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Phys. Rev. Lett. **114**, 157002 — Published 17 April 2015

DOI: [10.1103/PhysRevLett.114.157002](https://doi.org/10.1103/PhysRevLett.114.157002)
Structural and magnetic phase transitions near optimal superconductivity in BaFe$_2$(As$_{1-x}$P$_x$)$_2$

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(Dated: March 23, 2015)

We use nuclear magnetic resonance (NMR), high-resolution x-ray and neutron scattering to study structural and magnetic phase transitions in phosphorus-doped BaFe$_2$(As$_{1-x}$P$_x$)$_2$. Previous transport, NMR, specific heat, and magnetic penetration depth measurements have provided compelling evidence for the presence of a quantum critical point (QCP) near optimal superconductivity at $x = 0.3$. However, we show that the tetragonal-to-orthorhombic structural ($T_s$) and paramagnetic to antiferromagnetic (AF, $P_N$) transitions in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ are always coupled and approach to $T_s \approx T_N$ for $x = 0.29$ before vanishing abruptly for $x \geq 0.3$. These results suggest that AF order in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ disappears in a weakly first order fashion near optimal superconductivity, much like the electron-doped iron pnictides with an avoided QCP.

PACS numbers: 74.70.Xa, 75.30.Gw, 78.70.Nx

A determination of the structural and magnetic phase diagrams in different classes of iron pnictide superconductors will form the basis from which a microscopic theory of superconductivity can be established [1–5]. The parent compound of iron pnictide superconductors such as BaFe$_2$As$_2$ exhibits a tetragonal-to-orthorhombic structural transition at temperature $T_s$ and then orders antiferromagnetically below $T_N$ with a collinear antiferromagnetic (AF) structure [Fig. 1(a)] [3, 4]. Upon hole-doping via partially replacing Ba by K or Na [6, 7], the structural and magnetic phase transition temperatures in Ba$_{1-x}$A$_x$Fe$_2$As$_2$ ($A = K, Na$) decreases simultaneously with increasing $x$ and form a small pocket of a magnetic tetragonal phase with the c-axis aligned moment before disappearing abruptly near optimal superconductivity [8–11]. For electron-doped Ba(Fe$_{1−x}$T$_x$)$_2$As$_2$ ($T =$Co,Ni), transport [12, 13], muon spin relaxation ($\mu$SR) [14], nuclear magnetic resonance (NMR) [15–17], x-ray and neutron scattering experiments [18–23] have revealed that the structural and magnetic phase transition temperatures decrease and separate with increasing $x$ [18–23]. However, instead of a gradual suppression to zero temperature near optimal superconductivity as expected for a magnetic quantum critical point (QCP) [15, 16], the AF order for Ba(Fe$_{1−x}$T$_x$)$_2$As$_2$ near optimal superconductivity actually occurs around 30 K ($＞T_s$) and forms a short-range incommensurate magnetic phase which competes with superconductivity and disappears in the weakly first order fashion, thus avoiding the expected magnetic QCP [20–23].

Although a QCP may be avoided in electron-doped Ba(Fe$_{1−x}$T$_x$)$_2$As$_2$ due to disorder and impurity scattering in the FeAs plane induced by Co and Ni substitution, phosphorus-doped BaFe$_2$(As$_{1-x}$P$_x$)$_2$ provides an alternative system to achieve a QCP since substitution of As by the isovalent P suppresses the static AF order and provides an alternative to antiferromagnetic ($P_N$) transitions in BaFe$_2$(As$_{1-x}$P$_x$)$_2$, which competes with superconductivity and disappears in the weakly first order fashion, thus avoiding the expected magnetic QCP [20–23].
the structural and magnetic phase transitions at all studied P-doping levels are first order and occur simultaneously within the sensitivity of the measurements (~0.5 K), thus casting doubt on the presence of a QCP [34]. While these results are interesting, they were carried out on powder samples, and thus are not sensitive enough to the weak structural/magnetic order to allow a conclusive determination on the nature of the structural and AF phase transitions near optimal superconductivity.

In this Letter, we report systematic transport, NMR, x-ray and neutron scattering studies of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ single crystals focused on determining the P-doping evolution of the structural and magnetic phase transitions near $x = 0.3$. While our data for $x \leq 0.25$ are consistent with the earlier results obtained from powder samples [34], we find that nearly simultaneous structural and magnetic transitions in single crystals of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ occur at $T_s \approx T_N \geq T_c = 29$ K for $x = 0.28$ and 0.29 (near optimal doping) and disappear suddenly at $x \geq 0.3$. While superconductivity dramatically suppresses the static AF order and lattice orthorhombicity below $T_c$ for $x = 0.28$ and 0.29, the collinear static AF order persists in the superconducting state. Our neutron spin echo and NMR measurements on the $x = 0.29$ sample reveal that only part of the sample is magnetically ordered, suggesting its mesoscopic coexistence with superconductivity. Therefore, in spite of reduced impurity scattering, P-doped BaFe$_2$As$_2$ has remarkable similarities in the phase diagram to that of electron-doped Ba(Fe$_{1-x}$T$_x$)$_2$As$_2$ iron pnictides with an avoided QCP.

We have carried out systematic neutron scattering experiments on BaFe$_2$(As$_{1-x}$P$_x$)$_2$ with $x = 0.19, 0.25, 0.28, 0.29, 0.30$, and 0.31 [37] using the C5, RITA-II, and MIRA triple-axis spectrometers at the Canadian Neutron Beam center, Paul Scherrer Institute, and Heinz Maier-Leibnitz Zentrum (MLZ), respectively. We have also carried out neutron resonance spin echo (NRSE) measurements on the $x = 0.29$ sample using...
TRISP triple-axis spectrometer at MLZ [35]. Finally, we have performed high-resolution x-ray diffraction experiments on identical samples at Ames laboratory and Advanced Photon Source, Argonne National Laboratory [36]. Our single crystals were grown using Ba$_2$As$_2$/Ba$_3$P$_3$ self-flux method and the chemical compositions are determined by inductively coupled plasma analysis with 1% accuracy [37]. We define the wave vector $Q$ at $(q_x, q_y, q_z)$ as $(H, K, L) = (q_x a/2\pi, q_y b/2\pi, q_z c/2\pi)$ reciprocal lattice units (r.l.u) using the orthorhombic unit cell suitable for the AF ordered phase of iron pnictides, where $a \approx b \approx 5.6$ Å and $c = 12.9$ Å. Figure 1(b) shows temperature dependence of the resistivity for $x = 0.31$ sample, confirming the high quality of our single crystals [28].

Figure 1(c) summarizes the phase diagram of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ as determined from our experiments. Similar to previous work on powder samples with $x \leq 0.25$ [34], we find that the structural and AF phase transitions for single crystals of $x = 0.19, 0.28$, and 0.29 occur simultaneously within the sensitivity of our measurements ($\sim$1 K). On approaching optimal superconductivity as $x \to 0.3$, the structural and magnetic phase transition temperatures are suppressed to $T_s \approx T_N \approx 30$ K for $x = 0.28, 0.29$ and then vanish suddenly for $x = 0.3, 0.31$ as shown in the inset of Fig. 1(c). Although superconductivity dramatically suppresses the lattice orthorhombicity and static AF order in $x = 0.28, 0.29$, there are still remnant static AF order at temperatures well below $T_s$. However, we find no evidence of static AF order and lattice orthorhombicity for $x = 0.3$ and 0.31 at all temperatures. Since our NMR measurements on the $x = 0.29$ sample suggest that the magnetic order takes place in about $\sim$50% of the volume fraction, the coupled $T_s$ and $T_N$ AF phase in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ becomes a homogeneous superconducting phase in the weakly first order fashion, separated by a phase with coexisting AF clusters and superconductivity [dashed region in Fig. 1(c)].

To establish the phase diagram in Fig. 1(c), we first present neutron scattering data aimed at determining the Neél temperatures of BaFe$_2$(As$_{1-x}$P$_x$)$_2$. Figure 2(a) shows scans along the $[H, 0, 3H]$ direction at different temperatures for the $x = 0.19$ sample. The instrumental resolution limited peak centered at $Q_{AF} = (1, 0, 3)$ disappears at 99 K above $T_N$ [Fig. 2(a)]. Figure 2(b) shows the temperature dependence of the scattering at $Q_{AF} = (1, 0, 3)$, which reveals a rather sudden change at $T_N = 72.5 \pm 1$ K consistent with the first order nature of the magnetic transition [34]. Figure 2(c) plots $[H, 0, 0]$ scans through the (1, 0, 3) Bragg peak showing the temperature differences between 28 K (4 K) and 82 K for the $x = 0.28$ sample. There is a clear resolution-limited peak centered at (1, 0, 3) at 28 K indicative of the static AF order, and the scattering is suppressed but not eliminated at 4 K. Figure 2(d) shows the temperature dependence of the scattering at (1, 0, 3), revealing a continuously increasing magnetic order parameter near $T_N$ and a dramatic suppression of the magnetic intensity below $T_c$. Figures 2(e) and 2(f) indicate that the magnetic order in the $x = 0.29$ sample behaves similar to that of the $x = 0.28$ crystal without much reduction in $T_N$. On increasing the doping levels to $x = 0.3$ [36] and 0.31 [Fig. 2(f)], we find no evidence of magnetic order above 2 K. Given that the magnetic order parameters near $T_N$ for the $x = 0.28, 0.29$ samples look remarkably like those of the spin cluster phase in electron-doped Ba(Fe$_{1-x}$Ta)$_2$As$_2$ near optimal superconductivity [22, 23], we have carried out additional neutron scattering measurements on the $x = 0.29$ sample using TRISP, which can operate as a normal thermal triple-axis spectrometer with instrumental energy resolution of $\Delta E \approx 1$ meV and a NRSE triple-axis spectrometer with $\Delta E \approx 1$ μeV [35]. Fig. 2(h) shows the triple-axis mode data which reproduces the results in Fig. 2(f). However, identical measurements using NRSE mode reveals that the magnetic scattering above 30.7 K is quasielastic and the spins of the system freeze below 30.7 K on a time scale of $\tau \sim h/\Delta E \approx 6.6 \times 10^{-10}$ s [23]. This spin freezing temperature is almost identical to those of nearly optimally electron-doped Ba(Fe$_{1-x}$Ta)$_2$As$_2$ [21–23].

Figure 3 summarizes the key results of our x-ray scattering measurements carried out on identical samples as those used for neutron scattering experiments. To facilitate quantitative comparison with the results on Ba(Fe$_{1-x}$Ta)$_2$As$_2$, we define the lattice orthorhombicity $\delta = (a - b)/(a + b)$ [19, 22]. Figure 3(a) shows the temperature dependence of $\delta$ for BaFe$_2$(As$_{1-x}$P$_x$)$_2$ with $x = 0.19$, obtained by fitting the two Gaussian peaks in longitudinal scans along the $(8, 0, 0)$ nuclear Bragg peak.
Estimated for the previous neutron scattering results [34, 36]. We also note a first order like jump below $T_N = 28.5$ K. Consistent with the P-doping dependence of $M^2$ [Fig. 4(b)] and $T_N$ [Fig. 1(c)], we find that $T_N$ approaches to $\sim 3 \times 10^{-4}$ K near optimal superconductivity before vanishing at $x \geq 0.3$.

Summarizing the results in Figs. 2-4, we present the refined phase diagram of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ in Fig. 1(c). While the present phase diagram is mostly consistent with the earlier transport and neutron scattering work on the system at low P-doping levels [30, 34], we have dis-
covered that the magnetic and structural transitions still occur simultaneously above $T_c$ for $x$ approaching optimal superconductivity, and both order parameters vanish at optimal superconductivity with $x = 0.3$. Since our NMR and TRISP measurements for samples near optimal superconductivity suggests spin-glass-like behavior, we conclude that the static AF order in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ disappears in the weakly first order fashion near optimal superconductivity. Therefore, AF order in phosphorus-doped iron pnictides coexists and competes superconductivity near optimal superconductivity, much like the electron-doped iron pnictides with an avoided QCP. From the phase diagrams of hole-doped Ba$_{1-x}$A$_x$Fe$_2$As$_2$ [8–11], it appears that a QCP may be avoided there as well.

We thank Q. Si for helpful discussions. The work at IOP, CAS, is supported by MOST (973 project: 2012CB21400, 2011CBA00110, and 2015CB921302), NSFC (11374011 and 91221303) and CAS (SPRP-B: 2012CB821400, 2011CBA00110, and 2015CB921302), and TRISP measurements for samples near optimal superconductivity, much like the electron-doped iron pnictides with an avoided QCP. From the phase diagrams of hole-doped Ba$_{1-x}$A$_x$Fe$_2$As$_2$ [8–11], it appears that a QCP may be avoided there as well.

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