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Successive magnetic transitions in $\text{RECoAsO}$

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Abstract

In order to elucidate the details of successive magnetic transitions in the rare earth cobalt arsenic oxides ($\text{RECoAsO}$), we have measured muon-spin rotation and relaxation ($\mu^+\text{SR}$) spectra of powder samples with $\text{RE} = \text{La, Ce, Pr, Nd, Sm, and Gd}$. Together with the result of magnetization measurements, it was found that all the compounds enter into a bulk static ferromagnetic ordered phase below around 70 K ($=T_C$). Furthermore, additional transitions into a static antiferromagnetic ordered phase were found for the $\text{RE} = \text{Nd, Sm, and Gd}$ compounds; namely $T_{N1} = 15 \text{ K}$ and $T_{N2} = 7 \text{ K}$ for Nd, $T_{N1} = 41.5 \text{ K}$ and $T_{N2} = 17.5 \text{ K}$ for Sm, and $T_N = 3 \text{ K}$ for Gd.

Keywords: Pnictides and chalcogenides, Antiferromagnetics, Other ferromagnetic metals and alloys, Muon-spin rotation and relaxation

1. Introduction

Although LaFeAsO enters into an itinerant spin-density-wave (SDW) antiferromagnetic (AF) phase below $T_N \sim 140 \text{ K}$ [1, 2], LaCoAsO (LaCoPO) is an itinerant ferromagnet with $T_C = 60 \text{ K (50K)}$ down to the lowest $T$ measured [3]. Recently, Ohta et al. found that $\text{RECoAsO}$ with $\text{RE} = \text{Nd, Sm, Gd}$ undergo an additional transition ($T_m$) below $T_C$ by bulk magnetization measurements [4]. Since the magnetization suddenly decreases at $T_m$, the additional transition is thought to be a transition from a high-$T$ ferromagnetic (FM) phase to a low-$T$ antiferromagnetic (AF) phase; i.e. $T_m = T_N$ [4]. In order to elucidate the microscopic magnetic nature of $\text{RECoAsO}$ ($\text{RE} = \text{La, Ce, Pr, Nd, Sm, Gd}$), we have measured their $\mu^+\text{SR}$ spectra using powder samples.

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2. Experimental

Polycrystalline samples of RECoAsO were prepared by a solid state reaction technique using reagent grade RE, As, and CoO powders [5, 4]. At first, REAs was prepared by the reaction; \(\text{RE} + \text{As} \rightarrow \text{REAs}\), in an evacuated quartz tube at 550°C for 5 h and then 800°C for 12 h. And finally, the RECoAsO was prepared by the reaction; \(\text{REAs} + \text{CoO} \rightarrow \text{RECoAsO}\), in an evacuated quartz tube at 1100°C for 12 h. Powder X-ray diffraction analyses showed that all the samples are single phase of a tetragonal symmetry with space group \(P4/nmm\). Susceptibility (\(\chi\)) was measured below 300 K under a \(H \leq 1\) kOe field with a SQUID magnetometer (MPMS, Quantum Design).

The \(\mu^+\)SR spectra were measured at the 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 packed in an envelope with 1 cm \(\times\) 1 cm area, which is made of very thin Al-coated Mylar tape, and then the envelope was attached to a low-background sample holder in a liquid-He flow-type cryostat in the \(T\) range between 1.7 and 150 K.

3. Results and Discussions

![Figure 1](image)

Figure 1: (a) The zero field (ZF) \(\mu^+\)SR time-spectrum at 1.7 K for LaCoAsO, (b) the \(T\) dependence of its Fourier amplitude spectrum, (c) the \(T\) dependences of \(f_\mu\) and \(\chi\), and (d) the \(T\) dependences of \(A_i\). In (a), a solid (red) line represents the fitting result using Eq. (1). \(\chi\) was measured with \(H = 1\) kOe in field cooling mode.

Figures 1(a) and 1(b) show the zero field (ZF) \(\mu^+\)SR time-spectrum at 1.7 K and the \(T\) dependence of its Fourier amplitude spectrum. A clear oscillation indicates the formation of static FM order in LaCoAsO. Also, since there is 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 non-oscillatory relaxing signal;

\[
A_0 P_{ZF}(t) = A_{FM} \cos(2\pi f_\mu t + \phi) \exp(-\lambda_{FM} t) + A_{slow} \exp(-\lambda_{slow} t),
\]

where \(A_i\) are the asymmetries and \(\lambda_i\) are exponential relaxation rates. \(2\pi f_\mu(\equiv \omega)\) is the muon Larmor frequency and \(\phi\) is the initial phase of the oscillatory signal.

Figures 1(c) and 1(d) show the \(T\) dependences of \(f_\mu\) and \(\chi\) and \(A_i\) 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. In fact, the \(f_\mu(T)\) curve is in very good agreement with the \(\chi(T)\) curve in the whole \(T\) range measured, besides the temperatures at the vicinity of \(T_C\). Since \(\phi \sim -17^\circ\) at 1.7 K and is almost \(T\)-independent until the vicinity \(T_C\), the FM order is commensurate to the lattice, as expected. The relative amplitude of the oscillatory signal (\(A_{FM}/A_0\)) is about 0.6, and that for the non-oscillatory signal (\(A_{slow}/A_0\)) is about 0.4. Also, they are \(T\)-independent until the vicinity of \(T_C\). \(\lambda_{slow}\) is smaller by two orders of magnitude than \(\lambda_{FM}\) in the whole \(T\) range measured and \(\lambda_{slow}\) approaches 0 with \(T \rightarrow 0\). Therefore,
Figure 2: The ZF-spectra at (a) 1.7 K and 20 K for NdCoAsO, (b) 1.7 K and 50 K for SmCoAsO, and (c) 1.7 K and 3.5 K for GdCoAsO. The $T$ dependences of $f_{\mu}$ and $\chi$ for (d) NdCoAsO, (e) SmCoAsO, and (f) GdCoAsO. In (a)-(c), the spectra at 20, 50, and 5 K are shifted by 0.15 for clarity of display. In (b), the top horizontal axis is for the spectrum at 50 K, while the bottom horizontal axis for the spectrum at 1.7 K. In (e') and (f'), the $f_{\mu}$ axis is a linear scale. $\chi$ was measured with $H = 1$ kOe in a field cooling mode.

The $A_{\text{slow}}$ signal is assigned as the “1/3” tail, which is caused by the internal magnetic field ($H_{\text{int}}$) component parallel to the initial muon-spin polarization. This means that essentially the whole sample enters into the FM ordered phase below $T_C$.

Figures 2(a)-2(c) show the $T$ variation of the ZF-spectrum for NdCoAsO, SmCoAsO, and GdCoAsO. Although the ZF-spectrum shows a clear oscillation at each $T$ below $T_C$, $f_{\mu}(1.7 \text{ K})$ is rather high compared with $f_{\mu}$ at high-$T$. This means that each sample enters into an AF ordered phase, as speculated from magnetization measurements [4]. In fact, the spectrum was fitted by a combination of Eq. (1) and an additional cosine term, $A_{\text{FM}} \cos(2\pi f_{\mu}t + \phi) \exp(-A_{\text{FM}}t)$, where $A_{\text{FM}}=0$ below $T_N$, whereas $A_{\text{AF}}=0$ above $T_N$. Figures 2(d)-2(f) show the $T$ dependences of $f_{\mu}$ and $\chi$ for NdCoAsO, SmCoAsO, and GdCoAsO. In contrast to LaCoAsO, all the three samples are found to enter into an static AF ordered phase below $T_N = 16 \text{ K}$ for NdCoAsO, below 41 K for SmCoAsO, and below 3 K for GdCoAsO. Since $A_{\text{FM}}/A_0 = A_{\text{AF}}/A_0 \approx 0.6$ below $T_C$, the whole volume of the samples exhibit 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 $f_{\mu}$ and $\lambda_{\text{AF}}$ increase rapidly particularly below $\sim 7 \text{ K}$, indicating the presence of an additional AF transition, i.e. $T_{N1} \sim 15 \text{ K}$ and $T_{N2} \sim 7 \text{ K}$. Indeed, recent neutron scattering measurements [6] revealed the evolution of the ordered Nd moments with decreasing $T$ below $T_{N2} \sim 3.5 \text{ K}$, but the Nd moment looks to starts 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 posses a commensurate spin structure.

As $T$ decreases from $T_C$, $f_{\mu}$ for SmCoAsO increases abruptly by $\sim 40$ times at $T_{N1}(= 41 \text{ K})$, although $f_{\mu}$ 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 the slope ($df_\mu/dT$) around 17.5 K, at which the $\lambda_{AF}(T)$ curve exhibits a broad maximum (not shown). This suggests the presence of an additional magnetic transition ($T_{N2} = 17.5$ K), as for NdCoAsO. This could correspond to the transition at 5 K recently reported by specific heat measurements [7]. Besides the vicinity 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.

For GdCoAsO, $f_\mu$ does not exhibit a typical $T$ dependence, but rapidly increases with decreasing $T$. And then, $f_\mu$ leaps at 3 K, at which $\lambda_{AF}$ increases with further lowering $T$ (not shown). This behavior indicates the appearance of the AF ordered phase ($T_{N} = 3$ K). Although $|\phi| \leq 10^\circ$ above $T_{N}$, $\phi$ ranges between -46 and -70° below $T_{N}$ and reaches -55° at 1.7 K. This suggests the formation of incommensurate AF order below $T_{N}$ [8, 9].

We also found a static FM ordered phase for PrCoAsO and CeCoAsO in the $T$ range between ~ 70 K and 1.8 K, being consistent with the results of magnetization measurements [4, 10]. The characteristic feature of the FM phase is that $f_\mu$ ranges between 20 MHz and 35 MHz for the $RE$ =La, Ce, and Gd compounds, but $f_\mu$ is very small for PrCoAsO, NdCoAsO and SmCoAsO. This indicates that the FM order of the former compounds is very different from that of the latter compounds. Also, if the presence of incommensurate SDW order is essential for the parent compound of superconductivity, GdCoAsO would be the most promised candidate for superconducting cobalt pnictides among $RECoAsO$.

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