Magnetic phase diagram in the Co-rich side of LnCo$_{1-x}$Fe$_x$AsO (Ln=La, Sm) system

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The magnetic phase diagram has been mapped out via the measurements of electronic resistivity, magnetization and specific heat in the cobalt-based layered LnCo$_{1-x}$Fe$_x$AsO (Ln=La, Sm) compounds. The ferromagnetic (FM) transition at $\sim$63 K for LaCoAsO is rapidly suppressed upon Fe doping, and ultimately disappears around $x=0.3$ in the LaCo$_{1-x}$Fe$_x$AsO system. When La is replaced by magnetic rare earth element Sm, the 3d–electrons first undergo a FM transition at $T_c \sim 75$ K, followed by an antiferromagnetic (AFM) transition at a lower temperature $T_{N1} \sim 45$ K. With partial Fe doping on the Co site, both FM ($T_c$) and AFM ($T_{N1}$) transition temperatures are significantly suppressed, and finally approach zero kelvin at $x=0.3$ and 0.2, respectively. Meanwhile, a third magnetic transition at $T_{N2} \sim 5.6$ K for SmCoAsO, associated with the AFM order of the Sm$^{3+}$ 4f–moments, is uncovered and $T_{N2}$ is found to be almost robust against the small Fe-doping. These results suggest that the 4f–electrons of Sm$^{3+}$ have an important effect on the magnetic behavior of 3d electrons in the 1111 type Co-based LnCo$_{1-x}$Fe$_x$AsO systems. In contrast, the magnetism of the f–electrons is relatively unaffected by the variation of the 3d electrons. The rich magnetic phase diagram in the Co-rich side of the LnCo$_{1-x}$Fe$_x$AsO system, therefore, is established.

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I. INTRODUCTION

Correlated electron systems LnTmPnO [Ln=rare earth element, Tm=transition metal element, Pn=pnictogen element] have attracted great attention due to their various electronic and magnetic properties, such as high transition temperature superconductivity, itinerant ferromagnetism, giant magnetoresistance, spin density wave (SDW), and structural instability. For example, iso-structural LaOMnAs is an AFM semiconductor, and LaONiAs shows superconductivity below 3 K. In the case of $T_{\text{M}}=\text{Co}$, LnCoAsO was reported to be an itinerant ferromagnet with the Curie temperature $T_c$ between 60 and 80 K for La and Sm, respectively. Among them, the compound LaFeAsO, which is a parent compound of well-known iron-based superconductors, exhibits a spin-density wave antiferromagnetic transition at about 150 K. When Fe is partially replaced by Co atoms, the AFM order from Fe ions is suppressed and then superconductivity emerges, and the compound exhibits a good metallic behavior down to superconducting (SC) transition temperature. Similar results have also been reported for Co-doped CeFeAsO, PrFeAsO, NdFeAsO, and SmFeAsO systems. Thus, magnetism is closely related to superconductivity in these iron-based high-temperature superconductors.

On the other hand, the LnCoAsO compounds (also referred to as Co-1111 system) with the same space group as ZrCuSiAs exhibit rich magnetic properties at low temperature. LaCoAsO is reported to be an itinerant ferromagnet with 2D ferromagnetic spin fluctuations. When La is substituted by other magnetic rare earth elements, LnCoAsO (Ln=Nd, Sm, and Gd) under-goes multiple magnetic phase transitions as the temperature decreases. Furthermore, the AFM order due to the magnetic sublattice of Ln ions at very low temperature can be also observed in those compounds, almost irrelevant to the doping at $T_{\text{M}}$ or $Pn$ sites. For example, in the case of SmCoAsO, a ferromagnetic (FM) transition occurs around $T_c \sim 75$ K, followed by a FM-AFM transition from the magnetic coupling between the CoAs layers around 45 K, and finally another AFM order from Sm ion forms at 5.6 K recently reported by other groups. Indeed, several groups have suggested that the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction may play a role in the FM-AFM transition. It is ascribed to the interaction between the localized magnetic moments of lanthanide 4f electrons and the ferromagnetic ordered magnetic moments of cobalt 3d itinerant electrons. The neutron diffraction experiments and specific heat measurements have detected the localized magnetic moment of Ln 4f electrons in those parent compounds.

Up to now, main studies about Co-containing 1111 system focus on these low Co concentrations and LnCoPnO parent compounds. There are few reports on the study of chemical doping in LnCoAsO and the magnetic phase diagram on the Co-rich side of LnCoAsO is less known. In this paper, we report our detailed study of the magnetic properties of Fe-doped LnCo$_{1-x}$Fe$_x$AsO (Ln=La, Sm) system on the Co-rich side. In order to study the interplay between 4f electrons and 3d electrons, LaCo$_{1-x}$Fe$_x$AsO system is employed as a comparison. We performed powder X-ray diffraction, electrical resistivity, and magnetization measurements, as well as the first-principles calculations. The results of these measurements and calculations indicate that, the FM order is quickly suppressed by Fe doping in
LaCo$_{1-x}$Fe$_x$AsO system, and finally disappears at about $x = 0.3$. In the case of SmCo$_{1-x}$Fe$_x$AsO, the FM and AFM transitions of the 3d-electrons are gradually suppressed and then disappear at $x = 0.3$ and 0.2, respectively. However, the AFM order at low temperature due to Sm$^{3+}$ is robust and $T_{N2}$ slightly varies with increasing Fe content. A rich magnetic phase diagram for $x \leq 0.3$ LnCo$_{1-x}$Fe$_x$AsO system is therefore established.

II. EXPERIMENTAL

The polycrystalline samples of LnCo$_{1-x}$Fe$_x$AsO ($Ln$=La, Sm) were synthesized by two-step solid state reaction methods in vacuum, similar to our previous reports. The pellets of LnCo$_{1-x}$Fe$_x$AsO ($x = 0$, 0.05, 0.1, 0.2, 0.3) were annealed in an evacuated quartz tube at 1423 K for 40 hours and furnace-cooled to room temperature.

Crystal structure measurement was performed by powder X-ray diffraction (XRD) at room temperature using a D/Max-rA diffractometer with Cu K$_\alpha$ radiation and a graphite monochromator. Lattice parameters were calculated by least-squares fitting using at least 20 XRD peaks. The electrical resistivity was measured by four-terminal method. The temperature dependence of d.c. magnetization was measured on a Quantum Design Magnetic Property Measurement System (MPMS-5). The measurement of specific heat was performed on a Quantum Design Physical Property Measurement System (PPMS-9).

The magnetic properties of LaCo$_{1-x}$Fe$_x$As was calculated using planewave basis pseudopotential method implemented in Quantum Espresso package. The exchange-correlation interactions were modeled with Perdew, Burke and Enzerhoff flavor of generalized gradient approximation. To model the dilute substitutional iron doping effect, a virtual crystal approximation (VCA) was employed to treat Fe/Co sites.

III. RESULTS AND DISCUSSION

A. Magnetic properties in LaCo$_{1-x}$Fe$_x$AsO

Fig. 1(a) shows the powder XRD patterns of the typical LaCo$_{1-x}$Fe$_x$AsO samples and Fig. 1(b) shows the variations of lattice parameters with respect to the Fe content ($x$). Where the main diffraction peaks of those samples can be well indexed based on a tetragonal cell of ZrCuSiAs-type structure, weak peaks exist due to impurity phase CoAs. The content of impurity phase CoAs estimated by Rietveld fitting is less than 5%. It is worth noting that CoAs has been reported to be non-magnetic from 4.2 to 300 K. The $a$-axis decreases slightly with increasing Fe content, and the $c$-axis increases accordingly, resulting in the increase of the cell volume, since the ionic radius of tetrahedrally coordinated Fe$^{2+}$ ions are larger than that of Co$^{2+}$. The systematic increase in the $c$-axis indicates successful substitution of Fe by Co. Similar variations of lattice constants were also observed in the NdFe$_{1-x}$Co$_x$AsO in previous reports.

![FIG. 1. Structural characterization of LaCo$_{1-x}$Fe$_x$AsO samples. (a) Powder X-ray diffraction patterns of representative LaCo$_{1-x}$Fe$_x$AsO samples. The asterisked peak positions designate the impurity phase of CoAs. (b) Lattice parameters as functions of Fe content.](image)

Fig. 2 shows the temperature dependence of the electric resistivity ($\rho$) and magnetic susceptibility ($\chi$) of LaCo$_{1-x}$Fe$_x$AsO samples. The inset shows magnetic susceptibility vs. temperature between 100 to 300 K. In Fig. 2(a), for LaCoAsO, the resistivity falls monotonically with decreasing temperature from 300 K, a resistivity hump can be clearly identified at about 63 K, which is related with FM transition temperature $T_c$. As Fe content increases to 0.1, this hump shifts to below 2 K at $x = 0.3$, the anomaly in resistive is not observed. Actually, the anomaly around $T_c$ becomes more obvious in the derivative of $\rho$ shown in Fig. 2(b), where $T_c$ decreases with increasing Fe content and shifts to below 2 K at $x = 0.3$. Meanwhile, the resistivity value gradually increases with the Fe doping levels, which can be attributed to the less itinerant nature of Fe 3d electron than that of Co. The magnetic susceptibility for the LaCo$_{1-x}$Fe$_x$AsO under $H = 1$ kOe in zero field cooled (ZFC) configuration was plotted in Fig. 2(c). For the parent LaCoAsO sample, the magnetic susceptibil-
ity increases dramatically below $T_c$ of 63 K, suggesting that the Co sublattice forms FM order in the CoAs layer. The similar magnetic behavior has been reported in the literature. As Co is partially replaced by Fe, FM transition temperature ($T_c$) is sharply suppressed and shifts to lower temperature. For $x = 0.3$, the formation of long range FM order cannot be identified in $\chi(T)$ down to 2 K. Furthermore, the magnetic susceptibility value drops to several orders of magnitude of LaCoAsO. On the other hand, it can be seen from inset that the magnetic susceptibility curve above 100 K exhibits the Curie-Weiss behaviors for LaCoAsO. As Fe content increases, the susceptibility gradually becomes less $T$-dependence and final remains constant for $x = 0.3$, indicating that Fe doping strongly reduces the moment of 3d-electrons in Co-based 1111 compounds.

Fig. 2. (a)Temperature dependence of resistivity ($\rho$) for the LaCo$_{1-x}$Fe$_x$AsO ($x = 0, 0.1, 0.2, 0.3$) samples. (b) The derivative of resistivity near the ferromagnetic phase transition. (c)Temperature dependence of magnetic susceptibility ($\chi$) under a magnetic field of 1000 Oe in the zero-field-cooled (ZFC) configuration.

Fig. 3 shows the M-H loop curves at several temperatures for LaCo$_{1-x}$Fe$_x$AsO. For $x \leq 0.2$, the M-H curves are nearly linear above $T_c$, indicating that those compounds are paramagnetic at these temperatures. Below $T_c$, these curves deviate from linearity and become slightly S-shaped, suggesting the emergence of FM order. Further decreasing temperature to 3 K, the molar magnetization sharply increases and then saturates with the increase of magnetic field, and the small finite hysteresis can be distinguished (the data is not shown here). These results suggest that the ground state of these samples is FM. For $x = 0.3$, the M-H curve always shows the linear behaviors above 3 K, indicating that this sample remains paramagnetic. The magnetic moment $M_{s0}$ estimated by extrapolating the Ms-H curves to $T = 0$ K are 0.35 $\mu_B$ per Co for LaCoAsO, which is very close to the value reported previously. With increasing Fe content, $M_{s0}$ quickly decreases, consistent with the fact that the FM transition temperature $T_c$ shifts to lower temperature.

Fig. 3. Field dependence of magnetization at various temperatures for the LaCo$_{1-x}$Fe$_x$AsO ($x = 0, 0.1, 0.2, 0.3$) samples.
order. Furthermore, the magnetic coupling strength is suppressed with increasing $x$ from $x = 0.2$ to 0.5, as suggested by increasing configuration energy of both FM and SDW-AFM orders. With these considerations, we conclude that the actual ground state should be paramagnetic with local magnetic fluctuations.

We then compare the LDA lattice structure variation in Fig. 4(b). As the experimental measurements were performed at room temperature when the long range magnetic order was not yet formed, we compare the NM lattice constants. It could be seen that between $x \in [0.0, 0.3]$, the LDA lattice constants show the same trend as the experimental results but with much larger variation. Beyond $x = 0.3$, the lattice constants show much less variation. For the FM phase of LaCo$_{1-x}$Fe$_x$AsO, we also examine its magnetic moment per transition metal $m_{\text{TM}}$ and the arsenic height $z_{\text{As}}$ (Fig. 4(c)). At $x = 0.0$, the LaOCOAs compound has a small moment of 0.6 $\mu_B$/Co, indicating weak FM ground state with low Curie temperature. As the doping level $x$ increases, the moment almost linearly decreases to $x = 0.3$ $\mu_B$/TM at $x = 0.3$ at the VCA level. As discussed above, the disorder effect will further suppress the moment. Meanwhile, $z_{\text{As}}$ also increases almost linearly with respect to $x$ from $\sim1.18\text{Å}$ to $\sim1.24\text{Å}$. The variation of $z_{\text{As}}$ is consistent with the change of the super-exchange via arsenic, which becomes less FM and more AFM with increasing $x$.

**B. Magnetic properties in SmCo$_{1-x}$Fe$_x$AsO**

Fig. 5(a) shows the powder XRD patterns of SmCo$_{1-x}$Fe$_x$AsO samples and Fig. 5(b) shows the variations of lattice parameters with Fe content ($x$). All those samples are single phase since no extra peak is observed. Similar to the case of LaCo$_{1-x}$Fe$_x$AsO, Fe doping causes slight decrease in the $a$-axis, while the $c$-axis monotonously increases.

Fig. 6 shows the temperature dependence of the electric resistivity and magnetic susceptibility of the SmCo$_{1-x}$Fe$_x$AsO samples. In Fig. 6(a), for the undoped parent compound SmCoAsO$^{20}$, the resistivity monotonically decreases with decreasing temperature from 300 K, followed by a distinguishable kink around 45 K which can be associated with the FM-AFM transition temperature (defined as $T_{N1}$). As Fe content increases to 0.1, this kink becomes more pronounced and moves to lower temperatures, and no anomaly is observed below $T_{N1}$. For $x = 0.2$, the resistivity anomaly related with $T_{N1}$ disappears, but another tiny kink can be identified around 5.1 K, which can be attributed to the AFM transition ($T_{N2}$) due to the magnetic sublattice of Sm ions. As $x$ increases to 0.3, $T_{N2}$ in the resistivity becomes more remarkable (shown in inset of Fig. 6(a)). In order to identify the magnetic ordering transition more clearly, the derivative of resistivity below 150 K is plotted in Fig. 6(b), which shows a maximum around $T_c$, a minimum near $T_{N1}$, and a peak at $T_{N2}$. With increasing Fe content, the maximum around $T_c$ shifts to lower temperatures, and the minimum near $T_{N1}$ even becomes more pronounced for $x = 0.1$ and disappears as $x = 0.2$. The magnetic susceptibility data is shown in Fig. 6(c), it can be seen that SmCoAsO shows a sharp peak around 45 K. This peak is ascribed to FM to AFM transition of the cobalt sublattice, which has been reported for $Ln = \text{Nd, Sm, and Gd}^{22–24}$. As Fe substitutes Co, $T_{N1}$ is gradually suppressed and shifts to lower temperatures. Meanwhile, the intensity of the peaks becomes weaker, consistent with the resistivity data. At $x = 0.2$, it is noted that a tiny hump around 6.5 K is observed, which may not be explained by the AFM transition $T_{N1}$ according to our M-H data (see Fig. 8). The detailed discussion is beyond the scope of the current work and will be given in the future. When $x$ increases to 0.3, the magnetization sharply drops and a tiny peak is detected at 5.5 K. Considering the specific heat data in Fig. 7, this transition ($T_{N2}$) is attributed to the AFM ordering of Sm$^{3+}$ sublattice$^{22–24}$. Similar results can be found in the previous papers $^{15,17,24}$. For $x < 0.3$ samples, such low temperature peak in mag-
are observed in the case of SmFeAsO

FIG. 5. Structural characterization of SmCo\textsubscript{1−x}Fe\textsubscript{x}AsO samples. (a) Powder X-ray diffraction patterns of representative SmCo\textsubscript{1−x}Fe\textsubscript{x}AsO samples. (b) Lattice parameters as functions of Fe content.

netization curves is not observable due to the magnetic ordering of 3d–electrons.

In order to further study the magnetic phase transition, the zero field specific heat versus temperature curves for those samples are summarized in Fig. 7. For all the samples, no anomaly in the curves is found around \(T_c\) associated with the FM transition, which is also the case in NdCoAsO\textsuperscript{17}. A small broad peak related to the AFM transition \(T_{N1}\) can be observed at 45 K for SmCoAsO and then shifts to 22 K for \(x = 0.1\) (The data is not shown here). However, it is worth noticing that another clear broad peak from the AFM ordering of Sm\textsuperscript{3+} sublattice can be observed at 5.5 K and 3.5 K, respectively. As \(x\) increases to 0.2, no extra peak is detected except for the large anomaly near \(T_{N2}\) of 5 K, which then shifts to 5.5 K for \(x = 0.3\), consistent with the magnetic susceptibility data shown in Fig. 6(c). Similar results are observed in the case of SmFeAsO\textsuperscript{18}, SmCoAsO\textsuperscript{18} and SmCoPO\textsuperscript{22}. However, the hump in SmCoAsO related to the Sm AFM ordering becomes sharper and higher with increasing Fe content, which suggests that the increase of \(c\) lattice weakens the coupling of 3d electron and 4f electron. Low temperature specific heat measurements also confirms that the peak associated with \(T_{N2}\) is robust as \(x \leq 0.3\).

Fig. 8 shows the field dependence of the magnetization at various temperatures for all the samples. As reported in previous works\textsuperscript{18,20} SmCoAsO undergoes three magnetic phase transitions at \(T_c\), \(T_{N1}\), and \(T_{N2}\), respectively. The magnetization sharply increases and saturates with increasing field between \(T_c\) and \(T_{N1}\). In order to study the magnetic structure at different temperatures, these data are collected at temperature where PM or FM state dominates in Fig. 6(b), and 2 K. Obviously, for \(x \leq 0.1\), the \(M - H\) curve is linear at 2 K and above \(T_c\), and the "S" shape of FM behavior is only observed between \(T_c\) and \(T_{N1}\). As \(x\) increases to 0.2, the linear feature is observed only above \(T_c\), and the M-H curve displays FM behavior below 2 K, implying that the AFM transition \(T_{N1}\) approaches to zero. This feature is different from the case of NdCo\textsubscript{1−x}Fe\textsubscript{x}AsO\textsuperscript{17}, where both FM and AFM order are not observed around 0.2. At \(x = 0.3\), the M-H curves goes back to the linear behavior at 2 K, indicating that the FM order from the Co sublattice is completely destroyed. On the other hand, with increasing Fe content, both the saturation moment and the transition
temperature \((T_c)\) gradually decrease, implying that the 3d–electron magnetism becomes weaker.

Based on above data, the magnetic phase diagram of \(\text{LaCo}_{1−x}\text{Fe}_x\text{AsO}\) is established in Fig. 9. In \(\text{LaCo}_{1−x}\text{Fe}_x\text{AsO}\), the \(T_c\) associated with FM transition is sharply suppressed and disappears around \(x = 0.3\). At the same time, in the \(\text{SmCo}_{1−x}\text{Fe}_x\text{AsO}\) system, the \(T_{N1}\) from FM to AFM transition of Co sublattice is shifted to lower temperatures with increasing Fe content and such transition has not been observed at \(x = 0.2\). Meanwhile the \(T_c\), the FM order gradually decreases and is completely suppressed at \(x = 0.3\), similar to the case of \(\text{LaCo}_{1−x}\text{Fe}_x\text{AsO}\). Here, we note that for the Co-parent compounds \(T_c\) increases slightly when La is replaced by Sm. But a new FM-AFM transition of the 3d–electrons is induced in the later case. This manifests an interesting interplay between the 3d–electrons and the local Sm\(^{3+}\) moments.

Thus, in the 1111–type Co-based \(\text{LnCo}_{1−x}\text{Fe}_x\text{AsO}\) systems, 4f electrons of rare earth elements have an important effect on the magnetic behavior of 3d electrons. Whereas, the antiferromagnetic transition temperature of Sm moments \(T_{N2}\) almost does not change within the whole doping regime. It implies that the AFM ordering of the Sm 4f–electrons is robust against Fe/Co substitution within the CoAs layer. Therefore, the microscopic origin of the f–electron AFM order of this system should be mainly due to the superexchange interactions between the f–local moments\(^{25}\). These superexchange interactions are bridged by two kinds of f–p orbital hybridizations: one via Sm–O path and another the Sm–As path, respectively\(^{25}\). Meanwhile, the RKKY interaction mediated by the charge carries within the CoAs layer may not play a crucial role for the f–electron magnetism because the RKKY interaction would be explicitly dependent on the variations of 3d–electrons. Because the radius of Sm\(^{3+}\) ion is smaller than La\(^{3+}\), one may speculate that the FM-AFM transition is not related to the magnetic 4f–electrons, but rather due to the enhancement of three dimensionality as the lattice parameter \(c\) decreases. In order to clarify this possibility, we have also performed LDA calculations on \(\text{LaCoAsO}\) but using the lattice parameters of \(\text{SmCoAsO}\). We do find that the FM state of Co d–electrons is robust against the decreasing lattice constant. Experimentally, Similar results were always observed in \(\text{NdCoAsO}\) under pressure\(^{29}\). Therefore, we suggest that the FM-AFM transition at \(T_{N1}\) of the 3d–electrons should be due to their coupling (polarization) to the 4f–moments along the \(z\)-direction.

**FIG. 7.** The specific heat of \(\text{SmCo}_{1−x}\text{Fe}_x\text{AsO} (x = 0, 0.05, 0.1, 0.2, 0.3)\) samples under at zero field below 100 K.

**FIG. 8.** Magnetic field dependence of magnetization at several different temperature for the \(\text{SmCo}_{1−x}\text{Fe}_x\text{AsO} (x = 0, 0.05, 0.1, 0.2, 0.3)\) samples.
FIG. 9. Magnetic phase diagram for the SmCo$_{1-x}$Fe$_x$AsO (solid) and LaCo$_{1-x}$Fe$_x$AsO (open) system, respectively. The transition temperatures were determined from the measurements of magnetic susceptibility, magnetization and specific heat. $T_{N2}$ is taken from resistivity and specific heat data.

IV. CONCLUSION

In the 1111 Co-based $Ln$Co$_{1-x}$Fe$_x$AsO ($Ln$=La, Sm ) system, a series of $Ln$Co$_{1-x}$Fe$_x$AsO samples have been synthesized, and their transport and magnetic properties were investigated. A rich magnetic phase diagram of the $Ln$Co$_{1-x}$Fe$_x$AsO systems is then established. The FM order is observed in both $Ln$CoAsO ($Ln$ = La,Sm) systems, and is completely destroyed with increasing Fe doping content to 0.3. Meanwhile, in SmCo$_{1-x}$Fe$_x$AsO, $T_N$ is suppressed to below 2 $\text{K}$ as $x = 0.2$, but the AFM order of rare earth element Sm ion survives in the whole doping regime $x \leq 0.3$. This also indicates that the disorder effect induced by Fe/Co doping is very weak. Based on these results, it is concluded that in $Ln$Co$_{1-x}$Fe$_x$AsO systems, while the magnetic properties of the 4f electrons of rare earth elements are robust against the variations of 3d electrons, they do play an significant role in the magnetic behaviors of the 3d electrons. These materials therefore provide a prototypical testing ground for exploring the interplay between 4f and 3d electrons in transition metal compounds.

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