Nuclear spin-lattice relaxation rate in the superconducting state on La(Fe\(_{1-x}\)Zn\(_x\))AsO\(_{0.85}\) studied by \(^{75}\)As-NMR

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Abstract. \(^{75}\)As nuclear spin-lattice relaxation rate \(1/T_1\) was measured in Zn-free and Zn-substituted La(Fe\(_{1-x}\)Zn\(_x\))AsO\(_{0.85}\) \((x = 0, \) and 0.05), \(T_c\) of which is 25 K and 0 K, respectively. Although the temperature dependence of \(1/T_1\) above \(T_c\) is the same between two samples, \(1/T_1\) of \(x = 0\) shows \(T^{3.0\pm0.1}\) dependence \((1/T_1 \propto T^3)\) in the superconducting (SC) state, but \(1/T_1\) of non-SC \(x = 0.05\) sample continuously decreases below 50 K. The normalized \(1/T_1\) \(\left(1/T_1\right)_{x=0}/\left(1/T_1\right)_{x=0.05}\), which is related to the SC gap structure, is proportional to \(T^{2.4\pm0.1}\) below \(T_c\). These results indicate that the temperature dependence of \(1/T_1\) in the SC state can be affected by the temperature dependence of the normal-state \(1/T_1\).

Introduction
One of the most important issues in iron-based superconductors is to identify their superconducting(SC) gap structure and pairing symmetry experimentally. Until now, it has become clear that iron-based superconductors have a non-universal SC gap structure, i.e. various experiments suggest that \(R\)FeAs(O,F) \((R:\) rare-earth elements) with the “1111” structure and \((\text{Ba,K})\)Fe\(_2\)As\(_2\) with the “122” structure possess multi-SC gaps, but BaFe\(_2\)(As,P)\(_2\) and Ba(Fe,Co)\(_2\)As\(_2\) with heavily doping possess nodes in the SC gaps[1]. At present, the pairing symmetry and thus the SC mechanism are controversial issues, since the SC mechanism is closely related with the pairing symmetry. There are two candidates of the pairing symmetry for \(R\)FeAs(O,F); spin fluctuations mediated \(s_{\pm\pm}\)-wave[2, 3, 4] and orbital fluctuations mediated \(s_{++}\)-wave[5].

In general, nuclear magnetic resonance (NMR) measurements give important information about the pairing symmetry. To determine the parity of SC pairing, the Knight-shift measurements give crucial information about the spin state of a SC pair. In addition, the measurements of nuclear spin-lattice relaxation rate \(1/T_1\) give information about the SC gap structure. Existence of a significant coherence peak just below \(T_c\), as well as an exponential
temperature dependence of $1/T_1$ at low temperatures indicates that the SC gap is isotropic and finite. Temperature dependence of $1/T_1$ well below SC transition temperature $T_c$ is related to low-energy quasiparticle excitations, and thus to a nodal structure.

In iron-based superconductors, there are many NMR studies reported in the SC state. Most Knight-shift measurements show that spin susceptibility decreases below $T_c$, indicative of a spin singlet pairing[6, 7]. Moreover, $1/T_1$ shows absence of a coherence peak just below $T_c$, suggestive of sign-changed SC gaps[8, 9] since a coherence factor of the sign-changed SC gaps vanishes when the coherence factor is integrated over the Brillouin zone. However, various temperature dependences of $1/T_1 T$ below $T_c$ have been reported: $1/T_1 T \propto T^n$: $n \simeq 2 \sim 5$ has been observed[9, 8, 10, 11]. One of the reasons for this variety of temperature dependence of $1/T_1 T$ in the SC state might be due to temperature dependence of $1/T_1 T$ in the normal state. Temperature dependent normal-state is different with different carrier concentrations and affects temperature exponent of $1/T_1 T$ in the SC state. Indeed, the theoretical studies indicate that normal-state $1/T_1 T$ is temperature dependent and is changed by doping due to the characteristic band dispersion around the Fermi energy[12, 13].

In this paper, we measured temperature dependence of $1/T_1 T$ in Zn-free and Zn-substituted La(Fe$_{1-x}$Zn$_x$)$_2$AsO$_{y+0,05}$ ($x = 0$, and 0.05). Comparing with the SC $x = 0$ sample and the $x = 0.05$ sample in which superconductivity is suppressed by Zn-substitution, we found that $1/T_1 T$ in the normal state is temperature dependent below 50 K and normalized SC-state $1/T_1 T \propto T^{2.4 \pm 0.1}$ although $1/T_1 T$ at $x = 0$ is proportional to $T^{3.0 \pm 0.1}$ below $T_c$. When we discuss the SC gap symmetry from $1/T_1 T$, we should note that the temperature dependence of $1/T_1 T$ in the SC state is affected by the normal-state $1/T_1 T$, which is one of the reasons for various temperature dependences observed in the SC state.

![Figure 1](image_url)

**Figure 1.** (Color online)(a) Meissner signals for La(Fe$_{1-x}$Zn$_x$)$_2$AsO$_{y+0,05}$ ($x = 0$, and 0.05) measured by an identical NMR coil. The arrow indicates $T_c$ at $x = 0$. (b) Temperature dependence of $1/T_1 T$ for $x = 0$, and 0.05. On cooling, $1/T_1 T$ at $x = 0$ slightly increases down to 100 K, and decreases from $\sim 50 K$. $1/T_1 T$ in the normal state hardly changes by Zn substitution.

We performed $^{75}$As-NMR measurements in polycrystalline samples of Zn-substituted La(Fe$_{1-x}$Zn$_x$)$_2$AsO$_{y+0,05}$ ($x = 0$, and 0.05), which were used in the previous reports[14]. $T_c$ of the Zn-free $x = 0$ sample is 24 K, and the $x = 0.05$ sample does not show any Meissner signals as shown Fig. 1 (a), which is consistent with the previous reports[14, 15]. Conventional spin-echo technique was utilized for following NMR measurements.

Figure 1(b) shows the temperature dependence of $1/T_1 T$ at 72.1 MHz ($\mu_0 H = 9.90$ T) in La(Fe$_{1-x}$Zn$_x$)$_2$AsO$_{y+0,05}$ ($x = 0$, and 0.05). On cooling, $1/T_1 T$ at $x = 0$ slightly increases down to 100 K, and decreases from $\sim 50 K$ above $T_c$. From comparing this result with previous NMR measurements.
results in LaFeAsO$_{1-y}$ reported by Mukuda et al.,[10], electron doping of our $x = 0$ sample is lower, since $1/T_1T$ at 100 K is larger than those in their underdoped $y \sim 0.2$ sample. $1/T_1T$ at $x = 0$, and 0.05 are almost the same above 24 K, suggesting that Zn substitution modifies neither carrier doping level nor Fermi surface properties.

![Figure 2](image)

**Figure 2.** (Color online)(Main panel) Temperature dependence of $1/T_1T$ for $x = 0$, and 0.05. $1/T_1$ at $x = 0$ suddenly decreases due to opening SC gap and is proportional to $T^{3.0 \pm 0.1}$. On the other hand, $1/T_1$ at $x = 0.05$ is proportional to $T^{0.4 \pm 0.1}$ below 40 K although the $x = 0.05$ sample does not show superconductivity. Solid lines are corresponding to fitting lines. (Inset) Temperature dependence of normalized $1/T_1T/[(1/T_1T)_{x=0}/(1/T_1T)_{x=0.05}]$. Normalized $1/T_1T$ is proportional to $T^{2.4 \pm 0.1}$ below $T_c$. Solid line is corresponding to a fitting line.

Below 24 K, $1/T_1T$ in the Zn-free sample suddenly decreases due to opening SC gap, but $1/T_1T$ in the Zn-substituted sample gradually decreases below $\sim 50$ K. Since no Meissner signal is observed in the Zn-substituted sample, this decrease in $1/T_1T$ is not caused by superconductivity but can be ascribed to the characteristic band dispersion around the Fermi energy. In contrast, $1/T_1T$ of the Zn-free sample sharply decreases and is proportional to $T^{3.0 \pm 0.1}$ below 15 K down to 4.2 K, as shown in Fig. 2. In order to know the temperature dependence of $1/T_1T$ ascribed to the SC gap structure in the SC $x = 0$ sample, $1/T_1T$ of the $x = 0$ sample is divided by $1/T_1T$ of the non-SC $x = 0.05$ sample, which is shown in the inset of Fig. 2. Normalized $1/T_1T/[(1/T_1T)_{x=0}/(1/T_1T)_{x=0.05}]$ is proportional to $T^{2.4 \pm 0.1}$ below 20 K, which is close to the previous results ($1/T_1T \sim T^2$) in LaFeAs(O$_{0.89}$F$_{0.11}$) where $1/T_1T$ is constant in the temperature range between $T_c$ and 50 K[9, 16]. This suggests that temperature dependence of $1/T_1T$ in the SC state can be affected by $1/T_1T$ in the normal state, which is estimated from a sample where superconductivity is suppressed by non-magnetic impurity or magnetic field.

Measurements of the temperature dependence of $1/T_1T$ at low temperatures help to determine which type of SC pairing is realized. For an s-wave superconductor, $1/T_1T$ shows activated temperature dependence, as expected from the existence of an isotropic gap. For a line-node superconductor, $N_s(E) \propto E$ for $E < \Delta_0$, leading to $1/T_1T \propto T^2$ where $\Delta_0$ is a SC gap at 0 K. For a point-node superconductor, $N_s(E) \propto E^2$ for $E < \Delta_0$, leading to $1/T_1T \propto T^4$. These differences arise from quasiparticle excitations near the gap nodes. Then, normalized $1/T_1T/[(1/T_1T)_{SC}/(1/T_1T)_{normal}]$ can be described as follows:

$$\frac{1}{T_1T} \propto \begin{cases} 
\exp(-\Delta_0/k_\text{B}T) & \text{for full gap,} \\
T^2 & \text{for line node gap,} \\
T^4 & \text{for point node gap.}
\end{cases} \quad (1)$$

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In the case of a simple $s_{\pm}$-wave superconductor, $1/T_1T$ follows $\exp(-\Delta_0/k_B T)$ at low temperatures, which is the same as in the case of a $s_{++}$-wave superconductor. On the other hand, in the case of an anisotropic SC gap model incorporated with impurities or a multi-SC gap effect\cite{17, 18, 19}, $1/T_1T$ approaches $T^2$ similar to behaviors in nodal gaps. It should be also noted that a development of SC gap just below $T_c$ strongly affects the temperature variation of $1/T_1T$. Therefore, to distinguish type of SC pairing, we should check the temperature exponent of $1/T_1T$ well below $T_c$. Our experimental data can be explained by a line-node $d$-wave or an $s_{\pm}$-wave model with highly anisotropic SC gaps. However, in a superconductor with nodal SC gaps, residual density of states is easily introduced by tiny amount of impurities and $1/T_1T$ becomes constant at low temperatures. Considering that our samples are polycrystalline with oxygen deficiency, line node $d$-wave would be excluded. Then, an $s_{\pm}$-wave is the most promising pairing symmetry of LaFeAsO$_{0.85}$.

In summary, we have measured $^{75}$As-$1/T_1T$ in Zn-free and Zn-substituted La(Fe$_{1-x}$Zn$_x$)AsO$_{0.85}$ ($x = 0$, and 0.05). $1/T_1$ at $x = 0$, and 0.05 are almost the same above $T_c$ of $x = 0$, suggesting that the temperature dependent normal state are the same. $1/T_1T$ of the Zn-free sample sharply decreases and is proportional to $T^{3.0\pm0.1}$ below $T_c$ down to 4.2 K, but $1/T_1T$ in the non-SC $x = 0.05$ sample shows gradual decrease below $\sim 50$ K. Normalized SC-state $1/T_1T \times x = 0/(1/T_1T)_x = 0.05$ is proportional to $T^{2.4\pm0.1}$, which is close to the previous reports. We suggest that temperature dependence of $1/T_1T$ in the normal state is one of the reasons that various temperature dependences of $1/T_1T$ have been observed in the SC state in La-based “1111” superconductors.

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