magnetic phase diagram of three compounds. Figure 4 (a) shows the \( H \) versus \( T \) phase diagram of the three compounds. Closed and open circles show data of NdCoAsO and SmCoAsO, respectively. Inset of Fig. 4 (a) shows the data of GdCoAsO. Closed diamond shows the \( T_C \) (~75 K) of both NdCoAsO and SmCoAsO. Dashed lines are guides for the eyes. By naturally extrapolating the phase boundary of FAFT to \( T = 0 \), one can roughly estimate the value of transition field at the ground state (\( H_N \)) as 50 kOe for NdCoAsO, 250 kOe for SmCoAsO and 50 kOe for GdCoAsO. The FAFT line of SmCoAsO is quite similar to that of NdCoAsO in its shape. On the other hand, the FAFT line in the case of GdCoAsO is different from those of other two compounds. We showed the value of \( T_N \) at zero field except for the case of \( Ln = Gd \) scaling to the de Gennes factor (dGf) of \( Ln^{3+}[12] \). It seems interesting to compare the \( H \) vs \( T \) phase diagrams in a normalized form by the de Gennes factor. Figure 4 (b) shows the \( H/dGf \) versus \( T/dGf \) phase
Figure 4. (a) $H$ versus $T$ phase diagram of LnCoAsO. Closed and open circles show the data of NdCoAsO and SmCoAsO, respectively. Closed diamond shows Curie temperature of both samples ($\approx 75$ K). Dashed lines are guides for the eyes. Inset: $H$-$T$ phase diagram of GdCoAsO. (b) Modified magnetic ($H$/dGf vs $T$/dGf) phase diagram of LnCoAsO. Closed and open circles show the data of NdCoAsO and SmCoAsO, respectively and open triangles show those of GdCoAsO. The envelopes of the Nd and Sm cases almost overlap with each other, while in the case of Gd the envelope does not scale to those of the other two samples.

diagram of the compounds. Here, the values of dGf of Nd$^{3+}$, Sm$^{3+}$, and Gd$^{3+}$ are 81/44, 125/28, and 63/4, respectively. The FAFT lines of NdCoAsO and SmCoAsO almost overlap with each other, showing that the origins of FAFT in both cases are really the same with each other. On the other hand, the FAFT line of GdCoAsO is solely different from those of other two compounds, indicating some different mechanism induces the antiferromagnetic order in GdCoAsO. Since magnetic moments of Gd$^{3+}$ are large and have no orbital part, antiferromagnetically ordered moments may easily flop in relatively weak magnetic field. Finally, we summarize the data of magnetic measurements as the total magnetic phase diagram of LnCoAsO ($Ln =$ La - Gd) in Fig. 5. Dashed lines are guides for the eyes. PM, FM, and AFM denote a paramagnetic phase, a ferromagnetic phase and an antiferromagnetic phase, respectively. The dGf lines correspond to the de Gennes factor of $Ln^{3+}$ ions which are scaled to $T_N$ or $H_N$ of NdCoAsO and SmCoAsO.

4. Summary
We measured magnetizations of polycrystalline samples of LnCoAsO with $Ln =$ Nd, Sm and Gd as functions of temperature and magnetic field. We successfully observed the magnetic field dependence of the ferromagnetic-antiferromagnetic transition (FAFT) up to 55 kOe for each sample, and draw the magnetic phase diagram of the samples. The FAFT lines of NdCoAsO and SmCoAsO well scale to each other with the difference of de Gennes factors of Nd$^{3+}$ and Sm$^{3+}$. On the contrary, in the case of $Ln =$ Gd, some different situation may occur compared with Nd and Sm cases. We draw the total magnetic phase diagram of LnCoAsO ($Ln =$ La -Gd) from the results of magnetic measurements.


Figure 5. Total magnetic phase diagram of $LnCoAsO$ ($Ln = La - Gd$). Dashed lines are guides for eyes. PM, FM, and AFM denote a paramagnetic phase, a ferromagnetic phase and an antiferromagnetic phase, respectively.

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