Electron doping evolution of structural and antiferromagnetic phase transitions in NaFe$_{1-x}$Co$_x$As iron pnictides

Guotai Tan,1 Yu Song,2 Chenglin Zhang,2 Lifang Lin,1 Zhuang Xu,1 Tingting Hou,1 Wei Tian,3 Huibo Cao,3 Shiliang Li,4,5 Shiping Feng,1 and Pengcheng Dai2,1,*

1 Department of Physics, Beijing Normal University, Beijing 100875, China
2 Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA
3 Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
4 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
5 Collaborative Innovation Center of Quantum Matter, Beijing, China

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We use transport and neutron diffraction to study the electronic phase diagram of NaFe$_{1-x}$Co$_x$As. In the undoped state, NaFeAs exhibits a tetragonal-to-orthorhombic structural transition below $T_c$, followed by a collinear antiferromagnetic (AF) order below $T_N$. Upon codoping to form NaFe$_{1-x}$Co$_x$As, $T_c$ and $T_N$ are gradually suppressed, leading to optimal superconductivity near Co-doping $x = 0.025$. While transport experiments on these materials reveal an anomalous behavior suggesting the presence of a quantum critical point (QCP) near optimal superconductivity, our neutron diffraction results indicate that commensurate AF order becomes transversely incommensurate with $T_N > T_c$ before vanishing abruptly at optimal superconductivity. These results are remarkably similar to electron-doping and isovalent-doping evolution of the AF order in BaFe$_2$As$_2$ and BaFe$_2$(As$_{1-x}$P$_x$)$_2$, thus suggesting a universal behavior in the suppression of the magnetic order in iron pnictides as superconductivity is induced.

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I. INTRODUCTION

High-transition-temperature (high-$T_c$) superconductivity in copper oxides [1] and iron pnictides [2–5] generally appears in the vicinity of a magnetically ordered phase. For this reason, magnetism is believed to play a critical role in the pairing mechanisms of high-$T_c$ superconductors [4]. In the case of copper oxides, hole doping to La$_2$CuO$_4$ by partially substituting La by Sr will gradually suppress the static antiferromagnetic (AF) order before superconductivity emerges [6]. For iron pnictide superconductors such as electron-doped BaFe$_2$As$_2$, $T_c$ dependence on the AF order and compare with those of electron, hole, and isovalently doped BaFe$_2$As$_2$ [12,13,17,18], optimal superconductivity appears near the regime where the static collinear AF order has been suppressed, leading to optimal superconductivity near Co-doping $x = 0.025$. While transport experiments on these materials reveal an anomalous behavior suggesting the presence of a quantum critical point (QCP) near optimal superconductivity, our neutron diffraction results indicate that commensurate AF order becomes transversely incommensurate with $T_N > T_c$ before vanishing abruptly at optimal superconductivity. These results are remarkably similar to electron-doping and isovalent-doping evolution of the AF order in BaFe$_2$As$_2$ and BaFe$_2$(As$_{1-x}$P$_x$)$_2$, thus suggesting a universal behavior in the suppression of the magnetic order in iron pnictides as superconductivity is induced.

II. EXPERIMENTAL RESULTS

High-quality NaFe$_{1-x}$Co$_x$As single crystals with nominal doping level $x$ were synthesized by the self-flux method as described elsewhere [30]. Similar to previous work [32], we use inductively coupled plasma (ICP) atomic-emission spectroscopy measurements to determine the chemical
FIG. 1. The magnetic structure, neutron scattering geometry, and phase diagram of NaFe$_{1-x}$Co$_x$As as determined from transport and neutron diffraction experiments. (a) The in-plane magnetic structure of NaFeAs [31]. $a_o$ and $b_o$ ($a_o > b_o$) are orthorhombic crystal axes in the AF ordered state. (b) Neutron scattering geometry used to search for transverse incommensurate AF order for samples near optimal superconductivity. The scattering plane is $[0,K,0]$, and the scan direction to search for incommensurate magnetic order is along the $[1,K,1.5]$ direction shown the dashed line. (c) The phase diagram of NaFe$_{1-x}$Co$_x$As, where Ort, Tet, and SC indicate the orthorhombic, tetragonal, and superconducting phases, respectively. The C-AFM and IC-AF denote commensurate and incommensurate AF order, respectively. The green down-pointing triangles and blue squares are $T_N$ and $T_c$, respectively, determined from neutron diffraction experiments. The diamonds and stars are $T_c$ determined from resistivity (R-T) and heat capacity (C-T), respectively [30].

FIG. 2. Temperature dependence of the resistivity as a function of increasing Co doping for NaFe$_{1-x}$Co$_x$As with (a) $x = 0.01$, (b) 0.0125, (c) 0.015, (d) 0.0175, (e) 0.019, (f) 0.02, (g) 0.021, and (h) 0.023. The red solid line in the inset is a fit to the model: $\rho(T) = \rho_0 + AT^n$ up to 220 K in the normal state.

collinear AF order in NaFeAs and Co-doped samples should occur at $Q_{AF} = (1.0, L)$ where $L = 0.5, 1.5, \ldots$ rlu [31].

Figure 2 summarizes temperature dependence of the in-plane resistivity measurements for NaFe$_{1-x}$Co$_x$As with $x = 0.01, 0.0125, 0.015, 0.0175, 0.019, 0.02, 0.021$, and 0.023. The resistivity is normalized to the room temperature value per $\rho_{ab}(T)/\rho_{ab}(300 K)$ in the inset of Fig. 2(a). For all measured Co-doping levels, $\rho_{ab}(T)/\rho_{ab}(300 K)$ is metallic in the paramagnetic state, and the upturns above $T_c$ for lightly Co-doped samples are due to structural and magnetic phase transitions [12,19]. To compare the resistivity behavior in NaFe$_{1-x}$Co$_x$As with those of the doped BaFe$_2$As$_2$ family of materials [12,19,33], we performed fits for the data from $T_c + 10$ K to 220 K using the empirical model [12,19,33]: $\rho(T) = \rho_0 + AT^n$, where $\rho_0$ is a constant, $A$ is amplitude, and $n$ is the temperature exponent. For a typical Fermi liquid metal, one expects $n = 2$, and a material close to QCP typically has $n = 1$ with $n < 2$, suggesting non-Fermi liquid behavior [35,36]. The red solid line in the inset of Fig. 2(a) represents a fit to the resistivity data. The Co-doping dependence of the fitting exponent $n$ is shown in Fig. 3(e), which has a minimum value of $n \approx 1.3$ around $x \approx 0.02$ near optimal superconductivity. These results are similar to previous transport measurements on NaFe$_{1-x}$Co$_x$As [28,29] and compositions of the samples. For the nominal NaFe$_{0.95}$Co$_{0.05}$As samples, which contain an unknown amount of NaAs flux, ICP measurements suggest a total chemical composition of Na$_{0.94}$Fe$_{0.95}$Co$_{0.02}$As. Since the Na concentration of 0.94 is similar to the combined Fe and Co concentration of 0.91, we assume that the actual chemical compositions of NaFe$_{1-x}$Co$_x$As are similar to the nominal doping levels and quote the nominal doping level throughout the paper [32]. Resistivity measurements were carried out with the four-probe method using a physical property measurement system (PPMS). Neutron diffraction experiments were carried out on HB-1A thermal triple-axis spectrometer at the High-Flux Isotope reactor (HFIR), Oak Ridge National Laboratory. We define the wave vector $Q$ at $(q_x, q_y, q_z)$ as $(H, K, L) = (q_xa_o/2\pi, q_yb_o/2\pi, q_zc/2\pi)$ in reciprocal lattice units (rlu), where $a_o \approx b_o \approx 5.56$ Å, and $c = 6.95$ Å. In this orthorhombic unit cell notation, the
ordered moment square $M$ magnetic scattering has been normalized to a weak nuclear Bragg peak in $\AA$ as a function of Co doping. The shaded doping dependence of the ordered magnetic moment. (d) The spin-spin correlation length in a as a function of Co doping. The shaded area indicates that spin-spin correlation length is resolution limited. (e) Co-doping dependence of the exponent $n$ from fits to the resistivity data.

suggest the presence of a QCP near optimal superconductivity in NaFe$_{1-x}$Co$_x$As similar to that of BaFe$_{2-x}$T$_x$As$_2$.

Figures 3(a) and 3(b) summarize the magnetic order parameters for NaFe$_{1-x}$Co$_x$As with $x = 0.0, 0.005, 0.0125, 0.0175$, and $0.0215, 0.023, 0.0235$. The negative values are due to imperfect high-temperature background scattering subtraction. (c) Co-doping dependence of the ordered magnetic moment. (d) The spin-spin correlation length in A as a function of Co doping. The shaded area indicates that spin-spin correlation length is resolution limited. (e) Co-doping dependence of the exponent $n$ from fits to the resistivity data.

temperature, however, seems to saturate around $T_N \approx 30$ K on approaching optimal superconductivity with $x = 0.0235$. We also note that the AF phase transitions become rounded for samples near optimal superconductivity. This is consistent with the temperature dependence of the magnetic order parameters of underdoped BaFe$_{2-x}$T$_x$As$_2$ near optimal superconductivity, which has been attributed to a cluster spin glass state [38–40].

To determine Co-doping dependence of the spin-spin correlation length in the AF ordered phase of NaFe$_{1-x}$Co$_x$As, we carried out neutron diffraction measurements in two different scattering geometries. For the underdoped sample where we expect the static AF order to be commensurate, we aligned the single crystals in the $[H, 0, 0] \times [0, L, 0]$ scattering plane. For Co-doping level $x$ near optimal superconductivity, we aligned the crystals in the $[0, K, 0] \times [H, 0, 1.5H]$ scattering plane as shown in Fig. 1(b) in order to search for possible transverse incommensurate magnetic order, as seen in BaFe$_{2-x}$T$_x$As$_2$ [11,12]. For lightly Co-doped NaFe$_{1-x}$Co$_x$As, Fourier transforms of longitudinal scans along the $[H, H, 0]$ direction reveal that spin-spin correlation lengths are resolution limited and greater than or equal to 290 $\AA$ [Fig. 3(d)]. This is the case for all samples probed.

Figures 4(a) and 4(b) show transverse and longitudinal scans, respectively, for NaFe$_{1-x}$Co$_x$As with $x = 0.0125$ at different temperatures. The scattering is featureless at $T = 45$ K (above $T_N$) along both directions. On cooling to $T = 15$ K and 5 K, we see clear magnetic scattering at commensurate
FIG. 5. Temperature dependence of a strong nuclear Bragg peak scattering (4,0,0) as a function of Co doping (a) $x = 0.005$, (b) 0.0125, (c) 0.015, (d) 0.023, (e) 0.0235, and (f) 0.02375. The blue vertical arrows mark estimated $T_s$. The black arrows mark $T_N$ determined from neutron diffraction measurement, and the green arrows are $T_c$ determined from transport data.

positions along the longitudinal and transverse directions [Figs. 4(a) and 4(b)]. The situation is similar for the $x = 0.023$ sample [Figs. 4(c) and 4(d)]. However, the transverse scans for the $x = 0.0235$ sample show two incommensurate peaks at $T = 15$ K and 5 K [Fig. 4(e)], while longitudinal scans are commensurate at all measured temperatures [Fig. 4(f)]. The positions of incommensurate peaks are similar to those of electron-doped BaFe$_{2-x}$T$_x$As$_2$ [11,12]. These results thus suggest that the presence of transverse incommensurate magnetic order before optimal superconductivity may be a common feature of electron-doped BaFe$_2$As$_2$ and NaFeAs.

To determine electron-doping evolution of the orthorhombic-to-tetragonal structural transition in NaFe$_{1-x}$Co$_x$As, we measured the temperature dependence of the intensity at the (4,0,0) nuclear Bragg reflection position in the orthorhombic notation [7]. From previous neutron diffraction experiments on BaFe$_2$As$_2$, we know that the intensity of the (4,0,0) nuclear Bragg reflection [or the nuclear Bragg peak (2,2,0) in the tetragonal notation] shows a dramatic jump at $T_s$ arising from the neutron extinction release that occurs due to strain and domain formation related to the orthorhombic distortion [41,42]. Figure 5 summarizes the key results for NaFe$_{1-x}$Co$_x$As with $x = 0.005, 0.0125, 0.015, 0.023, 0.0235,$ and $0.02375$. In all cases, we see a clear enhancement of the scattering intensity below a characteristic temperature marked by vertical arrows. The resulting $T_s$ as a function of Co doping is plotted together with other information shown in Fig. 1(c), thus establishing the Co-doping dependence of the NaFe$_{1-x}$Co$_x$As phase diagram.

III. CONCLUSION

To summarize, we have mapped out the orthorhombic-to-tetragonal structural and AF ordering phase transition phase diagram in NaFe$_{1-x}$Co$_x$As as a function of Co doping up to optimal superconductivity. In spite of the rather different electron and hole Fermi surfaces between electron-doped BaFe$_{2-x}$T$_x$As$_2$ [43] and NaFe$_{1-x}$Co$_x$As [44–46], we show that the Co-doping evolutions of the structural and magnetic phase transitions in these two classes of materials are remarkably similar. These results confirm the universal nature of the Co-doping dependence of the structure and magnetic phase transitions and suggest that the AF order vanishes in the first-order fashion with an avoided magnetic QCP in iron pnictides. Since inelastic neutron scattering experiments on these two families of iron-based superconductors reveal that their Co-doping-dependent spin excitations are also similar [47–50], we conclude that magnetism and spin excitations must play a critical role in the pairing mechanisms of iron-based superconductors [4].

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