Magnetic properties of LCoAsO (L=La–Gd)

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We synthesized a series of CoAs based weakly itinerant ferromagnetic compound LCoAsO (L: 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^{3+}. In the cases of L=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 superconducting transition temperature T_c in FeAs-based high-T_c compound LFeAsO. We discussed the mechanism of ferromagnetic-antiferromagnetic transition and the lanthanoid dependence of T_C.

I. INTRODUCTION

The recent discoveries of superconductivity in doped LaFeAsO (Ref. [1]) and the subsequent discoveries of the marvelous increase in superconducting transition temperature T_c up to 55 K (Ref. [2]) have caused lots of excitements 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 (space group: $P4/nmm$, represented by LaFeAsO) and ThCr$_2$Si$_2$ type ($I4/mmm$, BaFe$_2$As$_2$), the successful substitutions of Fe for other transition-metal elements were reported by the German groups[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.[4] In the case of nickel, LaNiPO was reported to be a superconductor with $T_c \sim 2$ K.[5] In the case of cobalt, i.e., LaCoAsO and LaCoPO were reported to be ferromagnetic with the Curie temperature T_C of about 50 and 60 K, respectively,[6,7] and we analyzed magnetic properties around T_C in the case of LaCoAsO based on the self-consistent renormalization theory of spin fluctuations[8] and Takahashi's spin-fluctuation theory[9,10] in the previous report.[11]

Lanthanum in each transition-metal series was reported to be exchanged by other lanthanoid elements.[12] The recent studies on doped LFeAsO 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 LMAsO (L=lanthanoids, M=transition metals). Especially, in the case of LCoAsO, it is also interesting how the ordered moments in CoAs planes can be influenced by the localized $4f$-electrons' moments and/or the shrinkage of lattice. Though LCoAsO has already been synthesized by Zimmer et al.[3] and Quebe et al.,[12] the physical properties have not yet been studied. In the last

year, Krellner and Geibel[13] reported the detailed physical properties of CeCoPO and discussed interplay between magnetic moments of $3d$ electrons of Co and $4f$ electrons of Ce in their report. Their report arouses our interest about the physical properties of CeCoAsO and lanthanoid site substituted compounds LCoPnO (Pn=P and As).

In this paper, we showed the magnetization of polycrystalline samples of LCoAsO 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 (FAFT) observed in the cases of L=Nd, Sm, and Gd, and discuss its origin.

II. EXPERIMENTS

For the synthesis of polycrystalline samples of LCoAsO, we used powders of lanthanoids (La, Ce, Pr, Nd, Sm, and Gd) (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 (XRD) patterns of LCoAsO (L=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 LCoAsO. Although we tried to synthesize LCoAsO with L being heavier lanthanoid elements (Eu, Tm$\sim$Lu) and Y, the LCoAsO phase could not be obtained under the ambient conditions, being consistent with the report by Quebe et al.[12] 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
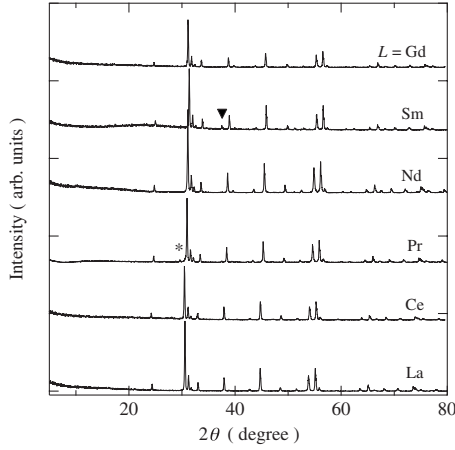
FIG. 1. Powder x-ray diffraction patterns of LCoAsO. Asterisk and closed triangle show quite small amounts of L_2O_3 and CoAs, respectively.

=La to 3.932 and 8.191 Å in the case of L=Gd, respectively. This result is good agreement with the previous report,[12] implying that we successfully change the lattice size of CoAs plane systematically.

III. RESULTS AND DISCUSSION

The magnetizations (M) of LCoAsO 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 for 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 LCoAsO 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,[6,7,11] LaCoAsO is the itinerant electron ferromagnet with $T_C \sim 55$ K. The M and the dM/dT of LaCoAsO rapidly increases around 55 K and shows a peak at 55 K, respec-
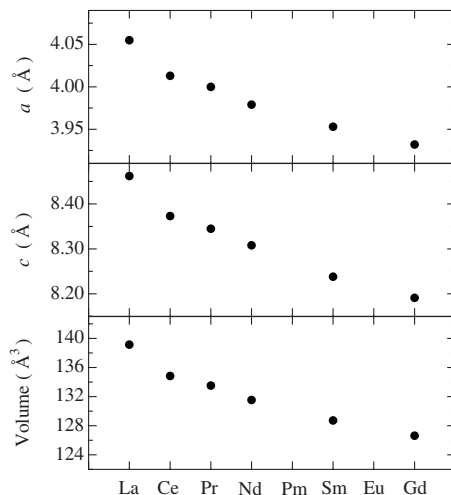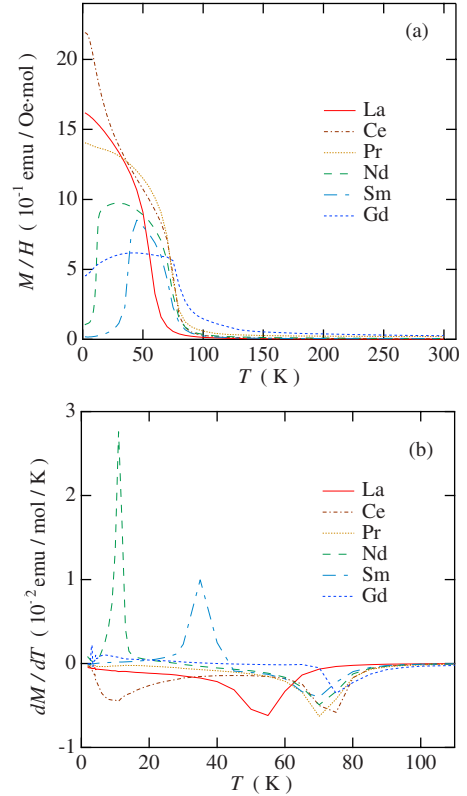

FIG. 2. Lattice parameters and cell volume of LCoAsO.

FIG. 3. (Color online) T dependences of (a) M/H and (b) dM/dT of LCoAsO measured at H=1 kOe.

tively, indicating the ferromagnetic transition and the M gradually increases at low T region with decreasing T, being consistent to the previous reports.[6,7,11] The M and dM/dT of other samples show the rapid increase and peak, respectively, around 70 K, indicating that the ferromagnetic transitions occur at rather higher temperatures than in LaCoAsO. The increase in T_C may be induced by the shrinkage of lattice to the c-axis direction and/or the existence of $4f$-electrons' magnetic moments. The relation among T_C, the ordered moment in the ground state P_s and lattice parameter is discussed later. It is noteworthy that the superconducting transition temperature T_c of LnFeAsO$_{1-x}$ also increases with the shrinkage of FeAs planes. At the low-T region, the M of the samples shows the different behavior from each other. In the case of Ce, the M shows one more rapid increase below 45 K as decreasing T, indicating the two steps transitions occur in CeCoAsO. The M of CeCoAsO showed a hysteresis against H below 45 K as shown in Fig. 5, whose behavior reminds us hard ferromagnets. On the other hand, no such a large hysteresis loop was observed between 45 K and $T_C \sim 75$ K like LaCoAsO. Other lanthanoid samples do not show such the hysteresis in the M-H curve. This anomalous T dependence of the M can be attributed to the anisotropic character of the $4f$ electrons of Ce^{3+} ion. In the case of CeCoPO, a homolog of CeCoAsO, the M was reported to show quite different behavior from CeCoAsO against T.[13] The M starts to decrease just below T_C (=75 K) and then increases with decreasing T, which is caused by the antiferromagnetic coupling between $3d$ and $4f$ magnetic moments. It is noteworthy that such the different behaviors of magnetism between ars-
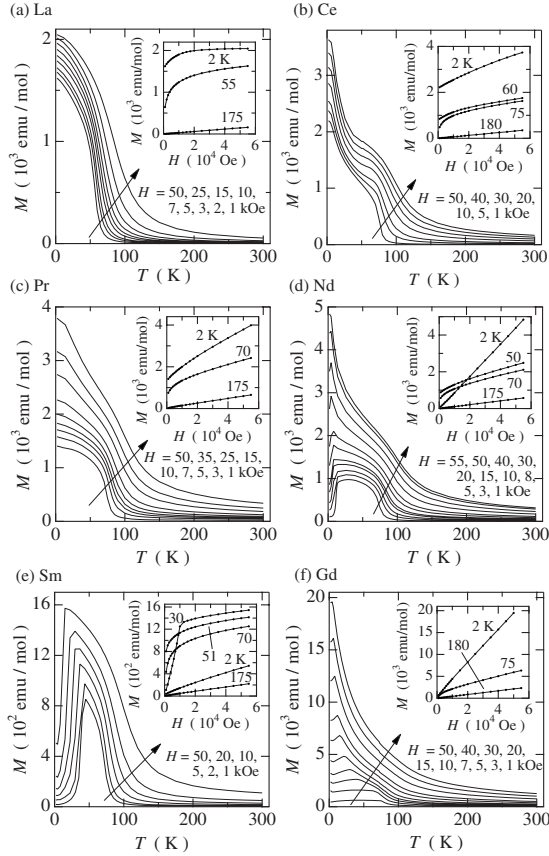
FIG. 4. *T* dependences of *M* of *L*=(a) La, (b) Ce, (c) Pr, (d) Nd, (e) Sm, and (f) Gd at various *H* up to 55 kOe. Inset of each panel shows *M*-*H* curves at several temperatures.

enide and phosphide was observed in the case of LaFe*Pn*O, 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 *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
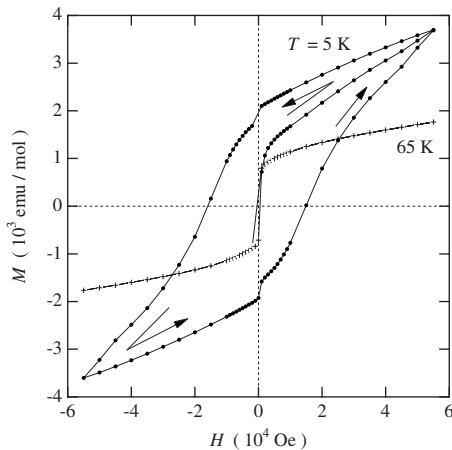

FIG. 5. Magnetization (*M*-*H*) curves of CeCoAsO at *T*=5 and 65 K. Both data were measured after zero-field cooling from room temperature.
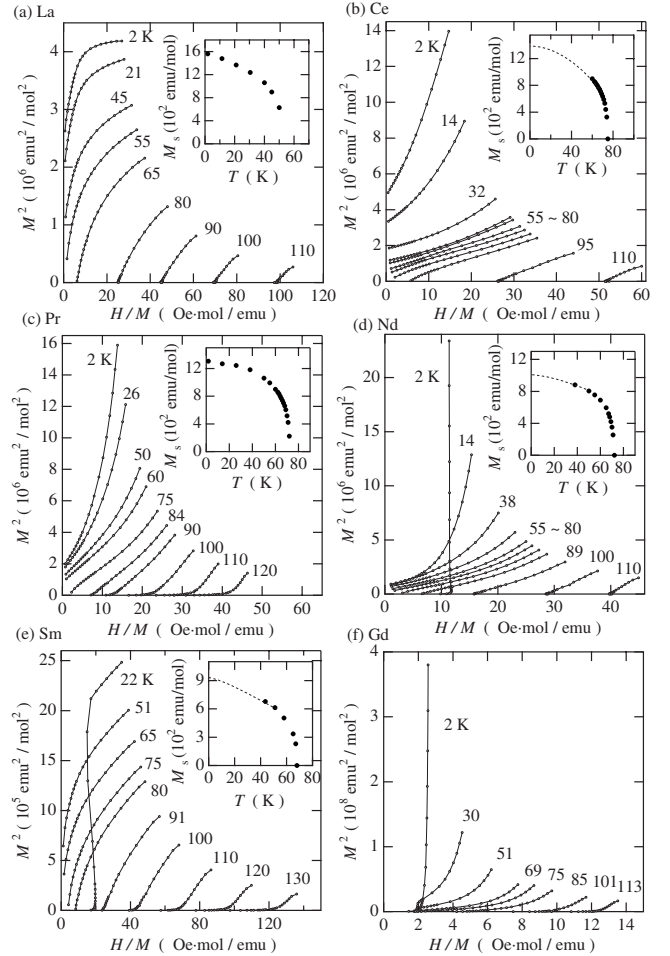

FIG. 6. Arrott plots of each sample. Inset: M_s of each sample estimated from Arrott plots.

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 P_{eff} 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 ~ 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 deceases with increasing *H* rather rapidly than that in the case of Nd. The sharp drop is cleary 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,[15] 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
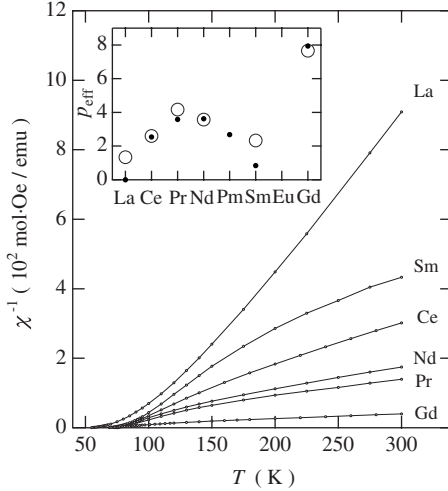
FIG. 7. T dependences of χ^{-1} of LCoAsO estimated from Arrott plots. Inset: T dependences of M_s also estimated from Arrott plot.

different behavior especially in the low-T region. We estimated T dependences of the spontaneous magnetization M_s and magnetic susceptibility χ as the extrapolations of the M 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 χ^{-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 χ^{-1}'s of samples except for La show convex behaviors, indicating that the dominating magnetic moments are gradually changing from $4f$ electrons of L^{3+} to $3d$ electrons of Co with decreasing T. We roughly estimated the values of effective magneton number P_{eff} of the samples by fitting χ^{-1} data to the Curie-Weiss law $\chi=C/(T-\theta)+\chi_0$ between 200 and 300 K, here $C=N_A P_{\text{eff}}^2/3k_B$ and χ_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 $4f$-electrons' magnetic moments which is larger than that of $3d$-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 $P_{\text{eff}}^2=(P_{\text{eff}}^{Co})^2+(P_{\text{eff}}^L)^2$.

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 $4f$ 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,[16] 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 re-
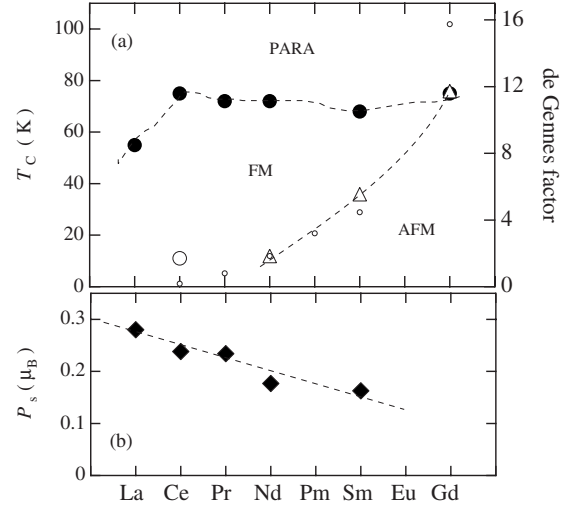

FIG. 8. (a) Magnetic phase diagram of LCoAsO. Closed and open circles show T_C and an anomaly temperature, respectively. Open triangles show T_N. Small open circles show de Gennes factor of L^{3+}. (b) P_s of LCoAsO. Dashed lines in both panels are the guides for the eyes.

ported in the Fe_xRh_{1-x} system[17] and La_2Ni_7.[18] 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 polarized.[19] 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 LCoAsO at $H \approx 0$. 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 $4f$ electrons can be given as the de Gennes factor dGf $=(g_J-1)^2 J(J+1)$, where g_J 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 $4f$-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-
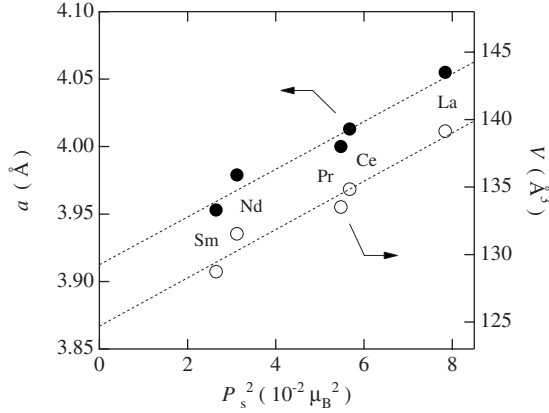
FIG. 9. Lattice parameter a and cell volume V versus P_s^2. Dashed lines are guides for the eyes.

tem because the bandwidth increases and the density of states (DOS) at Fermi level decreases with the shrinkage of the lattice. However, the T_C increases in spite of the decrease in the lattice parameters as shown in Fig. 8(a). 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 $T \rightarrow 0$ as shown in the insets of Fig. 6 and showed the results in Fig. 8(b). 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 ($\approx \langle S_L^2 \rangle \propto V_M$) ($V_M$: volume derived from magnetovolume effect), shown in Fig. 9. This relation is empirically proposed by experiment[20,21] and derived by spin-fluctuation theory.[22] 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=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 Å and/or V=125 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 interacted 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=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 μ^+SR are expected to help the validity of this scenario.

IV. CONCLUSION

In summary, we successfully synthesized polycrystalline samples of LCoAsO with L=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=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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