An NMR study on the F-doping evolution of the iron oxypnictide $\text{LaFeAs}(O_{1-x}F_x)$

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Abstract. We report the experimental results of $^{75}\text{As}$ and $^{139}\text{La}$ nuclear magnetic resonance (NMR) in the layered oxypnictide system $\text{LaFeAs}(O_{1-x}F_x)$ ($x = 0.0, 0.04, 0.07, 0.11$ and $0.14$) where superconductivity occurs at $x \gtrsim 0.03$. In the undoped $\text{LaFeAsO}$, $1/T_1$ of $^{139}\text{La}$ exhibits a distinct peak at $T_N \sim 142$ K below which the La-NMR spectra become broadened due to the internal magnetic field attributed to an antiferromagnetic (AFM) ordering. In the $x = 0.04$ sample, $1/T_1 T$ of $^{75}\text{As}$ exhibits a Curie–Weiss temperature dependence down to 30 K, suggesting the development of AFM spin fluctuations with a decrease in temperature. At $x = 0.11$ and 0.14, in contrast, pseudogap behavior is observed in $1/T_1 T$ at the $^{75}\text{As}$ site with a gap value of $\Delta_{\text{pg}} \sim 175$ and 165 K, respectively. The spin dynamics vary markedly with F-doping, which is ascribed to the change of the Fermi-surface structure because of the electron doping. As for the superconducting properties for $x = 0.04, 0.07$ and 0.11, the $1/T_1$ of $^{75}\text{As}$ in the three samples does not exhibit a coherence peak just below $T_c$ and follows a $T^3$ dependence at low temperatures. These results may suggest unconventional superconductivity with a zero gap along the lines, but neither the

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field-induced extra relaxation rate nor the residual density of states at the low temperatures is incompatible with the presence of the line nodes. We discuss the similarities and differences between LaFeAs(O$_{1-x}$F$_x$) and cuprates and also discuss the relationship between spin dynamics and superconductivity on the basis of the F-doping dependence of $T_c$ and $1/T_1$.

Contents

1. Introduction 2
2. Experimental results and discussion 2
   2.1. $^{139}$La NMR in LaFeAs(O$_{1-x}$F$_x$) 3
   2.2. $^{75}$As NMR in superconducting LaFeAs(O$_{1-x}$F$_x$) 6
3. Conclusion 14
Acknowledgments 14
References 14

1. Introduction

The discovery of the iron-based layered superconductor LaFeAs(O$_{1-x}$F$_x$) has opened a new route to high-temperature superconductivity [1], because it has been reported that the superconducting transition temperature $T_c$ of RFeAs(O$_{1-x}$F$_x$) ($R$ = Ce, Pr, Sm and Nd) rises to $\sim$55 K, which is the highest except for high-$T_c$ cuprates [2]–[4]. The crystal structure of LaFeAs(O$_{1-x}$F$_x$) is tetragonal ($P4/nmm$) and it consists of LaO and FeAs layers that are stacked along the $c$-axis, as shown in figure 1. The physical properties are considered to be highly two-dimensional (2D), similar to the case of cuprate, ruthenate and cobaltate superconductors [5, 6]. Comparing the Fe-based and cuprate superconductors, we notice similarities and differences between them. One of the similarities is that superconductivity is induced by doping. In LaFeAs(O$_{1-x}$F$_x$), superconductivity emerges when LaFeAsO is doped with 3% F. On the other hand, one of the differences is that the mother compound LaFeAsO is metallic in contrast to the Mott insulator La$_2$CuO$_4$, although LaFeAsO shows antiferromagnetic (AFM) ordering at about 150 K as shown later [7]–[9]. Another difference is that $T_c$ is not so sensitive to $x$, i.e. $T_c$ remains almost unchanged from $x$ = 0.04 to 0.11 [1]. The $T_c$ dependence on F-concentration is in contrast to the ‘dome dependence’ of $T_c$ in the hole-doped cuprates.

In order to shed light on the magnetic properties of undoped LaFeAsO and their evolution by F-doping as well as the superconducting properties, we have performed $^{139}$La- and $^{75}$As-nuclear magnetic resonance (NMR) measurements on LaFeAs(O$_{1-x}$F$_x$). In this paper, we report on the temperature dependence of the spin-lattice relaxation rate $1/T_1$ in the various F-doping compounds, which is related to the wave vector $q$-averaged dynamical susceptibility at low energies. Some of the experimental data have already been published [10].

2. Experimental results and discussion

Polycrystalline samples of LaFeAs(O$_{1-x}$F$_x$) ($x$ = 0.0, 0.04, 0.07, 0.11 and 0.14) synthesized by solid-state reactions [1] were ground into a powder for the NMR measurements. All the samples were examined by powder x-ray diffraction (XRD; Bruker D8 Advance TXS) with Cu Kα radiation, indicating that all the samples are mostly composed of a single phase. The contents
Figure 1. Crystal structure of LaFeAs(O$_{1-x}$F$_x$). For the drawings, the software Vesta was used [44].

of the dopant ($x$) were determined from lattice constants using Vegard’s volume rule [11]. Electrical resistivity ($\rho$) measurements were performed using the usual four-probe technique, and the temperature dependence of $\rho$ is shown in figure 2. The $T_c$’s determined from the zero resistivity are 16.3, 22.5, 22.5 and 12.5 K for $x = 0.04$, 0.07, 0.11 and 0.14, and the $T_c$ values determined by the onset of the Meissner signal are 17.5, 22.5 and 22.7 K for $x = 0.04$, 0.07 and 0.11, respectively. Two independent measurements reasonably coincided with each other.

2.1. $^{139}$La NMR in LaFeAs(O$_{1-x}$F$_x$)

Figure 3 shows the $^{139}$La ($I = 7/2$)-NMR spectra for undoped LaFeAsO obtained by sweeping an external field at a fixed frequency of 15.35 MHz. In general, when an electric field gradient is present at the La site, an La-NMR spectrum consists of seven peaks arising from ($m \leftrightarrow m - 1$) (where $m = 7/2$, 5/2, . . . and $-5/2$) transitions due to the electric–quadrupole interaction [12]. However, quite a different $^{139}$La-NMR spectrum is observed in undoped LaFeAsO at 10 K; the central peak arising from the 1/2 $\leftrightarrow$ $-1/2$ transition is split due to the internal magnetic field at the La site. With an increase in the temperature, the splitting of the NMR spectrum denoted by the two red arrows in figure 2 decreases gradually, and typical powder-pattern spectra consisting of seven transitions were observed above 150 K. The observed spectrum for the undoped LaFeAsO suggests an AFM ordering below $\sim$150 K, which is consistent with an anomaly of the electrical resistivity and susceptibility at about 150 K [1]. A similar temperature variation of the $^{139}$La-NMR spectra in LaFeAsO was also observed by Mukuda et al [13]. The $^{139}$La-NMR spectrum clearly indicates that the undoped LaFeAsO is in a magnetically ordered state below $\sim$150 K.

The internal field at the La site arises from the hyperfine field from adjacent Fe atoms, and is related to the Fe ordered moments. The internal field $H_{int}$ determined from the
Figure 2. Temperature dependence of resistivity $\rho$ in LaFeAs(O$_{1-x}$F$_x$). The inset is a plot of $\rho$ against $T^2$.

half-width of the splitting is shown in figure 4 (filled circles). From the As-NMR study on single-crystal BaFe$_2$As$_2$, it was revealed that the $c$-axis internal field arises at the As site in the ordered state with the stripe-type magnetic structure [14, 15] suggested by the neutron-scattering measurement [8]. Thus, the direction of $H_{\mathrm{int}}$ is considered to be the $c$-axis, since the La site is in the same geometrical configuration as the As site with respect to the magnetic Fe site. The dashed line in figure 4 is a fit to the following expression: $M(T)/M_0 = [1 - (T/T_N)]^{0.15}$. The growth of $M(T)/M_0$ below $T_N$ is much steeper than the 3D mean field value (0.5), and the transition to the AFM state is almost first-order-like. We consider that the two-dimensionality of magnetic fluctuations is also responsible for the reduced value of the critical exponent. A similar rapid growth was actually reported in the cuprate antiferromagnet La$_2$CuO$_4$ with a critical exponent $\beta \sim 0.1$ [16], which possesses magnetic fluctuations of 2D nature.

Further insights into the magnetic properties of the undoped LaFeAsO were obtained from $1/T_1$ measurements. Figure 4 shows the temperature dependence of $1/T_1$ of $^{139}$La, which was measured at $H = 2.54$ T in the $^{139}$La-NMR spectrum. $1/T_1$ exhibits a divergence at $T_N = 142$ K, and the overall temperature dependence of $1/T_1$ in figure 4 is fitted to the self-consistent renormalization (SCR) theory for weak itinerant antiferromagnets [17]:

$$\frac{1}{T_1} = \begin{cases} aT + bT/\sqrt{T - T_N}, & T > T_N, \\ cT/M(T), & T < T_N, \end{cases}$$

(1)
Figure 3. Field-sweep $^{139}$La-NMR spectra at a series of temperatures through $T_N \sim 142$ K in undoped LaFeAsO. The spectra have been offset vertically. The arrows indicate the fields at which we measured the internal magnetic field.

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 $M(T) = M_0(1 - T/T_N)^{0.15}$ is an AFM order parameter as mentioned above. The first term in (1) comes from the usual Korringa relaxation expected in a metal. It is worth noting that the $1/T_1$ 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 the characteristic features of an itinerant antiferromagnet observed in V$_3$Se$_4$, in which the ordered $q$-vector is far from $\vec{q} = 0$ [18].

Although the SCR expression roughly captures the behavior of $1/T_1$ in the undoped LaFeAsO, the sharp decrease of $1/T_1$ below $T_N$ cannot be reproduced by the expression. The discontinuous decrease of $1/T_1$ and the abrupt increase of $H_{int}$ were observed in single-crystal BaFe$_2$As$_2$ and CaFe$_2$As$_2$ [14, 15, 19] in which the structural and magnetic transitions occurs simultaneously with a first-order character. Therefore, the sharp decrease of $1/T_1$ and the abrupt increase of $H_{int}$ below $T_N$ suggest that the magnetic transition in LaFeAsO possesses a first-order-like character, although a hysteresis behavior through the magnetic transition temperature was not reported. It should be noted that the divergence of $1/T_1$ is affected by a structural
Figure 4. $T$-dependence of $1/T_1$ ($\circ$) and the internal magnetic field ($\bullet$) of undoped LaFeAsO ($x = 0$). The dotted line is a fit to the SCR theory for weak itinerant antiferromagnets (see text).

phase transition from the tetragonal ($P4/nmm$) to the orthorhombic ($Cmma$) occurring at 165 K upon cooling, which was observed by synchrotron x-ray diffraction in the same batch sample as ours [9]. In fact, as shown in figure 5, $1/T_1$ starts to increase just below 160 K, where the resistivity shows a kink due to this structural transition. It was found that the temperature derivative of the resistivity shows a sharp peak at $T_N$ determined by the peak of $1/T_1$. The $1/T_1$ result indicates that the characteristic frequency of the magnetic fluctuations starts to decrease below 160 K, where the structural transition occurs and becomes static below 142 K. The relationship between the structural and magnetic transitions suggests the importance of the spin Jahn–Teller effect in LaFeAsO, where the direction of the ordered moments is determined to lower the magnetic energy after the crystal distortion occurs. To understand the origin of magnetic ordering, it is necessary to investigate the relationship between the structural transition temperature and $T_N$ with the same technique in various samples.

The present $^{139}$La-NMR results are in good agreement with the neutron-scattering results [8]. The neutron-scattering measurements revealed a small ordered moment, 0.37 $\mu_B$/Fe, with the stripe-type magnetic structure $Q = (\pi, 0)$ in the ‘unfolded’ Brillouin zone in the undoped LaFeAsO below 134 K, which is slightly lower than the lattice anomalous temperature, 155 K.

2.2. $^{75}$As NMR in superconducting LaFeAs(O$_{1-x}$F$_x$)

Next, we turn to the $^{75}$As ($I = 3/2$)-NMR results for the superconducting compounds. Figure 6 shows the $^{75}$As-NMR spectra of the $x = 0.11$ powder sample at 30 K obtained by sweeping a magnetic field at 72.1 MHz. Note that this powder sample is mostly aligned along the $ab$-plane.
parallel to the field, which was inferred from the NMR line shape of an aligned sample. From a split between the first-satellite peaks in the $^{75}$As-NMR spectrum, we evaluated the nuclear quadrupole resonance (NQR) frequency to be about 11 MHz, which is in good agreement with previous reports [13, 20]. Actually, an NQR signal arising from the $\pm 1/2 \leftrightarrow \pm 3/2$ transition was observed, as shown in the inset of figure 6.

$1/T_1$ of $^{75}$As was measured at the intense peak of the central transition in figure 6, which corresponds to the applied field along the $ab$-plane. A single component of $T_1$ was consistently derived above 30 K, below which a short component of $T_1$ appears gradually [10]. Figure 7 shows the $T$-dependence of $1/T_1 T$ of $^{75}$As for $x = 0.04, 0.07, 0.11$ and 0.14. The $T$-dependence of $1/T_1 T$ above $T_c$ is markedly changed by F-doping, indicating that magnetic fluctuations strongly depend on F-doping. $1/T_1 T$ for $x = 0.04$ increases with a decrease in temperature down to $\sim 30$ K although the bulk susceptibility $\chi(q = 0)$ monotonically decreases below room temperature [21], and follows a Curie–Weiss law $1/T_1 T = C/(T + \theta)$ between 30 and 200 K with $C = 44$ (sK)$^{-1}$ and $\theta = 10.2$ K. These are the characteristics of the presence of AFM fluctuations away from $q = 0$. A similar Curie–Weiss behavior in $1/T_1 T$ was observed at the Cu site in underdoped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [22], which results from the AFM correlations due to neighboring Cu spins with $Q_{AF} = (\pi, \pi)$. In contrast, it is considered, from the neutron-scattering measurement, that the AFM fluctuations in LaFeAsO possess the stripe correlation with $Q_{stripe} = (\pi, 0)$ and $(0, \pi)$, which enhances $1/T_1 T$ at the As site since the stripe correlation is not filtered out at the As site [14]. Thus the $1/T_1 T$ at the As site is regarded as a good probe to detect the stripe-type AFM correlations.

$1/T_1 T$ for $x = 0.04$ shows an anomaly at about 30 K, which is $\sim 10$ K higher than $T_c$. Since the full-width at half-maximum $H_{FWHM}$ of the As-NMR spectrum in the powder sample starts to increase below 30 K (from $H_{FWHM} \sim 26$ mT at 30 K to $\sim 36$ mT at 10 K) and the resistive

\[ \frac{1}{T_1} \]
Figure 6. Field-swept $^{75}$As-NMR spectrum of powdered LaFeAs(O$_{0.89}$F$_{0.11}$) obtained with a fixed frequency of $f = 72.1$ MHz and at 30 K. The inset shows the $^{75}$As-NQR spectrum obtained by sweeping a frequency at 5 K.

anomaly was observed at 30 K seen in figure 2, this anomaly is considered to be a weak magnetic ordering. Further detailed measurements using an aligned powder sample or single crystal are needed to investigate the character of the weak magnetism occurring around the boundary between magnetism and superconductivity in LaFeAs(O$_{1-x}$F$_x$).

Spin dynamics markedly different from these of $x = 0.04$ were observed for the higher doping level samples, as shown in figure 8. The $1/T_1 T$ for $x = 0.07$ is $T$-independent down to 50 K, and decreases below $T^* \sim 40$ K. The $1/T_1 T$ for $x = 0.11$ and 0.14 decreases with a decrease in temperature from room temperature. The decrease of $1/T_1 T$ above $T_c$ is reminiscent of the pseudogap behavior in the underdoped regime of high-$T_c$ cuprates, e.g. underdoped YBa$_2$Cu$_3$O$_{6.6}$[23] and YBa$_2$Cu$_4$O$_8$[24]. However, $1/T_1 T$ for $x = 0.11$ and 0.14 approaches an almost constant value in a narrow $T$-region just above $T_c$. The temperature dependence of $1/T_1 T$ for $x = 0.11$ and 0.14 in the normal state is fitted with

$$\frac{1}{T_1 T} = A + B \exp (-\Delta_{PG} / T),$$

where $A = 0.04$ (sK)$^{-1}$, $B = 0.17 \pm 0.01$ (sK)$^{-1}$ and $\Delta_{PG} = 172 \pm 17$ K for $x = 0.11$ and $A = 0.012$ (sK)$^{-1}$, $B = 0.18 \pm 0.01$ (sK)$^{-1}$ and $\Delta_{PG} = 165 \pm 15$ K for $x = 0.14$. Similar results were reported from the $^{19}$F NMR and $^{75}$As NMR/NQR at $x = 0.10–0.11$[20, 25, 26]. We plot the estimated pseudogap temperature against the F-concentration in figure 9 and develop the phase diagram in LaFeAs(O$_{1-x}$F$_x$). Quite recently, it was reported by Terasaki et al[27] that $1/T_1 T$ of $^{57}$Fe shows a similar pseudogap behavior to that of $^{75}$As in LaFeAsO$_{0.7}$. This
indicates that the magnitude of the pseudogap is almost identical for both the Fe site and the As site and that the low-energy spin-fluctuations are suppressed over $q$-space with a decrease in temperature, since the $1/T_1 T$ of Fe is determined by the spin fluctuations over the whole $q$-space.

From the temperature dependence of $1/T_1 T$ and the doping dependence of the pseudogap temperature, we point out that the character of the pseudogap is quite different in LaFeAs($O_{1-x} F_x$) and the underdoped cuprates. In the cuprates, $1/T_1 T$ decreases from far above $T_c$ and no clear anomaly was observed at $T_c$. In contrast, for $x = 0.11$ and $0.14$, the extrapolation of $1/T_1 T$ from higher temperatures to $T_c$ does not intercept the temperature axis at positive values, and the Korringa behavior ($T_1 T = \text{constant}$) was observed in the narrow $T$-region from 30 K to $T_c$, which is related to the $T^2$ behavior of the resistivity (see the inset of figure 2).

Furthermore, a clear anomaly of $1/T_1 T$ was found at $T_c$. The temperature dependence of $1/T_1 T$ in LaFeAs($O_{1-x} F_x$) suggests the presence of the density of states (DOS) at the Fermi level $T_c$, and that the gap exists in a part of the Fermi surfaces even if the gap is present. In addition, the pseudogap behavior at $x = 0.11$ is more pronounced than that at $x = 0.07$, although the $T_c$ in the two samples is nearly the same. The $1/T_1 T$ result indicates that the pseudogap behavior in LaFeAs($O_{1-x} F_x$) becomes more significant with F-doping, whereas $T_c$ is insensitive to the F-doping, and that the doping dependence of the pseudogap behavior in LaFeAs($O_{1-x} F_x$) is opposite to that in the cuprate superconductors. In cuprates, the pseudogap behavior becomes more pronounced on approaching the AFM phase boundary (i.e. the underdoped regime).

Figure 7. $T$-dependence of $(T_1 T)^{-1}$ of $^{75}$As for $x = 0.04, 0.07, 0.11$ and $0.14$ in LaFeAs($O_{1-x} F_x$). The broken line is a fit to $(T_1 T)^{-1}$ for LaFeAs($O_{0.96} F_{0.04}$) and $(T_1 T)^{-1} = C/(T + \theta)$ with $C = 44 \text{ (sK)}^{-1}$ and $\theta = 10.2 \text{ K}$.
Taking theoretical studies into account, we consider that the strong AFM fluctuations observed in $x = 0.04$ originate from the nesting between the hole Fermi surfaces located at the Brillouin zone center (Γ) and the electron Fermi surfaces located at the corner (M), and that the marked suppression of the stripe-type AFM fluctuations implies strong dependence of the Fermi surfaces on electron-doping; the hole (electron) Fermi surfaces become smaller (larger) by F-doping, and as a result the nesting between these Fermi surfaces would be suppressed. Quite recently, Ikeda [29] pointed out that the pseudogap behavior in the NMR relaxation rate originates from the band structure effect near Fermi energy. The existence of the high DOS just below the Fermi level, which is assigned to a $d_{x^2-y^2}$ orbital around Γ′, gives rise to the temperature dependence of the DOS. The temperature and doping dependence of $1/T_1 T$ was calculated, which is in good agreement with our experimental results on $1/T_1 T$.

Next, we discuss the superconducting-gap properties from the $T$-dependence of $1/T_1 T$ in the superconducting state. Figure 10 shows the $T$-dependence of $1/T_1$ of $^{75}$As for $x = 0.04, 0.07$ and 0.11, which was measured at $H \sim 9.9$ T. As mentioned above, a short component of $T_1$ appears gradually in all samples below 30 K and its fraction increases with a decrease in $T$. The appearance of the short component of $T_1$ is considered to be due to a tiny amount of impurities and/or disorder, which is usually present in the polycrystal F-doped sample. The presence of vortices might be a source of the short component in the superconducting state. However, the

**Figure 8.** $T$-dependence of $(T_1 T)^{-1}$ of $^{75}$As for $x = 0.07, 0.11, 0.14$ in LaFeAs(O$_{1-x}$F$_x$). The broken and dotted lines are a fitting to $(T_1 T)^{-1}$ for $x = 0.11$ and 0.14 using the formula of $(T_1 T)^{-1} = A + B \exp(-\Delta_{PG}/T)$ with $A = 0.044$ (sK)$^{-1}$, $B = 0.17$ (sK)$^{-1}$, and $\Delta_{PG} = 172 \pm 17$ K for $x = 0.11$ and $A = 0.012$ (sK)$^{-1}$, $B = 0.18$ (sK)$^{-1}$, and $\Delta_{PG} = 165 \pm 15$ K for $x = 0.14$. 
Figure 9. Phase diagram determined from our NMR measurements on LaFeAs(O$_{1-x}$F$_x$). The closed (open) triangle designates the pseudogap energy determined from $1/T_1$ measurements at the $^{75}$As site (the Knight shift of $^{19}$F quoted from [26]). The closed square indicates the magnetic ordering temperature determined from NMR measurements [10]. The diamond corresponds to the peak temperature of temperature derivative of resistivity $d\rho/dT$, which seems to track the magnetic ordering temperature. The green open square is determined from $\mu$SR measurements (from [28]), indicating the onset temperature of spin glass like magnetism. The superconducting transition temperatures (the red circle) are determined from the temperature where the value of $\rho$ becomes half of that at the onset temperature (adapted from [1]).

Fraction of the longer component of $T_1$ is dominant even at low temperatures, and thus the longer component is shown in figure 10. It was found that $1/T_1$ decreases suddenly without showing a Hebel–Slichter (coherence) peak just below $T_c$, and that $T^3$ dependence of $1/T_1$ was observed in the superconducting state for all samples. In order to check whether or not the $T^3$ dependence is modified by applying external fields, we measured $1/T_1$ in different fields. Figure 11 shows the temperature dependence of $1/T_1$ for $x = 0.11$ at 5.2, 9.9 and 12 T. It was found that the $T^3$ behavior holds down to 4 K ($\sim 0.2T_c$) in the field range of 5.2–12 T within the experimental error (typically $\Delta T_1 \sim 10\%$), suggesting that the $T^3$ behavior is intrinsic to the superconducting state. Actually, we can reproduce the observed $T^3$ dependence of $1/T_1$ data for $x = 0.11$ by using a 2D line node ($\Delta(\phi) = \Delta_0 \sin(2\phi)$) model with $2\Delta/k_BT_c = 4.0$ as shown by the dotted curve in figure 11.

Although the absence of the coherence peak and the $T^3$ dependence observed in $1/T_1$ strongly suggest the presence of the line nodes, various experimental results are inconsistent with the presence of the line nodes. First, it is known, in anisotropic superconductors with nodes, that applied magnetic field induces the extra relaxation rate originating from the Volvik effect [30]. It was pointed out that the quasiparticle state is extended outside the vortex cores with the ungapped spectrum in a d-wave superconductor, which gives rise to a field-induced relaxation rate. However, such a field-induced relaxation rate was not observed in LaFeAs(O$_{1-x}$F$_x$). We also point out that a residual DOS suggested from the low-temperature Korringa behavior was not observed in the $x = 0.04$, 0.07 and 0.11 samples. In non-s-wave
superconductors with line nodes, it is well known that the residual DOS is easily induced by a tiny amount of impurities and crystal imperfections, and was observed in most of the unconventional superconductors [31, 32]. It seems that the absence of the residual DOS is contrary to non-s-wave models, since the LaFeAs(O\textsubscript{1−x}F\textsubscript{x}) is considered to possess the randomness related to the F substitution. Furthermore, various experimental results such as penetration-depth and photoemission measurements in the FeAs superconductors suggest the presence of a finite superconducting gap, which is inconsistent with the existence of line nodes [33, 34].

To reconcile with these experimental results, the \textit{s±} state with the anisotropic gap is considered as the most promising state in the FeAs superconductors at present. In this state, the superconducting gap is sign reverse between hole and electron Fermi surfaces across the nesting vector. In the case of the anisotropic s-wave gap ($\Delta(\phi) = |\Delta_0 \sin (2\phi)|$ [35]), a tiny coherence peak remains since the coherence factor does not vanish when the gap function is integrated over the Fermi surfaces. In contrast, the absence of the coherence peak is consistently understood by the sign-changed superconducting gaps realized in the \textit{s±} state [36]–[38]. Furthermore, it

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10}
\caption{\textit{T}-dependence of $1/T_1$ of $^{75}\text{As}$ for $x = 0.04$, 0.07 and 0.11 in LaFeAs(O\textsubscript{1−x}F\textsubscript{x}) at $H \sim 9.9$ T applied within the \textit{ab}-plane.}
\end{figure}
was reported that the $T^3$ dependence in the superconducting state can be reproduced with the $s_\pm$ state with an anisotropic character of the superconducting gap at the electronic Fermi surfaces together with some impurity effect [39]. However, since the exponential temperature dependence of $1/T_1$ should be observed in an impurity-free sample with the $s_\pm$ pairing, further NMR measurements using high-quality samples are important; in particular, $1/T_1$ measurements at low temperatures are crucial.

Finally, we would like to discuss the relationship between magnetic fluctuations and superconductivity. Since the electron–phonon coupling was shown to be too weak to account for the high-$T_c$ of the iron oxypnictide superconductors [40, 41], spin fluctuation is one of the plausible candidates for the pairing interaction [6, 42, 43]. Due to the disconnected Fermi surfaces in the iron oxypnictide, nesting-related spin fluctuations would be the origin of the pairing interaction. F-doping (corresponding to electron-doping) is likely to enhance the mismatch between the Fermi surfaces, leading to the suppression of the spin fluctuations. This is actually observed in the present NMR study; the significant AFM fluctuations in $x = 0.04$ are suppressed at $x = 0.07$. It should be noted that $1/T_1$ in the superconducting state of $x = 0.07$ is

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{\textit{T}-dependence of $1/T_1$ of $^{75}\text{As}$ in LaFeAs(O$_{0.89}$F$_{0.11}$) at 5.2, 9.9 and 12 T applied within the $ab$-plane. The dashed curve is a calculation assuming a line node gap $\Delta(\phi) = \Delta_0 \sin(2\phi)$ with $\Delta_0 = 2k_B T_c$.}
\end{figure}

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identical to that in $x = 0.11$, although $1 / T_1$ in the normal state is different for $x = 0.07$ and 0.11. The 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 spin fluctuations observed through the $1 / T_1$ measurements do not play a vital role in the superconductivity. However, it should be noted that the $1 / T_1$ measurements can detect the low-energy magnetic fluctuations (typically of the order of mK), and might fail to detect important magnetic fluctuations if their characteristic energy exceeds the limitaion of the NMR experiments. Therefore, inelastic neutron experiments over a wide $q$-sapce and energy range are needed for thoroughly uncovering magnetic fluctuations, and are important for clarifying the relationship between the superconductivity and magnetic fluctuations.

3. Conclusion

To conclude, the present NMR study revealed that an itinerant antiferromagnet LaFeAsO evolves into superconductors with F-doping. The spin fluctuations proved via the $^{75}$As nucleus vary markedly with F-doping, i.e. strong antiferromagnetic behavior for $x = 0.04$ and pseudogap behavior for $x = 0.11$. The observed $T$-dependence of $1 / T_1$ in the superconducting state suggests that an unconventional superconductivity with zero gap along the lines is realized in LaFeAs($O_{1-x}F_x$), whereas neither the field-induced extra relaxation rate nor the residual DOS at low temperatures is incompatible with d-wave superconductivity. In addition, since $T_c$ remains almost constant although the $1 / T_1 T$ of $^{75}$As in the normal state significantly varies with F-doping, it is considered that the low-energy antiferromagnetic fluctuations revealed by $1 / T_1$ of $^{75}$As do not play a vital role in the occurrence of superconductivity in LaFeAs($O_{1-x}F_x$).

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New Journal of Physics 11 (2009) 045004 (http://www.njp.org/)
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