Evolution from Itinerant Antiferromagnet to Unconventional Superconductor with Fluorine Doping in La(O$_{1-x}$F$_x$)FeAs Revealed by $^{75}$As and $^{139}$La Nuclear Magnetic Resonance

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We report experimental results of $^{75}$As and $^{139}$La nuclear magnetic resonance (NMR) in the iron-based layered La(O$_{1-x}$F$_x$)FeAs ($x = 0.0, 0.04$ and $0.11$). In the undoped LaOFeAs, $1/T_1$ of $^{139}$La exhibits a distinct peak at $T_N \sim 142$ K below which the spectra become broadened due to the internal magnetic field attributed to an antiferromagnetic (AFM) ordering. In the 4% F-doped sample, $1/T_1T$ exhibits a Curie-Weiss temperature dependence down to 30 K, suggesting the development of AFM spin fluctuations with decreasing temperature. In the 11% F-doped sample, in contrast, pseudogap behavior is observed in $1/T_1T$ both at the $^{75}$As and $^{139}$La site with a gap value of $\Delta_{PC} \sim 172$ K. The spin dynamics vary markedly with F doping, which is ascribed to the Fermi-surface structure. As for the superconducting properties for the 4% and 11% F-doped samples, $1/T_1$ in both compounds does not exhibit a coherence peak just below $T_c$ and follows a $T^3$ dependence at low temperatures, which suggests unconventional superconductivity with line-nodes. We discuss similarities and differences between La(O$_{1-x}$F$_x$)FeAs and cuprates, and also discuss the relationship between spin dynamics and superconductivity on the basis of F doping dependence of $T_c$ and $1/T_1$.

KEYWORDS: LaOFeAs, superconductivity, NMR

The recent discovery of iron-based layered superconductor La(O$_{1-x}$F$_x$)FeAs has opened up a new route to high-temperature superconductivity, because it has been reported that superconducting transition temperature $T_c$ of R(O$_{1-x}$F$_x$)FeAs ($R$: rare-earth) raises up to $\sim 50$ K, which is the highest other than high-$T_c$ cuprates. The crystal structure of La(O$_{1-x}$F$_x$)FeAs is tetragonal ($P4/nmm$), and consists of the LaO and FeAs layers which are stacked along the $c$ axis. Therefore, the physical properties are considered to be highly two dimensional, similar to the cuprate, ruthenate and cobaltate superconductors. Comparing between the Fe-based and cuprate superconductors, we notice their similarities and differences. One of similarities is that superconductivity of the two compounds is induced when carriers are introduced by means of elemental substitutions. In La(O$_{1-x}$F$_x$)FeAs, superconductivity emerges when 4% F is doped to LaOFeAs. On the other hand, one of differences is that the parent compound LaOFeAs is metallic in contrast to the Mott insulator La$_2$CuO$_4$, although LaOFeAs shows AFM ordering around 150 K.$^7,1,6,8$ Other difference is that $T_c$ seems to be insensitive to $x$, i.e., $T_c$ remains almost unchanged from $x = 0.04$ to 0.11.$^1$ The F-concentration dependence of $T_c$ is in contrast with the “dome dependence” of $T_c$ in the hole-doped cuprates. In order to shed light on magnetic properties in the undoped LaOFeAs and on their evolution with F doping as well as superconducting (SC) properties, we have performed La- and As-NMR measurements in La(O$_{1-x}$F$_x$)FeAs. In this paper, we mainly report temperature dependence of spin-lattice relaxation rate $1/T_1$, which is related to the wave vector $q$-averaged dynamical susceptibility. We show that LaOFeAs is an itinerant antiferromagnet with $T_N \sim 142$ K from the $T$-dependence of $1/T_1$. The magnetic ordering is suppressed by F doping, and is not observed in the SC samples. The magnetic fluctuations revealed by $1/T_1$ of As vary significantly with F doping, although $T_c$ is insensitive to F concentration. $1/T_1$ in the SC samples suggests that La(O$_{1-x}$F$_x$)FeAs is an unconventional superconductor with line-nodes in the SC gap. We consider that competition between itinerant antiferromagnetism and unconventional superconductivity also exists in the La(O$_{1-x}$F$_x$)FeAs system, as in unconventional superconductors realized in strongly correlated electron systems. Polycrystalline samples of La(O$_{1-x}$F$_x$)FeAs ($x = 0.04$ and $0.11$) synthesized by solid-state reactions$^4$ are ground into powder for NMR measurements. $T_c$ for $x = 0.04$ and 0.11 determined from the onset of the SC transition with ac susceptibility is 17.5 K and 22.7 K, respectively.

Figure 1(a) shows $^{139}$La($I = 7/2$)-NMR spectra for $x = 0.04$, and 0.11 in La(O$_{1-x}$F$_x$)FeAs obtained by sweeping magnetic field at a fixed frequency 15.35 MHz. In the 4% and 11% F-doped samples which exhibit superconductivity, typical powder-pattern NMR spectra broadened by the first-order electric-quadrupole interaction are observed, which consist of seven peaks. The pow-
A little anomaly of the susceptibility around 150 K, and the central peak arising from the hyperfine field from La site arises from the hyperfine field from La site. The dotted line is a fit to the SCR theory for weak itinerant antiferromagnet. The inset shows a plot of $T_1 T$ as a function of $T$, indicating an abrupt drop around $\sim 160$ K.

The recovery curves $m(t)$ of the nuclear magnetization of La in LaOF$_{e}$As fitted uniquely with $m(t) = 0.0119 e^{-(T/T_1)} + 0.0682 e^{-(6T/T_1)} + 0.2061 e^{-(15T/T_1)} + 0.7137 e^{-(28T/T_1)}$ (dotted lines).

dependence of $1/T_1$ in Fig. 2 can be fitted to the SCR theory for weak itinerant antiferromagnets:

$$\frac{1}{T_1} = \left\{ \begin{array}{ll} a T + b T / \sqrt{T - T_N} & T > T_N \\ c T / M(T) & T < T_N \end{array} \right.$$  

where $a = 0.005$ (sK)$^{-1}$, $b = 0.13$ s$^{-1}$K$^{-1/2}$ and $c/M_0 = 0.02$ (sK)$^{-1}$ are fitting parameters, and $M(T) = M_0(1-T/T_N)^{a}$. is the AFM order parameter mentioned above. The first term in (1) comes from usual Korringa relaxation expected in a metal. It is noteworthy that $1/T_1$ related to the $q$-averaged dynamical susceptibility shows a divergence at 142 K whereas a clear anomaly is not observed in the static susceptibility. These are characteristic of an itinerant antiferromagnet as seen in $V_3$Se$_4$, in which the ordered $q$-vector is far from $q = 0$. Although
the SCR expression roughly captures the behavior of \(1/T_1\) in LaOFeAs, the sharp decrease of \(1/T_1\) just below \(T_N\) cannot be reproduced with the expression. This reflects a structural phase transition from the tetragonal (\(P4/nmm\)) to orthorhombic (\(Cmca\)) at \(\sim 165\) K observed in the same batch sample as ours. In fact, the plot of \(T_1/T\) against \(T\) shown in the inset of Fig. 2 suggests that the magnetic fluctuations change around \(160\) K where the structural phase transition occurs. One of the plausible scenarios for the occurrence of the magnetic ordering below the structural phase transition is that the cylindrical Fermi surfaces are distorted, and thus the nesting between Fermi surfaces are enhanced. To check this scenario, it is designed to investigate the relation between the structural transition temperature and \(T_N\) with the same technique. Quite recently, it has been reported that the neutron scattering measurements revealed a small ordered moment 0.4 \(\mu_B/\text{Fe}\) in LaOFeAs below 134 K, which is slightly lower than the lattice anomalous temperature 155 K. Our La NMR results are consistent with this neutron-scattering measurement.\(^7\)

Next, we turn to \(^{75}\)As-NMR results on the SC F-doped compounds. Figure 5 shows the \(T\)-dependencies of \(1/T_1/T\) of As for \(x = 0.04\) and 0.11, in which \(T_1\) was measured at the intense peak of the central transition obtained in the fixed frequency of 72.1 MHz (see the inset of Fig. 4). Figure 4 shows the recovery curves \(m(t)\) at 80 and 6 K of 11\% F-doped sample. A single component of \(T_1\) was consistently derived from \(m(t)\) above 30 K, below which a short component of \(T_1\) appears gradually. The behavior of \(1/T_1/T\) for \(x = 0.04\) is strikingly different from that for \(x = 0.11\), suggesting that magnetic fluctuations strongly depend on the F-concentration. 1/T_1/T for \(x = 0.04\) increases with decreasing temperature down to \(\sim 30\) K. The \(T\)-dependence of \(1/T_1/T\) follows a Curie-Weiss law \(1/T_1/T \propto C/(T + \theta)\) between 30 and \(200\) K, which is clearly seen in the inset of Fig. 5. The obtained Weiss temperature is \(\theta = 10.3 \pm 2\) K, indicating that the \(1/T_1/T\) does not diverge at a finite temperature. This suggests that the superconductivity in the F-doped La(O_{1-x}Fe_x)FeAs emerges when a magnetic ordering is suppressed. This tendency is similar to that in 1/T_1/T of Cu in underdoped La_{2-x}Sr_xCuO_4,\(^{12}\) where superconductivity appears when a Weiss temperature obtained from 1/T_1/T becomes positive.

Markedly different spin-dynamics from that for \(x = 0.04\) is observed for \(x = 0.11\), as shown in Fig. 6. 1/T_1/T both at the \(^{75}\)As and \(^{139}\)La site decreases with lowered temperature, which is reminiscent of the pseudogap behavior in underdoped regime of high-\(T_c\) cuprates e.g. underdoped YBa_2Cu_3O_{6.6},13 and YBa_2Cu_3O_8,\(^{14}\) and approaches a nearly constant value in a narrow \(T\)-region
just above $T_c$. The dashed line in Fig. 6 is a fit to
\[ \frac{1}{T_1 T} = A + B \exp(-\Delta_{PG}/T), \]
where $A = 0.04 (sK)^{-1}$, $B = 0.17 \pm 0.01 (sK)^{-1}$, and $\Delta_{PG} = 172 \pm 17$ K. Recent $^{19}$F NMR measurements also report pseudogap behavior for $x = 0.11$. However, we point out a difference between the pseudogap behavior for $x = 0.11$ and that in the underdoped cuprate. In the cuprate, $1/T_1 T$ decreases from far above $T_c$ and no clear anomaly is observed at $T_c$. In contrast, for $x = 0.11$, the Korringa behavior ($T_1 T = \text{const.}$) is observed in the narrow $T$-region from 30 K to $T_c$, which is related to the $T^2$ behavior of the resistivity, and the clear anomaly of $1/T_1 T$ is found at $T_c$. These behaviors for $x = 0.11$ are related to the multiband nature of the Fermi surfaces. We consider that the pseudogap originates from one of the multibands, and that the superconductivity is related with a band without showing the pseudogap. The inset shows the plot of $1/T_1 T$ of La against $1/T_1 T$ of As. A good linear relation indicates the spin dynamics at both sites are determined by the same fluctuations arising from the Fe-3$d$ spins. From the linear coefficient $\langle 1/T_1 T \rangle \sim 0.135 \times \langle 1/T_1 T \rangle$, the ratio between the hyperfine coupling constant, $H_{hf}/H_{hf}$, is estimated to be $0.45$, showing that the coupling between two layers is not so small.

Next, we discuss the SC-gap properties from the $T$-dependence of $1/T_1 T$ in the SC state. Figure 7 shows the $T$-dependence of $1/T_1 T$ of As for $x = 0.04$ and 0.11, together with $1/T_1 T$ of La in the undoped LaOFcAs. In this figure, $1/T_1 T$ of La is normalized by the relation $\langle 139/1/T_1 T \rangle \sim 0.135$. As noted above, a short component of $T_1$ appears gradually in both samples below 30 K and its fraction increases with decreasing $T$. Since the short component in $m(t)$ is about 30% at 6 K for $x = 0.11$, the main component (corresponding to the longer component) of $T_1$ is shown in Fig. 7. We observed $T^3$ dependence of $1/T_1 T$ in the SC state for $x = 0.04$ and 0.11, suggesting that the SC gap has line-nodes. We also found that $1/T_1 T$ decreases suddenly without showing Hebel-Slichter (coherence) peak. In general, a tiny coherence peak remains in anisotropic s-wave SC with a line-node gap $(\Delta(\phi) = |\Delta_0 \sin(2\phi)|)$, since the coherence factor does not vanish when the gap function is integrated over the Fermi surfaces. The sharp decrease of $1/T_1 T$ just below $T_c$ and $T^3$ dependence in the SC state suggest that the superconductivity in La$(O_{1−x}F_x)$FeAs is classified into a non s-wave type. The observed $T^3$ dependence of $1/T_1 T$ for $x = 0.11$ can be reproduced using a 2-D line-node $(\Delta(\phi) = \Delta_0 \sin(2\phi))$ model with $2\Delta/k_B T_c = 4.0$. However, we point out that a residual density of states (DOS), which is suggested from the Korringa behavior at low temperatures, is not observed in both samples. In non s-wave superconductors, the residual DOS is usually induced by impurities and crystal imperfections. Since the absence of residual DOS appears to be contrary to non s-wave models, further NMR measurements using high quality samples are important in order to fully determine the SC symmetry.

Finally, we would like to discuss the evolution of the spin dynamics in the normal state with F doping (corresponding to electron doping) and the relationship between magnetic fluctuations and superconductivity. From the Fermi-surface structure, it is considered that there exists two different kinds of fluctuations in this system, e.g. the fluctuations arising from the interband and intraband scatterings. The former gives rise to the AFM fluctuations and the latter induces the fluctuation near $q = 0$. The AFM fluctuations observed in the undoped and 4% F-doped samples are considered to originate from the interband fluctuations. Upon F doping, such AFM fluctuations disappear in the 11% F-doped sample due to the shrinkage of the hole Fermi surfaces by the electron doping. Almost constant value of $T_c$ against the F concentration, irrelevant to the drastic change of $1/T_1 T$ in the normal state, suggests that the superconductivity is related to the intraband fluctuations of the electron Fermi surfaces. For further insight on the relation between magnetic fluctuations and superconductivity, $^{57}$Fe NMR measurements are needed.

In conclusion, the present NMR study revealed that an itinerant antiferromagnet in LaOFcAs evolves into superconductors with F doping. The spin fluctuations vary markedly with F doping, i.e. the strong AFM behavior for $x = 0.04$ and the pseudogap behavior for $x = 0.11$. The observed $T$-dependence of $1/T_1 T$ suggests unconventional superconductivity with a line-node SC gap in F-doped La$(O_{1−x}F_x)$FeAs.

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