Pressure-induced unconventional superconductivity near a quantum critical point in CaFe$_2$As$_2$

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Abstract

$^{75}$As-zero-field nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements are performed on CaFe$_2$As$_2$ under pressure. At $P = 4.7$ and 10.8 kbar, the temperature dependencies of nuclear-spin-lattice relaxation rate ($1/T_1$) measured in the tetragonal phase show no coherence peak just below $T_c(P)$ and decrease with decreasing temperature. The superconductivity is gapless at $P = 4.7$ kbar but evolves to that with multiple gaps at $P = 10.8$ kbar. We find that the superconductivity appears near a quantum critical point under pressures in the range 4.7 kbar $\leq P \leq 10.8$ kbar. Both electron correlation and superconductivity disappear in the collapsed tetragonal phase. A systematic study under pressure indicates that electron correlations play a vital role in forming Cooper pairs in this compound.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of high-transition temperature ($T_c$) superconductivity in LaFeAsO$_{1-x}$F$_x$ at $T_c = 26$ K [1], iron pnictides have become one of the most fascinating research areas in condensed matter physics. The electron doping suppresses the structural and magnetic phase transitions in undoped ReFeAsO and superconductivity appears near the border of magnetism [1], as seen in the high-$T_c$ cuprates. After the discovery of superconductivity in ReFeAsO, the high-$T_c$ superconductivity has also been found in a ThCr$_2$Si$_2$-type structure, BaFe$_2$As$_2$, by replacing Ba by K as hole doping [2]. One of the most remarkable features in these iron pnictide superconductors is their superconducting gap structure. Previous nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements on ReFeAsOF and Ba$_2$K$_3$Fe$_2$As$_2$ consistently found multiple gap superconductivity [3–5]. These observations were also confirmed by angle-resolved photoemission spectroscopy [6]. The multiple gap feature is believed to be relevant to their multiple electronic band structure [7]. On the other hand, the mechanism of the Cooper pair formation in iron pnictide is still unclear. Since the superconductivity in iron pnictides is induced by chemical doping, systematic investigation of the relationship between electron correlations and superconductivity has been difficult.

Recent discoveries of pressure-induced superconductivity in RFe$_2$As$_2$ (R = Ca, Sr, and Ba) provide a new route to investigate superconductivity in iron pnictides [8–11]. In RFe$_2$As$_2$, the parent compounds also show structural transition from a tetragonal (tetra.) to orthorhombic (orth.) structure with antiferromagnetic order [12–14]. In BaFe$_2$As$_2$ and SrFe$_2$As$_2$, the structural phase transition and antiferromagnetic orders are both suppressed by pressure, and superconductivity was found around the critical pressure, $P_c = 40–60$ kbar, with $T_c \sim 30$ K [8, 11]. On the other hand, pressure-induced superconductivity in CaFe$_2$As$_2$ has been observed with lower $P_c \sim 5$ kbar and lower $T_c(P) \sim 10$ K [9, 10]. The most
strikingly different feature in CaFe$_2$As$_2$ is the occurrence of another structural transition under pressure. Above $P \sim 5$ kbar, normal state tetra. phase changes to a collapsed tetragonal (c-tetra.) phase with a drastic reduction in both the unit cell volume (5%) and the $c/a$ ratio (11%) [15, 16]. Notably, when tetra. phase collapses, superconductivity disappears [17]. Since these structural phase transitions are sensitive to external pressure, the detailed information about pressure-induced superconductivity in CaFe$_2$As$_2$ is still unknown.

In this paper, we report results of a zero-field (ZF) NMR and NQR study in CaFe$_2$As$_2$. At $P = 4.7$ and 10.8 kbar, pressure-induced superconductivity in the tetra. phase is confirmed by ac-susceptibility and nuclear-spin-lattice relaxation time ($T_1$) measurements. The temperature dependencies of $1/T_1$ show no coherence peak just below $T_c(P)$. Below $T_c(P)$, the temperature dependencies of $1/T_1$ indicate the unconventional nature of pressure-induced superconductivity in CaFe$_2$As$_2$. The systematic measurements indicate electron correlations play a vital role in inducing unconventional superconductivity in this compound.

2. Experimental procedures

The single crystals of CaFe$_2$As$_2$ are grown by a self-flux method and crushed into coarse powder for $^{75}$As ($I = 3/2, \gamma = 7.292$ MHz T$^{-1}$) ZF-NMR/NQR measurements under pressure. The pressure was applied utilizing a NiCrAl/BeCu piston-cylinder type cell filled with Daphne 7373 as the pressure-transmitting medium [18]. The pressure at low temperatures was determined from the pressure dependence of the $T_c$ values of Sn metal measured by a conventional four-terminal method. The temperature dependence of $ac$-susceptibility is measured using an in situ NMR/NQR coil. The ZF-NMR/NQR spectra were taken by changing the $rf$ frequency and recording the spin echo intensity step by step. The value of $T_1$ was extracted by fitting the nuclear magnetization obtained by recording the spin echo intensity after the saturation pulse.

Figure 1 shows the schematic phase diagram of CaFe$_2$As$_2$ under pressure taken from the literature [15–17, 19]. Dashed lines indicate the first-order structural phase transitions, respectively. Arrows indicate the pressure at which the present experiments have been performed.

3. Pressure dependence of zero-field NMR and NQR spectra

Figure 2(a) shows the pressure dependence of ZF-NMR and NQR spectra measured at $T = 5$ K and $P = 0, 4.7,$ and 10.8 kbar, respectively. At $P = 0$, three $^{75}$As-NMR lines are observed due to the internal magnetic field ($H_{int}$) induced by the Fe ordered moment below $T_N$, which comes from the orth. phase. Actually, as seen in figure 2(b), the nuclear magnetization recovery curve measured at 19 MHz is well fitted by the theoretical curve for NMR ($-1/2 \leftrightarrow +1/2$ transition) which is given by $1 - M(t)/M_0 = 0.1 \exp(-t/T_1) + 0.9 \exp(-6t/T_1)$, where $M_0$ and $M(t)$ are the nuclear magnetization at thermal equilibrium and at a time $t$ after saturating pulse, respectively. Assuming that both $H_{int}$ at the As site and $v_0$ for the As nuclei are along the $c$-axis direction, $H_{int} = 2.6$ T and $v_0 = 12$ MHz are obtained. Here, the nuclear spin Hamiltonian is given as $H_{AFM} = -\gamma H \cdot H_{int} + (h/2v_0)\{3l^2 - I(I + 1)\}$. These parameters are in good agreement with previous As-NMR experiments on single crystalline CaFe$_2$As$_2$ [14].

While the ground state of CaFe$_2$As$_2$ at ambient pressure is in a single orth. phase, a phase separation is observed under pressure due to the first-order transition [14, 16] and pressure distribution [17]. As seen in figure 2(a), at $P = 4.7$ kbar, a phase separation between the orth. and tetra. phases is observed as the ground state. The peak around 18 MHz is due to the central transition ($-1/2 \leftrightarrow +1/2$ transition) for ZF-NMR of the orth. phase as observed at $P = 0$. However, the satellite peaks, which are clearly observed at ambient pressure, due to the nuclear quadrupole interaction are not observed, indicating an increase of $v_0$ for the orth. phase under pressure. On the other hand, another peak appears around 24 MHz. Since the nuclear magnetization recovery curve measured at 24 MHz is well fitted by the nuclear magnetization recovery curve for $^{75}$As-NQR ($\pm 1/2 \leftrightarrow \pm 3/2$ transition) given by the single exponential $1 - M(t)/M_0 = \exp(-3t/T_1)$, as seen in figure 2(c), we assigned this peak as coming from the tetra. phase which survives due to a pressure distribution. We have also confirmed this assignment by measuring the As-NMR spectrum at $P = 5.0$ kbar (not shown). Notably, it has been reported that the structural transition from tetra. to orth. under pressure is accompanied by a phase separation in a certain temperature range until a single orth. phase is established as the magnetic ground state [16, 19]. Since the present experiment is performed using coarse powdered single crystals, the local pressure distribution may cause the tetra. phase to coexist with the orth. phase even at the ground state.

As the pressure reaches $P = 10.8$ kbar another structural transition from tetra. to c-tetra. occurs [15, 16], the NMR signal around 18 MHz and the NQR signal from the tetra. around 25 MHz are still observed. In addition, a new peak appears around 30.4 MHz. As seen in figure 2(d), since the nuclear magnetization recovery curve at 30.4 MHz indicates...
Figure 2. (a) Pressure dependence of $^{75}$As-NMR/NQR spectra for CaFe$_2$As$_2$ measured at $T = 5$ K and $H = 0$. Solid arrows indicate the $^{75}$As ZF-NMR spectrum which comes from the orth. phase below $T_N$. Dotted and dashed arrows indicate NQR spectra at the tetra. and c-tetra. phases, respectively. Typical data sets of nuclear recovery curves measured in the (b) orth. phase (ZF-NMR), (c) tetra. phase (NQR), and (d) c-tetra. phase (NQR), respectively. Solid curves are theoretical fittings to obtain $T_1$ (see text).

From the NMR/NQR spectra, the volume fraction of orth.:tetra.:c-tetra. = 54%:46% and orth.:tetra.:c-tetra. = 45%:18%:37% are estimated for $P = 4.7$ and 10.8 kbar, respectively. It is clear that the effect of the pressure distribution on the evolution of the ground states in CaFe$_2$As$_2$ is larger than a previous NMR study under pressure using a large single crystal [19].

4. Pressure-induced superconductivity in CaFe$_2$As$_2$

Figure 3 shows the temperature dependence of ac-susceptibility measured using the in situ NMR/NQR coil. The pressure-induced superconducting transitions at $T_c(P)$ = 3.9 and 4.1 K at $P = 4.7$ and 10.8 kbar are clearly observed. Although the $T_c(P)$s are relatively lower, the superconducting transitions are much sharper than previous reports [19, 20].

5. Evolution of the electronic properties in CaFe$_2$As$_2$ under pressure

To investigate the evolution of the electronic properties in CaFe$_2$As$_2$ under pressure, we measured the $^{75}$As nuclear-spin-lattice relaxation time ($T_1$) at each phase. Figure 4 shows the temperature dependence of $1/T_1$ divided by temperature ($1/T_1T$) well below the structural transitions. In the orth. phases all of the data show a $1/T_1T = constant$ behavior, which is characteristic of a Fermi-liquid state. These results are consistent with previous NMR results on (Ba, Sr)Fe$_2$As$_2$ [12, 13], indicating that a small Fermi surface remains below antiferromagnetic order. Due to the large $H_{int} \sim 2.5$ T in the orth. phase, the coexistence of antiferromagnetism and superconductivity, which has frequently been observed in heavy fermion compounds [21], could not be confirmed. As
discussed later, pressure-induced superconductivity is clearly observed as a reduction of $1/T_1T$ for the tetra. phases at which the onset of diamagnetism is observed at $P = 4.7$ and 10.8 kbar, respectively.

In the normal state in the tetra. phases, $1/T_1T$ increases with decreasing temperature, which indicates that the antiferromagnetic correlation develops down to $T_c(P)$. To analyze the temperature dependence of $1/T_1T$ above $T_c(P)$, we employed the model for a weakly antiferromagnetically correlated metal, $1/T_1T = \text{const.} + C/(T + \theta)$ [22]. Here, the first term describes the contribution from the density of states (DOS) at the Fermi level, and the second term describes the contribution from the antiferromagnetic wavevector $Q$. As shown by the solid curves in figure 4, the temperature dependencies of $1/T_1T$ for the tetra. phases are well fitted by this model: $1/T_1T = 0.48 + 4.4/(T + \theta)$ with $\theta = 5.4 \pm 2.3$ K for $P = 4.7$ kbar and $1/T_1T = 0.57 + 5.2/(T + \theta)$ with $\theta = 6.0 \pm 1.1$ K for $P = 10.8$ kbar, respectively. Surprisingly, the values of $\theta$, which is a measure of the distance to an antiferromagnetic quantum critical point (QCP), are not only one order of magnitude smaller than $\theta = 39$ K observed in LaFeAsO$_{0.87}$F$_{0.13}$ ($T_c = 23$ K) [4], but also comparable to that observed in unconventional superconductors in strongly correlated electron systems [23–25]. This indicates that superconductivity in CaFe$_2$As$_2$ is induced near an antiferromagnetic QCP. Since the value of $\theta$ is insensitive to pressure, the present results indicate that the quantum criticality in the tetra. phase is robust against pressure. This may be the reason why a robust superconducting dome was observed under pressure [9, 10]. Such a situation is somewhat different from heavy fermion superconductivity around QCP, at which both $T_c$ and electron correlations are enhanced [24]. On the other hand, both the DOS at the Fermi level and the value of $C$ in the antiferromagnetic correlation slightly increase with increasing pressure. The small increase of $T_c$, from 3.9 K at 4.7 kbar to 4.1 K at 10.8 kbar, may be due to this small increase of both the DOS at the Fermi level and the antiferromagnetic correlations. To describe the detailed relationship between QCP and superconductivity in CaFe$_2$As$_2$, further systematic measurements under pressure are in progress.

The most important result is the difference of $1/T_1T$ between the tetra. and c-tetra. phases at $P = 10.8$ kbar. As seen in figure 4(b), $1/T_1T$ = constant behavior is established even below $T_c$, indicating that the electron correlation and also superconductivity disappear in the c-tetra. phase. Importantly, recent electronic band structure calculations for CaFe$_2$As$_2$ have shown that the tetra. phase has the multiple band structure seen in other iron pnictides [6], whereas the multiband nature along the $\Gamma$–M direction vanishes when it collapses [26, 27]. It is thus suggested that the candidate for the antiferromagnetic wavevector $Q$ observed in the tetra. phases and the driving force of the Cooper pair formation in CaFe$_2$As$_2$ is the interband correlations, which has been suggested as the origin for the spin-density-wave order in the LaFeAsOF superconductor [28].

6. Novel superconductivity in CaFe$_2$As$_2$

To focus on the superconducting gap structure for CaFe$_2$As$_2$, the plots of $T_1(T)^{-1}/T_1(T_c)^{-1}$ versus $T/T_c(P)$ are shown in figure 5. Here, the relaxation rate below $T_c(1/T_1)$ can be expressed as, $\frac{1}{T_1} = \frac{1}{T_1(0)} + \int N_f(E)\frac{\partial f}{\partial E} dE$ [28]. The coherence peak just below $T_c$ is absent at both pressures. At $P = 4.7$ kbar, $1/T_1$ decreases moderately and is saturated approaching $T = 0$. This means that there is a residual density of states in the superconducting gap. Since the present experiments are performed in zero magnetic field, it is clear evidence for the occurrence of gapless superconductivity.

On the other hand, at $P = 10.8$ kbar, $1/T_1$ continues to decrease steeply below $T_c$, as observed in other iron pnictide superconductors [3–5, 29–34]. Notably, as clearly seen in the inset to figure 5, $1/T_1T$ below $T_c$ has a hump structure around $T \sim 0.5 T_c$, which is a signature for multiple gap superconductivity, as observed in other pnictide superconductors [3–5]. By assuming two gaps of d-wave symmetry $\Delta(\phi) = \Delta_0 \cos(2\phi)$ with a mean-field temperature dependence $\Delta(\phi) = \alpha \Delta_1 + (1 - \alpha) \Delta_2$ and $\alpha = \frac{N_f}{N_f + N_s}$, we find that the $\Delta_1(0) = 3.9 k_B T_c$, $\Delta_2(0) = 1.7 k_B T_c$ and $\alpha = 0.65$ can fit the data reasonably well, as shown by the solid curve in figure 5. These values of superconducting gaps and $\alpha$ are comparable to other iron pnictide superconductors [3–5].

How can we understand this difference of the superconducting gap structure between $P = 4.7$ and 10.8 kbar? One possible scenario is the mechanism predicted in heavy fermion
superconductivity around the antiferromagnetic QCP at which gapless superconductivity has been observed [35–37]. When the system locates at the vicinity of the antiferromagnetic QCP, odd-frequency p-wave spin singlet superconductivity (pSS) prevails over the d-wave singlet superconductivity (dSS) [38]. Notably, for the pSS state, it is suggested that there is no gap in the quasiparticle spectrum anywhere on the Fermi surface due to its odd frequency, thus, gapless superconductivity is realized [38]. In the present case, the values of $\theta$, which is the measure of closeness to the QCP, are very small and comparable to the value of heavy fermion compounds around the QCP [23, 24]. In this model, gapless pSS and dSS compete near a QCP [38]. In addition, it would be difficult to realize gapless pSS when it competes against full-gap superconductivity, such as $\pm s$-wave pairing [39]. Thus, d-wave pairing is favored as the competing order against gapless pSS near a QCP [39]. In fact, it has been predicted that d-wave superconductivity can also be the candidate for iron pnictide superconductivity, although $\pm s$-wave pairing has been suggested in other iron pnictide superconductors [40]. The present results suggest that the pressure-induced superconductivity near a QCP in CaFe$_2$As$_2$ is a good candidate to investigate a variety of superconductivities in iron pnictides.

7. Concluding remarks

In conclusion, we report zero-field NMR/NQR experiments on the iron pnictide pressure-induced superconductor CaFe$_2$As$_2$.