Possible Multiple Gap Superconductivity with Line Nodes in Heavily Hole-Doped Superconductor KFe$_2$As$_2$

Studied by $^{75}$As-NQR and Specific Heat

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We report the $^{75}$As nuclear quadrupole resonance (NQR) and specific heat measurements of the heavily hole-doped superconductor KFe$_2$As$_2$ (superconducting transition temperature $T_c \approx 3.5$ K). The spin-lattice relaxation rate $1/T_1$ in the superconducting state exhibits quite gradual temperature dependence with no coherence peak below $T_c$. The quasi-particle specific heat $C_{QP}/T$ shows small specific heat jump which is about 30% of electronic specific heat coefficient just below $T_c$. In addition, it suggests the existence of low-energy quasi-particle excitation at the lowest measurement temperature $T = 0.4 K \approx T_c/10$. These temperature dependence of $1/T_1$ and $C_{QP}/T$ can be explained by multiple nodal superconducting gap scenario rather than fully gapped $s_\pm$-wave one within simple gap analysis.

KEYWORDS: KFe$_2$As$_2$, multiple superconducting gap, nuclear quadrupole resonance, specific heat

After the discovery of superconductivity in F-doped LaFeAsO with a superconducting transition temperature $T_c = 26$ K$^{1}$, K-doped (hole-doped) BaFe$_2$As$_2$ was reported as the first oxygen-free iron-pnictide superconductor with $T_c = 38$ K$^{2}$. The crystal structure of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is of the ThCr$_2$Si$_2$-type. We performed $^{75}$As-NMR measurements of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($T_c \approx 38$ K)$^{3}$ which also exhibits the first-order antiferromagnetic (AF) ordering associated with a structural phase transition. Our results clearly revealed that the coexistence of AF and superconducting (SC) states$^{4,5}$ is not a microscopic one but a phase separation, which is related with the fact that the structural transition is intrinsically of the first order.$^{6}$ Hence, the suppression of the structural phase transition rather than carrier doping seems to have a key role in achieving superconductivity in so-called 122 systems. Recent reports of pressure-induced superconductivity of BaFe$_2$As$_2$ ($T_c \approx 13$ K)$^{7}$ and SrFe$_2$As$_2$ ($T_c \approx 34$ K)$^{8,9}$ under hydrostatic pressure are consistent with this consideration.

The important feature of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is that superconductivity occurs even for $x = 1, 4, 5, 10$ though $T_c$ itself is much lower ($T_c \approx 3.5$ K) than the optimum $T_c$. This also implies the less essentiality of carrier doping for the occurrence of superconductivity in the 122 systems compared to high-$T_c$ cuprates. However, looking at the phase diagram of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ in ref. 4, $T_c$ once decreases to zero from maximum $T_c$ side toward $x = 0.75$ with increasing $x$, but remains lower value ($T_c \approx 10$ K) above about $x = 0.75$. Nearby the same tendency of the phase diagram is also seen in Sr$_{1-x}$K$_x$Fe$_2$As$_2$.$^{10}$ This is probably related with the disappearance or the shrinkage of the electron-like Fermi surface around the M point in the Brillouin zone by hole doping, which is indeed observed by angle resolved photoemission spectroscopy (ARPES)$^{11}$ or confirmed by the band calculation in KFe$_2$As$_2$.$^{12}$ Furthermore, this might bring the change of the SC symmetry. In iron arsenide superconductors, it has been proposed that the multiple fully gapped $s_\pm$-wave Cooper pairing is preferable from many experimental and theoretical approaches.$^{13-20}$ On the other hand, the nodal-line SC symmetry scenario is new and promising candidate for verifying the general tendency of SC symmetry in Fe-based superconductors, since it is potentially cleaner than other substituted SC compounds and SC even with extremely modified Fermi surface. In this Letter, we report the $^{75}$As nuclear quadrupole resonance (NQR) and specific heat measurements of KFe$_2$As$_2$ ($T_c \approx 3.5$ K). Characteristic temperature $T$ dependence of spin-lattice relaxation rate $1/T_1$ and quasi-particle specific heat $C_{QP}/T$ can be understood by multiple nodal SC gap scenario.

Polycrystalline KFe$_2$As$_2$ was synthesized by a high-temperature and high-pressure method.$^{3}$ X-ray diffraction analysis revealed that the sample was of nearly single phase. The obtained lattice parameters, $a = 3.846$ Å, $c = 13.87$ Å, were consistent with the previous reports.$^{4,5}$

In order to check the sample quality, we measured resistivity $\rho(T)$ by a standard four-probe method (Fig. 1). The residual resistivity ratio (RRR) is $\rho(300 K)/\rho(4.2$ K) = 67, which is comparable with the reported value ($= 87$) for single crystal of KFe$_2$As$_2$ ($T_c = 2.8$ K).$^{23}$ The onset of $T_c$ is about 4.0 K and the $\rho$ becomes nearly zero at 3.5 K. We also determined the $T_c$ and SC volume frac-
tation with a commercial SQUID magnetometer (the inset of Fig. 1). To reduce demagnetization effect, we used the plate-shape sample with $3.0 \times 3.0 \times 1.0$ mm$^3$ and applied magnetic field parallel to the largest plane. The $T_c$ of the sample is about 3.5 K and the SC volume fractions is 80%. These results indicate that the quality of our sample is reasonably good enough and that the superconductivity in KFe$_2$As$_2$ is bulk property of the sample.

The NQR experiment on the $^{75}$As nucleus ($I = 3/2$, $\gamma / 2\pi = 7.292$ MHz/T) was carried out using phase-coherent pulsed NQR spectrometers. The samples were crushed into powder for use in the experiments. The measurement above 1.4 K was performed using a $^4$He cryostat, and between 0.3 and 1.2 K with a $^3$He refrigerator. We measured specific heat by a thermal relaxation method between 0.4 and 10 K with a commercial calorimeter.

In Fig. 2(a), we show the $^{75}$As-NQR spectra of KFe$_2$As$_2$ at various $T$. Clear single peak signal was successfully observed. With decreasing $T$, the spectral center decreases and remains nearly constant below about 70 K. Below this temperature, the NQR frequency $\nu_Q$ was 12.4 MHz. The principal axis of the electric field gradient is along the crystal c-axis since the As site has a local four-fold symmetry around the c-axis. With increasing $x$, the $\nu_Q$ in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ increases from $\nu_Q = 2.2$ MHz ($x = 0$) to 12.4 MHz ($x = 1$) through intermediate value $\sim 5$ MHz ($x = 0.4$). The full width at half maximum ($FWHM$) remains nearly constant above $T_c$ and is about 740$\pm$20 kHz. This is about half magnitude of linewidth of oxygen-deficient LaFeAsO$_{1-x-F_2}$ and F-doped LaFeAsO$_{1-x-F_2}$. The $FWHM$ slightly increases below $T_c$ and becomes about 850 kHz at 0.38 K. However, we cannot conclude that this is due to magnetic order since the increase of the width is too small.

In Fig. 2(b), we show nuclear magnetization recovery curves of KFe$_2$As$_2$ at 0.3, 3.7 and 120 K. All the obtained recovery curves followed single exponential curve expected for $^{75}$As NQR ($I = 3/2$, $^{28}$)

$$1 - \frac{m(t)}{m_0} = \exp(-\frac{3t}{T_1}),$$

where $m(t)$ and $m_0$ are nuclear magnetizations after a time $t$ from the NQR saturation pulse and thermal equilibrium magnetization. Small deviation of data points from the fitting curve for 0.3 K may be due to the distribution of $T_c$. However, its fitting error is within marker size in Fig. 3. We checked the absence of sample heat up by changing the NQR pulse width and power.

In Fig. 3, we show the $T$ dependence of $1/T_1$ of KFe$_2$As$_2$. In the normal state, $1/T_1$ follows $T^{0.8}$ between 5 and 160 K. This is slightly gradual compared to $T$ linear dependence of usual Korringa law, which suggests that antiferromagnetic fluctuation is much suppressed and that the system is nearly Pauli paramagnetic. The most striking feature of $1/T_1$ is $T$ dependence below $T_c = 3.5$ K. No coherence peak was observed just below $T_c$, and the $1/T_1$ follows only $T^{1.4}$ between 0.6 K and $T_c$. This is quite different from the $1/T_1$ below $T_c$ in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $T_c \approx 38$ K in which $1/T_1$ follows $T^3$-$T^5$ without coherence peak. The $1/T_1$ of KFe$_2$As$_2$ more steeply decreases below about 0.6 K. Such kind of gradual $T$ dependence of $1/T_1$ in the SC state was observed in La$_{0.87}$Ca$_{0.13}$FePO$_2$.

In order to understand the nature of this anomalous $T$ dependence, we analyzed the data by assuming simple two-independent SC-gap model with gap with line

**Fig. 1.** (Color online) Resistivity of KFe$_2$As$_2$. The inset shows the magnetic susceptibility of KFe$_2$As$_2$ in the paramagnetic state. Solid and open symbols denote the data obtained after zero-field-cooling (ZFC) and field-cooling (FC), respectively.

**Fig. 2.** (Color online) (a) $^{75}$As NQR spectra of KFe$_2$As$_2$ at various temperatures. (b) Nuclear magnetization recovery curves of KFe$_2$As$_2$ at 0.3, 3.7 and 120 K. Solid lines denote the fitting curve using the formula written in the text.
node or full gap (s± wave type). Similar analysis procedure was adopted in refs. 20, 30. Larger two hole Fermi surfaces (α and β in ref. 11) are observed around the Γ point by ARPES in KFe2As2.11 These Fermi surfaces have different sizes of gap in Ba1−xKxFe2As2 (Tc ≃ 38 K)18–20,30 and are consider to have main contribution to total density of states (DOS) at the Fermi level in KFe2As2.11,12 Therefore, it is natural to analyze two SC gap model. Furthermore, we assumed two SC gap symmetries because these symmetries are experimentally and theoretically favorable for iron-based superconductors.13–21,30 The 1/T1 in the SC state is proportional to,

\[ \frac{1}{T_1} \propto \sum_{i=1,2} n_i^2 \int_0^\infty \{N_i^2(E)^2+M_i^2(E)^2\} f(E)\{1-f(E)\}dE, \]

where \( N_i^2(E) \), \( M_i^2(E) \), \( f(E) \) are the DOS, the anomalous DOS arising from the coherence effect of Cooper pairs, and the Fermi distribution function, respectively. \( n_i \) represents the fraction of DOS of the \( i \)-th gap and \( n_1 + n_2 = 1 \). For both cases of SC gaps, we assumed that the integral of \( M_i^2(E) \) becomes zero because of the sign-changing SC gaps. For the full gap case, we averaged \( N_i^2(E) \) around \( E \approx \Delta_i(T) \) with the width \( 2\delta_i < \Delta_i(T) \) in order to reduce the coherence peak.31,32 Here, \( \Delta_i(T) \) is the SC gap; for simplicity, \( (\theta, \varphi) \) dependence is given by \( \Delta_i(T, \theta, \varphi) = \Delta_i(T) \cos \theta \) for nodal gap and \( \Delta_i(T, \theta, \varphi) = \Delta_i(T) \) for full gap. Concrete function for the averaged \( N_i^2(E) \) is described in ref. 31. This procedure corresponds to consider the anisotropy of the SC gaps or finite lifetime of Cooper pairs arising from pair breaking.33 In order to distinguish the nodal gap model and the full gap model, we utilized the above procedure different from that described in refs. 20, 34, in which finite DOS appears at the Fermi level in the full gap model. The clear difference of total DOS is depicted in Fig. 4 by using the parameters described below.

In the inset of Fig. 3, we show the normalized results of the experiment and analysis. In Table. I, we summarized the obtained parameters of \( 2\Delta_i(0)/T_c \), \( n_i \), and \( \delta_i/\Delta_i \) (for the full gap model). The gap parameters are nearly the same for each model and the fitting to the experimental results is good enough. This suggests that the 75As-NQR down to the lowest measurement temperature \( T_c/10 \) cannot solely determine the SC symmetry of KFe2As2. The larger gap is of moderate strong coupling while the smaller gap is of quite weak coupling. This indicates that the smaller gap is induced by the emergence of the larger gap. Note that the single gap analysis \( (n_1 = 1) \) did not entirely work for both SC symmetries.

In Fig. 5, we show specific heat divided by temperature \( C(T)/T \) of KFe2As2. Clear specific heat jump was observed, which again indicates the bulk nature of superconductivity. The midpoint of the jump is 3.4 K. In order to estimate the electronic-specific-heat coefficient \( \gamma_e \) and the lattice contribution, we performed the fitting \( (C_{\text{fit}}/T = \gamma_e + \beta T^2 + \epsilon T^4) \) for the data between 4 and 10 K (a solid curve in Fig. 5. The obtained \( \gamma_e \) is 69.1(2) mJ/K2mol, which is comparable with 63.3 mJ/K2mol for single crystal of Ba0.9K0.1Fe2As2.35) Note that the Schottky specific heat of 75As is negligible since the calculated Schottky specific heat from the NQR frequency \( \nu_0 = 12.4 \) MHz becomes significant below about 0.3 K.

By subtracting the lattice contribution \( \beta T^2 + \epsilon T^4 \), we obtained the quasi-particle specific heat \( C_{\text{QP}}/T \). The most obvious feature of \( C_{\text{QP}}/T \) is that the specific heat jump is only about 30% of \( \gamma_e \). One of reasons is the broadening of the SC transition arising from the small distribution of \( T_c \). However, by taking into account this broadening, the specific heat jump is roughly expected to be at most 60% of \( \gamma_e \). Another important feature is the finite \( C_{\text{QP}}/T \sim 45 \) mJ/K2mol-fu even at the lowest measurement temperature \( T_c/10 \). This suggests the existence of low-energy quasi-particle excitation.

In the inset of Fig. 5, we compared the normalized results of experiment and numerical calculation. Here,
The influence of residual DOS becomes significant. Further, \( \Delta C / T \) and reasonably large \( \Delta \gamma_e \) can be seen in the results of specific heat (Fig. 7 in ref. 35) that such correspondence between \( T \) total DOS for nodal gap model in Fig. 4 gives rise to wide gap analysis. The \( E \) linear part in \( C(T)/T \) fit shows small specific heat jump just below \( T_c \). In addition, it suggests the existence of low-energy quasi-particle excitation at \( T = 0.4 \) K \( \leq T_c/10 \). These \( T \) dependence of \( 1/T_1 \) and \( C_{QP}/T \) can be explained by multiple nodal superconducting gap scenario rather than multiple fully-gapped \( s_\pm \)-wave one which is the most plausible scenario to describe SC state in Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) with \( T_c \approx 38 \) K. Further studies including theory and other experimental methods (ARPES, de Haas-van Alphen effect, penetration depth etc) especially using single crystal at lower temperatures are required to more precisely determine the SC gap symmetry. Moreover, Knight shift measurement below \( T_c \) is also urgently required to determine the spin part symmetry of KFe\(_2\)As\(_2\).

In summary, we performed the \(^{75}\)As NQR and specific heat measurements of the heavily hole-doped superconductor KFe\(_2\)As\(_2\) (\( T_c \approx 3.5 \) K). The \( 1/T_1 \) in the normal state reflects nearly Korringa-like \( T \) dependence. The \( 1/T_1 \) in the SC state exhibits quite gradual \( T \) dependence with no coherence peak. The quasi-particle specific heat \( C_{QP}/T \) shows small specific heat jump just below \( T_c \).

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