Superconductivity in LaFe$_{1-x}$Co$_x$AsO

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Here we report the synthesis and basic characterization of LaFe$_{1-x}$Co$_x$AsO for several values of $x$. The parent phase LaFeAsO orders antiferromagnetically ($T_N$=145 K). Replacing Fe with Co is expected both to electron dope and introduce disorder in the FeAs layer. For $x$=0.05 antiferromagnetic order is destroyed and superconductivity is observed at $T_{c\text{onset}}$=11.2 K. For $x$=0.11 superconductivity is observed at $T_{c\text{onset}}$=14.3 K and for $x$=0.15 it is observed at $T_{c\text{onset}}$=6.0 K. For $x$=1, and the material appears to be ferromagnetic as judged by magnetization measurements. We conclude that Co is an effective dopant to induce superconductivity. Somewhat surprisingly, the system appears to tolerate considerable disorder in the FeAs planes.

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I. INTRODUCTION

The recent reports of $T_c$~26 K in LaFeAsO$_{1-x}$F$_x$ ($x \sim 0.11$) (Refs. 1–10) and related materials have attracted a great deal of attention as these appear to be unconventional high-$T_c$ superconductors that are based on iron instead of copper. It is interesting to compare and contrast the behavior of the iron arsenide superconductors with the cuprates. For high-$T_c$ copper oxides, the parent compounds are antiferromagnetic Mott insulators and the magnetic order is suppressed and superconductivity emerges by doping with either electrons or holes. Much like copper oxide superconductors, high $T_c$ in the Fe-based family of RFeAsO ($R=$rare-earth) is caused by doping. Here is a report of superconductivity in LaFeAsO by electron doping by means of cobalt substitution in the layers of FeAs$_4$ tetrahedra in LaFe$_{1-x}$Co$_x$AsO (Fig. 1).

The parent LaFeAsO crystallizes with the ZrCuSiAs-type structure in $P4/mmm$ space group (No. 129; $Z=2$). Electronic structure calculations describe the structure as quasi-two dimensional (2D), composed of sheets of metallic Fe$^{2+}$ in between cubic blocks of LaOAs$^{2-}$ along the c axis. Although there is bonding between Fe and As ($d$=2.3–2.4 Å), the states near the Fermi level are dominated by Fe $d$ states lightly mixed with As $p$ states. LaFeAsO undergoes a continuous or weakly first-order structural phase transition from tetragonal ($P4/mmm$) to orthorhombic (Cmmm) upon cooling below 155–160 K (Refs. 8, 17, and 18); this is followed by a commensurate antiferromagnetic order just below 135–150 K. 

Ab initio calculations yield Fe magnetic moments ranging from 1.5 to 2.3 $\mu_B$ while weak superlattice reflections in neutron scattering and Mössbauer spectra indicate a much smaller value of 0.25–0.35 $\mu_B$/Fe.

Carrier doping plays a major role in the appearance of superconductivity by suppressing the magnetic order and structural phase transition in LaFeAsO$_{1-x}$F$_x$. Substitution of La for other rare earths ($R$) has resulted in finding F-doped RFeAsO$_{1-x}$F$_x$ ($R=$Pr, Sm, Nd, and Gd) superconductors, giving $T_c$ as high as 55 K in SmFeAsO$_{0.4}$F$_{0.6}$–30. Thi$^{2+}$ doping in Gd$_{1-x}$Th$_x$FeAsO gives slightly higher $T_c$ at 56 K. Hole doping, by substituting Sr$^{2+}$ for La$^{3+}$, results in $T_c$=25 K. A series of oxygen deficient RFeAsO$_{1-x}$ gives highest $T_c$=55 K for SmFeAsO$_{0.85}$. Here we report the synthesis and characterization of Co-doped LaFeAsO and find superconductivity for $x=4$–12% doping levels. Chemically, Co is a better mean electron doping as carriers are doped directly into the FeAs planes. This also provides information as to how well the superconductors tolerate in-plane disorder.

For LaFe$_{1-x}$Co$_x$AsO, experimental details below are followed by a discussion of the crystal structure from powder x-ray and neutron diffractions for ($0 \leq x \leq 1$). The thermodynamic and transport properties of this material will then be presented and discussed. The measurements include field- and temperature-dependent magnetic susceptibility, electrical resistivity, and Seebeck coefficient.

![FIG. 1. (Color online) Crystal structure of LaFe$_{1-x}$Co$_x$AsO with tetragonal ZrCuSiAs type. It is composed of layers of edge-sharing OLax tetrahedra alternating with layers of Fe(Co)As$_4$ along the $c$ axis. The unit cell is represented in gray lines.](Image)
TABLE I. Crystallographic data of LaFeAsO.

| $T$ (K) | 4 | 300 |
|---------|---|-----|
| Space group | $P4/nmm$ | $P4/nmm$ |
| $a$ (Å) | 5.6823(2) | 4.0345(1) |
| $b$ (Å) | 5.7103(2) | $=a$ |
| $c$ (Å) | 8.7117(4) | 8.7387(4) |
| $V$ (Å³) | 282.67(2) | 142.24(1) |
| $Z$ | 4 | 2 |
| $d$ range (Å) | 0.8–10.6 |
| $\omega R_p$ | 3.17 | 3.20 |
| $\chi^2$ | 7.14 | 5.92 |

Atomic parameters:

| | | |
|---|---|---|
| La | $4g(0,\frac{1}{4},z), z=0.1424(3)$ | $2c(\frac{1}{4},\frac{1}{4},z), z=0.1420(3)$ |
| | $U_{iso}=0.0025(8) \times 10^{-2}$ | $U_{iso}=0.0066(11) \times 10^{-2}$ |
| Fe | $4b(\frac{1}{2},0,\frac{1}{2}), U_{iso}=0.0011(6)$ | $2b(\frac{1}{2},\frac{1}{2},\frac{1}{2}), U_{iso}=0.0055(8) \times 10^{-2}$ |
| As | $4g(0,\frac{1}{4},z), z=0.6501(4)$ | $2c(\frac{1}{4},\frac{1}{4},z), z=0.6498(4)$ |
| | $U_{iso}=0.0099(10) \times 10^{-2}$ | $U_{iso}=0.0045(12) \times 10^{-2}$ |
| O | $4a(\frac{1}{4},0,0), U_{iso}=0.0049(11) \times 10^{-2}$ | $2a(\frac{1}{4},\frac{1}{4},0), U_{iso}=0.0096(13) \times 10^{-2}$ |

II. EXPERIMENTAL DETAILS

Polycrystalline samples with LaFe$_{1-x}$Co$_x$AsO ($x=0$, 0.05, 0.11, 0.15, 0.2, 0.5, and 1) nominal compositions were synthesized by stoichiometrically mixing fine powders of LaAs, Co$_2$O$_4$ (99.9985%), Fe$_2$O$_3$ (99.99%, calcined at 900 °C for 12 h), and Fe (99.998%), pressing into a pellet, and rapidly heating in silica tubes. The silica tubes were sealed under partial pressure of argon and heated at 1220 °C for 12 h, then rapidly cooled by shutting off the furnace. Each pellet was reground and reannealed. The source of all elements or compounds was Alfa Aesar.

The initial phase purity and structural identification were made via powder x-ray diffraction using a Scintag XDS 2000 θ-θ diffractometer (Cu $K\alpha$ radiation). The cell parameters for LaCoAsO were refined using least-squares fitting of the measured peak positions in 2$\theta$=20°–70° using JADE 6.1 MDI package.

Neutron powder-diffraction data on LaFe$_{1-x}$Co$_x$AsO with $x=0$, 0.11, and 0.15 were collected on the C2 diffractometer$^{36}$ operated by the Neutron Program for Materials Research of the National Research Council of Canada. Each sample of 1–2 g was placed in a helium-filled vanadium can that was sealed with an indium gasket. Data were collected at two different wavelengths of 1.330910 and 2.372630 Å. For $x=0$ and 0.15, powder-diffraction data were collected at 4 and 300 K. For $x=0.11$, data were collected at 4, 10, 15, 30, 50, 100, 150, 200, and 300 K.

TABLE II. Crystallographic data of LaFe$_{1-x}$Co$_x$AsO: $x=0.11$.

| $T$ (K) | 4 | 300 |
|---------|---|-----|
| Space group | $P4/nmm$ | $P4/nmm$ |
| $a$ (Å) | 4.02771(1) | 4.0351(1) |
| $b$ (Å) | $=a$ | $=a$ |
| $c$ (Å) | 8.6860(3) | 8.7132(3) |
| $V$ (Å³) | 140.908(6) | 141.871(11) |
| $Z$ | 2 | 2 |
| $d$ range (Å) | 0.8–10.6 |
| $\omega R_p$ | 3.38 | 3.61 |
| $\chi^2$ | 3.94 | 4.25 |

Atomic parameters:

| | | |
|---|---|---|
| La | $2c(\frac{1}{4},\frac{1}{4},z), z=0.1412(3)$ | $2c(\frac{1}{4},\frac{1}{4},z), z=0.1412(3)$ |
| | $U_{iso}=0.0038(8) \times 10^{-2}$ | $U_{iso}=0.0049(9) \times 10^{-2}$ |
| Fe/Co | $2b(\frac{1}{2},\frac{1}{2},\frac{1}{2}), U_{iso}=0.0015(8) \times 10^{-2}$ | $2b(\frac{1}{2},\frac{1}{2},\frac{1}{2}), U_{iso}=0.0087(11) \times 10^{-2}$ |
| As | $2c(\frac{1}{4},\frac{1}{4},z), z=0.6502(3)$ | $2c(\frac{1}{4},\frac{1}{4},z), z=0.6505(4)$ |
| | $U_{iso}=0.0012(9) \times 10^{-2}$ | $U_{iso}=0.0054(12) \times 10^{-2}$ |
| O | $2a(\frac{1}{4},\frac{1}{4},0), U_{iso}=0.0057(11) \times 10^{-2}$ | $2a(\frac{1}{4},\frac{1}{4},0), U_{iso}=0.0057(14) \times 10^{-2}$ |
Neutron powder-diffraction data for both wavelengths were jointly refined for the main and impurity phases of FeAs and La₃O₅ using GSAS (Refs. 37 and 38) with the EXPGUI (Ref. 39) interface. For all the refinements, the pseudo-Voigt function profile function 3 in GSAS was used and both Lorentzian and Gaussian widths were allowed to vary. Zero-point parameter was also allowed to change. The background was modeled using a ten-term Chebyshev polynomial function. The lattice parameters for the main as well as impurity phases were refined. Isotropic thermal parameters and fractional coordinates were refined for all the atoms in the primary phase. For \( x = 0.11 \) and 0.15 samples, a single thermal parameter was used for both Fe and Co and the occupancy factors were refined with the constraint that they add up to the full occupancy of the site. The details of the neutron powder refinement conditions and the atomic parameters at 4 or 300 K are given in Tables I and II for \( x = 0 \) and 0.11, respectively.

Powder x-ray diffraction patterns were collected at beamline X16C of the National Synchrotron Light Source utilizing x-rays of wavelength 0.69869 Å from a Si(111) channel-cut monochromator and a Ge(111) analyzer. The data for LaFe\(_{1-x}\)Co\(_x\)AsO with \( x = 0.05, 0.11, 0.2, \) and 0.5 were collected at room temperature. Samples were ground in air and diluted with ground glass wool and flame sealed in 1 mm capillaries. Total exposure to the atmosphere before sealing was approximately 1 min for each sample. Capillaries were spun during data collection to improve counting statistics. The high-resolution x-ray data were modeled in a similar fashion as the neutron data described above.

dc magnetization was measured as a function of temperature and field using a Quantum Design magnetic property measurement system. For a temperature sweep experiment, the sample was cooled to 1.8 K in zero-field (zfc) and data were collected by warming from 1.8 to 300 K in an applied field. The sample was then cooled in the applied field (fc) and the measurement was repeated from 1.8 K. The magnetic-susceptibility results are presented per mole of LaFe\(_{1-x}\)Co\(_x\)AsO (0 \( \leq x \leq 1 \)) formula unit (cm\(^3\)/mol). Electrical resistivity, Seebeck coefficient, and specific-heat measurements were obtained using a Quantum Design physical property measurement system. For dc resistance measurements, electrical contacts were placed on samples in standard four-probe geometry using Pt wires and silver epoxy (EPO-TEK H20E). Gold-coated copper leads were used for Seebeck coefficient measurements.

### III. RESULTS AND DISCUSSION

#### A. Structure

For LaFe\(_{1-x}\)Co\(_x\)AsO, neutron-diffraction data were collected on \( x = 0, 0.11, 0.15 \), while x-ray diffractions were done on \( x = 0.05, 0.11, 0.2, \) and 0.5 compositions.

The structure of LaFe\(_{1-x}\)Co\(_x\)AsO at 300 K for all compositions of \( x \) was refined with the tetragonal space group \( P4/nnm \) (No. 129, origin choice 2; \( Z = 2 \)) (Refs. 14 and 15) (Fig. 1). La and As atoms are located at Wyckoff positions...
The structure of LaFeAsO at 4 K was refined with orthorhombic space group *Ccma* (No. 67; *Z*=4), earlier reported at 120 K by Nomura et al.\(^\text{18}\) As a result of this phase transition, the *a*- and *b*-crystallographic axes rotate by 45°. Splitting of several reflections of the room-temperature tetragonal phase (111,112,322) was observed at 150 K as the temperature was lowered to 4 K. The atoms in this low-temperature orthorhombic phase are characterized by the same coordination as that of tetragonal structure. La and As atoms are located on Wyckoff positions 4*g*, Fe on 4*b*, and O on 4*a*.

For LaFe\(_{1-x}\)Co\(_x\)AsO with *x*=0.11, similar peak splitting to LaFeAsO was, however, not observed in the diffraction data down to 4 K. The data was refined within the tetragonal *P4/nmm* framework, comparable to that for 14% F-doped LaFeAsO structure at 120 K.\(^\text{18}\) The refined neutron-diffraction pattern at 4 K is shown in Fig. 3(a). The data were refined for the main (89.8%) and impurity phases of FeAs (4.1%) and La\(_2\)O\(_3\) (6.1%).

For *x*=0.11, the temperature dependence of lattice parameters and the cell volumes are shown in Fig. 3(b). The *a* and *c* parameters seem to vary nonlinearly with increasing temperature and by 0.18% and 0.31%, respectively, over the 4 to 300 K region; the cell volume change is 0.68%. It has been suggested that the *R*-As distance and Fe-As-Fe angle are the two crucial parameters in the structure of RFeAsO that control the effective bandwidths in these materials and, hence,

**TABLE III. Bond distances as a function of temperature for LaFe\(_{1-x}\)Co\(_x\)AsO: *x*=0 and *x*=0.11.**

| *T* (K) | LaFe\(_{1-x}\)Co\(_x\)AsO | LaFe\(_{1-x}\)Co\(_x\)AsO |
|---------|--------------------------|--------------------------|
|         | Fe-As (Å) | La-As (Å) | La-O (Å) | Fe-O (Å) | Fe-Fe (Å) |
| 4       | 2.408(5)  | 3.3741(31) | 2.351(4)  | 4.3430(9) | 2.8478(3)  |
| 10      | 2.4024(25) | 3.3738(15) | 2.3559(19) | 4.3423(2) | 2.8477(1)  |
| 15      | 2.4028(25) | 3.3739(15) | 2.3552(19) | 4.3421(2) | 2.8476(1)  |
| 30      | 2.4019(25) | 3.3745(15) | 2.3559(19) | 4.3425(2) | 2.8478(1)  |
| 50      | 2.4023(25) | 3.3756(15) | 2.3558(20) | 4.3434(2) | 2.8482(1)  |
| 100     | 2.4024(25) | 3.3776(15) | 2.3555(19) | 4.3447(2) | 2.8487(2)  |
| 200     | 2.4044(26) | 3.3799(15) | 2.3576(20) | 4.3495(2) | 2.8506(1)  |
| 300     | 2.4110(5)  | 3.3832(31) | 2.356(4)   | 4.3555(9) | 2.8528(3)  |

**TABLE IV. Two selected sets of bond angles as a function of temperature for LaFe\(_{1-x}\)Co\(_x\)AsO: *x*=0 and *x*=0.11.**

| *T* (K) | LaFe\(_{1-x}\)Co\(_x\)AsO | LaFe\(_{1-x}\)Co\(_x\)AsO |
|---------|--------------------------|--------------------------|
|         | Fe-As-Fe | O-La-O   |
| 4       | 113.5(4), 72.51(18) | 117.86(34), 74.55(15) |
| 10      | 113.90(18), 72.70(9) | 117.46(15), 74.37(7)   |
| 15      | 113.86(18), 72.68(9) | 117.51(15), 74.39(7)   |
| 30      | 113.93(19), 72.71(9) | 117.46(15), 74.37(7)   |
| 50      | 113.94(19), 72.71(9) | 117.50(16), 74.39(7)   |
| 100     | 113.96(18), 72.72(9) | 117.56(15), 74.42(7)   |
| 200     | 113.93(19), 72.71(9) | 117.51(16), 74.39(7)   |
| 300     | 113.6(4), 72.73(9)  | 117.81(35), 74.53(16)  |

**LaFeAsO**

| *T* (K) | LaFeAsO |
|---------|---------|
| 4       | 113.97(14), 72.52(7), 72.94(7) | 116.76(11), 74.26(5), 73.83(5) |
| 300     | 114.02(15), 72.76(7) | 116.82(12), 74.07(6) |

2c. O site is at 2*a*, while Fe/Co may be shared at site 2*b*. For LaFeAsO, the lattice constants obtained from neutron data were *a*=4.0345(1) Å and *c*=8.7387(4) Å (see Fig. 2) and compare well with the reported *a*=4.038(1) Å and *c*=8.753(6) Å.\(^\text{15}\) The incorporation of Co in *x*=0.11 in the Fe site reduces the cell volume by 0.26% due to contraction of the lattice constant *c*=8.7132(3) Å. For F-doped LaFeAsO\(_{1-x}\)F, with *x*=0.11, the lattice constants are found to shrink by 0.17% [4.0277(2) Å] and 0.30% [8.7125(4) Å], respectively.\(^\text{2}\)

The structure of LaFeAsO at 4 K was refined with orthorhombic space group *Ccma* (No. 67; *Z*=4), earlier reported at 120 K by Nomura et al.\(^\text{18}\) As a result of this phase transition, the *a*- and *b*-crystallographic axes rotate by 45°. Splitting of several reflections of the room-temperature tetragonal phase (111,112,322) was observed at 150 K as the temperature was lowered to 4 K. The atoms in this low-temperature orthorhombic phase are characterized by the same coordination as that of tetragonal structure. La and As atoms are located on Wyckoff positions 4*g*, Fe on 4*b*, and O on 4*a*.

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For *x*=0.11, the temperature dependence of lattice parameters and the cell volumes are shown in Fig. 3(b). The *a* and *c* parameters seem to vary nonlinearly with increasing temperature and by 0.18% and 0.31%, respectively, over the 4 to 300 K region; the cell volume change is 0.68%. It has been suggested that the *R*-As distance and Fe-As-Fe angle are the two crucial parameters in the structure of RFeAsO that control the effective bandwidths in these materials and, hence,
the superconductivity. At 300 K, the variation of the bond distance and angle of the $x=0.11$ versus Fe parent (Tables III and IV) is very small (La-As: 0.06%; Fe-As-Fe: 0.05%). However, these differences are significantly larger at 4 K (La-As: 0.11%; Fe-As-Fe: -0.14%). It is interesting to note that the large distortion of the FeAs$_4$ tetrahedron in $x=0.11$ is accompanied by a similarly large distortion in La$_2$O tetrahedron, whereas F doping in the LaO layer in LaFeAsO causes no distortion in FeAs$_4$ tetrahedron. F doping in the La$_2$O layer changes the Fe-As bond only slightly; however, Co doping in the FeAs$_4$ layer changes the La-O bond significantly (Table III).

The occupancy of Co on Fe 2b site refines as LaFe$_{0.92}$Co$_{0.08}$Fe$_{0.003}$AsO for $x=0.11$. Also, the average occupancy of Co for nominally prepared $x=0.15$ sample refines as $x=0.12(1)$. Assuming a linear dependence between nominal $x$ and the Co concentration, the $x=0.05$, 0.2, and 0.5 samples are likely to have ~4%, 16%, and 40% cobalt. Despite the variance between the nominal and measured compositions, they will continue to be presented with their nominal $x$ values. The three compositions are stoichiometric in oxygen content as 2a site was refined to unity at every temperature that the data were collected.

From $x=0$ to 1, the reduction in the $a$ and $c$ parameters and cell volumes are 0.04%, 3.20%, and 2.79%, respectively (Fig. 4). It was suggested that the $T_c$ in $R$FeAs$_{1−x}$ is strongly dependent on the tetrahedral distortion represented by As-Fe-As bond angle. We also observe similar trend from our x-ray data at various concentration of Co. From $x=0.11$ to 0.2, As-Fe-As bond angle decreases from 107.35° to 106.99° (see Fig. 5). It should be mentioned here that at $x=0.2$, superconductivity is lost (Sec. III B).

**B. Physical properties**

The temperature dependence of molar magnetic susceptibility in 1 T for the LaFe$_{1−x}$Co$_x$AsO system is shown in Fig. 6. For $0 \leq x \leq 0.5$, $\chi$ values vary between $3 \times 10^{-3}$ and $3.5 \times 10^{-3}$ cm$^3$/mol at 300 K. These values are smaller than that reported for LaFeAsO$_{0.89}F_{0.11}$ ($1.8 \times 10^{-3}$ cm$^3$/mol at 300 K and 0.1 T). For LaFeAsO (Fig. 6), magnetic susceptibility decreases with decreasing temperature, with an anomaly at ~150 K and a rise below 50 K. For $x=0.2$ and 0.5, $\chi$ is weakly temperature dependent with a gradual increase below 50 K. The field-dependent magnetization data for $x=0$, 0.2, and 0.5 are shown in the inset of Fig. 6 and none of the samples approach saturation at 7 T, reaching $<0.003$ $\mu_B$/f.u.

The temperature dependence of magnetization in 1 T for LaCoAsO is shown in Fig. 7(a). The $M(T)$ decreases below ~80 K, indicating possible ferromagnetic ordering. The inset of Fig. 7(a) shows a plot of the inverse magnetization and the fit to a Curie-Weiss law, where $M/H = C/(T−\theta) + \chi_o$; $C$ is the Curie constant, $\theta$ is the paramagnetic Weiss temperature, and $\chi_o$ is a temperature-independent term. The fit was...
done for $T > 150$ K. Assuming Co is the only moment-bearing ion, then the term $C$ is related to the effective moment in paramagnetic state and the theoretically expected $3.87 \mu_B = 3/2$. Experimentally, the Curie-Weiss fit gives $\mu_{\text{eff}} = 1.4 \mu_B$ per Co. This result is comparable to that recently reported for LaCoAsO. The Weiss temperature is positive and $90$ K; $\theta = -6 \times 10^{-6}$ mol. Field-dependent magnetization data, $M(H)$, at $1.8$ K are shown in Fig. 7(b). The magnetization rises rapidly up to $\sim 500$ G and changes weakly thereafter. The precipitous rise in magnetization at low fields again suggests ferromagnetism. An applied field of $5$ T gives $0.46 \mu_B$/f.u.; this field is insufficient to saturate the magnetic data to $3 \mu_B$/Co$^{2+}$ as expected for localized high-spin Co$^{2+}$ ions.

In order to locate the ferromagnetic transition, magnetization isotherms in the vicinity of Curie temperatures have been measured for the construction of Arrott plots in the form of $M^2$ versus $H/M$ at temperatures in the vicinity of magnetic transition (inset).

ferromagnetic interactions but extremely weak out-of-plane interactions. In this scenario, LaCoAsO would be a strongly exchange-enhanced paramagnet and that application of even a small field produces a large ferromagnetic response.

Figure 8 shows the temperature dependence of magnetic susceptibility, measured under zfc and fc conditions at $20$ Oe for LaFe$_{1-x}$Co$_x$AsO with $x = 0.05$ (top), $0.11$, and $0.15$ (bottom). The enlarged regions around $T_c$ are shown in the insets.

Figure 9(a) shows the temperature dependence of the electrical resistivity ($\rho$) in zero field. Similar to the other reports for LaFeAsO, $\rho_{300}$ K $\approx 4$ m$\Omega$ cm, then it increases
slightly with decreasing temperature peaking at \( 160 \) K. This upturn in \( \rho \) is likely associated with the increased charge-carrier scattering by lattice fluctuations related to the onset of the structural transition. The samples with \( x = 0.05, 0.11, \) and 0.15 exhibit superconductivity. Higher doping levels of \( x = 0.2, 0.5, \) and 1 give only metallic behavior. The electrical conductivity increases by a factor of 8 from \( \text{LaFeAsO} \) to \( \text{LaCoAsO} \).

The resistive transitions for the superconducting compositions shift to lower temperatures by applying a magnetic field [Fig. 9(b)]. The transition width for each sample becomes wider with increasing \( H \), a characteristic of type-II superconductivity. Here we define a transition temperature \( T_c \), which satisfies the condition that \( \rho(T_c, H) \) equals a onset of the structural transition. The samples with \( x = 0.05, 0.11, \) and 0.15 exhibit superconductivity. Higher doping levels of \( x = 0.2, 0.5, \) and 1 give only metallic behavior. The electrical conductivity increases by a factor of 8 from \( \text{LaFeAsO} (3d^6) \) to \( \text{LaCoAsO} (3d^7) \).

The resistive transitions for the superconducting compositions shift to lower temperatures by applying a magnetic field [Fig. 9(b)]. The transition width for each sample becomes wider with increasing \( H \), a characteristic of type-II superconductivity. Here we define a transition temperature \( T_c(H) \), which satisfies the condition that \( \rho(T_c, H) \) equals a
2.3, and 3.9 K, respectively. The transition width \( T_c \) was measured and subtracted from zero-field data. Figure 10 gives the temperature dependence of \( S \) for each field \( H \). In all cases we find that \( H_c(T) \) has a linear dependence with no sign of saturation. \( T_c \) at zero field for \( 0.1 \) \( \rho_N \) are 11.2, 14.3, and 6.0 K for \( x = 0.05, 0.11, \) and 0.15, respectively. The transition width \( \Delta T_c = T_c(90\%) - T_c(10\%) \) are 3.2, 2.3, and 3.9 K, respectively. The \( \Delta T_c \) values are smaller than the reported 4.5 K for \( \text{LaFeAsO}_{0.89}\text{F}_{0.11} \) with \( T_{c\text{onset}}^{\text{nominal}} = 28.2 \) K.  

Figure 10(a) shows the temperature dependence of specific heat in the form of \( C/T \) versus \( T \) from 1.8 to 20 K. For each \( x = 0.05 \) and 0.11, there is a broad specific-heat anomaly below \( T_c \). For \( x = 0.2, 0.5, \) and 1 samples, the \( C/T \) vs \( T \) plot is linear between \(-2 \) and 6 K [Fig. 10(a), bottom]. This allows the estimation of electronic \( \gamma \) and lattice \( \beta \) values as \( C = \gamma T + \beta T^3 \). The fits yield \( \gamma \) in units of mJ/(K\(^2\) mol atom) for \( x = 0.2, 0.5, \) and 1, respectively, as 1.405(1), 1.68(1), and 4.02(1). The value of the Debye temperature \( (\theta_D) \) was subsequently calculated in the low-temperature limit \( \beta = 12\pi^2R/5\theta_D^3 \) and \( \theta_D = 342(9) \) K for these samples. This value is comparable to the Debye temperature of \(-280 \) K for \( \text{LaFeAsO} \) (Ref. 5) and \(-325 \) K for \( \text{LaFeAsO}_{0.89}\text{F}_{0.11} \).  

For \( x = 0.05 \), the specific heat under magnetic fields of 14 T was measured and subtracted from zero-field data. Figure 10(b) gives the temperature dependence of \( \Delta C/T \) data and illustrates a deviation from high-temperature behavior below \( T_c \sim 11 \) K, peaking at 7 K. The broadened transition reflects the inhomogeneity of superconducting phase, likely due to the random Co distribution. Nevertheless, the observation of specific-heat anomaly at \( T_c \) indicates bulk superconductivity in the discovered Co-doped \( \text{LaFeAsO} \). The origin of the field dependence of the background is not understood and has yet to be investigated.  

The Seebeck coefficient \( S \) of \( \text{LaFe}_{1-x}\text{Co}_{x}\text{AsO} \) with \( x = 0.11 \) at 0 T is shown in the inset of Fig. 11. \( S \) is negative over the entire temperature range, indicating dominant electron conduction. This result is similar to F doping (\( x = 0.11 \)) in \( \text{LaFeAsO} \) and provides evidence for electron doping. S varies from \(-50 \) \( \mu \)V/K at 300 K to a value of \(-65 \) \( \mu \)V/K at \(-160 \) K then decreases in magnitude as the temperature is lowered further. The maximum in the data is probably due to the competition between dominant electron-like bands and the expected proximity of holelike bands near the Fermi energy. Figure 11 gives the magnetic-field effect below 25 K; \( T_c \) at \(-14 \) K is clearly suppressed at 8 T.  

IV. CONCLUSIONS  

In this work we report the synthesis, structure, magnetization, resistivity, specific heat, and Seebeck coefficient of \( \text{LaFe}_{1-x}\text{Co}_{x}\text{AsO} \) for several values of \( x \). The most important observation is that Co acts as an effective dopant and produces superconductivity in this system. In most respects, \( \text{LaFe}_{1-x}\text{Co}_{x}\text{AsO} \) behaves similarly to \( \text{LaFeAsO}_{1-x}\text{F}_x \) but with a smaller \( T_c \). This is likely due to the stronger effects of disorder produced by doping in the FeAs layers rather than in the LaO layers. It is actually somewhat surprising that the superconductivity in \( \text{LaFe}_{1-x}\text{Co}_{x}\text{AsO} \) is quite robust to in-plane disorder and this behavior will need to be understood as part of a comprehensive theory of the superconducting mechanism.  

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