Reemergent phase of antiferromagnetic order in iron-based superconductor LaFe(As$_{1-x}$P$_x$)O probed by $^{31}$P-NMR

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Abstract. We report $^{31}$P-NMR studies of LaFe(As$_{1-x}$P$_x$)O compounds that revealed the reemergence of a novel antiferromagnetic (AFM) order phase (AFM2) at $0.4 \leq x \leq 0.7$ intervening between two superconductivity phases. The AFM2 state at $x=0.6$ is characterized by low Néel temperature $T_N = 35$ K and small AFM moment $0.18$ μB, which is in strong contrast to the AFM order phase (AFM1) at $x=0$ with larger AFM moment and higher $T_N$. This finding provides a reasonable explanation for the previous experimental fact that the AFM spin fluctuations and $T_c$ are unexpectedly enhanced in $x=0.6$ of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) even though its lattice parameters deviate from the optimum values, that is, the AFM spin fluctuations at low energies are enhanced as a result of the depression of AFM2 by electron doping through fluorine substitution.

1. Introduction

Iron(Fe) oxypnictide antiferromagnet LaFeAsO exhibits superconductivity (SC) with $T_c \approx 26$ K in LaFeAsO$_{1-y}$F$_y$ through the substitution of O$^{2-}$ with F$^-$[1]. In Fe-arsenic(FeAs) superconductors, it is well known that the $T_c$ reaches a maximum of 55 K[2, 3] when a FeAs$_4$ block forms into a nearly regular tetrahedral structure[4]: The optimal values of the As-Fe-As bonding angle ($\alpha$), the height of pnictogen ($h_{Pn}$) from the Fe plane, and the $a$-axis length are $\alpha = 109.5^{\circ}$ [4], $h_{Pn} \sim 1.38 \text{Å}$ [5], and $a \sim 3.9 \text{Å}$ [3, 6], respectively. The isostructural Fe-phosphorus (FeP) compound LaFeP(O$_{1-y}$F$_y$) also exhibits a superconducting transition with $T_c = 4\sim 7$K, which is much lower than that of FeAs compounds [7]. Thus, in the solid solution compounds LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$), it is anticipated that $T_c$ might decrease monotonically as $x$ increases, since the substitution of As with P makes $a$-axis length shorter, $\alpha$ wider, and $h_{Pn}$ lower than that in the optimal values for high $T_c$ Fe-pnictides. However, the $T_c$ exhibits a peak at $x=0.4$ when $y=0.1$ and at $x=0.6$ when $y=0.05$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) in spite of monotonic variation of lattice parameters with $x$[8, 9, 10]. Previous $^{31}$P-NMR study on LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) with $y=0.05$ and 0.1 revealed that the antiferromagnetic (AFM) spin fluctuations at low energies are markedly enhanced in the compounds that $T_c$ exhibits the maximum[11]. This finding provides clear evidence that the $T_c$ could be enhanced by AFM spin fluctuations at low energies even though its lattice parameters deviates from the optimum values: On the one hand, it gives rise
to another question why the AFM spin fluctuations are enhanced in such lattice parameter region being far from that of the AFM state in the parent compound LaFeAsO.

In this paper, we present NMR evidence for the novel AFM2 order phase of that appears between $0.4 \leq x \leq 0.7$ of LaFe(As$_{1-x}$P$_x$)O, which is apart from parent AFM phase of LaFeAsO($x=0$). This finding provides a reasonable explanation for the previous experimental fact that the AFM spin fluctuations and $T_c$ are unexpectedly enhanced in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) compounds even though its lattice parameters deviate from the optimum values. The result is summarized as phase diagram shown in Fig. 3. We also discuss the characteristics of AFM2 phase and the origin of the unexpected phase transition in LaFe(As$_{1-x}$P$_x$)O.

2. Experimental Procedures

Polycrystalline samples of LaFe(As$_{1-x}$P$_x$)O with nominal contents $x=0.3$, 0.4, 0.5, 0.6, 0.7, 0.8, and 1.0 were synthesized by the solid-state reaction method [8, 9, 10, 12]. The $^{31}$P-NMR spectra were obtained by sweeping a magnetic field at a fixed frequency $f_0=107$ MHz for coarse powder samples of LaFe(As$_{1-x}$P$_x$)O ($0.3 \leq x \leq 1$). The nuclear spin lattice relaxation rate ($1/T_1$) of $^{31}$P-NMR was obtained by fitting a recovery curve for $^{31}$P nuclear magnetization to a single exponential function, $m(t) \equiv (M_0 - M(t))/M_0 = \exp(-t/T_1)$. Here, $M_0$ and $M(t)$ are the nuclear magnetizations for a thermal equilibrium condition and at time $t$ after a saturation pulse, respectively.

3. Results and Discussion

![Figure 1](image-url)

**Figure 1.** $T$ dependence of $^{31}$P-NMR spectra for (a) $x=0.3$, (b) $x=0.4$, (c) $x=0.5$, (d) $x=0.6$, (e) $x=0.7$, and (f) $x=0.8$ of LaFe(As$_{1-x}$P$_x$)O.

Figure 1 shows the temperature ($T$) dependences of the $^{31}$P-NMR spectra for $0.3 < x < 0.8$ of LaFe(As$_{1-x}$P$_x$)O. In particular, the $^{31}$P-NMR spectrum for $x=0.6$ exhibits a rectangular-like spectral shape at 4.2 K, which is characteristic for a randomly-oriented powder of commensurate
AFM ordered compounds[13]. The internal hyperfine field at \( ^{31}\text{P} \) nucleus (\(^{31}\text{H}_{\text{int}} \)) is estimated to be \( \approx 0.12 \pm 0.05 \text{ T} \) for \( x=0.6 \) at 4.2 K. Since the \( ^{31}\text{P} \) nucleus experiences a uniform off-diagonal internal hyperfine field associated with a stripe-type AFM order of Fe-3d electron spins[14], the \(^{31}\text{H}_{\text{int}} \)(\( T \)) is proportional to an AFM moment at Fe site (\( M_{\text{AFM}} \)). Using the relation of \(^{31}\text{H}_{\text{int}}=A_{\text{hf}}M_{\text{AFM}} \), the \( M_{\text{AFM}} \) is evaluated to be \( \approx 0.18 (\pm 0.07) \mu_B \) by assuming the hyperfine-coupling constant at \( ^{75}\text{As} \) site, \( ^{75}\text{A}_{\text{hf}}=2.0 \sim 2.5 \text{ T} / \mu_B \) in \( \text{LaFeAsO}(x=0) \), and the ratio \( ^{75}\text{A}_{\text{hf}}/^{31}\text{A}_{\text{hf}}=\frac{^{75}\text{H}_{\text{int}}/^{31}\text{H}_{\text{int}}=3.05 \text{ in } (\text{Cu}_4\text{Al}_2\text{O}_6)\text{Fe}_2(\text{As,P})_2}{[13]} \). Here, \(^{75}\text{A}_{\text{hf}} \) was evaluated from the data of \( ^{75}\text{H}_{\text{int}} \)=1.6 T [15] and \( M_{\text{AFM}}=0.63 \mu_B \) [16] \( \sim 0.8 \mu_B \) [17] for the AFM ordered \( \text{LaFeAsO} \). Figure 2(a) shows the \( T \) dependence of a full-width at half maximum (FWHM) of \(^{31}\text{P}-\text{NMR} \) spectra for \( 0.3 \leq x \leq 0.8 \). It indicates Néel temperature of \( x=0.6 \) is \( T_N=35 \text{ K} \), which is also corroborated by the peak of the \( 1/T_1T \), as shown in Fig. 2(b). Note that the \( M_{\text{AFM}} \approx 0.18 \mu_B \) and \( T_N=35 \text{ K} \) at \( x=0.6 \) are smaller than \( M_{\text{AFM}} \approx 0.8 (0.63) \mu_B \) [17] [16]) and lower than \( T_N=140 \text{ K} \) in the parent AFM phase of \( \text{LaFeAsO}(x=0) \), respectively.

As shown in Fig. 1, the \(^{31}\text{P}-\text{NMR} \) spectra for \( x=0.4, 0.5, \) and 0.7 except \( x=0.6 \) do not resemble the rectangular shape even at sufficiently low temperatures, which is probably due to tiny AFM moments and an inevitable distribution of \( M_{\text{AFM}} \). Related to this fact, the \( 1/T_1T \) shows a broad maximum that differs from the case at \( x=0.6 \), as shown in Fig. 2(b), suggesting that the \( T_N \) is not homogeneous within the sample owing to the possible nonuniform distribution of P content. It is consistent with the previous report for \( x=0.5 \) [18]. Thus here, the spatially-averaged value of \( T_N \) for these compounds is deduced by the temperature where the FWHM rapidly increases in Fig. 2(a). On the other hand, the \( x \) dependence of the FWHM indicates that the broadening of \(^{31}\text{P}-\text{NMR} \) spectra is significantly suppressed at \( x=0.3 \) and 0.8, which is due to being in paramagnetic state. The AFM2 order state dominates in the \( x \) range between \( x=0.4 \) and 0.7, which is apart from the AFM1 phase in \( x \leq 0.2 \) [18]. As a result, the phase diagram of \( \text{LaFeAs}_{1-x}\text{P}_x(\text{O}_{1-y}\text{F}_y) \) is summarized in Fig. 3 [20, 8, 10, 18, 22, 11, 12, 21] that presents the reemergent AFM2 phase intervening the SC1 phase in low \( x \) region[19] and the SC2 phase in high \( x \) region[12]. Previous \(^{31}\text{P}-\text{NMR} \) studies of these compounds have revealed that \( T_c \) reaches its respective maxima of 27 and 24 K for \( x=0.4 \) with \( y=0.1 \) and for \( x=0.6 \) with \( y=0.05 \), as a result of the marked enhancement of AFM spin fluctuations at low energies [11]. The finding

Figure 2. (Color online) \( T \) dependence of (a) a full-width at half maximum (FWHM) of \(^{31}\text{P}-\text{NMR} \) spectra and (b) \( 1/T_1T \) for \( 0.3 \leq x \leq 0.8 \) of \( \text{LaFeAs}_{1-x}\text{P}_x \).
Figure 3. (Color online) Phase diagram of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) against P content ($x$) and F content ($y$)[20, 8, 10, 18, 22, 11, 12, 21]. The present study on LaFe(As$_{1-x}$P$_x$)O has revealed the presence of the AFM2 phase that intervenes between the SC-1 at $0 < x < 0.4$ [19] and the SC-2 at $x > 0.7$ [12].

of AFM2 phase provides a reasonable explanation for the previous experimental fact that the AFM spin fluctuations and $T_c$ are unexpectedly enhanced in these compounds even though its lattice parameters deviate from the optimum values: Namely, the enhancement of AFM spin fluctuations at low energies occurs as a result of the depression of AFM2 by electron doping through fluorine substitution.

The discontinuous phase transition of the ground states, AFM1–SC1–AFM2–SC2, is quite unusual. The AFM1 of LaFeAsO at $x=0$ disappears rapidly around $x \sim 0.2$[18] where $h_{\text{Pn}}$ is approximately 1.29 Å, which coincides with that at the border between the AFM and SC phases observed in many Fe pnictides in the Fe$^{2+}$-like state with neither electron nor hole doping [13]. The AFM2 phase, however, appears in the $h_{\text{Pn}}$ range of 1.2–1.25 Å, which is smaller than 1.29 Å. Such unexpected reemergence of AFM2 phase and the drastic variation of the ground state may be attributed to the multiband nature of the Fe-based superconductors. The recent band calculation has suggested that Fermi surface nesting at bands mainly composed of $d_{XZ}/d_{YZ}$ orbits becomes better again at the intermediate $x$ of LaFe(As$_{1-x}$P$_x$)O [23]. This will be clarified in the future. From other context, we note that AFM spin fluctuations at low energies are not always highly significant in Fe pnictide compounds with $T_c > 50$ K [24]. It has been reported that the new SC phase of heavily electron-doped LaFeAs(O,H) that exhibits a $T_c$ higher than that of LaFeAs(O,F) [25, 26] occurs owing to the development of AFM spin fluctuations at high energies in the vicinity of the AFM(H) phase despite the Fermi surface nesting condition being
significantly worse [27]. Therefore, the origins of the AFM and SC phases are yet unresolved underlying issues in LaFeAsO-based compounds, which should be clarified through a unified picture in the future.

4. Summary

In summary, the present $^{31}$P-NMR measurements in LaFe(As$_{1-x}$P$_x$)$_2$O have revealed the reemergence of the AFM2 order with the moment $\sim$0.18$\mu_B$ at $x=0.6$ that develops homogeneously below $T_N=35$K. The AFM2 phase occurs between $0.4 \leq x \leq 0.7$, being apart from the parent AFM order phase of LaFeAsO($x=0$). In the previous study in LaFe(As$_{1-x}$P$_x$)$_2$(O$_{1-y}$F$_y$), it was reported that the enhanced AFM spin fluctuations at low energies bring about the increase of $T_c[11]$. As a result of this study, the reason why the compound LaFe(As$_{1-x}$P$_x$)$_2$(O$_{0.95}$F$_{0.05}$) with $x=0.6$ exhibits a maximum $T_c=24$ K has been found, that is, the marked enhancement of AFM spin fluctuations at low energies as a result of the depression of AFM2 by electron doping. It should be noted that high SC transition of $T_c>50$K in Fe-pnictides appears when AFM spin fluctuations at low energies is not so significant[24]. To elucidate the mechanism of Fe-pnictides, the origin of AFM and high/low $T_c$ SC phases widely seen in Fe-pnictides should be clarified in the future.

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