Novel Superconducting Characteristics and Unusual Normal-State Properties in Iron-based Pnictide Superconductors: \( ^{57}\text{Fe-NMR} \) and \( ^{75}\text{As-NQR/NMR} \) studies in \( \text{REFeAsO}_{1−\gamma} \) (\( \text{RE} = \text{La, Pr, Nd} \)) and \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \)

H. Mukuda\( ^{a,c} \), N. Terasaki\( ^a \), M. Yashima\( ^{a,c} \), H. Nishimura\( ^a \), Y. Kitaoka\( ^a \), A. Iyo\( ^{b,c} \)

\( ^{a} \)Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
\( ^{b} \)National Institute of Advanced Industrial Science and Technology (AIST), Umezono, Tsukuba 305-8568, Japan
\( ^{c} \)JST-TRIP, 1-2-1 Sengen, Tsukuba 305-0047, Japan

Abstract

We discuss the novel superconducting characteristics and unusual normal-state properties of iron (Fe)-based pnictide superconductors \( \text{REFeAsO}_{1−\gamma} \) (\( \text{RE} = \text{La, Pr, Nd} \)) and \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \) by means of \( ^{57}\text{Fe-NMR} \) and \( ^{75}\text{As-NQR/NMR} \). In the superconducting state of \( \text{LaFeAsO}_{0.7} \) \( (T_c = 28 \text{ K}) \), the spin component of the \( ^{57}\text{Fe-Knight shift} \) decreases to almost zero at low temperatures, which provide firm evidence of the superconducting state formed by spin-singlet Cooper pairing. The nuclear spin-lattice relaxation rates \( (1/T_1) \) in \( \text{LaFeAsO}_{0.7} \) and \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \) exhibit a \( T^3 \)-like dependence without a coherence peak just below \( T_c \), indicating that an unconventional superconducting state is commonly realized in these Fe-based pnictide compounds. All these events below \( T_c \) are consistently argued in terms of an extended \( s_\pm \) wave pairing with a sign reversal of the order parameter among Fermi surfaces. In the normal state, \( 1/T_1 \) decreases remarkably upon cooling for both the Fe and As sites of \( \text{LaFeAsO}_{0.7} \). In contrast, it gradually increases upon cooling in \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \). Despite the similarity between the superconducting properties of these compounds, a crucial difference was observed in their normal-state properties depending on whether electrons or holes are doped into the Fe layers. These results may provide some hint to address a possible mechanism of Fe-based pnictide superconductors.

Key words: superconductivity, iron-based pnictide, \( \text{LaFeAsO} \), \( \text{(Ba,K)}\text{Fe}_{2}\text{As}_2 \), NMR, NQR 74.70.-b, 74.20.Rp, 76.60.-k

1. Introduction

The discovery of superconductivity (SC) in the iron (Fe)-based oxypnictide \( \text{LaFeAsO}_{1−\gamma} \), reaching a superconducting transition temperature \( T_c = 26 \text{ K} \), has attracted considerable interest in the fields of condensed-matter physics and material science [1]. Shortly after this discovery, it was reported that \( T_c \) of \( \text{LaFeAsO}_{0.85}\text{Fe}_{0.11} \) increases up to 43 K upon the application of pressure [2], and the replacement of the La site by other rare earth (RE) elements significantly increases \( T_c \) up to more than 50 K [3, 4, 5, 6]. These findings have provided a new material base for searching high-\( T_c \) SC. The structure of mother materials contains an alternate stacking of \( \text{RE}_2\text{O}_3 \) and \( \text{Fe}_2\text{As}_2 \) layers along the \( c \)-axis where the Fe atoms of the FeAs layer are located in a fourfold coordination forming a FeAs\( _4 \) tetrahedron. The mother material \( \text{LaFeAsO} \) is a semimetal with a stripe antiferromagnetic (AFM) order with \( \text{Q} = (0, \pi) \) or \( (\pi, 0) \) [7]. The substitution of fluorine for oxygen and/or oxygen deficiencies at the LaO layer yield a novel SC [7, 8, 9, 10]. In particular, a very sharp superconducting transition in resistance under \( P \) for \( \text{NdFeAsO}_{0.6} \) ensures a homogeneous electronic state even in an oxygen-deficient sample [8]. Remarkably, Lee et al. found that \( T_c \) increases to the maximum value of 54 K when the FeAs\( _4 \) tetrahedron is transformed into a regular one [9].

Another family of FeAs-based superconductors without oxygens has been reported in the ternary compound \( \text{Ba}_{1−\gamma}\text{K}_{\gamma}\text{Fe}_{2}\text{As}_2 \) with \( T_c = 38 \text{ K} \) [10]. In this compound, layers consisting of edge-sharing FeAs\( _4 \) tetrahedra are separated by Ba(K) layers. Moreover, SC was also reported in \( \alpha\text{-FeSe} \) with \( T_c = 8 \text{ K} \) [11]. This compound is composed of stacking layers of FeSe, resembling the FeAs layers in \( \text{LaFeAsO}_{1−\gamma} \), but containing neither any Ba(K) atoms nor LaO sheets. The present experimental facts suggest that systematic studies of the local electronic state at the Fe site are quite important to elucidate the origin of SC in the iron-based compounds.

In this paper, we report \( ^{57}\text{Fe-NMR} \) and \( ^{75}\text{As-NQR/NMR} \) studies of the superconducting and normal-state properties of Fe-based pnictide high-\( T_c \) superconductors. We review the previous results on \( \text{REFeAsO}_{1−\gamma} \) published elsewhere [12, 13], and present the recent results on \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \).

2. Experimental

Polycrystalline samples of \( \text{LaFeAsO}_{1−\gamma} \), \( \text{PrFeAsO}_{0.6} \), \( \text{NdFeAsO}_{0.6} \), and \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2 \) were synthesized via the high-pressure synthesis technique described elsewhere [4]. Although the real oxygen content of the samples may be greater than the nominal (intended) values due to the oxidation of the starting RE elements, powder X-ray diffraction measurements indicate that these samples are almost entirely composed of a single phase. The \( T_c \)s for all samples were determined by susceptibility measurement, which indicated a marked decrease due to the onset of SC below \( T_c \) = 20 K, 28 K, 28
K, 22 K, 46 K, and 53 K for \( \text{LaFeAsO}_0 \). \( ^{57}\text{Fe-enriched \text{LaFeAsO}}_0 \), \( \text{LaFeAsO}_6 \), \( \text{LaFeAsO}_{6.6} \), \( \text{PrFeAsO}_{6.6} \), and \( \text{NdFeAsO}_{6.6} \), respectively. Note that the lattice parameters \( a = 4.0226 \text{ Å} \) and \( c = 8.7065 \text{ Å} \) of \( ^{57}\text{Fe-enriched \text{LaFeAsO}}_0 \) are very close to those of \( \text{LaFeAsO}_6 \) \( (a = 4.0220 \text{ Å} \) and \( c = 8.7110 \text{ Å} \), indicating that the physical properties of both samples are compatible. \( T_c \) of \( \text{LaFeAsO}_{6.6} \) is lower than that of \( \text{LaFeAsO}_6 \) because the former is in an overdoped regime. This result is corroborated by the fact that the lattice parameters of \( \text{LaFeAsO}_{6.6} \) are smaller than those of \( \text{LaFeAsO}_6 \) \( (T_c = 28 \text{ K}) \). The samples were moderately crushed into powder for the NQR/NMR measurements. \( ^{57}\text{Fe-NMR} \) and \( ^{75}\text{As-NQR/NMR} \) measurements were performed by using the phase coherent pulsed NMR/NQR spectrometer in the temperature \( (T) \) range between 4 K and 280 K. \( 1/T_1 \) was measured using the saturation recovery method.

3. Results and discussion

3.1. \( ^{57}\text{Fe-NMR study of \text{LaFeAsO}}_{1−}\)

Figure[1(a)] shows the \( ^{57}\text{Fe-NMR} \) spectra for \( \text{LaFeAsO}_{0.7} \) obtained by a sweeping frequency \( f \) at a magnetic field \( H = 11.97 \text{ T} \) at 30 K. For \( H \) parallel to the \( ab \)-plane, a single NMR spectrum is observed with a very narrow linewidth with \( \sim 20 \) kHz. This result indicates that the FeAs layers of this sample are rather homogeneous irrespective of the oxygen deficiency in the LaO layer. For \( H \) parallel to the \( c \)-axis, respective symmetric peaks are observed in the spectra, corresponding to the crystal directions with \( \theta = 90^\circ \) and \( 0^\circ \), where \( \theta \) is the angle between the field and the \( c \)-axis. Anisotropic Knight shifts, defined as a shift from \( f_0 = ^{57}\gamma_nH \) \( (^{57}K = 0) \), 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.

Figures[1(b) and (c)] show the \( T \) dependences of the \( ^{57}\text{Fe-NMR} \) spectra at \( H = 6.309 \text{ T} \) and 11.97 T parallel to the \( ab \)-plane \( (\theta = 90^\circ) \) with \( T_c(H) \sim 24 \text{ K} \) and 20 K, respectively. The \( T \) dependence of \( ^{57}K^\perp \) for \( H \) parallel to the \( ab \)-plane is shown in Fig.[2(a)]. The Knight shift comprises the \( T \)-independent orbital contribution and the \( T \)-dependent spin contribution, denoted as \( ^{57}K_{\text{orb}} \) and \( ^{57}K_s \), respectively. Note that it increases upon cooling, exhibiting a \( T \) dependence opposite to those of the \( ^{75}\text{As} \) and \( ^{57}\text{Fe} \) sites \[14, 15, 16\]. This is because the hyperfine-coupling constant \( ^{57}A_{\text{As}} \) at the Fe site is negative, originating from the inner core-polarization. In this compound, note that \( ^{57}A_{\text{As}} = A + 4B \), where \( A \) is the on-site negative term dominated by the inner core polarization, and \( B \) is the transferred positive one from the neighboring Fe sites through direct Fe-Fe and/or indirect Fe-As-Fe bondings. A transferred hyperfine-coupling constant at the As site \( ^{57}A_{\text{As}} = 4C \) consists of two contributions in the isotropic term of a transferred hyperfine field \( (C_{\text{dir}}) \), and the anisotropic one of a pseudo-dipole field \( (C_{\text{dp}}) \) \[17\], both of which are induced by neighboring Fe-\( d \)-spin polarization. From a plot of \( ^{57}K^\perp(T) \) versus \( ^{57}K^\perp(T) \) with \( T \) as an implicit parameter, \( ^{57}K^\perp_{\text{orb}} \) is estimated to be \( 1.425\% \) \[13\] using the orbital shift \( ^{57}K^\perp_{\text{orb}} \) at the \( ^{75}\text{As} \) site reported in literature \[13\]. Eventually, a spin component of the Knight shift \( \left| ^{57}K^\perp_{\text{As}} \right| \sim \left| ^{57}K^\perp_{\text{orb}} \right|, \) as shown in Fig.[2(b)], decreases to almost zero well below \( T_c \).

This result suggests the possible existence of an isotropic gap in a very-low-temperature regime, providing firm evidence of spin-singlet Cooper pairing through the direct measurement of the local spin susceptibility by means of the \( ^{57}\text{Fe-Knight shift} \).

The nuclear spin-lattice relaxation rate \( ^{57}(1/T_1) \) at the \( ^{57}\text{Fe} \) site was determined from a single exponential recovery curve of \( ^{57}\text{Fe nuclear magnetization} \) as follows:

\[
^{57}m(t) = \frac{M(\infty) - M(t)}{M(\infty)} = \exp \left( -\frac{t}{T_1} \right),
\]

where \( M(\infty) \) and \( M(t) \) are the respective nuclear magnetizations for the thermal equilibrium condition and at time \( t \) after the saturation pulse. In fact, as shown in Fig.[3] \( ^{75}T_1 \) was uniquely determined from a single exponential function of \( ^{57}(1/T_1) \) in the entire \( T \) range, revealing that the electronic state of the present sample is homogeneous. We have confirmed that \( ^{57}(1/T_1) \) is isotropic regardless of the crystal direction.

Figure[4] shows the \( T \) dependences of \( ^{75}(1/T_1) \) at \( H = 6.309 \) and 11.97 T in the \( T \) range of 4–80 K and 30–240 K, respectively. In the SC state, \( ^{57}\text{Fe-NMR} \) \( (1/T_1) \) exhibits a \( T^3 \)-like dependence without a coherence peak just below \( T_c(H) = 24 \text{ K} \) at \( H = 6.309 \text{ T} \). Note that any deviation from the \( T^3 \) dependence was not observed even at \( T_c \). Here, it should be noted that in most \( d \)-wave superconductors with a line-node gap, such as copper oxides high-\( T_c \) superconductors, \( 1/T_1 \) tends to exhibit a \( T \) linear dependence at low temperatures, probing the residual density of states (RDOS) at the Fermi level in association with an impurity effect.

3.2. \( ^{75}\text{As-NQR study of \text{LaFeAsO}}_{1−}\)

Here, we review the \( ^{75}\text{As-NQR} \) \( 1/T_1 \) results for \( \text{LaFeAsO}_{0.6} \) \( (T_c = 28 \text{ K}) \) at \( f = 10.05 \text{ MHz} \) and zero field \[12\]. In the \( ^{75}\text{As-NQR} \) \( T_1 \) measurements at \( H = 0 \), the recovery curve of \( ^{75}\text{As nuclear magnetization} \) with \( I = 3/2 \) is also expressed by a single exponential function as follows:

\[
^{75}m(t)_{\text{NQR}} = \frac{M(\infty) - M(t)}{M(\infty)} = \exp \left( \frac{3t}{T_1} \right),
\]

As shown in Fig.[5] \( ^{75}(1/T_1)_{\text{NQR}} \) was almost fitted by a single exponential function in the SC state and the normal state, ensuring that \( 1/T_1 \) is uniquely determined over the entire \( T \) range.

Figure[4] shows the \( T \) dependence of \( ^{75}\text{As-NQR} \) \( 1/T_1 \) for \( \text{LaFeAsO}_{0.6} \) with \( T_c = 28 \text{ K} \). In the SC state, \( 1/T_1 \) at the As site exhibits a \( T^3 \)-like dependence without a coherence peak just below \( T_c \). \( T_c \) resembles the \( ^{57}\text{Fe-NMR} \) \( 1/T_1 \) result. Considering that \( ^{57}\text{Fe-NMR} \) \( 1/T_1 \) measured in the SC mixed state under \( H = 6.309 \text{ T} \) exhibits a \( T \) dependence similar to that of \( ^{75}\text{As-NQR} \) \( 1/T_1 \), it would be expected that the presence of vortex cores would not affect the quasiparticle excitations in the SC state considerably. This implies that the \( 1/T_1 \) measurements can clarify the SC gap structure although it has been measured under \( H \). Therefore, the \( 1/T_1 \sim T^3 \)-like behavior with no coherence peak gives firm evidence for an unconventional superconducting nature inherent to the Fe-pnictide superconductors.

In \( d \)-wave superconductors, which also exhibit \( 1/T_1 \sim T^3 \)-like
behavior with no coherence peak, a \(T_1 T = \text{const.}\)-like behavior was observed at low temperatures, indicating the presence of the RDOS at the Fermi level. This event is well understood in terms of the impurity scattering effect in a unitarity limit in unconventional superconductors with a line-node gap, such as \(d\)-wave superconductors. This is not the case in the Fe-based superconductors. When noting that similar results have been reported in the \(^{75}\text{As-NMR}\) studies on Fe-substituted \(\text{LaFeAsO}(\text{O}_1-x\text{F}_x)\) \([14,18]\) and \(\text{PrFeAs(O}_1-x\text{F}_x)\) \([19]\), and the \(^{77}\text{Se-NMR}\) study on FeSe \([20]\) and considering that these materials are far from a clean system, a \(d\)-wave model is not suitable for understanding these unconventional \(T_1\) behaviors in Fe-based pnictide superconductors.

3.3. \(^{75}\text{As-NMR study of Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\)

Figure 6 shows the typical \(^{75}\text{As-NMR}\) spectra for the oriented powder of \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) with \(T_c(H = 0) = 38\) K at \(f = 37.5\) MHz. The sharp central peak observed around \(H \sim 5.1\) T originates from the central transition (+1/2 ↔ −1/2) in the \(^{75}\text{As-NMR}\) spectrum. The satellite peaks (+1/2 ↔ ±3/2) around \(H \sim 4.7\) and 5.5 T originate from the first-order perturbation effect of the nuclear quadrupole interaction (NQI), allowing us to estimate the nuclear quadrupole frequency \(\nu_Q \sim 5(\pm 2)\) MHz to be larger than 2.2 MHz for the mother compound \(\text{BaFe}_2\text{As}_2\) \([21]\).

Next, we deal with the SC characteristics probed by the \(T_1\) measurement. The recovery curve of \(^{75}\text{As}\) nuclear magnetization \((I = 3/2)\) for the \(^{75}\text{As-NMR}\) measurement is expressed by a theoretical curve as follows:

\[
^{75}m(t)_{NMR} \equiv \frac{M(\infty) - M(t)}{M(\infty)} = 0.1 \exp\left(-\frac{t}{T_1}\right) + 0.9 \exp\left(-\frac{6t}{T_1}\right)
\]

Figures 7(a) and (b) show \(^{75}m(t)_{NMR}\) in the SC state and the normal state, respectively.

Figure 8 shows the \(T\) dependence of \(^{75}\text{As-NMR} 1/T_1\) for \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) at \(H \sim 5.1\) T along with the \(1/T_1\) data of \(\text{LaFeAsO}_{0.7}\). We note that the present data on \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) are consistent with the result reported by another group \([22]\). In the SC state, \(1/T_1\) decreases sharply below \(T_c(H) = 37\) K upon cooling without a coherence peak just below \(T_c\), strongly suggesting an unconventional SC nature. Furthermore, the \(1/T_1\) seems to be close to a \(T^3\) dependence well below \(T_c\). However, we note that the \(T\) dependence of \(1/T_1\) cannot be exactly reproduced by any simple SC gap model, either with line nodes or without nodes, which may relate to the characteristics of the multiband SC state observed in \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) \([23]\).

These unconventional features of \(1/T_1\) below \(T_c\) were commonly observed in most FeAs-based superconductors \([12,13,14,18,19,20,22]\). In contrast, a fully-gapped SC state was observed in experiments such as ARPES \([23]\) and magnetic penetration depth \([24]\). To reconcile these issues, \(1/T_1\) was theoretically calculated on the basis of a nodeless extended \(s_\pm\)-wave pairing model with a sign reversal of the order parameter between the hole and electron Fermi surfaces \([25,26]\). In the framework of either a two-band model, where the unitary scattering due to impurities is assumed \([27]\), or a five-band model in a rather clean limit \([28]\), the experiments are well reproduced by such calculations. In fact, the results of \((1/T_1)s\) for \(^{75}\text{As}\) in the SC state are consistent with the latter model. This may be because the intrinsic behavior of \(1/T_1\) is measured for a highly homogeneous sample, which is guaranteed by the very sharp NMR linewidth. In this context, our results are consistently argued in terms of the extended \(s_\pm\)-wave pairing with a sign reversal of the order parameter among Fermi surfaces. Further, it would be desirable to measure \(1/T_1\) at temperatures lower than 4 K and to systematically examine an impurity effect in these compounds.

3.4. Normal-state properties of \(\text{LaFeAsO}_{1-y}\) and \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\)

Next, we address the normal-state properties of \(\text{LaFeAsO}_{1-y}\) and \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) through the \((1/T_1T)\) results. As shown in Fig. 9 \(^{57}(1/T_1T)\) at the Fe site for \(\text{LaFeAsO}_{0.7}\) gradually decreases upon cooling down to \(T_c\), resembling the behavior of \(^{75}(1/T_1T)\) measured by NQR at the As site. Actually, \(^{57}(1/T_1T)\) at the Fe site is well scaled to \(^{57}(1/T_1T)_{\text{NQR}}\) at the As site down to 60 K with a ratio of \(^{57}(1/T_1T)_{\text{NQR}} = 1.85\). It has been theoretically proposed that the multiple spin-fluctuation modes with \(Q = (\pi/4, \pi/4)\) and \((0,\pi/4)\) originating 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 of \((1/T_1T)\) results \([13]\), we could only state that the spin fluctuations at finite wave vectors are more significant than the ferromagnetic spin fluctuation 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 a decrease in the low-energy spectral weight of spin fluctuations over the entire \(q\) space from room temperature. In contrast, in the case of the copper-oxide superconductors, \((1/T_1T)\)s of \(^{63}\text{Cu}\) and \(^{57}\text{As}\) exhibit a different \(T\) dependence due to the difference in the \(q\)-dependence of \(^{63,17}\text{As}-NQR(q)\) and the development of AFM spin fluctuations around \(Q = (\pi/a, \pi/a)\) \([29]\). The suppression of spin fluctuations over the entire \(q\) space upon cooling below room temperature was observed in FeAs-based superconductors, which has never been observed for other strongly correlated superconductors where an AFM interaction plays a vital role in mediating the Cooper pairing.

Figure 10 shows the \(T\) dependence of \(1/T_1T\) in the normal state of \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) along with the results of \(^{75}\text{As-NQR} 1/T_1\) for the electron-doped \(\text{LaFeAsO}_{0.6}\) and \(^{75}\text{As-NMR} 1/T_1\) for the undoped \(\text{BaFe}_{2}\text{As}_2\) \([21]\) and the electron-doped \(\text{BaFe}(\text{Fe}_{0.95}\text{Cu}_{0.05})_{2}\text{As}_2\) \([30]\). It gradually increases upon cooling down to \(T_c(H) = 37\) K, in contrast to a significant decrease in the case of \(\text{LaFeAsO}_{0.7}\). However, it should be noted that \(1/T_1T\) in the electron-doped \(\text{BaFe}(\text{Fe}_{1-x}\text{Co}_x)_{2}\text{As}_2\) gradually decreases upon cooling and remains almost constant down to \(T_c = 20\) K below \(-100\) K \([30]\). It is remarkable that the \(T\) dependence of \(1/T_1T\) in the hole-doped \(\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_{2}\text{As}_2\) is significantly different from those in the electron-doped compounds such as \(\text{BaFe}(\text{Fe}_{1-x}\text{Co}_x)_{2}\text{As}_2\) and \(\text{LaFeAsO}_{1-y}\); nevertheless, the SC characteristics possess common features in these compounds. Recently, on the basis of the fluctuation exchange approximation (FLEX) on an effective five-band Hubbard model, Ikeda found...
that with decreasing temperatures, $1/T_1 T$ is enhanced in undoped and hole-doped systems. On the other hand, in electron-doped systems, it decreases significantly upon cooling, exhibiting a pseudogap behavior that originates from the band structure effect, that is, the existence of a high density of states just below the Fermi level. The effect becomes more remarkable with electron-doping. This qualitatively explains the NMR results. Such a pseudogap behavior exists even without electron correlation in the present band structure. Currently, the mechanism responsible for a pairing glue causing a possible extended $s_\pm$-wave pairing remains unknown.

3.5. $^{75}\text{As-NQR studies of REFeAsO}_{1-y}$ ($\text{RE} = \text{La, Pr, Nd}$)

Figure 11 shows the $^{75}\text{As-NQR}$ spectra just above their $T_c$s for $\text{LaFeAsO}_{0.75}$ ($T_c = 20$ K), $\text{LaFeAsO}_{0.6}$ ($T_c = 28$ K), $\text{LaFeAsO}_{0.6}$ ($T_c = 22$ K), $\text{PrFeAsO}_{0.6}$ ($T_c = 46$ K), and $\text{NdFeAsO}_{0.6}$ ($T_c = 53$ K). A $^{75}\text{As-NQR}$ frequency ($^{75}\nu_Q$) is obtained from the frequency at the peak of their $^{75}\text{As NQR}$ spectra. Figure 12 shows a plot of $T_c$ versus $^{75}\nu_Q$ for $\text{REFeAsO}_{1-y}$ ($\text{RE} = \text{La, Pr, Nd}$). In the case of the $\text{LaFeAsO}_{1-y}$ system, this plot appears to exhibit a dome-like shape, having a maximum $T_c = 28$ K at $^{75}\nu_Q = 10$ MHz. Note that the respective $T_c$s are 46 K and 53 K of the optimally doped samples of $\text{REFeAsO}_{0.6}$ ($\text{RE} = \text{Pr and Nd}$) become larger than $T_c = 28$ K of $\text{LaFeAsO}_{0.6}$ as $^{75}\nu_Q$ increases from 10 MHz in $\text{LaFeAsO}_{0.6}$ to 12 MHz in $\text{PrFeAsO}_{0.6}$ and $\text{NdFeAsO}_{0.6}$. This correlation between $T_c$ and $^{75}\nu_Q$ suggests an intimate relationship between the maximum value of $T_c$ and an optimum local structure, as revealed in literature [9].

$^{75}\nu_Q$ is proportional to the electric field gradient (EFG) along the $c$-axis $V_{zz}$. Here $\nu_Q = eQV_{zz}/2\sqrt{1+\eta^2/3}$, where $Q$ is the nuclear quadrupole moment of $^{75}\text{As}$ and $\eta$ is the asymmetry parameter of the EFG. The EFG is generally given by two contributions: one is a non-cubic charge distribution of $4\rho$ orbitals at the $^{75}\text{As}$ site and the other is the charge distribution arising from the surrounding ions around the $^{75}\text{As}$ site, denoted by $V_{zz}^{\text{in}}$ and $V_{zz}^{\text{out}}$, respectively. The former originates from the hybridization between the $4\rho$ orbitals and $3\text{-d}$ orbitals in the FeAs layer, and the latter may have a predominant contribution relevant to the Madelung potential originating from the charge distributions of the neighboring Fe atoms and REO$_{1-y}$ layers. The variation of lattice parameters through doping significantly influences $V_{zz}^{\text{out}}$, resulting in a dome-like shape in the plot of $T_c$ versus $^{75}\nu_Q$ for $\text{LaFeAsO}_{1-y}$, as shown in Fig. 12. In fact, the lengths of the $a$- and $c$-axes in the tetragonal structure decrease with oxygen content in $\text{LaFeAsO}_{1-y}$, and it decreases upon the replacement of La with Nd in $\text{REFeAsO}_{0.6}$. Despite the reduction in the lattice volume, the neutron diffraction experiment by Lee et al. has revealed that the distance between the Fe- and As-planes becomes larger in $\text{NdFeAsO}_{0.6}$ than in $\text{LaFeAsO}_{0.6}$ [9]. By assuming the point charges of the surrounding ions around the $^{75}\text{As}$ site, a simple calculation of $V_{zz}^{\text{out}}$ has revealed that the $V_{zz}^{\text{out}}$ becomes larger for $\text{NdFeAsO}_{0.6}$ than for $\text{LaFeAsO}_{0.6}$ and $\text{FeAsO}$. However, the calculated values of $^{75}\nu_Q$ cannot reproduce the experiments quantitatively, indicating that the on-site contribution $V_{zz}^{\text{in}}$ is also important in these compounds. Namely, the change in the distance between the Fe- and As-plane varies the charge distribution of the $\text{As}-4\rho$ orbitals, increasing $^{75}\nu_Q$ in going from non-superconducting $\text{LaFeAsO}$ to $\text{NdFeAsO}_{0.6}$ with $T_c = 53$ K. The variation of the hybridization between $\text{As}-4\rho$ orbitals and $\text{Fe}-3\text{d}$ orbitals induces the modification of the Fe-As layer-derived band structure as well. Here, we note that $^{75}\nu_Q = 2.2$ MHz for undoped $\text{BaFe}_2\text{As}_2$ is significantly lower than the value of 8.7 MHz for undoped $\text{LaFeAsO}$. The variation of lattice parameters due to the change in the crystal structure is expected to mainly influence $V_{zz}^{\text{out}}$. Interestingly, $^{75}\nu_Q$ in the $\text{BaFe}_2\text{As}_2$ system increases with K doping, suggesting that an increase in either the carrier density or the hybridization between $\text{As}-4\rho$ orbitals and $\text{Fe}-3\text{d}$ orbitals leads to an increase in $^{75}\nu_Q$.

Therefore, the intimate relationship between $\nu_Q$ and $T_c$ in $\text{REFeAsO}_{1-y}$ suggests that the local configuration of Fe and As atoms is significantly related to the $T_c$ of Fe-based pnictide superconductors, that is, $T_c$ can be enhanced up to 50 K when the local configuration of Fe and As atoms becomes optimal. Here, it may be relevant that $T_c$ becomes maximum when the bonding angle between Fe-As-Fe coincides with that of a regular tetrahedron of FeAs$_4$ [9].

4. Summary

$^{57}\text{Fe-NMR}$ and $^{75}\text{As-NQR/NMR}$ studies have clarified the novel SC and normal-state characteristics of $^{57}\text{Fe}$-enriched $\text{LaFeAsO}_{0.7}$ ($T_c = 28$ K) and $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ ($T_c = 38$ K). In the SC state of $\text{LaFeAsO}_{0.7}$ ($T_c = 28$ K), the spin component of the $^{57}\text{Fe-Knight}$ shift decreases to almost zero at low temperatures, which provide firm evidence of a superconducting state formed by spin-singlet Cooper pairing. The measurements of the Knight shift and $T_1$ have revealed that an extended $s_\pm$-wave pairing with a sign reversal of the order parameter can be a promising candidate.

In the normal state of $\text{LaFeAsO}_{0.7}$, we have found a remarkable decrease in $1/T_1 T$ upon cooling for both the Fe and As sites, whereas $1/T_1 T$ gradually increases upon cooling down to $T_c$ in the case of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. Remarkably, the $T$ dependence of $1/T_1 T$ in the normal state drastically changes when going from the hole-doped compound $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ to electron-doped compounds such as $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_{2}\text{As}_2$ and $\text{LaFeAsO}_{1-y}$; nevertheless, the SC characteristics are not drastically different among these compounds.

Recently, on the basis of the fluctuation exchange approximation (FLEX) on an effective five-band Hubbard model, Ikeda found that with decreasing temperatures, $1/T_1 T$ in an electron-doped system decreases significantly upon cooling, exhibiting a pseudogap behavior that originates from the band structure effect, that is, the existence of a high density of states just below the Fermi level [11]. This qualitatively explains the NMR results. Such pseudogap behavior exists even without electron correlation in the present band structure. Currently, the mechanism responsible for a pairing glue causing a possible extended $s_\pm$-wave pairing remains unknown. Further experiments on the $T_c$ dependences of $1/T_1$ and $K$ at both the Fe and As sites us-
ing a single crystal are required to understand the nature of spin fluctuations.

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Figure 1: (color online) (a) $^{57}$Fe-NMR spectra of LaFeAsO$_{0.7}$ at 30 K and $H$ = 11.97 T in the field parallel (●) and perpendicular (○) to the ab-plane. The T dependence of $^{57}$Fe-NMR spectra was obtained at (b) $H$ = 6.309 T and (c) $H$ = 11.97 T parallel to the ab-plane (θ = 90°).

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from evidence for a spin-singlet Cooper pairing state. (b) Its spin part indicates that the hyperfine-coupling constant $^{57}K_{ab}$ is negative at the Fe site, originating from the inner core-polarization. Figure 3: The recovery curves of $^{57}$Fe nuclear magnetization under the (a) normal state (30 K) and (b) SC state (10 K) for LaFeAsO$_{0.7}$ at $T = 30$ K ($T_c (H) = 28$ K). Note that it increases upon cooling, exhibiting a $T$ dependence opposite to those of the $^{75}$As and $^{19}$F sites [14, 15, 16]. This indicates that the hyperfine-coupling constant $^{57}K_{ab}$ is negative at the Fe site, originating from the inner core-polarization. (b) Its spin part $[^{57}K_{zz}]$ evaluated from $[^{57}K_{zz} - ^{57}K_{ab}]$ decreases to zero in the SC state, which provides firm evidence for a spin-singlet Cooper pairing state.

Figure 2: $T$ dependence of $^{57}K_{zz}$ at $H = 11.97$ T ($T_c (H) = 28$ K) measured by Fe-NMR for LaFeAsO$_{0.7}$. In a entire range of $M$ at $T = 28$ K, and $^{75}$As-NQR $1/T_1$ for LaFeAsO$_{0.6}$. In the SC state, $1/T_1$ is negative at the Fe site, which provides firm evidence for a spin-singlet Cooper pairing state.

Figure 4: $T$ dependence of $^{57}$Fe-NMR $1/T_1$ at $H= 6.309$ and 11.97 T for Fe-NMR $1/T_1$ at $H= 6.309$ and 11.97 T for $^{75}$As-NQR $1/T_1$ for LaFeAsO$_{0.6}$. In the SC state, $1/T_1$s at both the Fe and As sites follow a $T^3$-like dependence upon cooling without a coherence peak just below $T_c$.

Figure 5: The recovery curves of $^{75}$As nuclear magnetization for $^{75}$As-NQR ($H = 0$) at (a) the normal state (50 K) and (b) the SC state (20 K) for LaFeAsO$_{0.6}$. In the entire $T$ range, the recovery curves are uniquely fitted by $^{75}m(t)_{NQR} = (M(\infty) - M(t))/M(\infty) = \exp(-t/T_1)$ (dashed line).
Figure 6: (color online) $^{75}\text{As}$-NMR spectra of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ at 30 K (SC state), 100 K, and 150 K (normal state). The sharp central peak around $H \sim 5.1$ T originates from the $(\pm 1/2 \leftrightarrow -1/2)$ transition and the satellite peaks around $H \sim 4.7$ and $5.5$ T originate from the $(\pm 1/2 \leftrightarrow \pm 3/2)$ transitions.

Figure 7: The recovery curves of $^{75}\text{As}$ nuclear magnetization for the $^{75}\text{As}$-NMR measurement of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ at (a) the normal state (60 K) and (b) the SC state (10 K), which are uniquely determined by the theoretical function $75m(t)_{\text{NMR}} = (M(\infty) - M(i))/M(\infty) = 0.1 \exp(-t/T_1) + 0.9 \exp(-6t/T_1)$ (solid lines) in the entire $T$ range.

Figure 8: (color online) $T$ dependence of $^{75}\text{As}$-NMR $1/T_1$ at $H = 5.1$ T for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, along with the results for LaFeAsO$_{0.7}$ (T$_c = 28$ K). In the SC state of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, $^{75}\text{As}$-$1/T_1$ drops sharply below $T_c$($H$) = 37 K upon cooling without a coherence peak just below $T_c$. Although the $T$ dependence of $1/T_1$ well below $T_c$ appears to be similar to the $T^3$ behavior, it cannot be exactly reproduced by any simple SC gap model either with line nodes or without nodes. It may be related to the characteristics of the multiband SC state observed in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$.

Figure 9: $T$ dependence of $^{57}\text{Fe}$-$1/T_1$ at $H = 6.309$ T (•) and $H = 11.97$ T (closed diamond), along with $^{75}\text{As}$-NQR-$1/T_1$ in LaFeAsO$_{0.6}$ (o) [12]. The inset shows the plot of $^{75}(1/T_1)_{\text{NQR}}$ as the implicit parameter of $T$ between 30 and 240 K.
Figure 10: (color online) $T$ dependence of $1/T_1T$ for hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ by $^{75}$As-NMR and for electron-doped LaFeAsO$_{0.6}$ by $^{75}$As-NQR, along with the $^{75}$As-NMR results for the undoped BaFe$_2$As$_2$ (cited from Fukazawa et al. [21]) and the electron-doped Ba(Fe$_{0.895}$Co$_{0.105}$)$_2$As$_2$ (cited from Ning et al. [30]).

Figure 11: $^{75}$As NQR spectra just above their $T_c$s for LaFeAsO$_{0.75}$ ($T_c$ = 20 K), LaFeAsO$_{0.6}$ ($T_c$ = 28 K), LaFeAsO$_{0.6}$($\sharp$2) ($T_c$ = 22 K), PrFeAsO$_{0.6}$ ($T_c$ = 46 K), and NdFeAsO$_{0.6}$ ($T_c$ = 53 K).

Figure 12: (color online) A plot of $^{75}$As NQR frequency ($^{75}\nu_Q$) versus $T_c$ for LaFeAsO$_2$, LaFeAsO$_{0.75}$, LaFeAsO$_{0.6}$, PrFeAsO$_{0.6}$, and NdFeAsO$_{0.6}$. We have found an intimate relationship between the nuclear quadrupole frequency $\nu_Q$ of $^{75}$As and $T_c$ for the samples used in this study, revealing that $T_c$ is sensitive to the local configuration of the FeAs$_4$ tetrahedron.