Successive magnetic transitions and static magnetic order in $R\text{CoAsO}$ ($R = \text{La, Ce, Pr, Nd, Sm, Gd}$) confirmed by muon-spin rotation and relaxation

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The presence of antiferromagnetic (AF) order seems to be a common feature for the parent compounds of cuprate as well as some pnictide high-temperature superconductors. In order to search for antiferromagnetic order in the closely related rare-earth cobalt arsenic oxides ($R\text{CoAsO}$), we have measured muon-spin rotation and relaxation ($\mu^+\text{SR}$) spectra on a series of powder samples with $R = \text{La, Ce, Pr, Nd, Sm, and Gd}$. It was found that, besides GdCoAsO , all the other five compounds enter into a static ferromagnetic ordered phase below around 70 K ($=T_C$), while additional transitions into a static AF ordered phase were found for NdCoAsO and SmCoAsO . For GdCoAsO , a static ferrimagnetic phase appeared below 60.5 K and then an incommensurate spin-density-wave ordered phase followed below 3.2 K. The AF spin structure was also found to strongly depend on R .

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I. INTRODUCTION

The emergence of pnictides¹ and other Fe-based superconductors,² such as $\text{LaFeAsO}_{1-x}\text{F}_x$,³ has appealed the importance of the interplay between magnetism and superconductivity (SC). This is because the phase diagram of $\text{LaFeAsO}_{1-x}\text{F}_x$ ⁴ and related compounds⁵ seems to be similar to those for high- T_c cuprates. For instance, the parent compound, LaFeAsO , enters into an itinerant spin-density-wave (SDW) antiferromagnetic (AF) phase below $T_N \sim 140$ K,^{6,7} while the parent compounds of high- T_c cuprates are an AF Mott insulator. Upon F-doping for LaFeAsO , T_N is steadily reduced, until finally the AF order is annihilated and superconductivity emerges. In the case of F doping into the $[\text{La}_2\text{O}_2]$ layers, the expected result is that the number of Fe-3d electrons increases.

A more straightforward method is a partial substitution for Fe by Co—i.e., doping one more 3d electron, and hereby doped electrons directly into the $[\text{Fe}_2\text{As}_2]$ layers. It has been recently shown that for $\text{LaFe}_{1-x}\text{Co}_x\text{AsO}$ the AF order is destroyed at $x = 0.05$ and maximum $T_c^{\text{onset}} = 14.3$ K is achieved for $x = 0.11$.⁸ For $x = 1$, namely LaCoAsO , neither AF order nor SC appears, but instead metallic resistivity and ferromagnetic (FM) order with $T_C = 60$ K.⁹ This is rather surprising, since the crystal structure (see Fig. 1) as well as the electronic structure around the Fermi level, consisting of Co-3d and As-3p hybridized orbitals, are similar to that of $\text{LaFe}_{1-x}\text{Co}_x\text{AsO}$. However, when La is replaced by Nd, Sm, or Gd, such rare-earth-CoAsO ($R\text{CoAsO}$) exhibits an additional magnetic transition at T_m ($T_m < T_C$) according to susceptibility (χ) measurements.¹⁰ A sudden decrease in χ at T_m is likely to indicate the occurrence of an AF transition at T_m .¹⁰ In the context of competing AF order and SC, details of

the magnetic ground state in the $R\text{CoAsO}$ compound series is of high importance.

Indeed, recent neutron experiments on NdCoAsO ^{11,12} clarified the existence of long-range FM order below 70 K and long-range AF order below 15 K. Thus T_m is confirmed as T_N for NdCoAsO . Besides these works, the magnetic nature of $R\text{CoAsO}$ has been investigated by macroscopic measurement techniques, such as magnetization, resistivity, and heat-capacity measurements for LaCoAsO ,^{13,14} CeCoAsO ,¹⁵ NdCoAsO ,¹⁴ and SmCoAsO .^{14,16,17} Furthermore, the magnetism of LaCoAsO and CeCoAsO was studied by ^{75}As - and ^{139}La -NMR,^{15,18} while there are no reports on the microscopic magnetic properties of the other $R\text{CoAsO}$ compounds.

According to neutron measurements on NdCoAsO ,^{11,12} the ordered Co moment is estimated as about $0.2\mu_B$ in the FM state, but about $0.4\mu_B$ in the AF state. Furthermore, the Nd moment orders only in the AF state, and the ordered value reaches about $1.4\mu_B$ at 0.3 K. Since such FM/AF order generates a static internal magnetic field (H_{int}) at the interstitial sites where implanted muons are located, we can expect clear precession signals in the muon-spin rotation and relaxation ($\mu^+\text{SR}$) spectra under zero applied field (ZF) below T_C/T_N . If there are multiple muon sites with different H_{int} in the lattice, we could reconfirm and/or deduce the spin structure from the intensity ratios of several H_{int} signals, as in BaCoO_3 ,¹⁹ Ba_2CoO_4 ,²⁰ and NaV_2O_4 .²¹ We have, therefore, measured ZF- $\mu^+\text{SR}$ spectra in the $R\text{CoAsO}$ ($R = \text{La, Ce, Pr, Nd, Sm, Gd}$) compounds, as $\mu^+\text{SR}$ is especially sensitive to local magnetic environments.

II. EXPERIMENT

Polycrystalline samples of $R\text{CoAsO}$ were prepared by a solid-state reaction technique using reagent grade R , As, and

FIG. 1. (Color online) Crystal structure of LaCoAsO is tetragonal, space group $P4/nmm$, with lattice parameters of $a = 4.055 \text{ \AA}$ and $c = 8.462 \text{ \AA}$.^{10,22}

CoO powders.^{10,22} At first, RAs was prepared by the reaction $R + \text{As} \rightarrow \text{RAs}$ in an evacuated quartz tube at 550°C for 5 h and then at 800°C for 12 h. Finally, the RCoAsO was prepared by the reaction $\text{RAs} + \text{CoO} \rightarrow \text{RCoAsO}$ in an evacuated quartz tube at 1100°C for 12 h. Powder x-ray-diffraction analyses showed that all the samples are a single phase of a tetragonal symmetry with space group $P4/nmm$. The magnetic susceptibility χ was measured below 400 K under a $H \leq 1 \text{ kOe}$ field with a superconducting quantum interference device (SQUID) magnetometer.

The $\mu^+\text{SR}$ spectra were measured on surface muon beam lines using the Dolly spectrometer of PSI in Switzerland and the LAMPF spectrometer of TRIUMF in Canada. The approximately 500-mg powder sample was placed in an envelope with $1 \times 1 \text{ cm}^2$ area made of 0.05-mm-thick Al-coated Mylar tape in order to minimize the signal from the envelope. The envelope was then attached to a low-background sample holder in a liquid-He flow-type cryostat in the T range between 1.7 and 150 K. The experimental techniques are described in detail elsewhere.²³

III. RESULTS

A. LaCoAsO, CeCoAsO, and PrCoAsO

Figure 2(a) shows the zero-field (ZF) $\mu^+\text{SR}$ time spectra at 50 and 1.7 K for LaCoAsO. A clear oscillation indicates the

formation of static ferromagnetic (FM) order in LaCoAsO. Also, since there is only one oscillatory signal in the whole T range below T_C , all the implanted muons are found to locate at one magnetically equivalent site. In fact, the ZF spectrum was well fitted by a combination of the oscillatory signal and a nonoscillatory relaxing signal:

$$A_0 P_{\text{ZF}}(t) = A_{\text{FM}} \cos(2\pi f_\mu t + \phi) \exp(-\lambda_{\text{FM}} t) + A_{\text{S}} \exp(-\lambda_{\text{S}} t), \quad (1)$$

where A_i are the asymmetries (A_0 is the maximal asymmetry measured in Ag, where the muon polarization $P = 1$), λ_i is the exponential relaxation rate, $2\pi f_\mu (\equiv \omega_\mu)$ is the muon Larmor frequency, and ϕ is the initial phase of the oscillatory signal.

Figure 2 shows the T dependences of f_μ and χ , the normalized A_{FM} (A_{FM}/A_0), and λ_i for LaCoAsO, CeCoAsO, and PrCoAsO. For LaCoAsO, the $f_\mu(T)$ curve exhibits an order-parameter-like T dependence, suggesting that the FM phase is stable down to 1.7 K. Indeed, the $f_\mu(T)$ curve is in very good agreement with the $\chi(T)$ curve over the whole T range measured, except for temperatures in the vicinity of T_C .

Since $\phi \sim -17^\circ$ at 1.7 K and is almost T independent until the vicinity of T_C (not shown), the FM order is commensurate with the lattice, as expected. In principle, ϕ should be zero for a powder sample with commensurate magnetic order and an ideal Lorentzian or Gaussian field distribution at the muon site. Nevertheless, a fit using a nonzero ϕ gives an overall more acceptable result for the ZF spectrum of LaCoAsO. This is most likely due to a systematic delay in the electronic setup of the present apparatus, since the -17° delay corresponds to about 1.4 ns, when $f_\mu = 34.5 \text{ MHz}$. Unfortunately, there is no theoretical prediction for the critical ϕ beyond which the magnetic order is incommensurate. However, when $\phi \leq -45^\circ$, such a phase shift empirically suggests possible formation of incommensurate magnetic order.

The relative amplitude of the oscillatory signal (A_{FM}/A_0) is about 0.67, and that for the nonoscillatory signal (A_{S}/A_0) is about 0.33. Both are T independent until the vicinity of T_C . Therefore, the A_{S} signal is assigned as the “1/3 tail”, which is caused by the internal magnetic-field (H_{int}) component parallel to the initial muon spin polarization. This means that the whole sample enters into the FM ordered phase below T_C . This is also supported by weak transverse field (wTF) $\mu^+\text{SR}$ measurements, in which the normalized TF asymmetry (A_{TF}/A_0) drops from 1 to ~ 0 at T_C [see Fig. 2(g)]. Here, A_{TF}/A_0 is proportional to the volume fraction of paramagnetic phases in the sample.

For CeCoAsO, the overall behavior is similar to that for LaCoAsO. However, below $\sim 20 \text{ K}$, f_μ decreases slightly with decreasing T , whereas λ_{FM} increases, suggesting a shift of the field distribution at the muon site(s). Note that the $\chi(T)$ curve also changes slope around 20 K. We wish to point out that recent specific-heat measurements showed the presence of a broad anomaly below approximately 20 K for CeCoAsO, although it was thought to be a Schottky-type anomaly.¹⁵

For PrCoAsO, as T decreases from $T_C (= 71 \text{ K})$, f_μ ranges below 4.2 MHz down to 50 K ($= T_{m1}$), and then eventually becomes undetectable below T_{m1} due to the increase in λ_{FM} . When T is lowered further, two oscillatory signals appear below 32 K ($= T_{m2}$). Thus the ZF spectrum was fitted by a

FIG. 2. (Color online) Top: the ZF- μ^+ SR time spectra (a) at 1.7 and 50 K for LaCoAsO, (b) at 1.7 and 50 K for CeCoAsO, and (c) at 1.7 and 70 K for PrCoAsO. Bottom: T dependences of [f_μ and χ , the normalized P_i ($\equiv A_i/A_0$), and λ_i] for [(d), (g), (j)] LaCoAsO, [(e), (h), (k)] CeCoAsO, and [(f), (i), (l)] PrCoAsO. The data (except for χ and A_{TF}) were obtained by fitting the ZF-spectra using Eq. (1). A_{TF} represents a weak transverse field asymmetry measured with wTF = 30 Oe. The susceptibility χ was measured with $H = 1$ kOe in field cooling mode. Note that the time axis of (c) is a log scale.

combination of Eq. (1) and a second exponentially relaxing cosine function, $A_{FM2} \cos(2\pi f_{\mu 2} t + \phi_2) \exp(-\lambda_{FM2} t)$. Although $f_{\mu 2}$ ranges around 30 MHz as in the case for LaCoAsO, the larger signal shows an oscillation with $f_{\mu 1} \sim 3$ MHz down to 1.8 K. Note that, despite the absence of anomalies in the $\chi(T)$ curve below T_C , μ^+ SR clearly detects a change in the magnetic behavior of PrCoAsO in the T range between T_{m1} and T_{m2} .

B. NdCoAsO and SmCoAsO

For NdCoAsO, SmCoAsO, and GdCoAsO, although the ZF spectra show a clear oscillation at each T below T_C , as T decreases from T_C , f_μ increases abruptly at a certain T . This means that each sample enters into an AF ordered phase, as speculated from χ measurements.¹⁰ In fact, the spectrum was fitted by a combination of Eq. (1) and a second exponentially relaxing cosine function:

$$A_0 P_{ZF}(t) = A_{FM} \cos(2\pi f_\mu t + \phi) \exp(-\lambda_{FM} t) + A_{AF} \cos(2\pi f_\mu t + \phi) \exp(-\lambda_{AF} t) + A_S \exp(-\lambda_S t), \quad (2)$$

where $A_{FM} = 0$ below T_N , whereas $A_{AF} = 0$ above T_N .

Figure 3 shows the T dependences of f_μ , χ , A_i/A_0 , and λ_i for NdCoAsO, SmCoAsO, and GdCoAsO. In contrast to LaCoAsO, all three samples are found to enter into a static AF ordered phase below $T_N = 15$ K for NdCoAsO and below

41 K for SmCoAsO. The result on GdCoAsO is explained in Sec. IV C. Since $A_{FM}/A_0 = A_{AF}/A_0 \sim 0.67$ below T_C , the whole volume of the samples exhibits successive magnetic transitions from a paramagnetic phase to an FM phase, and then to an AF phase, with decreasing T .

For NdCoAsO, as T decreases from T_N , both f_μ and λ_{AF} increase rapidly, particularly below ~ 7 K, indicating the presence of an additional AF transition, i.e., $T_{N1} \sim 15$ K and $T_{N2} \sim 7$ K. Recent neutron-scattering measurements¹² revealed the evolution of the ordered Nd moments with decreasing T below $T_{N2} \sim 3.5$ K, but the Nd moment appears to start increasing below 7 K. In addition, since $\phi \sim -10^\circ$ in the T range between 1.7 K and below the vicinity of T_C , the FM and two AF phases should possess a commensurate spin structure. This is consistent with the neutron result.^{11,12}

As T decreases from T_C , f_μ for SmCoAsO increases abruptly by ~ 40 times at $T_{N1} (= 41$ K), although f_μ for SmCoAsO in the FM phase is comparable to that for NdCoAsO. This implies that the FM spin structure for SmCoAsO is very similar to that for NdCoAsO. Below T_{N1} , the $f_\mu(T)$ curve changes slope (df_μ/dT) around 17.5 K, where the $\lambda_{AF}(T)$ curve exhibits a broad maximum. This suggests the presence of an additional magnetic transition ($T_{N2} = 17.5$ K), which could correspond to the transition at 5 K recently reported by specific-heat measurements.¹⁶ Outside the vicinities of T_C , T_{N1} , and T_{N2} , since $|\phi| \leq 20^\circ$, the FM and two AF orders are thought to be commensurate with the lattice.

FIG. 3. (Color online) Top: the ZF- μ^+ SR spectra (a) at 1.7 and 20 K for NdCoAsO, (b) at 1.7 and 50 K for SmCoAsO, and (c) at 1.7 and 3.5 K for GdCoAsO. Bottom: T dependences of [f_μ and χ , A_i/A_0 , and λ_i] for [(d), (g), (j)] NdCoAsO, [(e), (h), (k)] SmCoAsO, and [(f), (i), (l)] GdCoAsO. χ was measured with $H = 1$ kOe in field cooling mode. Note that the T axis for GdCoAsO is a log scale. In (e') and (f'), the f_μ axis is a linear scale.

C. GdCoAsO

For GdCoAsO, f_μ does not exhibit a typical T dependence, but rapidly increases with decreasing T . Then, as seen in Fig. 4, f_μ splits into $f_{\mu 1}$ and $f_{\mu 2}$ at 3.2 K, below which the relaxation rates for the two signals are rather large compared with λ_{FM} . This behavior indicates the appearance of a complex magnetic-ordered phase below $T_m = 3.2$ K. Although $|\phi| \leq 10^\circ$ above T_m , ϕ for the predominant $f_{\mu 2}$ signal ranges between -90° and -54° below T_m and reaches -54° at 1.7 K, suggesting the formation of incommensurate (IC) SDW order below T_N .^{23,24} Thus T_m should be T_N . In fact, the ZF spectrum below T_N is fitted by a combination of a Gaussian relaxing cosine function, a Gaussian relaxing zeroth-order Bessel function of the first kind [$J_0(2\pi f_{\mu 2}t)$], and an exponentially relaxation function:

$$\begin{aligned}
 A_0 P_{\text{ZF}}(t) = & A_{\text{AF1}} \cos(2\pi f_{\mu 1}t + \phi) \exp\left(-\frac{\sigma_{\text{AF1}}^2 t^2}{2}\right) \\
 & + A_{\text{AF2}} J_0(2\pi f_{\mu 2}t) \exp\left(-\frac{\sigma_{\text{AF2}}^2 t^2}{2}\right) \\
 & + A_S \exp(-\lambda_S t),
 \end{aligned} \quad (3)$$

where $f_{\mu 2} > f_{\mu 1}$ and $f_{\mu 2}$ corresponds to the upper limit of H_{int} at the muon site, whereas $f_{\mu 1}$ corresponds to the lower limit of H_{int} (see the Appendix).

The $f_{\mu 2}(T)$ curve suggests an order-parameter-like T dependence [see Fig. 3(f)]. This indicates evolution of the

FIG. 4. (Color online) Fourier amplitude spectrum for GdCoAsO at 3.5 and 1.7 K. The magnitude of the spectrum at 1.7 K is about 1/20 of that at 3.5 K.

FIG. 5. (Color online) Temperature dependence of magnetization (M) for GdCoAsO obtained with various H ($=10, 20, 50, 100$, and 150 Oe). Broken lines at 3.2 and 60.5 K represent the transition temperatures determined by the present ZF- μ^+ SR.

IC-SDW field with decreasing T . It would therefore be very interesting to investigate the AF spin structure using neutrons, but the large neutron absorption cross sections of ^{157}Gd and ^{155}Gd may make this difficult.

Although μ^+ SR clearly detects the additional AF transition at 3.2 K, there is no anomaly in the $\chi(T)$ curve below ~ 80 K, when we measured it with $H = 1$ kOe [see Fig. 3(f)]. In order to know the magnetic nature of GdCoAsO at low fields, Fig. 5 shows the T dependence of magnetization (M) measured with $H \leq 150$ Oe. As T decreases from 80 K, the $M(T)$ curve shows an abrupt increase at T_N . Since M decreases with further decreasing T , the phase below $T_N^{\mu\text{SR}}$ is found to be an AF ordered phase, as expected from the IC-SDW nature.

TABLE I. μ^+ SR parameters for $R\text{CoAsO}$ and the calculated f_μ (f_μ^{calc}), where f_μ is converted into the local field (H_{int}) using $f_\mu = H_{\text{int}} \times 13.55342$ kHz/Oe. The field distribution width (Δ) was determined by fitting the ZF and LF spectra above T_C using a dynamic Kubo-Toyabe function. For GdCoAsO, since the ZF spectrum shows a rapidly relaxing behavior even at 140 K, it was impossible to determine Δ .

R	T_C (K)	T_{N1} (K)	T_{N2} (K)	$f_{\mu,\text{FM}}$ (MHz)	$f_{\mu,\text{AF}}$ (MHz)	Δ (10^6 s^{-1})
La	59	—	—	34.5(1) [at 1.7 K]	—	0.22(2) [at 140 K]
Ce	76	—	—	19.6(2) [at 1.8 K]	—	0.300(4) [at 80 K] ^a
Pr	71	—	—	3.07(2) & 34.2(4) [at 1.8 K]	—	0.31(1) [at 120 K]
Nd	70	15	7	3.05(1) [at 15.3 K]	5.97(1) [at 1.7 K]	0.192(4) [at 140 K]
Sm	69	41.5	17.5	1.07(2) [at 42.5 K]	45.3(1) [at 1.7 K]	0.164(1) [at 140 K]
Gd	60.5 ^b	60.5 ^b	3.2	25.9(4) [at 3.5 K]	22.2(1.6) & 66.2(2) [at 1.7 K] ^c	—

^aOnly by ZF spectrum.

^bNot ferromagnetic, but ferrimagnetic.

^cThe AF order is incommensurate.

Concerning the variation of M around $T_C = 60.5$ K, a broad peak is clearly seen at T_C in the $M(T)$ curve measured with $H = 10$ and 20 Oe [Fig. 5(b)], suggesting that the transition is not a typical FM transition. Since such an anomaly shifts toward a higher T side with H , an FM interaction plays a significant role for determining T_C . Furthermore, as H increases further, the anomaly was reported to disappear with $H > \sim 10$ kOe, and the $M(T)$ curve showed a typical Curie-Weiss behavior.¹⁰ This suggests that GdCoAsO is not a ferromagnet, but a ferrimagnet below T_C , i.e., $T_C = T_f$.¹⁰

IV. DISCUSSION

The parameters obtained by the present study are summarized in Table I and a magnetic phase diagram for the $R\text{CoAsO}$ series is shown in Fig. 6. We also determined the field distribution width (Δ) caused by nuclear moments in the paramagnetic state from ZF- and longitudinal field (LF-) μ^+ SR measurements. The characteristic feature of the FM phase is that f_μ ranges between 20 and 35 MHz for the $R = \text{La}$, Ce , and Gd compounds, but f_μ is very small for PrCoAsO , NdCoAsO , and SmCoAsO . In order to explain this difference, we attempt to speculate on the FM and AF spin structures of these compounds.

For ferromagnets, the internal magnetic field at a muon site (H_{int}) is represented by^{25,26}

$$H_{\text{int}} = H_{\text{dip}} + H_L + H_{\text{hf}}, \quad (4)$$

where H_{dip} is the dipole field, H_L is the Lorentz field, and H_{hf} is the hyperfine field. Furthermore, H_L and H_{hf} are connected to the saturated magnetization (M_s) and the local spin density at the muon sites (ρ_{spin}) as follows:

$$H_L = 4\pi/3 \times M_s, \quad H_{\text{hf}} = 8\pi/3 \times \rho_{\text{spin}}. \quad (5)$$

Since M_s ranges between 0.28 and $0.16 \mu_B/\text{Co}$ for $R\text{CoAsO}$,^{10,17} H_L is calculated as 78 – 48 Oe ($f_L = 1.1$ – 0.65 MHz). However, we can not obtain the correct H_{hf} without muon Knight shift measurements under high TF using a single crystal sample. Note that H_L should be zero for antiferromagnets, and H_{hf} for antiferromagnets is, in principle, very small compared with those for ferromagnets.

FIG. 6. (Color online) Schematic magnetic phase diagram for the $R\text{CoAsO}$ series determined by our ZF- μ^+ SR experiments. Here, we assumed that $T_C = T_f (= T_{N1})$ for GdCoAsO .¹⁰

A. NdCoAsO

We now begin the discussion of the AF state of NdCoAsO . First we attempt to determine the muon sites in the lattice by evaluating $H_{\text{dip}}(f_{\text{dip}})$ using dipole field calculations. First-principles calculations for LaFeAsO ²⁷ and CeFeAsO ²⁸ predicted that muons locate either at (0.25, 0.25, 0.41) in the FeAs layer (A site) or at the vicinity of the O^{2-} ion (B site). Assuming the same muon sites for NdCoAsO , the nuclear dipole field width (Δ) in the paramagnetic state, which is caused by ^{143}Nd , ^{145}Nd , ^{59}Co , and ^{75}As moments, is calculated to be $\Delta^{\text{calc}} = 0.399 \times 10^6 \text{ s}^{-1}$ for the A site and $0.092 \times 10^6 \text{ s}^{-1}$ for the B site (see also Table II). Here, the B site is assigned at (0.25, 0.96, 0.93) by electrostatic potential calculations using a point-charge model. On the other hand, based on ZF- and LF- μ^+ SR measurements²⁹ for NdCoAsO far above T_C , i.e., at 140 K (see Fig. 7), Δ was estimated to be $\Delta^{\text{expt}} = 0.192 \times 10^6 \text{ s}^{-1}$. Since Δ^{calc} corresponds to the highest limit of Δ^{expt} ($\Delta^{\text{calc}} > \Delta^{\text{expt}}$), muons are unlikely to be located at the B site.

Recent neutron experiments led to the proposal that, for the spin structures for NdCoAsO ^{11,12} in the FM state, only the Co moments align along the $[100]$ direction, with $\mu_{\text{Co,FM}}^{\text{ord}} \sim 0.3\mu_B$ at 15 K. In the AF state between T_{N1} and $T_{N2} = 7 \text{ K}$ —i.e., in the AF1 phase—both the Co and Nd moments align antiferromagnetically with propagation vector (0 0 1/2). The Co moments still align along the $[100]$ direction, while the Nd moments align along the $[\bar{1}00]$ direction. The ordered moments $\mu_{\text{Co,AF}}^{\text{ord}} = \mu_{\text{Nd,AF}}^{\text{ord}} \sim 0.4\mu_B$ are almost T independent. Below T_{N2} —i.e., in the AF2 phase— μ_{Nd} increases with decreasing

TABLE II. Prediction of the nuclear dipole field width (Δ) at the A site and B site for $R\text{CoAsO}$. Making comparison with the experimental data in Table I, the implanted muons are most unlikely to locate at the B site in the $R\text{CoAsO}$ lattice.

R	$\Delta_A^{\text{calc}} (10^6 \text{ s}^{-1})$	$\Delta_B^{\text{calc}} (10^6 \text{ s}^{-1})$
La	0.391	0.199
Ce	0.397	0.087
Pr	0.439	0.310
Nd	0.399	0.092
Sm	0.409	0.095
Gd	0.422	0.095

FIG. 7. (Color online) ZF- and longitudinal (LF-) μ^+ SR spectra for NdCoAsO obtained at 140 K. The magnitudes of the LF were 10 and 30 Oe. Solid lines represent the fit result using a dynamic Kubo-Toyabe function.²⁹

T , reaching $1.39\mu_B$ at 300 mK. Using the proposed AF model, $H_{\text{dip}} (= H_{\text{int}})$ at the A site for NdCoAsO is predicted as a function of $\mu_{\text{Co,AF}}^{\text{ord}}$ and $\mu_{\text{Nd,AF}}^{\text{ord}}$ (see Fig. 8). It is clearly found that $f_{\mu}^{\text{calc}} = 12.2 \text{ MHz}$ for $\mu_{\text{Co,AF}}^{\text{ord}} = 0.4\mu_B$ and $\mu_{\text{Nd,AF}}^{\text{ord}} = 0$. Since $f_{\mu} = 4 \text{ MHz}$ at 8 K (in the AF1 phase) and 6 MHz at 1.7 K (in the AF2 phase), the ordered moments satisfy the following relations:

$$\begin{aligned} \mu_{\text{Co,AF}}^{\text{ord}} &= 0.13 - 0.22 \times \mu_{\text{Nd,AF}}^{\text{ord}} \quad \text{at } 8 \text{ K}, \\ \mu_{\text{Co,AF}}^{\text{ord}} &= 0.20 - 0.22 \times \mu_{\text{Nd,AF}}^{\text{ord}} \quad \text{at } 1.7 \text{ K}, \end{aligned} \quad (6)$$

where $0 \leq \mu_{\text{Co,AF}}^{\text{ord}} < 0.20\mu_B$ and $0 \leq \mu_{\text{Nd,AF}}^{\text{ord}} < 0.91\mu_B$. If we assume that $\mu_{\text{Co,AF}}^{\text{ord}}$ is T independent below T_{N1} , $\mu_{\text{Nd,AF}}^{\text{ord}}$ increases by $0.3\mu_B$ with decreasing T from 8 to 1.7 K, while the increase in $\mu_{\text{Nd,AF}}^{\text{ord}}$ is about $1\mu_B$ from neutron data. Also, $\mu_{\text{Nd,AF}}^{\text{ord}}$ should be below $0.2\mu_B$ in the whole T range. The discrepancy between μ^{ord} estimated by μSR and neutrons is probably due to the different time windows of the two techniques.

FIG. 8. (Color online) Prediction of the muon precession frequency (f_{μ}) for NdCoAsO due to the dipole field [$H_{\text{dip}} = f_{\mu}/13.55342 \text{ (kHz/Oe)}$] at the A site in the AF state. f_{μ} was calculated using the AF model, in which the ordered Co and Nd moments (μ_{Co} and μ_{Nd}) are parallel/antiparallel to the $[100]$ direction. The planes with $f_{\mu} = 4$ and 6 MHz represent the experimental results at 8 and 1.7 K. The line at which the two planes intersect corresponds to the combination of μ_{Co} and μ_{Nd} to satisfy the experimental result.

Returning to the FM state of NdCoAsO, we note that M_s ($\sim 0.18\mu_B$) determined by dc-magnetization measurements is less than $\mu_{\text{Co,FM}}^{\text{ord}}$ ($\sim 0.3\mu_B$) estimated by neutrons. Since the time window of μ^+ SR is between those of dc-magnetization and neutrons, μ^+ SR should at least sense an FM ordered moment with a magnitude of $0.18\mu_B$. Thus the dipole field calculations for the A site show that $f_{\mu,\text{FM}}^{\text{calc}} = 4.0$ MHz, which corresponds to $H_{\text{dip}} = 292$ Oe. Also, $H_L = 53$ Oe from Eq. (5) and $M_s \sim 0.18\mu_B$. Therefore, $H_{\text{hf}} = -120$ Oe for NdCoAsO, since $H_{\text{int}} = 225$ Oe ($= 3.05$ MHz/ 13.553 kHz/Oe) at 3.05 K.

B. SmCoAsO

For SmCoAsO, M_s was reported as $0.16\mu_B$ by magnetization measurements,^{16,17} but there is no information regarding the FM and AF spin structures. Since $f_{\mu,\text{FM}} (= 1.07$ MHz) for SmCoAsO is comparable to $f_{\mu,\text{FM}}$ for NdCoAsO, the FM structure is likely the same as that for NdCoAsO. Indeed, $f_{\mu,\text{FM}}^{\text{calc}}$ is predicted to be 3.4 MHz ($H_{\text{dip}} = 249$ Oe), resulting in $H_L = 48$ Oe and $H_{\text{hf}} = -240$ Oe at 42.5 K.

It is, however, difficult to explain H_{int} in the AF phase of SmCoAsO by the AF model for NdCoAsO, because $f_{\mu,\text{AF}}$ for SmCoAsO is about eight times larger than that in NdCoAsO at 1.7 K. In fact, if we use such an AF model and fix $\mu_{\text{Co,AF}}^{\text{ord}}$ at $0.4\mu_B$, which is the value proposed for NdCoAsO from neutron experiments, $\mu_{\text{Sm,AF}}^{\text{ord}}$ should be in the range $\sim 5\mu_B$, inconsistent with the fact that the theoretical value of μ_{eff} of Sm^{3+} is $0.845\mu_B$. Therefore, we need to find another AF model for SmCoAsO, although μ^+ SR is not an ideal tool for determining unknown magnetic structures—particularly for cases where there is only one muon spin precession frequency in the magnetic state. Nevertheless, assuming that an AF structure with the same propagation vector but $\mu_{\text{Co,AF}}^{\text{ord}} \parallel [001]$ and $\mu_{\text{Nd,AF}}^{\text{ord}} \parallel [00\bar{1}]$ instead, $f_{\mu,\text{AF}}$ reaches 45.3 MHz (see Fig. 9) when $\mu_{\text{Co,AF}}^{\text{ord}} = (0.73\text{--}0.20) \times \mu_{\text{Sm,AF}}^{\text{ord}}$, in which

$0.56 \leq \mu_{\text{Co,AF}}^{\text{ord}} < 0.73\mu_B$ and $0 \leq \mu_{\text{Sm,AF}}^{\text{ord}} < 0.845\mu_B$. Such a simple structure could be a good candidate for the magnetic ground state for SmCoAsO. Here the ordered moments along the $[100]$ direction are most likely rapidly fluctuating compared with those along the $[001]$ direction, because of the tetragonal symmetry of RCoAsO. Therefore, it would be acceptable that both $\mu_{\text{Co,AF}}^{\text{ord}}$ and $\mu_{\text{R,AF}}^{\text{ord}}$ for SmCoAsO are larger than those for NdCoAsO, within the time window of μ^+ SR.

C. GdCoAsO

For GdCoAsO, the IC-SDW field ranges between ~ 22 and 66 MHz at 1.7 K. Since μ_{eff} of Gd^{3+} is about $8\mu_B$, either of the two AF models mentioned above could be used for the basis of the IC modulated spin structure. However, due to the large neutron absorption cross section of Gd, it would be difficult to determine the AF spin structure of GdCoAsO by a neutron-scattering technique.

The variation of the μ^+ SR parameters of RCoAsO with R demonstrates the importance of an interaction between $3d$ and $4f$ electrons to the electronic properties. For such cases, the electronic properties of $4f$ ions in ZF could be described by the following Hamiltonian:³¹

$$\begin{aligned} \mathcal{H}_R &= \mathcal{H}_{\text{s-o}} + \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{ex}} \\ &= \lambda \mathbf{L} \cdot \mathbf{S} + \mathcal{H}_{\text{CF}} + g_s \mu_B \mathbf{S} \cdot \mathbf{H}_{\text{ex}}, \end{aligned} \quad (7)$$

where $\mathcal{H}_{\text{s-o}}$ stands for the spin-orbit coupling energy, $\mathcal{H}_{\text{CF}}$ is the crystal electric-field energy, $\mathcal{H}_{\text{ex}}$ the exchange energy, λ the spin-orbit coupling parameter, $\mathbf{L}$ and $\mathbf{S}$ the orbital and spin momenta, g_s the spin gyromagnetic factor ($=2$), and $\mathbf{H}_{\text{ex}}$ the exchange field at R due to neighboring $3d$ electrons. Note that $\lambda > 0$ for R^{3+} with $n < 7$, $\lambda = 0$ for Gd^{3+} with $n = 7$, and $\lambda < 0$ for R^{3+} with $n > 7$, where n denotes the number of $4f$ electrons.

For most of the R ions, the spin-orbit coupling dominates the other terms in Eq. (7)—that is, $\mathbf{L}$ and $\mathbf{S}$ are coupled. As a result, the total angular momentum ($\mathbf{J}$) becomes a good quantum number. As usual, Eq. (7) is further simplified as³²

$$\mathcal{H}_R = \mathcal{H}_{\text{CF}} + 2(g_J - 1)\mu_B \mathbf{J} \cdot \mathbf{H}_{\text{ex}}, \quad (8)$$

where g_J is the Landé factor given by

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (9)$$

Here, $g_J < 1$ for R^{3+} with $1 \leq n < 6$, $g_J > 1$ for R^{3+} with $7 \leq n \leq 13$, and $g_J = 1$ for R^{3+} with $n = 0, 6$, and 14 (La^{3+} , Eu^{3+} , and Lu^{3+}). This leads to a parallel configuration between $3d$ and $4f$ moments for light R ions, and an antiparallel configuration for heavy R ions, but no preference for La^{3+} , Eu^{3+} , and Lu^{3+} .

Although the overall magnetic properties of RCoAsO are determined not only by the $3d$ - $4f$ interaction but also by $3d$ - $3d$ and $4f$ - $4f$ interactions, it is reasonable that such a change of sign in the second term of Eq. (8) induces a complex magnetic order for GdCoAsO compared with those for the other five RCoAsO compounds. In fact, despite systematic magnetization measurements for the compounds with $R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$, and Gd , a reliable value of M_s for

FIG. 9. (Color online) Prediction of f_{μ} for SmCoAsO due to dipolar fields at the A site in the AF state. f_{μ} was calculated using the AF model, in which the ordered Co and Sm moments (μ_{Co} and μ_{Sm}) are parallel/antiparallel to the $[001]$ direction. The plane with $f_{\mu} = 45$ MHz represents the experimental result at 1.7 K. The line at which the two planes intersect corresponds to the combinations of μ_{Co} and μ_{Sm} that satisfy the experimental result.

FIG. 10. (Color online) Relationship between magnetic transition temperatures and the de Gennes factor (ξ) for $R\text{CoAsO}$.

GdCoAsO is still not available, suggesting that GdCoAsO is not a simple ferromagnet, but a ferrimagnet, as already mentioned.

Assuming that GdCoAsO is a ferrimagnet with $T_f = 60.5$ K, T_{N1} (T_f) is most likely to correlate with the de Gennes factor (ξ),¹⁰ where ξ is defined as

$$\xi = (g_J - 1)^2 J(J + 1). \quad (10)$$

This could indicate that the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction plays a certain role to determine the AF nature of $R\text{CoAsO}$, because, if crystal electric-field effects are not taken into account, T_N for a series of isostructural and isoelectronic metals are expected to scale ξ .³³ However, as seen in Fig. 10, the slope of the $T_{N1}(\xi)$ curve decreases with ξ , indicating that T_{N1} is not simply determined by the RKKY interaction.

In order to further understand the role of the $3d$ - $4f$ and/or RKKY interaction on the magnetic nature of $R\text{CoAsO}$, it is important to study the compounds with $R = \text{Eu}$ and Tb-Lu by both muons and neutrons.

D. LaCoAsO and FM nature

Although M_s is reported as $0.28\mu_B/\text{Co}$ by magnetization measurements, a reliable FM ordered moment ($\mu_{\text{Co,FM}}^{\text{ord}}$) and FM spin structure are still unavailable for LaCoAsO . We therefore calculated a proportional coefficient ($F_{\text{Co,FM}}^{\text{calc}}$) between $f_{\mu,\text{FM}}^{\text{calc}}$ and $\mu_{\text{Co,FM}}^{\text{ord}}$, i.e., $f_{\mu,\text{FM}}^{\text{calc}} = F_{\text{Co,FM}}^{\text{calc}} \times \mu_{\text{Co,FM}}^{\text{ord}}$. For the A site, $F_{\text{Co,FM}}^{\text{calc}} = 41.8$ MHz/ μ_B when $\mu_{\text{Co,FM}}^{\text{ord}} \parallel [001]$, but 20.9 MHz/ μ_B when $\mu_{\text{Co,FM}}^{\text{ord}} \parallel [100]$. If we assume that

FIG. 11. (Color online) Relationship between (a) H_{hf} and M_s of the Co ion and (b) H_{hf} and μ_{eff} of the R^{3+} ion.

$M_s = \mu_{\text{Co,FM}}^{\text{ord}}$, $f_{\mu,\text{FM},[001]}^{\text{calc}} = 11.7$ MHz, whereas $f_{\mu,\text{FM},[100]}^{\text{calc}} = 5.8$ MHz; that is, $H_{\text{dip},[001]} = 863$ Oe and $H_{\text{dip},[100]} = 428$ Oe. Therefore, even for the case where $\mu_{\text{Co,FM}}^{\text{ord}} \parallel [001]$, $f_{\mu,\text{FM}}^{\text{calc}}$ is found to be about 1/3 of the experimental value [34.5 MHz ($=2546$ Oe) at 1.7 K]. As a result, we obtain $H_{\text{hf}} = 1604$ Oe, since $H_L = 78$ Oe.

By means of the same procedure for the other compounds, H_L , H_{dip} , and H_{hf} were estimated (Table III), based on the present H_{int} and M_s in the literature. Figure 11 shows the relationships between H_{hf} and M_s of Co ions, and between H_{hf} and theoretical μ_{eff} of R^{3+} . This is because H_{hf} is proportional to the spin density at the muon site [see Eq. (5)]. Considering the fact that muons locate in the CoAs layer (A site) and the $4f$ electrons well localize at the R site, H_{hf} is expected to increase with M_s . Indeed, there is a good correlation between H_{hf} and M_s ^{25,26} except for PrCoAsO , for reasons currently unknown. On the contrary, if we note the $3d$ - $4f$ interaction, H_{hf} could be proportional to μ_{eff} of R^{3+} , as in the case for an itinerant ferromagnetic system, $\text{R}_2\text{Fe}_{14}\text{B}$.³⁴ In fact, except for SmCoAsO , H_{hf} decreases monotonically with μ_{eff} of R^{3+} [Fig. 11(b)]. Here, the slope ($dH_{\text{hf}}/d\mu_{\text{eff}}$) is steeper for $\text{R}_2\text{Fe}_{14}\text{B}$ than for

TABLE III. Internal magnetic field (H_{int}) of $R\text{CoAsO}$ in their FM state obtained by the present μ^+ SR work, the saturated magnetization (M_s), and the estimation of the Lorentz field (H_L), the dipole field (H_{dip}), and the hyperfine field (H_{hf}).

R	H_{int} (Oe)	M_s (μ_B)/Co	H_L (Oe)	$H_{\text{int}} - H_L$ (Oe)	H_{dip} (Oe)	FM structure	H_{hf} (Oe)
La	2546 [at 1.7 K]	0.28 ^b	78	2467	863	$\mu_{\text{Co}} \parallel [001]$	1604
Ce	1446 [at 1.8 K]	0.24 ^b	69	1377	764	$\mu_{\text{Co}} \parallel [001]$	613
Pr	227 [at 1.8 K] ^a	0.24 ^b	70	157	386	$\mu_{\text{Co}} \parallel [100]$	-229
Nd	225 [at 15.3 K]	0.18 ^b	53	172	292	$\mu_{\text{Co}} \parallel [100]$	-120
Sm	79 [at 42.5 K]	0.16 ^c	48	31	271	$\mu_{\text{Co}} \parallel [100]$	-240
Gd	1911 [at 3.5 K]	—	—	—	—	—	—

^aOnly for the main signal with $f_{\mu} = 3.07$ MHz.

^bReference 10.

^cReference 17.

RCoAsO. However, such difference is reasonable, because the muons locate at the center of the tetrahedron consisting of two R and two Fe in the $R_2\text{Fe}_{14}\text{B}$ lattice. Although we cannot judge which is the predominant factor for H_{hf} at present, $4f$ electrons might strongly affect H_{int} through H_{hf} . However, $4f$ electrons are most unlikely to contribute to the FM order in RCoAsO.

For PrCoAsO, f_{μ} and $f_{\mu 1}$ are comparable to f_{μ} of NdCoAsO in the FM phase, while $f_{\mu 2}$ is comparable to that of LaCoAsO. This suggests a crossover of the FM spin structure from the high- T NdCoAsO-type order to a complex low- T order in the T range between T_{m1} and T_{m2} .

Finally, we wish to point out the possibility that H_{hf} has a finite value even in the AF phase of RCoAsO, since the neighboring Co spins are reported to align parallel in the AF phase of NdCoAsO.^{11,12} This means that H_{hf} listed in Table III should be subtracted from H_{int} in the AF phase for NdCoAsO and SmCoAsO. For NdCoAsO, the two planes in Fig. 8 are shifted upward by 120 Oe ($= 1.6$ MHz), resulting in an increase in the ordered moments in the AF phase by about $0.05\mu_B$. For SmCoAsO, due to its large H_{int} in the AF phase, the effect of H_{hf} on the total magnetic nature is considered to be negligible small.

V. SUMMARY

In summary, our systematic $\mu^+\text{SR}$ study of RCoAsO has clarified the successive transitions from a high- T FM phase to a low- T AF phase for NdCoAsO, SmCoAsO, and GdCoAsO, and confirmed the absence of AF transitions for LaCoAsO, CeCoAsO, and PrCoAsO down to 1.8 K. Also, the FM and AF spin structures were found to vary with R due to coupling between $3d$ and $4f$ electrons. Finally, if an SDW order between $3d$ electrons is an essential component for the parent materials of superconductors,³⁵ it is very important to clarify the AF spin structure of GdCoAsO. Such information in combination with further studies of similar compounds with $R = \text{Eu}$ and Tb-Lu could provide a valuable insight into the interplay between magnetism and superconductivity.

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APPENDIX: FIT FOR IC FIELD

Although $J_0(2\pi f_{\mu}t)$ is widely used for fitting the ZF- $\mu^+\text{SR}$ spectrum in an IC-SDW state, it should be noted that J_0 only provides an approximation of the generic IC magnetic-field distribution. This is because the lattice sum calculation of the dipolar field at the muon site (H_{IC}) due to an IC magnetic structure lies in a plane and traces out an ellipse. The half-length of the major axis of the ellipse corresponds to H_{max} , whereas half of the minor axis corresponds to H_{min} . As a result, the IC magnetic-field distribution P_{IC} is generally given by³⁸

$$P_{\text{IC}} = P(H_{\text{IC}}) = \frac{2}{\pi} \frac{H}{\sqrt{(H^2 - H_{\text{min}}^2)(H_{\text{max}}^2 - H^2)}}. \quad (\text{A1})$$

This distribution diverges as H approaches either H_{min} or H_{max} . Thus J_0 describes the field distribution very well except in the vicinity of H_{min} , and the value of f_{μ} should be interpreted as an accurate measure of H_{max} . However, J_0 provides no information on H_{min} . Hence the first term $A_{\text{AF1}} \cos(2\pi f_{\mu 1}t + \phi)$ is added in Eq. (3) to account for the van Hove singularity around H_{min} and to determine the value of $H_{\text{min}} = 2\pi f_{\mu 1}/\gamma_{\mu}$ ²⁴ (γ_{μ} is the muon gyromagnetic ratio and $\gamma_{\mu}/2\pi = 13.55342$ kHz/Oe). In other words, only when $H_{\text{min}} = 0$ is Eq. (A1) well approximated by J_0 . Field distributions well described by Eq. (A1) were observed for Ag_2NiO_2 ,³⁹ Co_3O_4 ,⁴⁰ and NaV_2O_4 .^{21,41}

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