Antiferromagnetic Spin Fluctuation above the Superconducting Dome and the Full-Gaps Superconducting State in LaFeAsO$_{1-x}$F$_x$ Revealed by $^{75}$As-Nuclear Quadrupole Resonance

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We report a systematic study by $^{75}$As nuclear-quadrupole resonance in LaFeAsO$_{1-x}$F$_x$. The antiferromagnetic spin fluctuation (AFSF) found above the magnetic ordering temperature $T_N = 58 K$ for $x = 0.03$ persists in the regime of $0.04 \leq x \leq 0.08$ where superconductivity sets in. A dome-shaped $x$-dependence of the superconducting transition temperature $T_c$ is found, with the highest $T_c = 27 K$ at $x = 0.06$ which is realized under significant AFSF. With increasing $x$ further, the AFSF decreases, and so does $T_c$. These features resemble closely the cuprates La$_{2-x}$Sr$_x$CuO$_4$. At $x = 0.06$, the spin-lattice relaxation rate $(1/T_1)$ below $T_c$ decreases exponentially down to 0.13 $T_c$, which unambiguously indicates that the energy gaps are fully-opened. The temperature variation of $1/T_1$ below $T_c$ is rendered nonexponential for other $x$ by impurity scattering.

The discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ at the transition temperature $T_c = 26 K$ has gained much attention in the condensed-matter physics community. The electron doping (F-doping) suppresses the antiferromagnetic ordering at $T_N = 140 K$ in LaFeAsO and high-$T_c$ superconductivity appears[1]. The $T_c$ significantly increases up to 55 K in RFeAsO$_{1-x}$F$_x$ ($R$: Ce, Pr, Nd, Sm) [2, 3]. To elucidate the mechanism of Cooper pairs formation in these arsenides, it is essential to know the superconducting gap symmetry and the normal-state properties. Previous nuclear-magnetic resonance (NMR) and nuclear-quadrupole resonance (NQR) measurements have found that the superconductivity is in the spin-singlet state with multiple gaps [4, 5]. Recent systematic measurements on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [6], CaFe$_2$As$_2$ under pressure [7], LaNiAsO$_{1-x}$F$_x$ [8], and BaFe$_2$(As$_{1-x}$S$_x$)$_2$ [9] have suggested that the antiferromagnetic spin fluctuation (AFSF) originated from their multiple electronic bands correlates with the appearance of the pertinent superconducting properties. On the other hand, there are also reports suggesting that AFSF is not important to realize high $T_c$ [11].

For prototypical LaFeAsO$_{1-x}$F$_x$, several issues remain elusive. One is the role of AFSF. In cuprates, it has been believed that AFSF plays a crucial role to induce high-$T_c$ superconductivity, but the situation in LaFeAsO$_{1-x}$F$_x$ is still unclear [5, 12, 16]. Some previous studies by NMR found no AFSF [12, 13].

The second issue is the doping dependence of $T_c$. It was initially reported that $T_c$ forms a wide plateau at $0.04 \leq x \leq 0.12$ [1], which raises a question about the effect of doping. The third unresolved issue is the superconducting gap symmetry. The spin-lattice relaxation rate $(1/T_1)$ decreases sharply below $T_c$, but the data were insufficient for distinguishing between $d$-wave from sign-reversal $s$-wave [5, 12, 16]. From other experimental probes, some measurements suggested the existence of node [17], but the photoemission spectroscopy and the point contact Andreev reflection measurement suggested a nodeless gap [18, 19].

Here we report results of systematic $^{75}$As NQR studies on LaFeAsO$_{1-x}$F$_x$ ($x = 0.03, 0.04, 0.06, 0.08, 0.10$, and $0.15$). An antiferromagnetic order with $T_N = 58 K$ is found for $x = 0.03$. Bulk superconductivity sets in at $T_c = 21 K$ for $x = 0.04$, with strong AFSF. A dome-shaped $x$-dependence of $T_c$ is found, with the highest $T_c = 27 K$ at $x = 0.06$ which is realized under significant AFSF. With further doping, the AFSF is weakened and disappears for $x \geq 0.10$. Concomitantly, $T_c$ decreases. These features resemble closely the case of cuprates La$_{2-x}$Sr$_x$CuO$_4$, and suggests that the AFSF is important in producing the superconductivity in LaFeAsO$_{1-x}$F$_x$ as well. The systematic observation of the AFSF in the low-doping regime is unprecedented, and the high quality samples enable us to reveal a dome shape of the $T_c$ which has a maximum at quite low $x$. In the superconducting state, $1/T_1$ for $x = 0.06$ decreases exponentially down to $0.13 T_c$, which is clear and direct evidence for a fully-gapped superconducting state. The $T$-variation of $1/T_1$ below $T_c$ is rendered nonexponential for $x$ either smaller or larger than 0.06, showing a seemingly $T^3$ behavior for $x = 0.10$, which is accounted for by impurity scattering.

The polycrystalline samples of LaFeAsO$_{1-x}$F$_x$ ($x = 0.03, 0.04, 0.06, 0.08, 0.10$, and $0.15$) were synthesized by the solid state reaction method [20, 21]. Here, $x$ indicates the nominal composition of the starting material. Quite often, resistivity measurements give a higher $T_c$ than magnetic susceptibility or NQR. We define $T_c$ by the latter methods. ac susceptibility measurements using the in-situ NQR coil indicate $T_c = 21, 27, 23, 18$, and 12 K for $x = 0.04, 0.06, 0.08, 0.10$, and 0.15, respectively. The $1/T_1$ decreases exactly below such-determined $T_c$. The $T_1$ is determined by an excellent fit to the single

node.
exponential curve \(1 - \frac{M(t)}{M(0)} = \exp\left(\frac{-t}{\tau}\right)\) [21], where \(M_0\) and \(M(t)\) are the nuclear magnetization in the thermal equilibrium and at a time \(t\) after the saturating pulse, respectively.

Figure 1 (a) shows the \(^{75}\text{As-NQR}\) spectrum for LaFeAsO\(_{1-x}\)F\(_x\) measured above \(T_c\). Data for \(x = 0.08\) are from Ref. [5]. Solid curves are Lorentzian fittings which give a FWHM of \(\sim 0.95, 1.2, 1.8,\) and \(2.3\) MHz for \(x = 0.06, 0.08, 0.10,\) and \(0.15,\) respectively. (b) The spectra above and below \(T_N = 58\) K for \(x = 0.03,\) 0.04 and 0.06 (a) and for \(x = 0.08, 0.10,\) and 0.15 (b). Data for \(x = 0.03\) were collected at the high-frequency (H) NQR peaks. For \(x = 0.04, 1/T_1\) was measured at both the low-frequency (L) and the H peak. Solid curves below \(T_c\) for \(x \geq 0.04\) are the simulations based on a \(s^\pm\) wave superconducting gap model with impurity scattering (see the text). The dashed line indicates the relation \(1/T_1 \propto T^3\). The dotted and solid arrows indicate \(T_N\) and \(T_c\), respectively.

Before going into the detail of the superconducting state, we first discuss the normal-state property. For this purpose, we plot \(1/T_1 T\) vs \(T\) in Fig. 3. None of the samples shows a Korringa relation \(1/T_1 T = \text{const.}\) expected for a conventional metal. Above \(T_N\) of \(x = 0.03, 1/T_1 T\) increases with decreasing \(T\) due to the AFSC. Such AFSC persists in \(x = 0.04, 0.06,\) and 0.08, where \(1/T_1 T\) increases with decreasing \(T\) down to \(T_c\). To model the \(1/T_1 T\) above \(T_N\) or \(T_c\), we employed the theory for a weakly antiferromagnetically-correlated metal [22], \(1/T_1 T = (1/T_1 T)_\text{AF} + (1/T_1 T)_\theta = C/(T + \theta) + (1/T_1 T)_0\). Here, the first term described the contribution from the antiferromagnetic wave vector, and the second term is the contribution from the density of states (DOS) at the Fermi level. For \(x = 0.03, \theta\) is simply \(-T_N\), where the data can be well fitted except around \(T_N\) [24]. As seen in Fig. 3, \(1/T_1 T\) for \(x = 0.04, 0.06,\) and 0.08 are well
The present phase diagram is consistent with the broader (in fact, two-peak-featured) NQR spectrum [29]. Therefore, a maximal AF breaking [27]. The inset is the enlarged part for 0.06. The dotted line is a guide to the eyes. The shade indicates the region of phase separation. (b) $x$ dependence of $T_N$ and $T_c$ determined by NQR measurements.

FIG. 4: (color online) Phase diagram obtained in this study. AF and SC denote the antiferromagnetically ordered and superconducting states, respectively. (a) $x$ dependence of $\theta$. The dotted line is a guide to the eyes. The shade indicates the region of phase separation. (b) $x$ dependence of $T_N$ and $T_c$ determined by NQR measurements.

FIG. 3: (color online) $T$ dependence of $1/T_1 T$ for various $x$. The curves above $T_N$ or $T_c$ are fits to the AFSF theory (see the text). The inset is the enlarged part for 0.06 $\leq x \leq 0.15$.

replicated by this model with $\theta \sim 10$, 25 and 39 K, respectively. The low-frequency NQR peak for $x = 0.04$ gives a smaller $\theta \sim 5$ K. The increase of $\theta$ with increasing $x$ means that the system moves away from the magnetic instability (MI) where $\theta = 0$ K. With further doping, for $x = 0.10$ and 0.15, no enhancement of $1/T_1 T$ is seen. Instead, $1/T_1 T$ decreases with decreasing $T_c$, which was recently explained by the loss of the DOS due to a topological change of the Fermi surface [9, 25]. The results in previous reports of the lack of the AFSF for $x \geq 0.10$ [12, 13, 15] are consistent with our results for $x = 0.10$ and 0.15.

The remarkable finding is that the highest $T_c = 27$ K is realized at $x = 0.06$, which is away from the MI. This situation is quite similar to the cuprates La$_{2-x}$Sr$_x$CuO$_4$ [26]. In the scenario of spin fluctuation-mediated superconductivity, this can be understood as follows. At high doping levels, the decrease of $T_c$ is due to the weakening of the AFSF. In the vicinity of the MI, on the other hand, the too strong low-energy fluctuation acts as pair breaking [22]. Therefore, a maximal $T_c$ is realized at some point away from the MI with moderate AFSF.

Figure 4 shows the phase diagram for LaFeAsO$_{1-x}$F$_x$ obtained in the present study. The most important finding is that the highest $T_c$ is found in the low-doping regime, which makes our $T_c$ vs $x$ relation look like a dome shape. In the previous study [1, 28], the failure of obtaining higher $T_c$ in the low-doping regime is probably due to sample inhomogeneity as evidenced by the broader (in fact, two-peak-featured) NQR spectrum [29]. The present phase diagram is consistent with that for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [7] but is somewhat different from that for BaFe$_2$(As$_{1-x}$P$_x$)$_2$ [10], whose $T_c$ shows a maximum around $\theta = 0$. This slight difference may originate from the difference of the tuning parameter for their ground states. The ground states for both LaFeAsO$_{1-x}$F$_x$ and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ are tuned by electron doping. On the other hand, isovalent P doping acts as chemical pressure on BaFe$_2$(As$_{1-x}$P$_x$)$_2$. In any case, these phase diagrams support the intimate relationship between AFSF and superconductivity in iron arsenides. Furthermore, such a phase diagram has consistently been found in high-$T_c$ cuprate La$_{2-x}$Sr$_x$CuO$_4$ [26] and heavy fermion compounds [30], indicating that the AFSF plays a significant role to induce superconductivity in strongly correlated electron systems in general.
the solid line, the $1/T_1$ below $T \sim 0.4 T_c$ clearly follows the relation $1/T_1 \propto \exp(-\Delta_0/k_B T)$ with $\Delta_0/k_B T_c = 1.8$, where $\Delta_0$ and $k_B$ denote the gap size at $T = 0$ and the Boltzmann constant, respectively. This is clear and direct evidence that the superconducting state is fully gapped in LaFeAsO$_{0.94}$F$_{0.06}$.

The evolution of the superconducting-state properties can be seen in Fig. 2. For $x = 0.06$-0.10, $1/T_1$ shows a marked hump structure around $T \sim 0.4 T_c$ and is followed by a still sharper decrease below. However, the low-$T$ behavior of $1/T_1$ changes gradually, as to decrease less and less steeply as $x$ increases. Eventually, for $x = 0.15$, the hump structure disappears completely. Instead, a simple $T$ dependence emerges which is close to $T^3$. Such $T^3$ behavior has been reported previously [12–14] and was taken as evidence for line nodes. Below we show that it is a consequence of impurity scattering. Namely, the $T^3$ is an accidental one rather than an intrinsic one. In fact, in Ba$_{1-x}$K$_x$Fe$_2$As$_2$, the low-$T$ behavior of $1/T_1$ also changes when the sample purity differs [6, 31].

Assuming sign reversing s-wave symmetry [32, 33] with impurity scattering, one can reproduce the evolution of the $1/T_1$ below $T_c$. By introducing the impurity scattering parameter $\eta$ in the energy spectrum in the form of $E = \omega + i\eta$, the $1/T_1$ in the superconducting state is given by

$$\frac{T_c}{T_1(T)} = \frac{T_c}{T_1(0)} \frac{1}{\exp(\Delta/k_B T)} \int_{-\infty}^{\infty} \frac{d\omega}{\cosh(\Delta/k_B T)} (W_{GG} + W_{FF})$$

where

$$W_{GG} = \left[\langle |\Delta(\omega + i\eta)|^2 + |\Delta(\omega - i\eta)|^2 \rangle \right]_{k_F}$$

and

$$W_{FF} = \left[\langle |\Delta(\omega + i\eta)|^2 + |\Delta(\omega - i\eta)|^2 \rangle \Delta(\omega + i\eta) \Delta(\omega - i\eta) \right]_{k_F} \right)^2.$$

Here the $\Delta$ is the gap parameter, and $\langle \cdots \rangle$ is the average over the entire Fermi surface, and runs over three bands consisting of two hole pockets at the $\Gamma$ point and an electron pocket at the $M$ point, respectively [33]. Namely, for a quantity $F$, $\langle F \Delta(k_F) \rangle_{k_F} = [N_i F(\Delta_1^+ + N_2 F(\Delta_2^-) + N_3 F(\Delta_3^-)) / (N_1 + N_2 + N_3)]$, where $N_i$ is the DOS coming from band $i$ ($i = 1, 2, 3$). Here, it is tempting to assign bands 1, 2, and 3 to the $\gamma, \beta$, and $\alpha$ bands found in angle-resolved photoemission spectroscopy measurement [30]. It is noted that the weaker $T$ dependence in the $x = 0.15$ sample can be understood as due to the impurity scattering that brings about a finite DOS. For $x = 0.04$ where two As sites were found, $1/T_1$ for each site can also be fitted by the same model, with an additional feature that a large $\eta$ is needed to explain the low-$T$ behavior. This can be understood if the two phases coexist in the nanoscale [22], where one phase acts as an impurity scatterer for the other. The obtained fitting parameters are summarized in Table 1. Finally, we note that an $s^+$-wave [37] seems difficult to explain the lack of the coherence peak just below $T_c$ and the $x$ evolution of low-$T$ behavior of $1/T_1$.

In conclusion, we have presented the results of systematic NQR measurements on high quality samples of LaFeAsO$_{1-x}$F$_x$ ($x = 0.03, 0.04, 0.06, 0.08, 0.10$, and 0.15). The AF SF seen above $T_N = 58 \text{ K}$ of $x = 0.03$ persists in the $0.04 \leq x \leq 0.08$ regime. The highest $T_c = 27 \text{ K}$ is realized for $x = 0.06$ which is away from the magnetic instability but with significant AF SF. The phase diagram closely resembles those of the cuprates La$_{2-x}$Sr$_x$CuO$_4$ and other iron arsenides, which suggests that the AF SF is also important to produce the superconductivity in LaFeAsO$_{1-x}$F$_x$. In $x = 0.06$, $1/T_1$ below $T_c$ decreases exponentially down to 0.13 $T_c$, which unambiguously indicates that the superconducting gaps are fully-opened. The $T$-variation of $1/T_1$ below $T_c$ is rendered nonexponential for $x$ either smaller or larger than 0.06, which is accounted for by impurity scattering.

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