Spin Fluctuations and Unconventional Superconductivity in the Fe-based Oxypnictide Superconductor \( \text{LaFeAsO}_{0.7} \) probed by \(^{57}\text{Fe}-\text{NMR}\)

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We report \(^{57}\text{Fe}-\text{NMR}\) studies on the oxygen-deficient iron (Fe)-based oxypnictide superconductor \( \text{LaFeAsO}_{0.7} \) \((T_c = 28 \, \text{K})\) enriched by \(^{57}\text{Fe}\) isotope. In the superconducting state, the spin component of \(^{57}\text{Fe}-\text{Knight} \) shift \(^{57}K \) decreases almost to zero at low temperatures and the nuclear spin-lattice relaxation rate \(^{57}T \) exhibits a \(^{T^2} \)-like dependence without the coherence peak just below \(T_c \), which gives firm evidence of the unconventional superconducting state formed by spin-singlet Cooper pairing. All these events below \(T_c \) are consistently argued in terms of the extended \( s_\pm \)-wave pairing with a sign reversal of the order parameter \(\Delta\) among Fermi surfaces. In the normal state, we found the remarkable decrease of \(1/TcT \) upon cooling for both the Fe and As sites, which originates from the decrease of low-energy spectral weight of spin fluctuations over whole \( q \) space upon cooling below room temperature. Such behavior has never been observed for other strongly correlated superconductors where an antiferromagnetic interaction plays a vital role in mediating the Cooper pairing.

KEYWORDS: superconductivity, iron-based oxypnictide, LaFeAsO, NMR

After the discovery of iron (Fe)-based layered oxypnictide superconductor \( \text{LaFeAsO}_{1-x} \) \((x \approx 0.1)\),\(^1\) the replacement of La site by other rare earth elements significantly enhances a superconducting transition temperature \(T_c \) up to more than 50 K.\(^2,4\) A new route has opened up to deepen understanding of high-\(T_c \) superconductivity (SC) phenomena. Mother material \(\text{LaFeAsO} \) is a semimetal with a stripe antiferromagnetic (AFM) order with \( Q = (0, \pi) \) or \( (\pi, 0) \). The crystal structure contains alternate stacking of \( \text{LaO} \) and \( \text{FeAs} \) layers along the c-axis. In this structure, the Fe atoms of the FeAs layer are located in a four-fold coordination forming a FeAs\(_4\)-tetrahedron. Substitution of oxygen site with fluorine atoms and/or oxygen deficiency at \( \text{LaO} \) layer causes an exotic SC with a highest \(T_c \) besides copper-oxides superconductors.\(^1,4\) Remarkably, Lee et al. have found that \(T_c \) increases up to a highest value of \(T_c \approx 54 \, \text{K} \) when FeAs\(_4\) tetrahedron is transformed toward a regular one.\(^5\) Relevant with this fact, we reported that the nuclear quadrupole frequency at the As site relates to \(T_c \) for various FeAs-based oxypnictide superconductors, unraveling that \(T_c \) is sensitive to the local configuration of FeAs\(_4\) tetrahedron.\(^6\) The present experimental facts suggest that systematic understanding of local electronic state at the Fe site is quite important to elucidate the origin of SC in the iron-based compounds.

In this letter, we report \(^{57}\text{Fe}-\text{NMR}\) studies on the superconducting and normal-state properties of \( \text{LaFeAsO}_{0.7} \) with \(T_c = 28 \, \text{K} \) enriched by \(^{57}\text{Fe}\) isotope. It is reinforced that the \(^{57}\text{Fe}-\text{NMR} \)-\((1/Tc) \) exhibits a \(^{T^3} \)-like dependence without the coherence peak just below \(T_c \) and the spin component of \(^{57}\text{Fe}-\text{Knight} \) shift decreases almost to zero at low temperatures. These results pointing to the unconventional SC with spin-singlet Cooper pairings are consistent with the theoretical model which proposes that an extended \( s_\pm \)-wave pairing realizes with a sign reversal of the order parameter \(\Delta\) among Fermi surfaces. In the normal state, we discuss the characteristics of spin fluctuations in this compound by comparing \(^{57}\text{Fe}-(1/Tc) \) with the \( 75\text{As}-(1/Tc) \).

The polycrystalline sample of \(^{57}\text{Fe-enriched LaFeAsO}_{0.7} \) was synthesized via the high-pressure synthesis technique, as described in the elsewhere.\(^3\) In particular, starting materials of \( \text{LaAs, }^{57}\text{Fe, }^{57}\text{Fe}_2\text{O}_3 \) enriched by the \(^{57}\text{Fe} \) isotope \(^{57}\text{Fe} : \text{atomic spin } \text{I} = 1/2,^{57} \gamma_\text{n}/2\pi = 1.3757 \, \text{MHz/T} \) \) were mixed with nominal composition of \( \text{LaFeAsO}_{0.7} \). The powder X-ray diffraction measurement indicates that the sample composes of almost a single phase. The superconducting transition temperature \(T_c \) was determined to be \(28 \, \text{K} \) by distinct decrease in the dc susceptibility due to the onset of SC diamagnetism. Although the real content of oxygen is unclear, the lattice parameters \( a = 4.0226\AA \) and \( c = 8.7065\AA \) are almost the same as the \( \text{LaFeAsO}_{0.6} \) with \(T_c = 28 \, \text{K} \) in the previous work,\(^5\) which indicates that both samples are compatible in their physical properties. The \(^{57}\text{Fe}-\text{NMR}\) measurements were performed in the moderately crushed powder sample, which was oriented along the direction including the \( ab \) plane.

Figure 1(a) shows \(^{57}\text{Fe}-\text{NMR} \) spectra obtained by sweeping frequency \((f) \) at magnetic field \( H = 11.97 \, \text{T} \) at \(30 \, \text{K} \). When the field is applied parallel to the orientation direction, we observed a single peak, the linewidth of which is as narrow as \( \sim 20 \, \text{kHz} \) at \(11.97 \, \text{T} \), demonstrating that the FeAs layers of this sample are homogeneous irrespective of the oxygen deficiency in the \( \text{LaO} \) layer. In the field perpendicular to the orientation direction, two horn peaks are observed, which arises from crystals with \( \theta = 90^\circ \) and \( 0^\circ \), where \( \theta \) is the angle between field and...
c-axis of the crystal. Knight shifts of $^{57}$Fe, that is determined by the shift from $J_0 = \frac{57}{2} \gamma_0 H$ ($^{57}K = 0$), are $^{57}K^\perp \sim 1.413\%$ and $^{57}K^\parallel \sim 0.50\%$ at 30 K for $\theta = 90^\circ$ and $0^\circ$, respectively.

The Knight shift comprises generally of the $T$-independent orbital contribution and $T$-dependent spin contribution, denoted as $^{57}A^\text{orb}$ and $^{57}K^\text{s}$. Here, $^{57}K = ^{57}K^\text{orb} + ^{57}K^\text{s}$, with $^{57}K^\text{s} = ^{57}A^\text{hf}\chi_\text{s}$, where $^{57}A^\text{hf}$ is the hyperfine coupling constant and $\chi_\text{s}$ is the uniform spin susceptibility. Figure 1(b) shows the $T$ dependence of $^{57}K^\perp$ in the field parallel to the ab-plane. It is noteworthy that the $T$ dependence of $^{57}K^\perp$ is opposite to those of $^{75}$As and $^{19}$F sites, indicating that the hyperfine-coupling constant is negative at Fe site, originating from the inner core-polarization.

The nuclear spin-lattice relaxation rate $^{57}1/T_1$ of $^{57}$Fe was determined from the recovery curve of $^{57}$Fe nuclear magnetization, which is expressed by a simple exponential function as $m(t) \equiv (M(\infty) - M(t))/M(\infty) = \exp(-t/T_1)$. Here $M(\infty)$ and $M(t)$ are the respective nuclear magnetizations for the thermal equilibrium condition and at a time $t$ after the saturation pulse. Note that $^{57}1/T_1$ was uniquely determined from a single exponential function of $m(t)$ in the whole $T$ range, suggesting that the normal-state properties are homogeneous and the presence of vortex cores in the SC mixed state under $H$ does not prevent from probing quasiparticle excitations inherent to the novel SC state in LaFeAs$_{0.7}$O$_{0.3}$. We measured the $^{57}(1/T_1)$ in the field along the ab-plane, since it was the same with that along the c-axis at 30K.

Figure 3 shows the $T$ dependences of $^{57}(1/T_1)$ at $H = 6.309$ T and 11.97 T in the $T$ range of 4–80 K and 30–240 K, respectively. In the SC state, the $^{57}$Fe-NMR
(1/T_1) exhibits a T^3-like dependence without the coherence peak just below T_c(H) = 24 K at H = 6.309 T, which resembles the previous 75 As-NQR (1/T_1) in LaFeAsO_0.6. It is noteworthy that the residual density of states (RDOS) well below T_c was not observed at the Fermi level even for T_c/T = 0.17, although RDOS used to be observed in the unconventional superconductors with the line-node gap, easily induced by impurity scatterings especially in a unitarity limit. These features of 1/T_1 were commonly reported among other Fe-based superconductors. In contrast, a fully gapped SC state was revealed by the experiments such as ARPES in LaFeAsO_0.6. In order to reconcile these issues, the theoretical groups have carried out the calculation of 1/T_1 on the basis of a nodeless extended s_±-wave pairing model with a sign reversal of the order parameter between the hole and electron Fermi surfaces. In the framework of either a two-band model where the unitarity scattering due to impurities is assumed or a five-band model in a rather clean limit, the experiments are well reproduced by such the calculations. As a matter of fact, the results of (1/T_1)s for 57 Fe and 75 As in the SC state are consistent with the latter model. This may be because the intrinsic behavior of 1/T_1 is measured on the highly homogeneous sample, that is guaranteed by the very sharp NMR linewidth with as small as 20 kHz even at 12 T. In this context, our results is consistently argued on the basis of a nodeless extended s_±-wave pairing model.

Next we deal with the normal-state properties probed by the (1/T_1)s of both 57 Fe and 75 As. As shown in Fig. 4, 57 (1/T_1) in the normal state gradually decreases upon cooling down to T_c, resembling that of 75 (1/T_1) at As site. Actually, 57 (1/T_1) at Fe site is well scaled to 75 (1/T_1) at As site down to 60 K with a ratio of 57 (1/T_1)/75 (1/T_1) ∼ 1.85, as shown in the inset, whereas it deviates slightly from this linear relation in the range of T = 30 K–60 K. The respective 1/T_1s of 57 Fe and 75 As are expressed as,

\[ \frac{1}{T_1} \sim \sum_q \langle 57, 75 \gamma_n \rangle^2 \langle 57, 75 \rangle A_{hf}(q) \frac{\chi''(q, \omega_0)}{\omega_0}, \]  

where \( A_{hf}(q) \) is the wave-vector \( q \)-dependent hyperfine coupling constant, \( \chi''(q, \omega_0) \) is the imaginary part of the dynamical spin susceptibility, \( a \) is a distance between Fe atoms, and \( \omega_0 \) is the NMR/NQR frequency. An anisotropy of 57 (1/T_1) between the ab-plane and the c-axis is negligibly small for Fe site, which ensures that \( \chi''(q, \omega_0) \) and the hyperfine fields (A and B) are isotropic. Although the anisotropy of 75 (1/T_1) was observed in other 75 As-NMR measurement, it is predominantly derived from the anisotropy of \( C_{dip}(q) \), which is the inplane component of off-diagonal pseudo-dipole hyperfine field arising from the \( \chi''(q, \omega_0) \) along the c-axis.

Now let us consider three simple cases on the basis of the possible evaluation of hyperfine field. (i) First, we assume a case that spin fluctuations only around \( q = 0 \) are predominant. In this case, we would expect a ratio of \( 57 (1/T_1) / 75 (1/T_1) \sim 0.005 \) by using \( (\langle 57 A_{hf}^+ / 75 A_{hf}^+ \rangle)^2 = (-0.38)^2 \). However, it is three orders of magnitude smaller than the experimental value of 1.85 at \( T = 60–250 \) K, suggesting that the ferromagnetic spin-fluctuation modes around \( q = 0 \) are

Fig. 3. T dependence of 57 Fe-NMR 1/T_1 at H = 6.309 T and H = 11.97 T, along with the 75 As-NQR 1/T_1 for LaFeAsO_0.6 (T_c = 28 K). In the SC state, 57 Fe-1/T_1 follows a T^3-like dependence upon cooling without the coherence peak just below T_c(H) = 24 K, which resemble the result by 75 As-NQR.

Fig. 4. T dependence of 57 Fe-1/T_1T at H = 6.309 T (△) and H = 11.97 T (closed diamond), together with the 75 As-1/T_1T in LaFeAsO_0.6 (○), respectively. The inset shows the plot of 57 (1/T_1T) vs 75 (1/T_1T) as the implicit parameter of T between 30 K and 240 K.
not predominant in this compound. (ii) Second, we assume the case that the spin fluctuations only around $Q = (0, \pi/a)$ or $(\pi/a, 0)$ are predominant. It is characteristic that $|A_{1\pi}(q)|$ at the Fe site becomes large around the boundaries of the first Brillouin zone. For example, $|A_{1\pi}(0, \pi/a)| = |A - 4B_2|$ is roughly evaluated to be $\sim 204$ kOe/$\mu_B$ if $B_1$ and $B_2$ were comparable, which are one order of magnitude larger than that of As site. Even though the off-diagonal term $4C_{1\pi}^4(q)$ in eq. (2) is not clear for the paramagnetic state of LaFeAsO$_{0.7}$, it is tentatively assumed to be 4.3 kOe/$\mu_B$ obtained for the stripe AFM ordered phase in the orthorhombic BaFe$_2$As$_2$. Then we obtain $57(1/T_1T)/75(1/T_1T) \sim 5$, which is the same order of magnitude to the experimental value. (iii) Third, we assume the case that the spin fluctuations only around $Q = (\pi/a, \pi/a)$ are predominant. In this case, $|A_{1\pi}(\pi/a, \pi/a)|$ becomes largest, whereas $|A_{2\pi}(\pi/a, \pi/a)|$ is expected to be zero. Thus $57(1/T_1T)/75(1/T_1T)$ would be the extremely large value, which is inconsistent with the experiment.

Thus far it has been theoretically proposed that the multiple spin-fluctuation modes with $Q = (\pi/a, 0)$ and $(0, \pi/a)$ arising from the nesting across the disconnected Fermi surfaces would mediate the extended $s_\pm$-wave pairing with a sign reversal of the order parameter. However, in our simple analyses, we could state only that the spin fluctuations at finite wave vectors is more significant than the ferromagnetic spin fluctuations mode in this compound. Nevertheless, it is noteworthy that the $(1/T_1T)$s for both the Fe and As sites decrease upon cooling, indicating the decrease of low-energy spectral weight of spin fluctuations over whole $q$ space from the room temperature. In contrast, in the case of the copper-oxide superconductors, $1/T_1T$s of $^{63}$Cu and $^{17}$O exhibit a different $T$ dependence, due to the difference in the $q$-dependence of $A_{1\pi}(q)$ and strong AFM spin fluctuations with $Q = (\pi/a, \pi/a)$.

The suppression of spin fluctuations over whole $q$ space upon cooling below room temperature was observed in FeAs-derived high $T_c$ superconductor, which has never been observed for other strongly correlated superconductors where an AFM interaction plays vital role in mediating the Cooper pairing. In this context, it is an open question at the present what type of fluctuations are responsible for a pairing glue taking place a possible extended $s_\pm$-wave pairing.

In summary, the first $^{57}$Fe-NMR studies have unraveled the novel SC and normal-state characteristics for the $^{57}$Fe-enriched LaFeAsO$_{0.7}$ with $T_c = 28$ K. The measurements of the Knight shift and the $T_1$ of $^{57}$Fe have revealed that the extended $s_\pm$-wave pairing with a sign reversal of the order parameter can be a promising candidate in LaFeAsO$_{0.7}$ with $T_c = 28$ K. This novel SC is theoretically proposed to be realized by the multiple spin-fluctuation modes with $Q = (\pi/a, 0)$ and $(0, \pi/a)$ arising from the nesting across the disconnected Fermi surfaces. However, in the normal state, we found the remarkable decrease of $1/T_1T$ upon cooling for both the Fe and As sites, indicating the decrease of low-energy spectral weight of spin fluctuations over whole $q$ space upon cooling below room temperature, which has never been observed for other strongly correlated superconductors where an AFM interaction plays vital role in mediating the Cooper pairing. Further experiments on $T_c$-dependences of $1/T_1$ and $K$ at both Fe and As sites by using a single crystal are required to understand the nature of spin fluctuations of this compound.

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