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Magnetic properties of \(L\)CoAs\(O\) \((L=\text{La–Gd})\)

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We synthesized a series of CoAs based weakly itinerant ferromagnetic compound LCoAs\(O\) \((L=\text{lanthanoids})\) and systematically studied a \(L\) dependence on magnetic properties. Lattice constants \(a\) and \(c\) decrease monotonically with the decrease in the ion size of \(L\). In the cases of \(L=\text{Nd, Sm, and Gd}\), a ferromagnetic-antiferromagnetic transition was observed at \(T_N=15, 35,\) and \(75\) K, respectively, indicating the existence of unconventional interaction between ferromagnetically ordered itinerant electrons of Co. The Curie temperature \(T_C\) increases from \(55\) to \(75\) K by changing La to Ce while from Ce to Gd the \(T_C\) does not change so much, being quite similar to the \(L\) site dependence of the superconduing transition temperature \(T_c\) in FeAs-based high-\(T_c\) compound LFeAs\(O\). We discussed the mechanism of ferromagnetic-antiferromagnetic transition and the lanthanoid dependence of \(T_C\).

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I. INTRODUCTION

The recent discoveries of superconductivity in doped LaFeAs\(O\) \((\text{Ref. 1})\) and the subsequent discoveries of the marvelous increase in superconducting transition temperature \(T_c\) up to \(55\) K \((\text{Ref. 2})\) have caused lots of excitement not only in the superconductivity community but also almost all the condensed-matter communities. These discoveries have also aroused much interest in the Fe site substituted systems for other transition metals. In the groups of ZrCuSiAs type compounds \(\text{Ref. 3}\) about \(10\) years ago. They have become the target of intensive studies and it was found that they have rich and interesting variations in their physical properties depending on the transition elements: e.g., in the case of manganese, LaMnPO was reported to be an antiferromagnetic semiconductor. \(\text{Ref. 4}\) In the case of nickel, LaNiPO was reported to be a superconductor with \(T_c\sim 2\) K. \(\text{Ref. 5}\) In the case of cobalt, i.e., LaCoAs\(O\) and LaCoPO were reported to be ferromagnetic with the Curie temperature \(T_C\) of about \(50\) and \(60\) K, respectively, \(\text{Ref. 6,7}\) and we analyzed magnetic properties around \(T_C\) in the case of LaCoAs\(O\) based on the self-consistent renormalization theory of spin fluctuations \(\text{Ref. 8}\) and Takahashi’s spin-fluctuation theory \(\text{Ref. 9,10}\) in the previous report. \(\text{Ref. 11}\)

Lanthanum in each transition-metal series was reported to be exchanged by other lanthanoid elements. \(\text{Ref. 12}\) The recent studies on doped LFeAs\(O\) have revealed that the \(T_c\) increases with the substitution of La for heavier lanthanoids. Such the increase in \(T_c\) seems to be the result of the shrinkage of the lattice caused by the substitution. It is important issue how the lanthanoid substitution affects the physical properties in other transition-metal series \(LM\)As\(O\) \((L=\text{lanthanoids}, M=\text{transition metals})\). Especially, in the case of LCoAs\(O\), it is also interesting how the ordered moments in CoAs planes can be influenced by the localized 4\(f\)-electrons’ moments and/or the shrinkage of lattice. Though LCoAs\(O\) has already been synthesized by Zimmer \(\text{et al.}\) \(\text{Ref. 3}\) and Quebe \(\text{et al.}\) \(\text{Ref. 12}\) the physical properties have not yet been studied. In the last year, Krellner and Geibel \(\text{Ref. 13}\) reported the detailed physical properties of CeCoPO and discussed interplay between magnetic moments of 3d electrons of Co and 4\(f\)-electrons of Ce in their report. Their report arouses our interest about the physical properties of CeCoAs\(O\) and lanthanoid site substituted compounds LCo\(Pn\)\(O\) \((Pn=P\) and As\). In this paper, we showed the magnetization of polycrystalline samples of LCoAs\(O\) and also showed how the substitution of lanthanoid site influences on the magnetic properties including the \(T_C\). From the results of measurements, we report the ferromagnetic-antiferromagnetic transition \(\text{(FAFT)}\) observed in the cases of \(L=\text{Nd, Sm, and Gd}\) and discuss its origin.

II. EXPERIMENTS

For the synthesis of polycrystalline samples of LCoAs\(O\), we used powders of lanthanoids \((\text{La, Ce, Pr, Nd, Sm, and Gd})\) \((\text{purity: 99.9\%})\), As \((99.99\%))\), and CoO \((99.99\%))\) as starting materials. At first, powders of lanthanoid metal and As were mixed and put in an evacuated silica tubes. The mixtures of lanthanoid metal and As were carefully fired in a furnace at \(550\) °C for \(5\) h and then at \(800\) °C for \(12\) h. The obtained powders of LAs were mixed with the powders of CoO to a stoichiometric ratio and ground well in hexane to avoid an oxidation. The pelletized mixtures of LAs and CoO were put in an evacuated silica tube and fired at \(1100\) °C for \(12\) h.

Figure 1 shows the powder x-ray diffraction \(\text{(XRD)}\) patterns of LCoAs\(O\) \((L=\text{La, Ce, Pr, Nd, Sm, and Gd})\) measured at room temperature. All the peaks in the patterns, except for the marked ones which is quite small, can be indexed by the space group of \(P4/nmm\). Thus our samples are found to be almost in a single phase of LCoAs\(O\). Although we tried to synthesize LCoAs\(O\) with \(L\) being heavier lanthanoid elements \((\text{Eu, Tm} \sim \text{Lu})\) and \(Y\), the LCoAs\(O\) phase could not be obtained under ambient conditions, being consistent with the report by Quebe \(\text{et al.}\). We estimated the lattice parameters from the obtained XRD patterns and show the results in Fig. 2. The estimated lattice parameters \(a\) and \(c\) monotonically decreased from \(4.055\) and \(8.462\) Å in the case of \(L\).
La to 3.932 and 8.191 Å in the case of L=Gd, respectively. This result is good agreement with the previous report, implying that we successfully change the lattice size of CoAs plane systematically.

III. RESULTS AND DISCUSSION

The magnetizations ($M$) of $L$CoAsO were measured as functions of temperature ($T$) and magnetic field ($H$) by using magnetic property measurement system (MPMS) (Quantum Design Inc.) up to 5.5 T. All the magnetization data except the $M$-$H$ curves of CeCoAsO shown in Fig. 5 were measured after field cooling. Figure 3(a) shows the $T$ dependence of the $M$ of $L$CoAsO at $H=1$ kOe and Fig. 3(b) shows that of the $dM/dT$ at $H=1$ kOe. We also show the $T$ dependences of the $M$ at various $H$ in Fig. 4 and $H$ dependences of $M$ at various $T$ in the insets of Fig. 4. As reported in previous papers, $L$CoAsO is the itinerant electron ferromagnet with $T_C\approx55$ K. The $M$ and the $dM/dT$ of $L$CoAsO rapidly increases around 55 K and shows a peak at 55 K, repec-
enide and phosphide was observed in the case of LaFePO, where LaFePO shows a Pauli paramagnetic behavior down to about 5 K (Ref. 14) while LaFeAsO shows an antiferromagnetic transition at about 120 K. 1 In the case of Pr, the magnetic transition at about 120 K. 1 In the case of Pr, the magnetization $M$ is reduced in compared with that of LaCoAsO in the low $T$ and low $H$ regions, and obvious anomalies are not seen below $T_C$, except for the small dent at $H=1$ kOe and the kink above 15 kOe seen around 10 K. The evolution of the $M$ with increasing $H$ seen below 50 K is due to the paramagnetic magnetic moments of Pr$^{3+}$ whose effective Bohr magneton number $\mu_B$ is $3.58 \mu_B$, being much larger than that of Co. In the case of Nd, the $M$ starts to decrease at about 35 K with decreasing $T$ and then abruptly decreases at $T_N \sim 11$ K at $H=1$ kOe. This abrupt drop of the $M$ at $H=1$ kOe is also seen in the cases of Sm and Gd at about 35 and 75 K, respectively. The $T_N$ in the case of Nd slowly decreases with increasing $H$ and the abrupt drop almost vanishes at $H=50$ kOe. In the case of Sm, the abrupt drop in the $M$ looks more prominent and the $T_N$ decreases with increasing $H$ rather rapidly than that in the case of Nd. The sharp drop is clearly observed up to $H=50$ kOe. We observed metamagnetic transition below 40 K as seen in the inset of Fig. 4(e). In the case of Gd, the ferromagnetic transition and abrupt drop seem to occur simultaneously at about 75 K. The $T_N$ rapidly decreases with increasing $H$. At $H=50$ kOe, the $M$ looks almost to obey the Curie law because of the large local magnetic moments of Gd$^{3+}$ ions.

Figure 6 shows the $M^2$ versus $H/M$ plots, so-called Arrott plots, of the samples. LaCoAsO shows the convex behavior around $T_C=55$ K. We discussed the magnetic properties of LaCoAsO on the basis of the theory of spin fluctuations in our previous report.11 As seen in Fig. 6, Arrott plots show the

FIG. 4. $T$ dependences of $M$ of $L=$ (a) La, (b) Ce, (c) Pr, (d) Nd, (e) Sm, and (f) Gd at various $H$ up to 55 kOe. Inset of each panel shows $M$-$H$ curves at several temperatures.

FIG. 5. Magnetization ($M$-$H$) curves of CeCoAsO at $T$=5 and 65 K. Both data were measured after zero-field cooling from room temperature.

FIG. 6. Arrott plots of each sample. Inset: $M_s$ of each sample estimated from Arrott plots.
different behavior especially in the low-$T$ region. We estimated $T$ dependences of the spontaneous magnetization $M_s$ and magnetic susceptibility $\chi$ as the extrapolations of the $M_s$ to the longitudinal and horizontal axes, respectively. We show the $T$ dependence of the $M_s$ of each sample (except for Gd) in the inset of Fig. 6. We estimated ordered moment at ground state, $P_s$, from the intersection of the natural extrapolation (dotted lines) of the $M_s$ and vertical axis. We will discuss $L$ dependence of $P_s$ later.

Figure 7 shows $T$ dependence of the reciprocal magnetic susceptibility $\chi^{-1}$ of each sample estimated from the Arrott plot as shown in Fig. 6. Above 200 K almost linear behavior is seen in each sample while below 150 K $\chi^{-1}$'s of samples except for La show convex behaviors, indicating that the dominating magnetic moments are gradually changing from 4$f$ electrons of $L^{3+}$ to 3$d$ electrons of Co with decreasing $T$. We roughly estimated the values of effective magneton number $P_{eff}$ of the samples by fitting $\chi^{-1}$ data to the Curie-Weiss law $\chi=C/(T-\theta)+\chi_0$ between 200 and 300 K, here $C=NA_{eff}P_{eff}^2/3k_B$ and $\chi_0$ is the constant susceptibility. Inset of Fig. 7 shows the estimated values of $P_{eff}$ as open circles together with the theoretical ones of free $L^{3+}$ ion as closed circles. The estimated and theoretical values of $P_{eff}$ are almost the same except for the cases of La and Sm, indicating that above 200 K magnetic properties are dominated by 4$f$-electrons' magnetic moments which is larger than that of 3$d$-electrons' moments of Co. In the case of Sm, the value of $P_{eff}$ of Sm$^{3+}$ is small and comparable to that of Co, thus the estimated value of $P_{eff}$ may look as the sum of them as $P_{eff}^2=(P_{Co}^{eff})^2+(P_{Sm}^{eff})^2$.

The differences in the $T$ dependence of $M$ seen in the low-$T$ region may be induced by either the shrinkage of lattice or the existence of localized 4$f$ electrons of lanthanoids. The $T_C$ and $T_N$ estimated from $dM/dT$ versus $T$ plots are summarized in Fig. 8(a). According to the Moriya’s report, the ferromagnetically ordered state in the intermediate $T$ region cannot be theoretically induced from the paramagnetic ground state by $T$ without structural phase transitions, therefore we regarded the abrupt drop of the $M$ in the cases of $L=$Nd, Sm, and Gd as a FAFT. Such an FAFT is also reported in the Fe$_x$Rh$_{1-x}$ system and La$_2$Ni$_2$. In the case of the ordered alloy FeRh, it has been pointed out that the magnetic polarization of Rh favors the ferromagnetic phase while the interaction between the magnetic moments of Fe always favors the antiferromagnetic state in which the magnetic moments of Rh do not polarize. If the similar scenario is realized, the magnetic moments of Co and lanthanoids correspond to the moments of Rh and Fe, respectively. In next paragraph, we discuss on the origin of the FAFT transition.

Figure 8(a) shows the electronic phase diagram of LaCoAsO at $H=0$. Closed and open circles show $T_C$ and anomaly temperature, respectively, defined as the temperature where the $dM/dT$ shows the local minimum. Open triangles show the $T_N$ defined as the local maximum of the $dM/dT$. In the case of Gd, we defined $T_N$ as the temperature where the kink is seen in the $T$ dependence of the $M$. Dashed lines are the guides for the eyes. Here, the $T_C$ increases from 55 K to about 75 K by changing La to Ce while the $T_C$ does not change by changing $L$ from Ce to Gd. On the other hand, the $T_N$ increases rather rapidly with the substitution of lanthanoid site. The effective spin part of the magnetic moments of 4$f$ electrons can be given as the de Gennes factor dGf $=(g_f-1)^2J(J+1)$, where $g_f$ is Landeé’s $g$ factor and $J$ the total angular momentum quantum number. We plotted the value of dGf for each $L^{3+}$ ion in Fig. 8(a) as small open circles. The $T_N$ and dGf show quite similar behaviors against $L$, indicating that the value of $T_N$ is strongly correlated with the effective spin moments of $L^{3+}$ ions. Not the full magnetic moments but the effective spin part of the magnetic moments can interact with each other by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction, so that the $L$ dependence of $T_N$ is governed by de Gennes factor, suggesting strongly that the FAFT is caused by the antiferromagnetic ordering of 4$f$-electrons’ moments of each $L^{3+}$ ion via the RKKY interaction.

Generally, the $T_C$ decreases when the chemical and physical pressures are applied to the itinerant ferromagnetic sys-

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![Figure 7](attachment:7.png)  
**FIG. 7.** $T$ dependences of $\chi^{-1}$ of LaCoAsO estimated from Arrott plots. Inset: $T$ dependences of $M_s$ also estimated from Arrott plot.

![Figure 8](attachment:8.png)  
**FIG. 8.** (a) Magnetic phase diagram of LaCoAsO. Closed and open circles show $T_C$ and an anomaly temperature, respectively. Open triangles show $T_N$. Small open circles show de Gennes factor of $L^{3+}$. (b) $P_s$ of LaCoAsO. Dashed lines in both panels are the guides for the eyes.
MAGNETIC PROPERTIES OF LCoAsO \((L=\text{La–Gd})\)

The behavior of \(T_C\) indicates that the relation between the lattice size and the volume effect are expected to decrease with \(x\). To elucidate which electrons or not. To understand the behavior of \(T_C\), we took notice of the behavior of \(P_s\). We estimated the values of \(P_s\) from the natural extrapolation of \(M_s\) with \(T\to0\) as shown in the insets of Fig. 6 and showed the results in Fig. 8(a). The value of \(P_s\) monotonically decreases with the decrease in the ionic size of \(L^{3+}\). To see the relation between the lattice size and \(P_s\), we plotted \(a\) and \(V\) against \(P_s^2 (\equiv (S_s^N)^2 \approx V_M) (V_M: \text{volume derived from magnetovolume effect})\), shown in Fig. 9. This relation is empirically proposed by experiment and derived by spin-fluctuation theory. Both \(a\) and \(V\) are well scaled to \(P_s^2\), indicating that the \(P_s\) decreases through the magnetovolume effect with the increase in the bandwidth and the decrease in the DOS at Fermi level by the chemical pressure effect. By considering the behavior of \(P_s\) against the lattice size, we can suggest the explanation of the lattice size dependence of the \(T_c\) shown in Fig. 8(a). As the lattice size decreases, both the \(T_C\) and \(P_s\) should decrease through the magnetovolume effect. On the other hand, the decrease in the lattice size along \(c\) axis may enhance the three dimensionality of the interaction between the magnetic moments of \(Co\) layers, which stabilizes the ferromagnetic state and makes the \(T_C\) increase. The behavior of \(T_C\) shown in Fig. 8(a) can be understood as the result of competition between the magnetovolume effect and the enhancement of three dimensionality. The \(L\) dependence of \(T_C\) can also be understood by another scenario. The \(T_C\) remains almost the same in the case of \(L=\text{Ce–Gd}\) while drastically changes between that of La and others. This indicates that the difference of \(T_C\) depends on whether lanthanoid element has the \(4f\) electrons or not. To elucidate which scenario is correct, it is thought to be important to study the behavior of \(T_C\) of \(La_{1-x}Y_xCoAsO\), whose lattice constants are expected to decrease with \(x\). Figure 9 also indicates that the quantum criticality of ferromagnetic state can be induced by the pressure corresponding to \(a=3.92 \text{ Å}\) and/or \(V =125 \text{ Å}^3\).

From our results, the following scenario is naturally proposed. The magnetic moments of Co are ferromagnetically ordered within the CoAs planes below \(T_C\) and are weakly interacting with each other to the \(c\)-axis direction. The ordered moments can be easily changed their directions by the rather weaker \(H\). This is because LaCoAsO is a quite soft ferromagnet. In the cases of other lanthanoids, if the \(4f\) electrons of \(L^{3+}\) are magnetically ordered, and then molecular field occurs, the ordered moments of Co are restricted to head to the direction of molecular field. The RKKY interaction works between \(4f\) electrons and they antiferromagnetically order at \(T_N\) especially in the cases of \(L=\text{Nd, Sm, and Gd}\). Below \(T_N\) the ferromagnetically ordered moments of Co, therefore, change their arrangements to the antiferromagnetic ones and lose their macroscopic ferromagnetic magnetization. To couple with two-dimensionally ordered Co moments, \(4f\)-electrons’ moments must be ordered antiferromagnetically between the planes and ferromagnetically in each plane. The detailed microscopic magnetic studies by using neutron diffraction, NMR and \(\mu^+\text{SR}\) are expected to help the validity of this scenario.

IV. CONCLUSION

In summary, we successfully synthesized polycrystalline samples of \(LCoAsO\) with \(L=\text{La–Gd}\) and measured the magnetizations as functions of \(T\) and \(H\). We observed the ferromagnetic transitions at 55 K for the La sample and at about 70 K for other lanthanoids samples. We showed that the \(L\) dependence of the Curie temperature can be understood by the competition between the magnetovolume effect caused by the chemical pressure effect and the enhancement of the three dimensionality. Below the Curie temperature, the magnetization shows the different temperature dependence from each other. We observed FAFTs in the cases of \(L=\text{Nd, Sm, and Gd}\), and the \(L\) dependence of the transition temperature was shown to be quite similar to that of de Gennes factor. We proposed the scenario that the ferromagnetically ordered moments of Co are antiferromagnetically rearranged by the molecular fields from the antiferromagnetically ordered \(4f\)-electrons’ moments below the antiferromagnetic-ferromagnetic transition temperature.

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