Multiple Antiferromagnetic Spin Fluctuations and Novel Evolution of $T_c$ in Iron-Based Superconductors LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) Revealed by $^{31}$P-NMR Studies

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We report on $^{31}$P-NMR studies of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) over wide compositions for $0 \leq x \leq 1$ and $0 \leq y \leq 0.14$, which provide clear evidence that antiferromagnetic spin fluctuations (AFMSFs) are one of the indispensable elements for enhancing $T_c$. Systematic $^{31}$P-NMR measurements revealed two types of AFMSFs in the temperature evolution, that is, one is the AFMSFs that develop rapidly down to $T_c$ with low-energy characteristics, and the other, with relatively higher energy than the former, develops gradually upon cooling from high temperature. The low-energy AFMSFs in low $y$ (electron doping) over a wide $x$ (pnictogen height suppression) range are associated with the two orbitals of $d_{xz/yz}$, whereas the higher-energy ones for a wide $y$ region around low $x$ originate from the three orbitals of $d_{xy}$ and $d_{xz/yz}$. We remark that the nonmonotonic variation of $T_c$ as a function of $x$ and $y$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) is attributed to these multiple AFMSFs originating from degenerated multiple $3d$ orbitals inherent to Fe-pnictide superconductors.

Since the discovery of superconductivity (SC) in a layered iron(Fe)-pnictide LaFeAs(O$_1$−yF$_y$), a number of researches have unraveled a rich variety of antiferromagnetic (AFM), structural, and SC phase diagrams in various Fe-pnictide families. The SC transition temperature ($T_c$) of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) exhibits a unique nonmonotonic variation, as shown in Fig. 1, where the respective compositions $x$ and $y$ control the local lattice parameter of the Fe-pnictogen (Pn) tetrahedron ($x$) through the isovalent substitution of As with P and an electron-doping level ($y$) through the substitution of O$^2$ with F$^−$. Previous NMR studies of this series ($0 \leq y \leq 0.1$) revealed that the AFM spin fluctuations (AFMSFs) are markedly enhanced at $x$ where $T_c$ exhibits a peak. The appearance of such unexpected AFMSFs was related to a reemergent AFM order phase at $(x, y)=(0.6, 0)$, denoted as AFM2 in Fig. 1, which is separated from the AFM1 at the parent LaFeAsO of $(x, y)=(0, 0)$. These results indicate that the AFMSFs are one of the important factors for enhancing the $T_c$ in Fe-pnictide SCs, even when the lattice parameters deviate from their optimum values for a FeP$_n$ regular tetrahedron.

On the other hand, the AFMSFs are not so distinct at low energies for the compounds with a high $T_c$($\sim 50$ K), which are characterized by the local lattice parameters of FeAs$_4$ close to the regular tetrahedron. It has been reported that once further electrons are doped in the hydrogen-substituted LaFeAs(O$_{1-y}$H$_y$), the new phases of SC and AFM orders are uncovered and denoted as SC3 and AFM3 in Fig. 1, respectively. The theory has pointed out that the electronic state for the onset of SC3 resembles that of the highest $T_c$($\geq 50$ K) state. Thus, further systematic studies over wide compositions of $x$ and $y$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) will provide an opportunity to unravel the universal relationship between the presence of AFMSFs and the onset of SC, including the unexpected relationship between the complicated effect of some electron doping and the deformation of the local structure of FeP$_n$.

![Fig. 1. (Color online) Superconducting and antiferromagnetic phase diagram of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) for $y=0.14$ (Uekubo et al.) and $0 \leq y \leq 0.10$. Together with schematic phases of SC3 and AFM3 for LaFeAs(O$_{1-y}$H$_y$).](image-url)

In this Letter, we report on $^{31}$P-NMR studies of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) over wide compositions for $0 \leq x \leq 1$ and $0 \leq y \leq 0.14$, revealing that AFMSFs are one of the indispensable elements for enhancing $T_c$. Systematic measurements of the $^{31}$P nuclear spin relaxation rate ($1/T_1$) have revealed that the multiple AFMSFs relevant to the multiple-orbital nature of Fe-pnictides are respon-
sible for increasing $T_c$ over wide compositions of $x$ and $y$. As a result, we remark that a nonmonotonic variation of $T_c$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) is attributed to the multiple AFMSFs originating from degenerated multiple 3d orbitals inherent to Fe-pnictides.

Detailed $^{31}$P-NMR ($I=1/2$) measurements were performed on coarse-powder polycrystalline samples of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) with nominal contents at $x=0.2$, 0.4, 0.6, and 1.0. These samples were synthesized by the solid-state reaction method. Powder X-ray diffraction measurements indicated that the lattice parameters exhibit a monotonic variation with $x$. $T_s$ were determined from an onset of SC diamagnetism in the susceptibility measurement, as shown in Fig. 1. Extensive studies over a wide composition of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) were also performed on the samples of $(x, y) = (0.2, 0.05)$ and $(x, y) = (0.2, 0.1)$. The Knight shift $K$ was measured at a magnetic field of $\sim 11.93$ T, which was calibrated using a resonance field of $^{31}$P in $\text{H}_2\text{PO}_4$. Generally, $K$ comprises the temperature($T$)-dependent spin shift $K_s(T)$ and the $T$-independent chemical shift $K_{\text{chem}}$, expressed as $K = K_s(T) + K_{\text{chem}}$. The nuclear-spin lattice-relaxation rate $^{31}$P-NMR was measured at the field of $\sim 11.93$ T by fitting a recovery curve for $^{31}$P nuclear magnetization to a single exponential function $m(t) = |M_0 - M(t)|/M_0 = \exp(-t/T_1)$. Here, $M_0$ and $M(t)$ are the respective nuclear magnetizations for a thermal equilibrium condition and at time $t$ after a saturation pulse.

Figures 2(a)-2(d) show the $T$ dependences of $(1/T_s)^{1/2}$ for $x=0.2$, 0.4, 0.6, and 1.0 of LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) with an implicit parameter of $T$ for these compounds, using data at high temperatures ($T > 160$ K). The empty diamonds are the previous data on $y=0.05$ and 0.1 ($T = 200$ K). The data for $x=0.4$ deviate from this line owing to the development of AFMSFs. (f) Contour plot of $(1/T_s)^{1/2}$ for $y=0.14$, indicating that the AFMSFs significantly develop where $T_c$ peaks a short pulse.

As a result, we remark that a nonmonotonic variation of $T_c$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) is attributed to the multiple AFMSFs originating from degenerated multiple 3d orbitals inherent to Fe-pnictides.

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As a result, we remark that a nonmonotonic variation of $T_c$ in LaFe(As$_{1-x}$P$_x$)(O$_{1-y}$F$_y$) is attributed to the multiple AFMSFs originating from degenerated multiple 3d orbitals inherent to Fe-pnictides.
\(\chi''(Q, \omega)\) significantly starts to increase upon cooling, roughly pointing to a characteristic energy of AFMSFs.

Note that the curves A, B, and C in Fig. 4(a) are along the values of \(T_c\) being relatively high for the wide compositions of \(x\) and \(y\).\(^{1-7}\) Figures 4(b) and 4(c) show the contour plots of \(T_{SF}\) and \((1/T_1 T)_{AFM}^{\max}\), respectively. The curve A is along the high values of \(T_{SF}\) in Fig. 4(b), demonstrating that the development of AFMSFs below \(T_{SF}\) is mostly responsible for increasing \(T_c\). Here, note that the high values of \(T_c\) are along the high values of \(T_{SF}\), in other words, roughly along the high values of the characteristic energy of AFMSFs. In fact, the theory predicted that the three orbitals of \(d_{xz}/d_{yz}+d_{xy}\) are relevant to the AFMSFs characteristic at finite energies rather than at low energies in association with the AFM1 order at \((x, y)=(0, 0)\).\(^{20-22}\) On the other hand, the high values of \(T_c\) along the curve B are along the large values of \((1/T_1 T)_{AFM}^{\max}\), as shown in Fig. 4(c), demonstrating that the development of AFMSFs at low energies is also responsible for increasing \(T_c\). Originating from the collapse of the AFM2 order at \((x, y)=(0.6, 0)\),\(^{3,10}\) Here, note that the very good nesting of the hole Fermi surfaces (FSs) at \(\Gamma(0,0)\) and electron FSs at \(M(0\pi/(\pi,0))\) in the unfolded FS regime is dominated mostly by the two orbitals of \(d_{xz}/d_{yz}\), bringing about the onset of the AFM2 order at \((x, y)=(0.6, 0)\).\(^{20,22}\) Hence, the present result suggests that these AFMSFs dominated by the two orbitals of \(d_{xz}/d_{yz}\) are gradually suppressed against the increase in the electron doping level as \(y\) increases from 0 to 0.14.

Theoretically, two different types of the \(T\)-evolution of AFMSFs shown in Fig. 3(b) were consistently reproduced by the fluctuation-exchange (FLEX) approximation in the multi-orbital Hubbard model. In this model, Arai et al. revealed that the \(d_{xz}/d_{yz}\)-derived AFMSFs around the AFM2 phase are largely enhanced at low energies, whereas the \(d_{xz}/d_{yz}+d_{xy}\) derived AFMSFs around the AFM1 are characteristic at finite energies rather than at low energies.\(^{20}\) In this context, it is notable that the highest \(T_c=27\) K is denoted at \((x, y)\) of (0.4, 0.1) by a star in Fig. 4(a) around which the curves A and B merge. It is instructive to note that the increase in the characteristic energy of AFMSFs from low to high energies brings about the increase in \(T_c\). This event is consistent with the spin-fluctuations mediated SC mechanism, which enables us to calculate a possible value of \(T_c\) on the basis of the integration of the AFMSF spectrum over a wide energy range.

We also note that as seen in Fig. 4(a), the high value of \(T_c\) at \((x, y)\) of (0.4, 0.1) is kept along the curve C toward \((x, y)=(0.4, 0.14)\) at which the AFMSFs from low to high energies slightly recover, as deduced from Figs. 4(b) and 4(c). This event may be associated with a reemergence of the \(d_{xz}/d_{yz}\)-derived AFMSFs since the low pionogen height at large \(x\) (0.5) will cause the FSs of the \(d_{xy}\) orbital to sink below \(E_F\) and the nesting of FSs of the \(d_{xz}/d_{yz}\) orbitals to become somewhat better.\(^{22}\) It is worth comparing this with the further electron-overdoped SC3 state in LaFeAs \((O_{1-y}H_y)\)\(^{17}\) shown in Fig. 1, since no nesting of FSs is expected. In these compounds, note that the hole FS in association with the \(d_{xz}/d_{yz}\) orbitals significantly shrinks owing to the heavy electron doping, whereas there still remain the hole FS relevant to the \(d_{xy}\) orbital and the large electron FSs.\(^{17}\) According to the spin-fluctuation model,\(^{19}\) the prioritized diagonal hopping on the \(d_{xy}\) orbitals reenhances the other type of AFMSFs in the high-\(T_c\) state of the SC3 phase, which is dominated by the high-energy AFMSFs,\(^{23}\) rather than the low-energy ones.\(^{24}\) It is interesting to unravel the systematic relationship between \(T_c\) and the evolution of different types of AFMSFs in the series going from LaFeAs \((As_{1-x}P_x)(O_{1-y}F_y)\) to LaFeAs \((O_{1-y}H_y)\).

Finally, we remark on the variation of \(N(E_F)\) over wide \(x\) and \(y\) regions, which can be seen from the contour plot of \(K_r(T\rightarrow0)\) estimated from an extrapolation to \(T\rightarrow0\), as shown in Fig. 4(d). Note that \(K_r(T\rightarrow0)\) is directly proportional to \(\chi(q=0)\) or \(N(E_F)\). As seen in the figure, \(K_r(T\rightarrow0)\) increases around \((x, y)\) of (1, 0) owing to the peak of DOS mainly arising from the \(d_{xz}/d_{yz}\)-derived three-dimensional hole pocket around \(Z(\pi,\pi,\pi)\).\(^{10,25}\) In fact, this contour plot of \(N(E_F)\) has no correlation with the \(T_c\) values. This indicates that the BCS-type SC mechanism through the electron-phonon interaction is not applicable even for the phosphorus-end members \((x=1.0)\),

Fig. 3. (Color online) (a) Contour plots of \((1/T_1 T)_{AFM}\) for \(y=0.0, 0.05, 0.10, 0.14\) in a common scale, providing clear evidence that the AFMSFs play a significant role in raising \(T_c\) for the present compositions of \(x\) and \(y\). (b) Typical \(T\) dependence of \((1/T_1 T)_{AFM}\) at \(x=0.2\) and 0.6 for \(y=0.05\). The AFMSFs at \(x=0.2\) gradually develop upon cooling from higher temperature, whereas the AFMSFs at \(x=0.6\) develop rapidly only at low temperature, although the value of \((1/T_1 T)_{AFM}\) at low temperature is smaller in the former case than in the latter case. We define \(T_{SF}\) as the temperature below which the AFMSFs start to develop, and \((1/T_1 T)_{AFM}^{\max}\) as the maximum value of \((1/T_1 T)_{AFM}\).
where the AFMSFs are significantly reduced and their \( T_c \) values are less than 10K.

In summary, the systematic \(^{31}\)P-NMR measurements for LaFe\((As_{1\rightarrow x}P_{x}) (O_{1\rightarrow y}F_{y})\) with \(0 \leq x \leq 1\) and \(0 \leq y \leq 0.14\) have unraveled two types of AFMSFs in the \( T_c \) evolution upon cooling, that is, one is the AFMSFs that develops rapidly down to \( T_c \), with low-energy characteristics, and the other, with relatively higher energy than the former, develops gradually upon cooling from high temperature. The low-energy AFMSFs in low \( y \) (electron doping) over a wide \( x \) (pnictogen-height suppression) range are associated with the nesting effect of FSs dominated mostly by the two orbitals of \( d_{xy}\), whereas the higher-energy ones for a wide \( y \) region around low \( x \) originate from the three orbitals of \( d_{xy} \) and \( d_{x\pm y\pm z} \). The intimate correlation between multiple AFMSFs and \( T_c \) values indicates that the AFMSFs are one of the indispensable elements for enhancing \( T_c \), even though the lattice parameters deviate from their optimum values for the \( FeP_{1.5} \) regular tetrahedron. We remark that the non-monotonic variation of \( T_c \) as a function of \( x \) and \( y \) in LaFe\((As_{1\rightarrow x}P_{x}) (O_{1\rightarrow y}F_{y})\) is attributed to these multiple AFMSFs originating from degenerated multiple 3d orbitals inherent to Fe-pnictide superconductors.

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