Doping Dependence of Normal-State Properties in Iron-Based Oxypnictide Superconductor \( \text{LaFeAsO}_{1-y} \) Probed by \(^{57}\text{Fe-NMR}\) and \(^{75}\text{As-NMR/NQR}\)

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We report systematic \(^{57}\text{Fe-NMR}\) and \(^{75}\text{As-NMR/NQR}\) studies on an underdoped sample \((T_c = 20 \text{ K})\), an optimally doped sample \((T_c = 28 \text{ K})\), and an overdoped sample \((T_c = 22 \text{ K})\) of oxygen-deficient iron (Fe)-based oxypnictide superconductor \(\text{LaFeAsO}_{1-y}\). A microscopic phase separation between superconducting domains and magnetic domains is shown to take place in the underdoped sample, indicating a local inhomogeneity in association with the density distribution of oxygen deficiencies. As a result, \(1/T_1T\) in the normal state of the superconducting domain decreases significantly upon cooling at both the Fe and As sites regardless of the electron-doping level in \(\text{LaFeAsO}_{1-y}\). On the basis of this result, we claim that \(1/T_1T\) is not always enhanced by antiferromagnetic fluctuations close to an antiferromagnetic phase in the underdoped superconducting sample. This contrasts with the behavior in hole-doped \(\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2\) \((T_c = 38 \text{ K})\), which exhibits a significant increase in \(1/T_1T\) upon cooling. We remark that the crucial difference between the normal-state properties of \(\text{LaFeAsO}_{1-y}\) and \(\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2\) originates from the fact that the relevant Fermi surface topologies are differently modified depending on whether electrons or holes are doped into the FeAs layers.

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

1. Introduction

The discovery of superconductivity (SC) in the iron (Fe)-based oxypnictide \(\text{LaFeAsO}_{1-x}\) \(x\) with SC transition temperature \(T_c=26 \text{ K}\) has attracted considerable interest in the fields of condensed-matter physics and materials science.\(^1\) Soon after this discovery, the \(T_c\) of \(\text{LaFeAsO}_{0.85}\text{Fe}_{0.1}\) was reported to increase up 43 K upon applying pressure,\(^2\) and the replacement of the La site by other rare-earth (RE) elements significantly increases \(T_c\) to more than 50 K.\(^3\) The structure of the mother material contains alternately stacked \(\text{RE}_2\text{O}_3\) and FeAs layers along the c-axis, where the Fe atoms of the FeAs layer are located in a fourfold coordination forming a FeAs tetrahedron. The mother material LaFeAsO is a semimetal with a stripe antiferromagnetic (AFM) order with \(Q = (0, \pi)\) or \((\pi, 0)\).\(^7\) The substitution of fluorine for oxygen and/or oxygen deficiencies in the LaO layer yields a novel SC.\(^1,3,6\) Remarkably, Lee \textit{et al.} found that \(T_c\) increases to a maximum value of 54 K when the FeAs tetrahedron is transformed into a regular tetrahedron.\(^8\)

Related to this fact, Shirage \textit{et al.} revealed that the \(a\)-axis length, corresponding to the distance among Fe atoms in the square lattice, also has a strong correlation with \(T_c\) in the RE-Fe-As-O system, as presented in Fig. 1.\(^9\)

In the normal state of \(\text{LaFeAsO}_{1-x}\) \(x\), pseudogap-like behavior was first reported on the basis of photoemission,\(^10\) \(^{75}\text{As-NMR,}\)\(^11\) and \(^{19}\text{F-NMR}\)\(^12\) measurements. Similar behavior was also reported by \(^{75}\text{As-NMR}\) probe for the electron-doped superconductor \(\text{Ba}(\text{Fe}_{0.89}\text{Co}_{0.105})\text{As}_2\)\(^13\) but not for the hole-doped \(\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2\)\(^14,15\). This suggests that the decrease of \(^{75}\text{As-NMR-(1/T_1T)}\) upon cooling, or pseudogap-like behavior, may characterize the normal-state properties in electron-doped Fe-pnictide systems. However, it has been reported by Nakai \textit{et al.}\(^11,16\) that \(^{75}\text{As-NMR-(1/T_1T)}\) is markedly enhanced upon cooling for underdoped \(\text{LaFeAsO}_{1-x}\) \(x\) \((x = 0.04)\). In addition, they observed a peak at \(\sim 30 \text{ K}\) in \(1/T_1\) below which the \(^{75}\text{As-NMR}\) spectral width starts to broaden gradually upon cooling.

In this paper, we report systematic studies on the doping dependence of the normal-state properties of electron-doped superconductors \(\text{LaFeAsO}_{1-y}\) by means of \(^{57}\text{Fe-NMR}\) and \(^{75}\text{As-NMR/NQR}\) measurements. A microscopic phase separation between SC and magnetic domains is demonstrated to take place in an underdoped sample, indicating a local inhomogeneity in association with the density distribution of oxygen deficiencies. As a result, it is highlighted that \(1/T_1T\) at both the Fe and As sites decreases markedly upon cooling, even in SC domains close to an AFM phase, and hence this behavior is a common feature regardless of electron-doping level. This, however, differs from the drastic doping dependence previously observed for \(^{75}\text{As-NMR-(1/T_1T)}\), which is markedly enhanced upon cooling in the underdoped sample.\(^16\) We also address the crucial difference observed between the normal-state properties of \(\text{LaFeAsO}_{1-y}\) and \(\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2\).
Table I. Transition temperatures and lattice parameters at room temperature for a nondoped sample (ND), an underdoped sample (UD), an optimally doped sample (OPT), and an overdoped sample (OVD) of LaFeAsO$_{1-y}$. Note that $T_c$ can be almost exactly reproduced when the $a$-axis length is identical, even though the nominal oxygen content is different.

| Sample   | $T_c$ [K] | $a$ [Å]   | $c$ [Å]   | References |
|----------|----------|-----------|-----------|------------|
| ND LaFeAsO$_{1-y}$ | $\sim$ | 4.0346 | 8.752 |
| UD LaFeAsO$_{1-y}$ | 20 | 4.0390 | 8.7136 |
| UD LaFeAsO$_{0.78}$ | 20 | 4.0297 | 8.7143 |
| OPT LaFeAsO$_{1-y}$ | 28 | 4.0226 | 8.7065 | (17) |
| OPT LaFeAsO$_{0.75}$ | 28 | 4.0220 | 8.7110 | (18) |
| OVD LaFeAsO$_{0.6}$ | 22 | 4.0087 | 8.6978 |

†)57Fe-enriched sample.
*)$T_N \sim 145$ K.

2. Experimental

Polycrystalline samples of LaFeAsO$_{1-y}$ were synthesized via a high-pressure synthesis technique described elsewhere. In particular, starting materials of La$_2$O$_3$, Fe$_2$O$_3$, and As$_2$O$_3$ were mixed at a nominal composition of LaFeAsO$_{1-y}$. Powder X-ray diffraction measurements indicate that these samples are almost entirely composed of a single phase, even though the oxygen content of the samples differs from the nominal content, depending on the oxidation of the starting RE elements. In fact, the SC transition temperature ($T_c$) for all samples was uniquely determined by a susceptibility measurement, which exhibits a marked decrease due to the onset of SC diamagnetism. There is a strong correlation between $T_c$ and the $a$-axis length in RE-Fe-As-O systems. As summarized in Table I and Fig. 1, the $T_c$ of LaFeAsO$_{1-y}$ is almost the same if the $a$-axis length is identical regardless of the process used to prepare samples. Bulk SC was not obtained in the sample with $a > 4.034$. $^{57}$Fe-NMR and $^{75}$As-NMR/NQR measurements were carried out on an underdoped sample (UD), an optimally doped sample (OPT), and an overdoped sample (OVD) with $T_c = 20$ K, 28 K, and 22 K, respectively. All samples were moderately crushed into powder. The nuclear spin-lattice relaxation rate $1/T_1$ was measured by the saturation-recovery method.

3. Results

3.1 $^{57}$Fe-NMR study on LaFeAsO$_{1-y}$

Figure 2 shows $^{57}$Fe-NMR spectra obtained by sweeping the frequency $f$ at magnetic field $H = 11.97$ T at 30 K for (a) UD, (b) OPT, and (c) OVD of LaFeAsO$_{1-y}$. For OPT, which was oriented along the direction including the $ab$-plane, we observed a single narrow peak when $H$ was applied parallel to the orientation direction, as shown in Fig. 2(b). In the field perpendicular to the orientation direction, two horn-shaped peaks were observed, which arise from crystals with $\theta = 90$ and 0°, where $\theta$ is the angle between the field and the $c$-axis of the crystal. Such a spectral shape originates from the anisotropy of the Knight shift with $^{57}$K$^\parallel \sim 1.413%$ and $^{57}$K$^\perp \sim 0.50%$ at 30 K for $\theta = 90$ and 0°, respectively. For UD, the $^{57}$Fe-NMR spectral width at 30 K is broader than that for OPT, even though it is as narrow as that for OPT at 200 K (see Fig. 10(a)). This suggests that the broad spectrum at 30 K for UD with the field parallel to the $ab$-plane is ascribed to the distribution of the $^{57}$Fe-NMR Knight shift. Figure 2(c) shows the spectrum of nonoriented OVD, which has an asymmetric powder pattern due to the anisotropy of the $^{57}$Fe-NMR Knight shift, as corroborated by the $^{75}$As-NMR spectrum (see Fig. 5(c)). The temperature ($T$) dependence of the $^{57}$Fe Knight shift was precisely measured for OPT as reported in the literature, but not for UD and OVD because of their broad NMR spectral width. Thus, we focus on the nuclear relaxation behavior to unravel the doping dependence of the normal-state properties in LaFeAsO$_{1-y}$.

The $^{57}$Fe was measured at $H = 11.97$ T along the $ab$-plane ($\theta = 90°$) for all samples. As shown in Fig. 3, $T_1$ was almost uniquely determined over the entire $T$ range from a single exponential function of $^{57}m(t)_{NMR}$, which is given by $^{57}m(t)_{NMR} = \frac{M(\infty) - M(t)}{M(\infty)} = \exp \left( - \frac{t}{T_1} \right)$, where $M(\infty)$ and $M(t)$ are the respective nuclear magnetizations for the thermal equilibrium condition and at time $t$ after the saturation pulse.

Figure 4 shows the $T$ dependences of $^{57}$Fe-(1/$T_1T$) for UD, OPT, and OVD. In the normal state, 1/$T_1T$ decreases significantly upon cooling for all samples, and the magnitude of 1/$T_1T$ decreases markedly as the doping level increases from UD to OVD. The relaxation behaviors of $^{57}$Fe-(1/$T_1T$) for OPT and OVD respectively resemble those of $^{75}$As-NMR(1/$T_1T$) for LaFeAsO$_{1-x}$F$_x$ with $x = 0.11$ and 0.14. In contrast, the relaxation behavior of $^{57}$Fe-(1/$T_1T$) for UD is considerably different from that of $^{75}$As-NMR-(1/$T_1T$) for the underdoped...
The broad spectrum of UD (a) with the field parallel to the ab-plane originates from the inhomogeneous distribution of the $^{57}$Fe Knight shift, which is caused by the phase separation into SC and magnetic domains at a microscopic scale in UD close to an AFM phase (see text). The spectrum of OVD (c), which was not oriented, indicates an asymmetric powder pattern due to the anisotropy of the $^{57}$Fe Knight shift.

In contrast, the relaxation behavior of $^{57}$Fe-(1/T$_1$T) for UD is considerably different from that of $^{75}$As-NMR-(1/T$_1$T) for the underdoped LaFeAsO$_{1-x}$F$_x$ with $x=0.04$, which is enhanced upon cooling.$^{11,16}$

Figures 5(a)-5(c) respectively show the $^{75}$As-NMR spectra at 30 K and $H = 11.97$ T for UD, OPT, and OVD of LaFeAsO$_{1-y}$. The sharp peak at approximately $f \sim 87.6$ MHz for all samples originates from the central transition ($I = +1/2 \leftrightarrow -1/2$) in the field parallel to the ab-plane ($\theta = 90^\circ$). The spectrum of OVD (c), which was not oriented, indicates an asymmetric powder pattern due to the anisotropy of the $^{75}$As Knight shift. Note that the resonance frequency for $\theta = 90^\circ$ is almost invariant for all samples, in contrast with that in the $^{57}$Fe-NMR spectra indicated in Fig. 2. This is because that the $^{75}$As Knight shift is smaller than the $^{57}$Fe Knight shift.

The recovery curve of $^{75}$As nuclear magnetization ($I = 3/2$) obtained by the $^{75}$As-NMR measurement is expressed by the following theoretical curve:

$$^{75}m(t)_{\text{NMR}} = 0.1 \exp \left( -\frac{t}{T_1} \right) + 0.9 \exp \left( -\frac{6t}{T_1} \right).$$

As shown in Fig. 6(a), $^{75}m(t)_{\text{NMR}}$ can be fitted by a theoretical curve at high temperatures ($T \geq 160$ K) for all samples. For UD, however, since it cannot be reproduced by a single component of $T_1$ below $\sim 150 \pm 10$ K, as shown in Fig. 6(b), a long component ($T_{1L}$) and a short component ($T_{1S}$) are tentatively estimated by assuming the expression $^{75}m(t)_{\text{NMR}} \equiv A_S^{75}m_S(t)_{\text{NMR}} + A_L^{75}m_L(t)_{\text{NMR}}$. Here, $A_S$ and $A_L$ (with $A_S + A_L = 1$) are the respective fractions of domains with $T_{1S}$ and $T_{1L}$. The respective $A_S$ for UD, OPT, and OVD are 0.7–0.8, 0.3–0.4, and $\sim 0.4$, revealing that the volume fraction of domains with $T_{1S}$ is increased when a sample approaches an AFM order and/or a structural transition. It should be noted that the $T_1$ of OVD was almost uniquely determined from a single component over the entire $T$ range, although the

LaFeAsO$_{1-x}$F$_x$ with $x=0.04$, which is enhanced upon cooling.$^{11,16}$ In order to reconcile why the $T$ dependence of 1/T$_1T$ for the present $^{57}$Fe-NMR differs from the previous results obtained by $^{75}$As-NMR measurements, in the next section we discuss with the $^{75}$As-NMR $T_1$ measurements on the same samples as those in $^{57}$Fe-NMR study.
fraction of oxygen deficiencies is larger for OVD than for UD, revealing that the inhomogeneity of electronic states may be significant in UD close to an AFM phase and/or a structural transition.

Figure 7 shows the $T$ dependences of $^{75}$As-NMR $(1/T_1T)$ at $H=11.97$ T along the $ab$-plane ($\theta = 90^\circ$) for all samples. In OVD, $^{75}$As-$(1/T_1T)$ gradually decreases upon cooling to $T_c$, resembling the results of $^{57}$Fe-$\nu_0$ (Fig. 4). $^{75}$As-$(1/T_1T)$ for UD and OPT also decrease upon cooling to their $T_c$ similarly to the results of $^{57}$Fe-$\nu_0$ (Fig. 4). In fact, Fig. 8 reveals that the $T$ dependence of $^{75}$As-$(1/T_1T)$ is well scaled to that of $^{57}$Fe-$\nu_0$ (Fig. 4) with a ratio of $^{57}$Fe-$(1/T_1T)$ to $^{75}$As-$(1/T_1T)$ of $\sim 1.3$. This suggests that these $^{75}$As-NMR properties of UD and OPT are not scaled to $^{57}$Fe-$\nu_0$, as indicated in Fig. 8. These results indicate that UD and OPT may contain unknown phases in addition to Fe-based oxypnictide superconductors. Here, we remark that the relaxation behaviors of $^{75}$As-$(1/T_1S$) for UD and OPT resemble those of LaFeAsO$_{1-x}$F$_x$ with $x = 0.04$ and 0.07, respectively.

In order to inspect whether or not the unknown phases are Fe-based oxypnictide phases, we measured $^{75}$As-NQR $T_1$ for UD at the $^{75}$As-NQR frequency inherent to LaFeAsO$_{1-y}$. Because the volume fraction of domains with $T_{1S}$ is increased when a sample approaches an AFM phase and/or a structural transition, it is likely that these domains arise from magnetic phases. In order to confirm this, we next present the relaxation behavior for the nondoped sample (ND).

3.3 Zero-field $^{75}$As-NMR in nondoped LaFeAsO

In magnetically ordered materials, the NMR spectrum can be observed at a zero field, since an internal field $H_{int}$ is induced by magnetically ordered moments. Figure 9 shows the $^{75}$As-NMR spectra at a zero field in the AFM state at 2.2 K for nondoped LaFeAsO (ND). The very sharp NMR spectra of ND indicate the good quality of the sample. Two narrow spectra at 11.7 and 20.6 MHz can be simulated using the NQR frequency $\nu_Q = 8.8$ MHz and $H_{int} = 1.60$ T along the $c$-axis, as shown by the solid curve in the figure. Note that $H_{int}$ at the As site is the off-diagonal pseudodipole field induced by the stripe-type AFM ordered moments in the $ab$-plane. Interestingly, $H_{int} = 1.60$ T for LaFeAsO is nearly equal to $H_{int} = 1.5$ T for BaFe$_2$As$_2$. The $^{75}$As-NMR $T_1$ of ND, which was measured in the paramagnetic state in the range $T=150-250$ K at $H=11.97$ T parallel to the $ab$-plane, was uniquely determined. $^{75}$As-NMR spectra have been published elsewhere. The $^{75}$As-$(1/T_1T)$ of ND is presented in Fig. 7, with those of UD, OPT, and OVD. The $^{75}$As-$\nu_0$ of ND appears to be markedly enhanced toward the AFM ordering temperature $T_N \sim 145$ K, resembling the results of $^{139}$La-NMR $1/T_1$. This relaxation behavior differs from those for the SC phases in UD, OPT, and OVD, which exhibit a significant decrease upon cooling. In this context, the reason for the increase in $^{75}$As-$\nu_0$ for UD upon cooling may be ascribed to the inclusion of some magnetic domains. We next focus on this issue.
the implicit parameter of \(T\) and OVD. The 75As-(1/\(T\)) for UD and OPT increase and stay a nearly constant upon cooling, respectively; neither of which are scaled to 57Fe-(1/\(T\)).

The observation of two components (\(T_{1S}\) and \(T_{1L}\)) of \(T_1\) in UD indicates some local inhomogeneity in association with the density distribution of oxygen deficiencies. Namely, it is likely that magnetic domains are nucleated owing to its relatively low density of oxygen deficiencies in UD. The fraction \(A_S\) of magnetic domains in UD, which exhibits the increase in 1/\(T_{1S}\) upon cooling, is 0.7–0.8, revealing that the magnetic domains appear to be separated from the SC domains when the doping level approaches an AFM phase and/or a structural transition. Here we comment on why 57Fe-NMR-\(T_1\) in UD was determined by an almost single component even though a phase separation into the magnetic and SC domains takes place. Figures 10(a) and 10(b) respectively show 57Fe-NMR and 75As-NMR spectra for UD. Figure 10(c) shows the \(T\) dependence of the linewidth of both spectra. The 57Fe linewidth increases significantly upon cooling below 130–150 K, whereas the 75As linewidth increases gradually below 130–150 K. These results suggest that a tiny magnetic moment is induced at the Fe site in the magnetic domains below 130–150 K. The further increase of 75As linewidth is seen below \(T_A\) ~40 K, suggesting that the increase of magnetic-domain size upon cooling stabilizes the static short-range magnetic order (SRMO) in UD, which is corroborated by the observation of the peak in 1/\(T_{1S}\) at \(T_A\) shown in Fig. 7. 57Fe-(1/\(T\)) was measured at the center of the broad 57Fe-NMR spectra that arises predominantly from the SC domains and hence was almost uniquely determined. On the other hand, since the broadening of the 75As-NMR spectra is much less than that of the 57Fe-NMR spectra and hence the center of the 75As-NMR spectra arises

4. Discussion

4.1 Phase separation in the underdoped sample (UD)

The observation of two components (\(T_{1S}\) and \(T_{1L}\)) of \(T_1\) in UD indicates some local inhomogeneity in association with the density distribution of oxygen deficiencies. Namely, it is likely that magnetic domains are nucleated owing to its relatively low density of oxygen deficiencies in UD. The fraction \(A_S\) of magnetic domains in UD, which exhibits the increase in 1/\(T_{1S}\) upon cooling, is 0.7–0.8, revealing that the magnetic domains appear to be separated from the SC domains when the doping level approaches an AFM phase and/or a structural transition. Here we comment on why 57Fe-NMR-\(T_1\) in UD was determined by an almost single component even though a phase separation into the magnetic and SC domains takes place. Figures 10(a) and 10(b) respectively show 57Fe-NMR and 75As-NMR spectra for UD. Figure 10(c) shows the \(T\) dependence of the linewidth of both spectra. The 57Fe linewidth increases significantly upon cooling below 130–150 K, whereas the 75As linewidth increases gradually below 130–150 K. These results suggest that a tiny magnetic moment is induced at the Fe site in the magnetic domains below 130–150 K. The further increase of 75As linewidth is seen below \(T_A\) ~40 K, suggesting that the increase of magnetic-domain size upon cooling stabilizes the static short-range magnetic order (SRMO) in UD, which is corroborated by the observation of the peak in 1/\(T_{1S}\) at \(T_A\) shown in Fig. 7. 57Fe-(1/\(T\)) was measured at the center of the broad 57Fe-NMR spectra that arises predominantly from the SC domains and hence was almost uniquely determined. On the other hand, since the broadening of the 75As-NMR spectra is much less than that of the 57Fe-NMR spectra and hence the center of the 75As-NMR spectra arises
comes less prominent. The AFM order in most mother going from UD to OVD, the fraction of magnetic do-

Fig. 11. As the oxygen deficiencies are increased when going from UD to OVD, the fraction of magnetic domains becomes smaller in OPT and disappears in OVD, since their spatial distribution of electronic states becomes less prominent. In UD, short-range magnetic order (SRMO) in the magnetic domain is suggested from the line broadening of NMR spectra. However no such broadening of the spectra was confirmed for OPT, probably due to the very small internal field.

Fig. 10. (color online) $T$ dependence of (a) $^{57}$Fe-NMR and (b) $^{75}$As-NMR spectra for the oriented UD sample in the field $H = 11.97$ T parallel to the ab-plane. (c) $T$-dependence of the linewidth of these $^{57}$Fe-NMR and $^{75}$As-NMR spectra. It is noteworthy that the broadening of the NMR spectra is more significant at the Fe site than at the As site.

from both the magnetic and SC domains. $^{75}$As-(1/$T_1 T$) includes two components, 1/$T_{1S}$ and 1/$T_{1L}$, corresponding to the magnetic and SC domains, respectively. Note that similar results were also reported in previous works in underdoped LaFeAsO$_{1-x}$F$_x$ ($x = 0.04$), and in which it was claimed that $T_A$ corresponds to the maximum of resistivity, implying the crossover from a bad metal to a somewhat better metal. We consider that the tiny moments induced in the magnetic domains below $\sim 150$ K may develop SRMO below $T_A$. Interestingly, the 1/$T_{1S}$ of the magnetic domains decreases markedly below $T_c$, as shown in Fig. 7, which is presumably due to an SC proximity effect in association with the mixture of magnetic and SC domains. In this context, $^{57}$Fe-NMR studies play a vital role in deducing the intrinsic normal-state properties of SC domains in Fe-based superconductors.

4.2 Phase diagram of LaFeAsO$_{1-y}$

The phase diagram of LaFeAsO$_{1-y}$ in Fig. 1 shows the evolution from AFM to SC as a function of the $a$-axis length, which becomes shorter as oxygen deficiencies are introduced into the LaO layer. As a result of the systematic $^{57}$Fe-NMR and $^{75}$As-NMR measurements, we reveal the phase transition between AFM and SC as a function of oxygen deficiencies in LaFeAsO$_{1-y}$, as illustrated in Fig. 11. As the oxygen deficiencies are increased when going from UD to OVD, the fraction of magnetic domains becomes smaller in OPT and disappears in OVD, since their spatial distribution of electronic states becomes less prominent. The AFM order in most mother materials of Fe pnictides takes place slightly below the temperature of the first-order structural phase transition from tetragonal to orthorhombic. Accordingly, it is likely that the local inhomogeneity of oxygen deficiencies in UD is responsible for the phase separation into magnetic and SC domains. The features presented here resemble the phase diagram of LaFeAsO$_{1-y}$ revealed by $\mu$SR. A phase separation has also been reported for the sample near the phase boundary between the AFM and SC states.

4.3 Normal-state properties of electron- and hole-doped Fe pnictides

Finally, we compare the normal-state properties of electron-doped LaFeAsO$_{1-y}$ and hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. Figure 12(a) shows the $T$ dependences of $^{57}$Fe-(1/$T_1 T$) in the SC domains of UD, OPT, and OVD along with that for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. In the case of electron-doped LaFeAsO$_{1-y}$, it is noteworthy that (1/$T_1 T$) decreases upon cooling for all superconducting samples, revealing that AFM fluctuations are not dominant, even approaching the AFM phase. By contrast, the 1/$T_1 T$ of the optimally hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ markedly increases upon cooling to $T_c$. A recent theoretical work appears to qualitatively explain this on the basis of a fluctuation-exchange approximation (FLEX) using an effective five-band Hubbard model; in electron-doped systems, 1/$T_1 T$ and spin susceptibility decrease significantly upon cooling, suggesting a band structure effect, that is, the existence of a high density of states slightly below the Fermi level. This is consistent with the experimental finding for electron-doped LaFeAsO$_{1-y}$ that the Knight shift in OPT of LaFeAsO$_{1-y}$ decreases upon cooling as well as 1/$T_1 T$. On the other hand, the $T$ dependence of 1/$T_1 T$ is markedly enhanced down to $T_c$ in hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, whereas the $T$ dependence of the Knight shift remains constant in this $T$ range. These results do not appear to be understandable in terms of only a simple band-structure effect in this compound; the evolution of AFM spin fluctuations should additionally be taken into account.

On the basis of these results, we claim that 1/$T_1 T$ is
not always enhanced by AFM fluctuations close to an AFM phase in the underdoped SC sample of Fe pnictides. According to the theoretical study by Kuroki et al., such AFM spin fluctuations may be attributed to the multiple spin-fluctuation modes arising from nesting across the disconnected Fermi surfaces. In this scenario, we deduce that a better nesting condition among the Fermi surfaces is realized in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ than in LaFeAsO$_{1-y}$. Consequently, we remark that the crucial difference between the normal-state properties of LaFeAsO$_{1-y}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ may originate from the fact that the relevant Fermi surface topologies are differently modified depending on whether electrons or holes are doped into the FeAs layers.

In the superconducting state, as shown in Fig. 13, 1/$T_1$ exhibits almost $T^3$-like dependence below $T_c (H)$ regardless of the doping level of LaFeAsO$_{1-y}$ in this $T$ range, which was significantly different from the $T^5$-like dependence of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (cited from ref. 24). As reported in a recent paper, the different behavior can be ascribed to the stronger coupling SC in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ ($T_{c}^{max} = 38$ K) than in LaFeAsO$_{1-y}$ ($T_{c}^{max} = 28$ K). Therefore, it is reasonable that the difference in the superconducting properties between LaFeAsO$_{1-y}$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ can be understood by the difference in their normal-state properties. In this context, we propose that the Fermi surface topology, namely a nesting condition among the disconnected Fermi surfaces, may be responsible for SC characteristics inherent to each Fe-based superconductor.

Fig. 13. (color online) $T$ dependences of $\gamma (1/T_1 T)$ for electron-doped LaFeAsO$_{1-y}$ and hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ (cited from ref. 24). 1/$T_1 T$ in the electron-doped LaFeAsO$_{1-y}$ decreases upon cooling, revealing that AFM spin fluctuations are not dominant, even approaching the vicinity of the AFM phase. By contrast, the 1/$T_1 T$ of the optimally hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ markedly increases upon cooling to $T_c$.

5. Summary

Systematic $^{57}$Fe-NMR and $^{75}$As-NMR/NQR studies on the oxygen-deficient Fe-oxypnictide superconductor LaFeAsO$_{1-y}$ have revealed a microscopic phase separation into SC and magnetic domains in an underdoped sample with $T_c = 20$ K. As oxygen-deficiencies are increased when going from an underdoped sample to the overdoped sample, the fraction of magnetic domains becomes smaller and disappears in the overdoped sample, since the spatial distribution of electronic states becomes less prominent. It was demonstrated that 1/$T_1 T$ in the SC domains of the underdoped sample decreases markedly upon cooling to $T_c$ for both the Fe and As sites as well as the results in the optimally doped and overdoped samples. As a result, we consider that the decrease of 1/$T_1 T$ upon cooling may be a common characteristic of the normal-state property of electron-doped LaFeAsO$_{1-y}$ superconductors, regardless of the electron-doping level. This contrasts with the behavior in hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, which exhibits a significant increase in 1/$T_1 T$ upon cooling. This crucial difference in the normal-state properties between LaFeAsO$_{1-y}$ and
\( \text{Ba}_0.0\text{K}_{0.4}\text{Fe}_2\text{As}_2 \) may originate from the fact that relevant Fermi surface topologies are differently modified depending on whether electrons or holes are doped into the FeAs layers. From the comparison between the superconducting and normal-state properties, we propose that the Fermi surface topology, namely a nesting condition among the disconnected Fermi surfaces, may be responsible for SC characteristics inherent to each Fe-based superconductor. A remaining important issue is to investigate the correlation between the electronic structure and SC characteristics in various Fe-pnictide superconductors, which may lead to a general SC mechanism of Fe-based superconductors. Experiments to investigate this issue are now in progress.

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