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Two superconducting gaps in $LaFeAsO_{0.92}F_{0.08}$ revealed by ^{75}As nuclear quadrupole resonance

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We report ^{75}As nuclear quadrupole resonance studies on superconducting oxypnictide $LaFeAsO_{0.92}F_{0.08}$ (T_c=23 K). The temperature dependence of the spin-lattice relaxation rate ($1/T_1$) decreases below T_c without a coherence (Hebel-Slichter) peak and shows a temperature dependence that is not simple power law nor exponential. We show that the result can be understood in terms of two superconducting gaps of either *d*- or $\pm s$-wave symmetry, with the larger gap $\Delta_1 \sim 4k_BT_c$ and the smaller one $\Delta_2 \sim 1.5k_BT_c$. Our result suggests that the multiple-gap feature is universal in the oxypnictide superconductors, which is probably associated with the multiple electronic band structures in this class of materials. We also find that $1/T_1T$ above T_c increases with decreasing temperature, which suggests weak magnetic fluctuations in the normal state.

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The discovery of superconductivity in $LaFeAsO_{1-x}F_x$ at T_c=26 K,[1] followed by that in $ReFeAsO_{1-x}F_x$ (Re: Ce, Pr, Nd, and Sm) (Refs. 2–6) with superconducting transition temperature (T_c) as high as 55 K, has attracted much attention. There are many issues remaining to be resolved regarding the physical properties and the pairing mechanism. To this end, it is important to unravel the nature of the superconducting energy gap. Nuclear-magnetic-resonance (NMR) measurements in $PrFeAsO_{0.89}F_{0.11}$ (T_c=45 K) found that the Knight shift with magnetic field parallel to the *ab* plane decreases below T_c and goes to zero, which is strong evidence for spin-singlet pairing in the superconducting state.[7] The Andreev reflection measurement on $SmFeAsO_{0.85}F_{0.15}$ suggested a Bardeen-Cooper-Schrieffer (BCS)-like gap.[8] On the other hand, both the Knight shift and the spin-lattice relaxation rate ($1/T_1$) in $PrFeAsO_{0.89}F_{0.11}$ suggest that there are two gaps opening below T_c, with the larger gap $\Delta_1(T=0)=3.5k_BT_c$ and the smaller gap $\Delta_2(T=0)=1.1k_BT_c$ in that compound. This observation was echoed by other measurements such as torque magnetometry measurements,[9,10] point-contact tunneling,[11,12] and angle-resolved photoemission spectroscopy.[13] Thus, the experimental results suggest that the superconducting gap structure resembles that of MgB_2.[14] These measurements, however, were performed for materials with T_c higher than 38 K. It is therefore natural to ask if the multiple-gap feature is unique to the materials with high T_c or it is universal in this class of materials.

In this Rapid Communication, we report a nuclear-quadrupole-resonance (NQR) study on $LaFeAsO_{0.92}F_{0.08}$ (T_c=23 K). NQR has several advantages over NMR. For example, it is performed at zero magnetic field, which gets rids of the complexity due to the vortex which makes the T_1 at low T ambiguous as pointed out by Grafe *et al.*[15] Also, a ^{75}As nucleus has a nuclear spin $I=3/2$, which results in only one transition line of NQR. Moreover, the recovery curve of the nuclear magnetization is simple, and thus the evaluation of T_1 is straightforward and unambiguous. Our careful and precise measurement shows that $1/T_1$ below T_c decreases without a coherence (Hebel-Slichter) peak but does not follow simple power-law nor exponential variation as found in high-T_c cuprates or MgB_2; instead it shows a stepwise temperature variation. The result can be fitted with two gaps of either *d*- or $\pm s$-wave symmetry with $\Delta_1(0) \sim 4k_BT_c$ and the smaller gap $\Delta_2(0) \sim 1.5k_BT_c$. We will compare our result with those reported earlier for $LaFeAsO_{1-x}F_x$ with different carrier concentrations (F content).[15–18]

The polycrystals of $LaFeAsO_{0.92}F_{0.08}$ was synthesized by the solid-state reaction method.[19] Fine powders of LaAs (presynthesized by La pieces and As powder), Fe, Fe_2O_3, and LaF_3 with purities better than 99.99% were mixed together according to the stoichiometric ratio, then ground thoroughly and pressed into small pellets. The pellets were sintered at temperature of 1150 °C for 50 h. The sample was characterized by powder x-ray diffraction (XRD) method with Cu $K\alpha$ radiation to be a tetragonal ZrCuSiAs-type structure ($P4/nmm$ space group). For NQR measurements, the pellet was crushed into coarse powders. ac susceptibility measurement using the NQR coil indicates that T_c for the powdered sample is 23 K. NQR measurements were carried out by using a phase-coherent spectrometer. The spin-lattice relaxation rate ($1/T_1$) was measured by using a single saturation pulse. To avoid possible heating effect due to the rf pulse, we used a small amplitude rf saturation pulse to obtain T_1 below T_c.

Figure 1 shows the ^{75}As-NQR spectrum in $LaFeAsO_{0.92}F_{0.08}$ (T_c=23 K). The clear single peak structure is observed, and it can be fitted by a single Lorentzian curve, indicating that there are no other phases in the present sample. The NQR frequency ν_Q is ~10.9 MHz, which is in good agreement with earlier reports,[15–17] but smaller than ν_Q=12.0 MHz in the higher-T_c compound $PrFeAsO_{0.89}F_{0.11}$ (T_c=45 K).[7]

Figure 2 shows the representative decay curves of the nuclear magnetization above and below T_c=23 K. Since the ^{75}As nucleus has nuclear spin $I=3/2$, the nuclear magnetization for NQR transition $\pm 1/2 \leftrightarrow \pm 3/2$ of yhe ^{75}As nucleus is given by single exponential $1-M(t)/M_0=\exp(-3t/T_1)$, where M_0 and $M(t)$ are the nuclear magnetization in the thermal equilibrium and at a time t after the saturating pulse, respectively. As seen in Fig. 2, T_1 is of a single component even well below T_c.

Figure 3 shows the temperature dependence of $^{75}(1/T_1)$

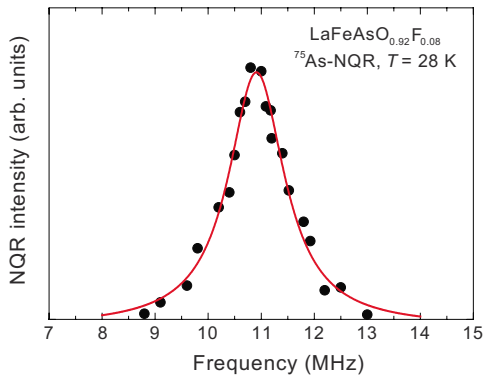

FIG. 1. (Color online) ^{75}As-NQR spectrum at $T=28$ K (above T_c). Solid curve is a Lorentzian fitting which gives a full width at half maximum (FWHM) ~1.2 MHz.

for $LaFeAsO_{0.92}F_{0.08}$. The onset of the superconducting transition is clearly observed in temperature dependence of $1/T_1$ below $T_c=23$ K. $1/T_1$ decreases with no coherence peak just below T_c, which is in contrast with a conventional BCS superconductor. Furthermore, the temperature dependence below T_c is neither a simple power law ($1/T_1 \propto T^3$ or T^5) as seen in heavy fermion compounds[20–22] or high-T_c cuprates[23] nor exponential as seen in conventional BCS superconductors.[24]

The most peculiar feature is that $1/T_1$ shows a stepwise decrease below T_c. Namely, the steep drop of $1/T_1$ just below T_c is gradually replaced by a slower change below $T \sim 10$ K then followed by a still steeper drop below. Such unusual decreases in $1/T_1$ leaves a broad humplike feature around 8 K. This behavior is clearly different from the case of usual superconductors that have a single superconducting gap. It should be emphasized that this uncommon temperature variation is not due to sample inhomogeneity, which would result in a two-component T_1 below T_c. We find that T_1 is of single component throughout the whole temperature range, as exemplified in Fig. 2. Thus, the two-step feature in the T dependence of $1/T_1$ appears to be universal in $ReFeAsO_{1-x}F_x$, as first found in $PrFeAsO_{0.89}F_{0.11}$.[7]

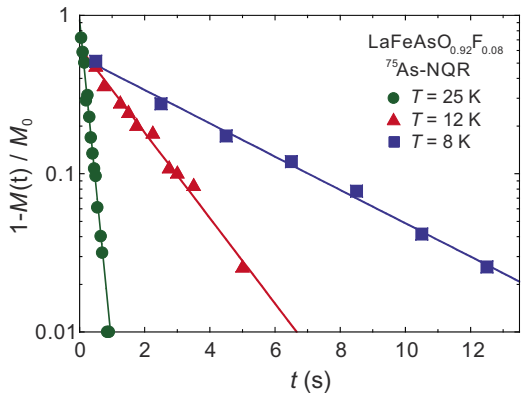

FIG. 2. (Color online) Decay curves of the nuclear magnetization observed at $T=25$, 12, and 8 K, respectively, which indicate a single component of T_1 and allow us an adequate determination of the values of T_1. Solid curves are the theoretical fittings to obtain T_1 (see text).

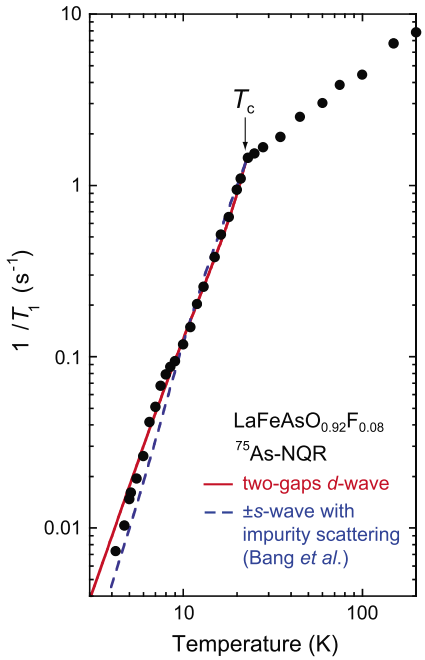

FIG. 3. (Color online) The temperature dependence of $^{75}(1/T_1)$ in $LaFeAsO_{0.92}F_{0.08}$ measured at zero magnetic field. Experimental error is within the size of the symbols. The solid curve is a two-gap fit assuming a d-wave symmetry with parameters $\Delta_1(0)=4.2k_BT_c$, $\Delta_2(0)=1.6k_BT_c$, and $\alpha=0.6$ (see text). The dotted curve is a simulation assuming two s-wave gaps that change signs with impurity scattering. The parameters are $\Delta_1(0)=3.75k_BT_c$, $\Delta_2(0)=1.5k_BT_c$, and $\alpha=0.38$ (Refs. 29 and 31). The solid arrow indicates T_c.

In the superconducting state, we find that two-gap models can explain the stepwise temperature variation in $1/T_1$. The underlying physics is that the superconducting density of states (DOS) just below T_c is dominantly governed by a larger gap, while at low temperature it starts to realize the existence of a smaller gap, resulting in another drop $1/T_1$ below 8 K. Here, the relaxation rate below T_c $(1/T_{1s})$ can be expressed as

$$\frac{T_{1N}}{T_{1s}} = \frac{2}{k_BT}\int\int\left(1+\frac{\Delta^2}{EE'}\right)N_s(E)N_s(E')f(E)[1-f(E')] \times \delta(E-E')dEdE',$$

where $1+\frac{\Delta^2}{EE'}$ is the coherence factor, $N_s=\frac{E}{\sqrt{E^2-\Delta^2}}$ is the DOS in the superconducting state, and $f(E)$ is the Fermi distribution function. In the d-wave model with two gaps, $N_{s,i}(E) = N_{s,i}\frac{E}{\sqrt{E^2-\Delta_i^2}}$, $1/T_{1s}$ is written as

$$\frac{T_{1N}}{T_{1s}} = \sum_{i=1,2}\frac{2}{k_BT}\int\int N_{s,i}(E)N_{s,i}(E')f(E)[1-f(E')] \times \delta(E-E')dEdE'$$

and

$$\alpha = \frac{N_{s,1}}{N_{s,1}+N_{s,2}}.$$

By assuming two gaps of d-wave symmetry $\Delta(\phi)$

$=\Delta_0 \cos(2\phi)$ with the mean-field temperature dependence, we find that $\Delta_1(0)=4.2k_BT_c$, $\Delta_2(0)=1.6k_BT_c$, and $\alpha=0.6$ can fit the data reasonably well as shown by the solid curve in Fig. 3. These values of the superconducting gap and α are slightly larger than that obtained in $PrFeAsO_{0.89}F_{0.11}$ [$\Delta_1(0)=3.5k_BT_c$, $\Delta_2(0)=1.1k_BT_c$, and $\alpha=0.4$].[7] The difference may arise from the difference in detail of the band structure.

We also compared our experimental results with the theoretical calculation assuming the so-called $\pm s$-gap symmetry. Several theoretical works proposed an s-wave gap opening on two different Fermi surfaces (with, respectively, hole and electron characters) but with opposite signs ($\pm s$ gap).[25–27] It has been shown that such $\pm s$-gap symmetry, with a nodal plane that does not intersect the Fermi surface, gives a higher T_c over d wave.[28–30] Calculations have shown that magnetic scattering and/or impurity scattering between the two different bands can reduce the coherence peak just below T_c.[29–34] The dotted curve in Fig. 3 is the result of Bang and Choi[29,31] with the fitting parameters $\Delta_1(0)=3.75k_BT_c$ with $-s$ symmetry, $\Delta_2(0)=1.5k_BT_c$ with $+s$ symmetry, $\alpha=0.38$, and $\Gamma/\Delta_1=0.04$. Here, $\Gamma=n_{\rm imp}/\pi N_{\rm tot}$, where $n_{\rm imp}$ is the nonmagnetic impurity concentration and $N_{\rm tot}$ is the total density of states of the two bands.[29,31] As seen in the figure, such a $\pm s$-gap model also reproduces the overall trend of the experimental results. More work is needed to distinguish between the d- and $\pm s$-gap symmetry.

Such a two-gap feature was first pointed out by the Knight shift and $1/T_1$ measurements in $PrFeAsO_{0.89}F_{0.11}$.[7] In Fig. 4, we compare the present data with $PrFeAsO_{0.89}F_{0.11}$ and with that reported by Grafe *et al.*[15] in $LaFeAsO_{1-x}F_x$ with higher F concentration. The data below T_c for $PrFeAsO_{0.89}F_{0.11}$ and $LaFeAsO_{0.92}F_{0.08}$ are quite similar. Even though the normal-state data between ours and Grafe *et al.*[15] are quite different as discussed later in detail, the data below T_c in $LaFeAsO_{1-x}F_x$ are quite similar, although Grafe *et al.*[15] analyzed their data in terms of a single gap. Thus, we suggest that the multiple-gap feature is an intrinsic property that is universal to the whole family of Fe-based pnictide superconductors.

Finally, we discuss the normal-state property in $LaFeAsO_{0.92}F_{0.08}$. As seen in Fig. 4, the quantity of $1/T_1T$ in our sample does not show a reduction above T_c which was ascribed to a possible pseudogap behavior observed in $LaFeAsO_{1-x}F_x$.[15,16,18] Instead, it increases with decreasing T. This may be due to the fact that our sample has a lower concentration of F than others.[15,16,18] The temperature dependence of $1/T_1T$ above T_c in $LaFeAsO_{0.92}F_{0.08}$ is well fitted by the relation for a weakly, antiferromagnetically correlated metal, $1/T_1T=C/(T+\theta)+\text{const.}$[35] Here, the first term describes the contribution from the antiferromagnetic wave vector Q and the second term describes the contribution from the density of states at the Fermi level. As shown by the solid curve in Fig. 4, the temperature dependence of $^{75}(1/T_1T)$ for

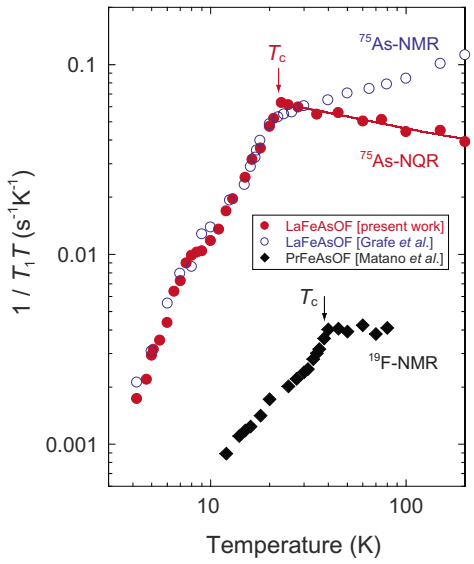

FIG. 4. (Color online) Temperature dependence of $1/T_1T$ for $LaFeAsO_{0.92}F_{0.08}$ together with $LaFeAsO_{0.9}F_{0.1}$ (Ref. 15) and $PrFeAsO_{0.89}F_{0.11}$ (Ref. 7) referred from the literature. Arrows indicate T_c. The solid curve indicates relation $1/T_1T=0.03+1.8/(T+39)$ in the unit of s^{-1} K^{-1} (see text).

$LaFeAsO_{0.92}F_{0.08}$ is well represented by this model with $\theta \sim 39$ K. Qualitatively similar behavior was also seen in underdoped high-T_c cuprates[36] or cobaltate superconductors,[37] but $1/T_1T$ increases much more steeply there with smaller θ. The result indicates that the spin correlations are much weaker in the present case.

In conclusion, we have presented the detailed NQR measurements on oxypnictide superconductor $LaFeAsO_{0.92}F_{0.08}$ ($T_c=23$ K). The temperature dependence of $1/T_1$ shows no coherence peak just below T_c, and it decreases with a small hump at around $T\sim 0.4T_c$, suggesting multiple gaps of the superconductivity. Assuming two gaps of either d or $\pm s$ wave can reproduce whole temperature dependence of $1/T_1$ qualitatively. We suggest that the multigap superconductivity is an intrinsic and universal feature in this class of materials which likely originated from their multiple electronic band structure. We also find that the normal state of $LaFeAsO_{0.92}F_{0.08}$ is governed by weak magnetic fluctuations which are commonly observed in underdoped high-T_c cuprates or superconducting cobaltate. We hope to address the relationship between the magnetic fluctuations and the high-T_c superconductivity in these compounds in the near future.

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