Phase diagram of the PrFeAsO$_{1-x}$F$_x$ superconductor

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The electronic phase diagram of PrFeAsO$_{1-x}$F$_x$ (0$\leq x \leq$0.225) has been determined using synchrotron X-ray powder diffraction, magnetization and resistivity measurements. The structural transition temperature is suppressed from 154 K to $\approx 120$ K and the magnetic phase transitions of both iron and praseodymium ions are completely suppressed by $x \approx 0.08$ fluorine doping, coinciding with the emergence of superconductivity. The optimal doping is $x \approx 0.15$ when $T_{c} = 47$ K, while the maximum solubility of fluorine in PrFeAsO$_{1-x}$F$_x$ is reached around $x = 0.22$. The structural, magnetic and superconducting phase diagram is presented.

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I. INTRODUCTION

The discovery of superconductivity in the oxypnictides $LnMnPO$ ($Ln$=La-Nd, Sm, Gd; $M$=Fe, Co, Ni, Ru; $Pn$=P and As)$_{1.2,3,4,5}$ with a ZrCuSiAs-type structure$^6,7$ sets a milestone in the field of superconductivity. The first step in the study of a newly discovered superconductor and towards elucidation of the nature of superconductivity itself is the determination of the phase diagram. It is natural then to compare the pnictide phase diagram with that of the only other class of high temperature superconductors, the cuprates$^7,8,9,10$. As in the cuprates, superconductivity arises when a so-called parent non-superconducting compound is doped with charge carriers. It has been demonstrated that the parent compound, $Ln$FeAsO, can be doped with holes when $Ln^{3+}$ is replaced partially by a divalent ion ($La_{1-x}Sr_xFeAsO_4$, $Pr_{1-x}Sr_xFeAsO_4$, $Sr^{2+}$). Correspondingly, $n$-type doping is realized either by substitution of $Ln^{3+}$ by a tetravalent ion ($Gd_{1-x}Th_xFeAsO_4$, $Th^{4+}$), or partially replacing $O^{2-}$ by $F^{-}$. Among the iron-pnictides, to-date, the electron-doped ($O_{1-x}F_x$) iron-arsenides $Ln$FeAsO$_{1-x}$F$_x$ have the highest $T_c$'s reported. Until now, there have been reports on the phase diagrams of $Ln$FeAsO$_{1-x}$F$_x$, $Ln$=La$^{1,10,14,15,16,17}$, Co$^{2,7}$, Nd$^{18}$, and Sm$^{19,20,21}$. Within the phase diagram of CeFeAsO$_{1-x}$F$_x$, J. Zhao et al.$^2$ argue for a suppression of the antiferromagnetism (AFM) with doping such that the magnetic order vanishes in close proximity to the superconductivity. This has been confirmed in other $Ln$FeAsO$_{1-x}$F$_x$ systems.$^{2,7,10,14,15,16,17,18,19}$ Yet, in SmFeAsO$_{1-x}$F$_x$ there are reports of coexistence of static AFM order with superconductivity.$^{2,20,21}$ Also, a signature of the Sm$^{3+}$ ions’ magnetism has been reported in optimal superconducting SmFeAsO$_{0.83}$F$_{0.17}$.$^{22}$ More recent studies on homologue systems$^{10,15,16,18}$ report a rather abrupt (first-order-like) change in the structural and magnetic order parameters at the boundary of superconductivity. Despite wide efforts toward a unified picture, a consensus has not yet been reached. Without any doubt, the correctness of the phase diagrams relies on an accurate determination of the fluorine ion concentration.$^{10,23}$ In this paper, we use synchrotron X-ray scattering, magnetization and resistivity measurements to map the structural, magnetic and superconducting phase diagram of the less studied PrFeAsO$_{1-x}$F$_x$.

II. EXPERIMENTAL PROCEDURE

PrFeAsO$_{1-x}$F$_x$ polycrystalline samples were synthesized through a two-step standard high temperature solid state chemical reaction using stoichiometric amounts of PrAs, Fe (4N8), Fe$_2$O$_3$ (5N), and PrF$_3$ (4N) as starting materials.$^{1,19}$ The PrAs binary used in the final reaction was synthesized by reacting Pr (3N) and As (4N) powders. The Pr:As=1:1 mix was encapsulated within a tantalum tube that was sealed inside a quartz tube under a low pressure Ar atmosphere, slowly heated to 500°C, and held at that temperature for 5 h. The powder was ground, mixed, re-sealed, and heated again to 900°C for 10 h. The stoichiometric constituents were then thoroughly ground, mixed, and finally pressed into pellets using a cold isostatic press with a pressure of 0.38 GPa. To avoid direct contact with the quartz tube and possible Si contamination, the pellets were wrapped in tantalum foil before being sealed under a low atmosphere of Ar gas in quartz tubes. They were heated to 1150°C for 50 h. All preparatory steps except the annealing were performed in a glovebox under a high purity Ar gas atmosphere. The single phase was checked after each step using XRD with Cu Kα radiation at room temperature.

A discrepancy between the nominal and real fluorine
content has been systematically reported in homologue systems. Therefore we determined the actual fluorine concentration by Wavelength Dispersive X-ray Spectroscopy (WDS) for each concentration. Therefore, all fluorine concentrations reported in this paper are the as-measured values and not the nominal starting compositions. Resistivity, dc- and ac-susceptibility measurements down to 1.8 K were performed using a Quantum Design Physical Property Measurements System. Electrical contacts with the samples for resistivity measurements were made using Pelco colloidal silver paste through attaching thin gold wires in a four-probe configuration. The silver paste was cured at 100 \degree C for up to 30 min in order to avoid sample degradation. The excitation current of 2 mA was optimized for the best signal-to-noise ratio and to prevent overheating of the samples by checking the linear I-V characteristic. Because the absolute values of the resistivity data carry an uncertainty of up to 30\% due to the slightly off-rectangular shape of the bar-shaped samples and the size of the contact pads, we report instead resistivity data as normalized to the room temperature values. The ac susceptibility was measured with a 10 Oe modulated field of frequency f=1 kHz, while dc measurements were carried out in 200 Oe. Synchrotron X-ray powder diffraction measurements with an incident-beam wavelength \( \lambda = 0.31 \) Å were performed at DND-CAT, Advanced Photon Source, Argonne National Laboratory.

III. RESULTS AND DISCUSSION

The parent PrFeAsO antiferromagnetic semimetal crystallizes in a \( P4/nmm \) tetragonal structure at high temperatures but undergoes a \( (Cmma) \) orthorhombic transformation at low temperatures, which is characteristic of all LnFeAsO systems. In order to obtain insight into the evolution of the crystallographic structure with fluorine doping and its relevance for superconductivity, we performed synchrotron X-ray powder diffraction measurements on the undoped parent PrFeAsO, two non-superconducting samples \( x=0.059 \) and \( x=0.078 \), and one under-doped superconducting concentration with \( x=0.082 \).

Figure 1 shows 2\( \theta \) scans through the (2 2 0)\(_T\) Bragg peak of the high temperature \( P4/nmm \) tetragonal structure. The peak broadens and splits into the (4 0 0)\(_O\) and (0 4 0)\(_O\) peaks of the \( Cmma \) orthorhombic phase upon cooling. "T" and "O" subscripts denote tetragonal and orthorhombic, respectively. The corresponding structural transition temperatures found within \( \pm 2 \) K resolution are \( T_S=154 \) K for the parent, \( T_S=142 \) K for \( x=0.059 \), and \( T_S=120 \) K for the fluorine doping preceding superconductivity \( x=0.078 \).

Figure 2 shows the evolution of the (2 2 0) Bragg peak for the superconducting \( x=0.082 \) sample upon cooling to 50 K. The full-width at half-maximum (FWHM) of the peak is plotted versus temperature in the inset of Fig. 2 and shows a continuous evolution down to 50 K. Upon cooling, we observe a continuous slight broadening of the (2 2 0) peak; yet we were not able to resolve any definite inflection point in the FWHM versus T indicative of a signature of the tetragonal to orthorhombic structural phase transition. Therefore, our data support a picture
of a rather abrupt suppression of the orthorhombic phase at the boundary of superconductivity. Our best estimate is a complete suppression of $T_S$ from 120 K within 1.5% fluorine doping of the critical value for superconductivity ($x$ between 0.072 and 0.087).

![Graph showing temperature-dependent magnetic susceptibility](image)

**FIG. 3:** The temperature-dependent magnetic susceptibility of PrFeAsO. The yellow (or light gray) curve is the result of a fit to Curie-Weiss law. The upper inset shows the susceptibility of PrFeAsO$_{1-x}$Fx, with $x=0$, 0.059 and 0.078 around the Pr ion ordering temperature along with their derivatives in the lower inset. In the lower panel the line is a guide-to-the-eye.

Now we turn to our magnetic susceptibility data. Figure 3 shows the temperature dependent, dc-magnetic susceptibility of PrFeAsO measured in 200 Oe fitted above the Pr ordering temperature with a Curie-Weiss law, $\chi(T) = \chi_0 + C/(T + \theta)$, where $\chi_0$ is the temperature independent susceptibility, $C = N\mu^2_{eff}/3k_B$ the Curie constant, $N$ is the number of Pr$^{3+}$ ions, and $\theta$ the Curie-Weiss temperature. The effective moment found is $\mu_{eff}$=3.75$\mu_B$, slightly larger than the isolated trivalent Pr ion value of 3.5$\mu_B$. The discrepancy could be due to the Pr$^{3+}$ CEF contribution to the susceptibility. It should be noted that the susceptibility data could be fitted with a Curie-Weiss law for LnFeAsO$_{1-x}$Fx, Ln=Ca$^{2+}$, Nd$^{3+}$ and Gd$^{3+}$, but not in the case of Ln=Sm$^{3+}$. The low temperature susceptibility is dominated by a sharp peak around 12 K in the pure PrFeAsO system, as well as in other non-superconducting F$^{-}$ concentrations. This is due to the AFM ordering (Néel temperature) of the Pr 4f/electrons (Fig. 5(b)), consistent with previous reports from neutron$^{22}$, magnetization$^{22}$, and resistivity$^{22,23}$ studies. The upper inset shows a moderated suppression of $T_N$(Pr) with fluorine doping for three different concentrations $x=0$, 0.059 and 0.078 in PrFeAsO$_{1-x}$Fx extending over the whole non-superconducting region. In the lower inset the temperature derivative of the susceptibility around the ordering temperature is shown. Again, it should be noted that there is a weak to moderate suppression of the ordering temperature with fluorine doping.

![Graph showing real component of ac susceptibility](image)

**FIG. 4:** Real component of ac susceptibility normalized to its maximum of PrFeAsO$_{1-x}$Fx, with $x=0$, 0.059, and 0.078.

Figure 4 presents the real components of the ac-susceptibilities normalized to their corresponding maxima for the same compositions ($x=0$, 0.059, 0.78) discussed previously. The 130 K sharp peak in magnetization of the parent compound coincides with the magnetic ordering temperature of the iron ion moments, as initially revealed by the neutron diffraction data$^{21}$. With fluorine doping, the magnetic ordering temperature of the iron moments is continuously reduced from 130 K ($x=0$) to 80 K for $x=0.078$.

In Fig. 5 we show resistivity data for PrFeAsO$_{1-x}$Fx with $x=0$, 0.044, 0.11, 0.138 and 0.225 divided by the room temperature value, $\rho$(297 K). The data are shifted for clarity. The behavior of $\rho(T)$ for the PrFeAsO compound is similar to that of the other LnFeAsO, Ln=La, Ce, Nd and Sm$^{10,27}$. Upon cooling, the resistivity decreases showing metallic behavior. Around 150 K there is a broad peak associated with both the structural phase transition from tetragonal to orthorhombic symmetry and the spin-density-wave (SDW) magnetic phase transition. Because of a smooth and continuous change in the physical properties around these transitions, an indicator of the transition temperature is the temperature derivative of the resistivity$^{16,27,30}$. Figures 5(c) and (d) show $\partial\rho/\partial T$ for the $x=0$ and 0.044 non-superconducting samples. $T_N$(Fe) and $T_S$ correspond to the two inflection points in $\partial\rho/\partial T$. At around 13 K, the resistivity of the parent PrFeAsO exhibits a shoulder-like feature (Fig. 5(b)) that was attributed to the AFM ordering of the Pr ion moments$^{27,29}$.

Fig. 6 shows the phase diagram of PrFeAsO$_{1-x}$Fx ($0\leq x\leq0.225$) as determined by the measurements reported in this paper. Superconductivity appears after
doping with charge carriers (electrons) the parent AFM semimetal PrFeAsO. In this system, doping is realized by substituting $O^{2−}$ by $F^{−}$. Upon doping, the coupled structural and AFM transitions are suppressed, in analogy with the behavior of the structural and magnetic transitions in $La_{2−x}Sr_{x}CuO_{4}$\textsuperscript{31}. The phase diagram showing close proximity between AFM and SC resembles that of the electron-doped cuprates where the AFM persists right up to the SC dome. The superconducting transition temperatures were determined by the onset of the diamagnetism in zero-field-cooled magnetization (data not shown) or the drop of the resistivity. Optimal doping is achieved at a fluorine concentration of $\approx0.15$, in agreement with values reported for the homologous systems CeFeAsO$_{1−\delta}$F$_{\delta}$\textsuperscript{27} and SmFeAsO$_{1−\delta}$F$_{\delta}$\textsuperscript{31,22} and as predicted by recent minimum principle energy calculations\textsuperscript{32}. $LnFeAsO_{1−\delta}$ oxygen deficient (optimally doped at $\delta=0.15$) with no fluorine doping obtained by high pressure synthesis has been reported to be a superconductor\textsuperscript{35}, this process is similar to the well known oxygenation of the cuprates. It is worthwhile to mention that a maximum superconducting temperature transition around 47 K has been reported previously for optimally doped samples synthesized by normal pressure solid state chemical reaction\textsuperscript{29,34}, while a slightly enhanced $T_{C}$ of 52 K was reported for the samples synthesized using a high pressure method\textsuperscript{35}. Our results show that the synthesis of a sample with nominal fluorine concentration of 0.35 resulted in an actual fluorine $x_{WDS}$ substitution of 0.225, which represents the maximum fluorine doping in PrFeAsO$_{1−x}$F$_{x}$. This value is consistent with recently reported WDS determined values in LaFeAsO$_{1−x}$F$_{x}$ and SmFeAsO$_{1−x}$F$_{x}$\textsuperscript{23} and the saturation of lattice parameters in LaFeAsO$_{1−x}$F$_{x}$\textsuperscript{35}.

IV. CONCLUSIONS

In summary, we have determined the complete structural, magnetic and superconducting phase diagram of PrFeAsO$_{1−x}$F$_{x}$ ($0≤x≤0.22$) using synchrotron X-ray powder diffraction, magnetization and resistivity measurements. We find a progressive suppression of the structural transition and magnetic ordering transitions of both iron and praseodymium ion moments with increasing fluorine doping. In superconducting samples, near the edge of the emergence of the superconductivity ($x=0.08$ fluorine doping), we were not able to detect any fraction of the orthogonal phase. The optimal doping was found to be at $x=0.15$ when $T_{C}=47$ K, and the maximum fluorine doping in PrFeAsO$_{1−x}$F$_{x}$ was reached around $x=0.22$ with superconductivity remaining robust.

The phase diagram is most similar to that of the hole-doped cuprates $La_{2−x}Sr_{x}CuO_{4}$. However, there are some important differences. First, in $La_{2−x}Sr_{x}CuO_{4}$ there is a spin glass phase in between the 3D Néel antiferromagnet and the superconductor; the stripe-like spin fluctuations in the cuprate spin glass phase are rotated by 45 degrees, relative to those in the superconductor...
and the spin glass-superconductor transition at 0 K as a function of hole concentration is first order. Second, the tetragonal-orthorhombic structural transition temperature in La$_{2-x}$Sr$_x$CuO$_4$ varies smoothly across the insulating to superconductor boundary and, indeed, persists in $x$ beyond the value at which $T_C$ is a maximum. By contrast, in the PrFeAsO$_{1-x}$F$_x$ system both the Néel order and the tetragonal-orthorhombic structural transition appear to vanish together quite rapidly, possibly in a first order way, as the fluorine concentration is varied. This will represent a significant technical challenge. It will also be necessary to elucidate this further it will be necessary to prepare homogeneous samples in which the fluorine concentration, $x$, is varied in quite fine steps. This will represent a significant technical challenge. It will also be necessary to characterize the magnetism in samples in the transition region using both neutron scattering and a local technique such as muon spin resonance. Of course, the ultimate goal is to determine which features are universal and which are details of a particular system. Specifically, one would like to determine whether or not the iron pnictides and the cuprates are in the same universality class or whether, in fact, the similarity in the phase diagrams is coincidental.

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