Emergence of Novel Antiferromagnetic Order Intervening between Two Superconducting Phases in LaFe(As$_{1-x}$P$_x$)O: $^{31}$P-NMR Studies

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Systematic $^{31}$P-NMR studies of LaFe(As$_{1-x}$P$_x$)O compounds have revealed the emergence of a novel antiferromagnetic ordered phase (AFM-2) at $0.4 \leq x \leq 0.7$ that intervenes between two superconductivity (SC) phases. This AFM-2 phase with Neel temperature $T_N=35$ K for $x=0.6$ is in strong contrast to the AFM order (AFM-1) at $x=0$ exhibiting $T_N$ of 140 K. Previous $^{31}$P-NMR studies of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) have revealed that $T_c$ reaches a maximum of 24 K for $x=0.6$ as a result of the marked enhancement of AFM spin fluctuations at low energies due to electron doping by the flourine substitution of $y=0.05$ for oxygen. The reason for this unexpected result has been found in the present work, that is, the emergence of AFM-2 at $0.4 \leq x \leq 0.7$ without electron doping. We note that AFM spin fluctuations arising from interband nesting on the $d_{xz}/d_{yz}$ orbit is a key factor for the occurrence of SC around AFM-2.

Iron (Fe) oxypnictide LaFeAsO with an orthorhombic structure exhibits antiferromagnetic (AFM) order, and the substitution of F$^-$ for O$^{2-}$ induces superconductivity (SC) with a maximum transition temperature of $T_c=26$ K in LaFeAs$_{0.95}$P$_{0.05}$F$_y$. The anisotropic compound LaFeP(O$_{1-y}$F$_y$) with P substituted for As also reveals the SC transition at $T_c=4 - 7$ K, which is lower than that in the case of LaFeAs(O,F). In Fe-pnictide superconductors, $T_c$ reaches a maximum of 55 K$^{3,4}$ when a FeAs$_2$ block forms a nearly regular tetrahedral structure:5 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 ($a$) are 109.5$^\circ$,~1.38 Å, and~3.9 Å, respectively. In this context, since the substitution of P for As makes the $a$-axis length smaller, $\alpha$ wider, and $h_{PN}$ smaller, it is anticipated that FePs might decrease monotonically as $x$ increases in solid solution compounds LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$). Unexpectedly, $T_c$ exhibits a nonmonotonic variation with $x$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) compounds.7-9 Previous $^{31}$P-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 (AFMSFs) at low energies.10 The result provides clear evidence that $T_c$ is enhanced by AFMSFs at low energies even though the lattice parameters deviate from their optimum values. However, another question should be addressed: Why are AFMSFs enhanced despite the fact that the lattice parameters of the compounds are far from those of the AFM mother compound LaFeAsO?

In this Letter, we report the results of our $^{31}$P-NMR studies that a novel AFM ordered phase (AFM-2) emerges at $0.4 \leq x \leq 0.7$, intervening between two SC phases (SC-1 and SC-2) in LaFe(As$_{1-x}$P$_x$)O. The $^{31}$P-NMR Knight shift indicates the appearance of a sharp density of states (DOS) at the Fermi level derived from a $d_{xz}/d_{yz}$ orbit, which is less relevant with the onset of SC-2. On the other hand, AFMSFs arising from interband nesting on the $d_{xz}/d_{yz}$ orbit is mainly responsible for the occurrence of SC around AFM-2.

Polycrystalline samples of LaFe(As$_{1-x}$P$_x$)O were synthesized by the solid-state reaction method.7-9,11 Powder X-ray diffraction measurements indicated that the lattice parameters of LaFe(As$_{1-x}$P$_x$)O exhibit a monotonic variation with $x$.11 $^{31}$P-NMR($I=1/2$) measurement was performed on coarse powder 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 $1.0$. The $^{31}$P-NMR spectra in the AFM ordered state were obtained by sweeping a magnetic field at a fixed frequency $f_0=107$ MHz. The Knight shift $K$ in the normal state was measured at a magnetic field of $\sim 11.95$ T, which was calibrated using a resonance field of $^{31}$P in $\mathrm{H}_3\mathrm{PO}_4$. The nuclear spin lattice relaxation rate $(1/T_1)$ of $^{31}$P-NMR was obtained at a field of $\sim 11.95$ T 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.

Figure 1(a) shows the temperature ($T$) dependence of the $^{31}$P-NMR spectrum at $x=0.6$, which exhibits significant broadening below 35 K. At 4.2 K, the $^{31}$P-NMR spectrum indicates a rectangle-like spectral shape, which is characteristic of a randomly oriented powder where a commensurate AFM order takes place.12 The $^{31}$P nucleus experiences a uniform off-diagonal internal hyperfine field, $^{31}H_{\text{int}}$, associated with a stripe-type AFM order of Fe-3d spins.13 Actually, the spectrum can be simulated by assuming $^{31}H_{\text{int}} \approx 0.12 \pm 0.05$ T at 4.2 K, as shown by the solid curve in Fig. 1(a). By using the relation $^{31}H_{\text{int}} = \gamma_{\text{hf}}M_{\text{AFM}}$, an AFM moment $M_{\text{AFM}}$ at the Fe site is estimated to be $\sim 0.18(\pm 0.07)\mu_B$. 

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by assuming the hyperfine-coupling constant at the $^{75}$As site, $^{75}$A$_{hf}$= 2.0–2.5 $T_1$/$\mu_B$ in LaFeAsO, and the ratio $^{75}$A$_{hf}$/3H$_{int}$= 3.05 in (CaAl$_2$O$_6$)Fe$_2$(As,P)$_2$. As shown in Fig. 1(b), $^{31}$H$_{int}$($T$) that is proportional to $M_{AFM}$ develops upon cooling below $T_N$= 35 K according to a mean-field type of $T$ dependence. The onset of AFM order is also corroborated by the peak in $(1/T_1 T)$ at $T_N$= 35 K. Note that $M_{AFM}$ ~ 0.18$\mu_B$ and $T_N$= 35 K for the $x=0.6$ compound are smaller than $M_{AFM}$=0.63$\mu_B$ and much lower than $T_N$= 140 K for the AFM compound LaFeAsO($x=0$), respectively.

Figure 1(c) shows the $x$ dependence of the $^{31}$P-NMR spectrum at low temperatures. The $^{31}$P-NMR spectra for $x=0.4$, 0.5, and 0.7 except $x=0.6$ are not rectangular even at 1.9 K, pointing to an inevitable distribution of $M_{AFM}$. Concomitantly, the peak in $(1/T_1 T)$ at approximately $T_N$ is broader for these compounds than for the $x=0.6$ compound [see Fig. 3(b)]. These results are indicative of some homogeneity of $T_N$ in association with an inevitable distribution of P content in the sample as noted in a previous report for $x=0.5$. In this context, the spatially averaged $T_N$ is tentatively evaluated as the temperature below which the full-width at half maximum (FWHM) of each spectrum rapidly increases as shown in Fig. 1(d). On the other hand, the spectra for $x=0.3$ and 0.8 do not undergo such significant broadening even at low temperatures, providing evidence that both are in a paramagnetic state. The unexpected onset of AFM-2 at $0.4 \leq x \leq 0.7$ is discontinuous from the AFM-1 emerging at $x \leq 0.2$. As a result, a novel phase diagram of LaFe(As$_{1-x}$P$_x$)O is summarized in Fig. 2, in which the re-emergent AFM-2 intervenes between the SC-1 at $0.2 < x < 0.4$ and the SC-2 at $0.7 < x$. Here, we focus on a possible P-derived evolution of the electronic state in LaFe(As$_{1-x}$P$_x$)O. The respective $T$ dependences of the Knight shift $K$ and $(1/T_1 T)$ are shown in Figs. 3(a) and 3(b), respectively. The Knight shift comprises the $T$-dependent spin shift $K_s(T)$ and the $T$-independent chemical shift $K_{chem}$. Figure 3(c) shows the $T$ dependence of $K_s(T)$ at $K$=200 K in Fig. 3(c) is close to the linear relation $(1/T_1 T)^{1/2} = K_{chem} + K_s(T)$ with $K_{chem} \sim 0.03$ ($\pm 0.01$)%.

Figure 4(a) shows $K_s(T)$ = $(K - K_{chem})$ for each $x$. For compounds at $x$ lower than 0.4, $K_s(T)$ decreases upon cooling as in LaFeAs(O,F) compounds. This is because the Fermi level is on the tail of the large peak of the DOS beneath $E_F$. However, in the intermediate $x$ range of $0.4 \leq x \leq 0.7$, once $K_s(T)$ increases in the high-temperature range, it then decreases toward $T$=0. At $x$ higher than 0.8, $K_s(T)$ monotonically increases upon cooling, suggesting the appearance of a sharp peak of DOS just at $E_F$. The band calculation has revealed that the Fermi surface (FS) of LaFeAsO is composed of two hole FSs at $\Gamma(0,0)$, one small hole FS at $\Gamma^\prime([\pi,\pi])$, and two electron FSs at $M([\pi,0],[0,\pi])$ in the unfolded FS regime; these nearly cylindrical FSs can be connected by the interband nesting vector $Q$. When the pnictogen height is as small as that in LaFePO, the $\Gamma^\prime$ mainly originating from the $d_{xy}$-$\Gamma$ orbit sinks below $E_F$, although the two nearly cylindrical hole FSs at $\Gamma$ and the two electron FSs at $M$ are maintained. On the other hand, the three-dimensional hole FS around $Z(\pi,\pi,\pi)$ arises from the $d_{xz}$-$\Gamma$ orbit, which brings about a sharp peak in the DOS just at $E_F$. As shown in the broken curves in Figs. 3(a) and 4(a), the $T$ dependence of $K_s(T)$ at
Fig. 3. (Color online) T dependences of (a) Knight shift (K) and (b) (1/T1 T) for LaFe(As1−xPx)O. (c) Plot of (1/T1 T)1/2 vs K at T=200 K. The thick line shows the linear relation (1/T1 T)1/2 = Kchem + Ks(T) with Kchem =0.03±0.01)% . Some Knight shift data in (a) are cited from Ref. 18.

Fig. 4. (Color online) (a) Systematic T dependences of KS(T) for each x for LaFe(As1−xPx)O and LaFeP(1−yFy)O.10 along with the x dependences of KS(T=240 K) and KS(T→0) estimated by extrapolation to T=0 in the paramagnetic state above TN or Tc . (b) Plot of KS(T→0) in the phase diagram.9, 19, 27 Note that KS(T→0) increases markedly at x≈0.7−0.8, but electron doping through F− substitution in LaFeP(O1−yFy) causes KS(T→0) to decrease markedly.10 The appearance of a sharp peak of DOS is due to the d3Z2−r2,z orbit for 0.7−0.8 < x.

Fig. 5. (Color online) Evaluation of AFMSFs for x=0.8 and 1.0 in SC-2. The 1/T1 T of these compounds increases upon cooling below 50 K even though Ks2 becomes nearly T-independent; hence the hatched area denoted as (1/T1 T)AFM corresponds to the component of 1/T1 T due to interband scattering process, i.e., AFMSFs at a finite Q.

Fig. 6. (Color online) (a) Quasiparticles derived from the hole FS at the Z point in Fe-pnictide SC in general. Finally, we deal with some differences of AFM-1 and AFM-2 in LaFe(As1−xPx)O. The AFM-1 of LaFeAsO at x=0 disappears rapidly around x≈0.2 where \( \mu_{pn} \) 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 Fe2+−like state with nei-
ther electron nor hole doping. AFM-2 appears in the $h_{\text{pn}}$ range of 1.2–1.25 $\text{Å}$, which is smaller than 1.29 $\text{Å}$. From the recent band calculation, Kuroki et al. suggested that FS nesting at bands mainly composed of $d_{xz}/d_{yz}$ orbits becomes better again at the intermediate $x$ of LaFeAs($\text{As}_1-x\text{P}_x$)$_2$O$_2$ consistent with the experimental results. From other context, the reason why the compound LaFeAs($\text{As}_1-x\text{P}_x$)$_2$O$_2$($O_{0.95}F_{0.05}$) with $x=0.6$ exhibits a maximum $T_c=24$ $\text{K}$ against $x$ is found, that is, the marked enhancement of AFMSFs at low energies as a result of the depression of AFM-2 by electron doping. Eventually, interband nesting on $d_{xz}/d_{yz}$ orbits must be a key factor for the emergence of SC around AFM-2.

However, note that AFMSFs at low energies are not always highly significant in Fe pnictide compounds with $T_c > 50$ $\text{K}$. Recently, another type of stripe AFM(H) phase carrying a large AFM moment but exhibiting a low $T_N$ has been reported for heavily electron-doped compounds LaFeAs(O,H):$_3$ with a homogeneous moment of $M$ from those of the mother compound with AFM-1 order. From another context, the reason why the compound LaFeAs(O,$\text{As}_1-x\text{P}_x$)$_2$O$_2$($O_{0.95}F_{0.05}$) with $x=0.6$ exhibits a maximum $T_c=24$ $\text{K}$ against $x$ is found, that is, the marked enhancement of AFMSFs at high energies in the vicinity of $1$ at $0.2 < x < 0.8$ in such a manner that a three-dimensional hole FS around $Z$. This result suggests that the appearance of $d_{3z^2-r^2}$-derived three-dimensional hole pocket causes AFM-2 to be unfavorable in association with the collapse of the nearly two-dimensional LaFeAsO-like band configuration. From another context, the reason why the compound LaFeAs($\text{As}_1-x\text{P}_x$)$_2$O$_2$($O_{0.95}F_{0.05}$) with $x=0.6$ exhibits a maximum $T_c=24$ $\text{K}$ against $x$ is found, that is, the marked enhancement of AFMSFs at low energies as a result of the depression of AFM-2 by electron doping. Eventually, interband nesting on $d_{xz}/d_{yz}$ orbits must be a key factor for the emergence of SC around AFM-2.

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