Unconventional superconducting gap in NaFe\(_{0.95}\)Co\(_{0.05}\)As observed by ARPES

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We have performed high resolution angle-resolved photoemission measurements on superconducting electron-doped NaFe\(_{0.95}\)Co\(_{0.05}\)As (\(T_c \sim 18\) K). We observed a hole-like Fermi surface around the zone center and two electron-like Fermi surfaces around the M point which can be connected by the momentum \(Q = (\pi, \pi)\) wavevector, suggesting that scattering over the near-nested Fermi surfaces is an important factor in the superconducting gap of this “111” pnicitide. Nearly isotropic superconducting gaps with sharp coherent peaks are observed below \(T_c\) at all three Fermi surfaces. Upon increasing temperature through \(T_c\), the gap size shows little change while the coherence vanishes. Large ratios of \(2\Delta/k_BT_c \sim 8\) are observed for all the bands, indicating a strong coupling in this system. These results are not expected from a classical phonon-mediated pairing mechanism.

PACS numbers: 74.25.Jb, 74.70.Xa, 74.20.Rp, 71.20.-b

The superconducting (SC) energy gap is one of the most important quantities in revealing the pairing mechanism of superconductors. For example, the conventional BCS superconductors have isotropic s-wave SC gaps (\(\Delta\)) with a \(2\Delta/k_BT_c \sim 3.5\) ratio, a characteristic of phonon-mediated pairing in the weak-coupling regime. In contrast, the high-\(T_c\) cuprate superconductors have an anisotropic \(d\)-wave gap with a much larger \(2\Delta_0/k_BT_c\) ratio. The discovery of a new class of high-\(T_c\) superconductors in Fe-pnictides\(^1\) with many unconventional properties raises the question of novel pairing mechanism in these materials. Due to the complexity of these multiband systems, no consensus has been reached yet on the SC gap symmetry and the pairing mechanism. In fact, literature contains many contradicting theoretical\(^2\)\(^4\) and experimental results\(^3\)\(^6\).

Angle-resolved photoemission spectroscopy (ARPES) is a powerful tool in probing directly the low-energy states of superconductors in the momentum (\(k\)) space. It thus allows a direct band-selective measurement of the size and \(k\)-profile of the SC gap. ARPES measurements on 122\(^2\)\(^12\)\(^12\), 11\(^1\)\(^13\) and 1111\(^4\)\(^14\) systems indicate isotropic nodeless gaps in the strong coupling regime (\(2\Delta/k_BT_c \sim 5–7\)). Among theoretical models promoted to explain these results, antiferromagnetic (AF) fluctuations have been regarded as a major candidate for pairing. Compared to other families of Fe-based superconductors, the 111 family has weaker magnetic correlations\(^15\). Recently, the consistency of the ARPES measurements on various families of Fe-based superconductors has been challenged by an ARPES report on the LiFeAs system (111)\(^16\). Phonon-mediated BCS pairing was proposed based on the observation of a \(2\Delta/k_BT_c \sim 3.1\) ratio\(^16\)\(^17\).

Here we report ultra-high resolution ARPES measurements on electron-doped 111 pnictide NaFe\(_{0.95}\)Co\(_{0.05}\)As (\(T_c \sim 18\) K). One hole-like Fermi surface (FS) centered at the zone center (\(\Gamma\)) is quasi-nested to two elliptical FSs centered at the M point (\(\pi, \pi\)). Signatures of an additional small hole pocket at \(\Gamma\) are also observed. The FSs have nearly isotropic gaps with variations smaller than \(\pm 0.5\) meV. These results are consistent with a \(s_\pm\) symmetry\(^14\)\(^18\) and exclude the possibility of symmetries with nodes. All gaps on hole and electron FSs have sizes of \(\sim 6–7\) meV, leading to a \(2\Delta/k_BT_c \sim 8\) ratio. The temperature dependence of the SC quasiparticles is similar to that of underdoped high-\(T_c\) cuprates. Our results point towards unconventional superconductivity in the 111 family of Fe-based superconductors.

High quality single crystals of NaFe\(_{1-x}\)Co\(_x\)As (\(x \approx 0.05\)) were synthesized by the flux method\(^18\). The cleaved surface, which is expected to happen between the two weakly-bonding Na layers, is symmetrical and non-polarized surface which is usually bulk representative and has less surface disorder. This is reflected by clear band dispersion and sharp quasiparticle peak observed by ARPES in this material, as described below. Samples were mounted in a gas protected glove box to prevent reaction with moisture. Samples with size of 1x1 mm\(^2\) were cleaved in \textit{ situ}, and yield flat, mirror like (001) surfaces. ARPES measurements were done at Tohoku University used a Scienta 2002 analyzer with a helium discharging lamp (He-I line, \(h\nu = 21.2\) eV), and at the Synchrotron Radiation Center, WI, using a Scienta R4000 analyzer. We performed experiments within the 4–100 K temperature range and in a vacuum better than...
Energy distribution curves (EDCs) along Γ–M in the normal state ($T = 30$ K) of a NaFe$_{0.95}$Co$_{0.05}$As sample are plotted in Fig. 1(a). The corresponding color plot of second derivative $\partial^2 I/\partial \omega^2$ as function of binding energy ($E_B$) and in-plane momentum ($k$) along Γ–M is plotted in Fig. 1(c). We identify three hole-like bands around the Γ point. Only one band, that we call α, clearly crosses $E_F$. According to LDA band calculations, there exist three hole-like bands around Γ, two of them being degenerate at Γ above the third one. Following this scheme, we assume that a second band (α’) crosses $E_F$ and intersects with the α band at the Γ point. As illustrated in Fig. 1(c), the intensity of the α’ band becomes much weaker when approaching toward Γ, likely due to the matrix element effect. In order to determine the top of the bands, we show the second derivative intensity plot along Γ–M at elevated temperature ($T = 100$ K) in Fig. 1(b). The Fermi function was removed to unmask the band dispersion above $E_F$. The α band crosses $E_F$ at $k_F \sim 0.15 \pi/a$ and reaches the top around 10-15 meV above $E_F$. A third band (β) that “sinks” 10-15 meV below $E_F$ is observed at 100 K [Fig. 1(b)] and 30 K [Fig. 1(c)].

In the vicinity of M, an electron-like band is clearly observed, as shown in the second derivative plot along Γ–M in Fig. 1(c). Along the perpendicular direction, as indicated by #c3 in panel (d), the intensity plot in Fig. 1(e) shows two electron-like bands crossing $E_F$ with slightly different $k_F$ values from Fig. 1(c). The observed bands are from two different electron-like bands, referred to as the γ, δ bands, in agreement with the LDA calculations and in an electron-doped “122” system.

Figure 2(a) shows the extracted band dispersions from the data in Fig. 1 with the suppressed portion of the α’ band linearly extrapolated to Γ. The estimated Fermi vector for the α dash band is $k_F \leq 0.05 \pi/a$. Figure 2(b) summarizes the FS topology of this sample: one large circular hole-like FS (α) and a possible much smaller one (α’) around Γ, and two elliptical electron-like FSs around M (γ, δ). We estimate that the net enclosed FS area (the area of electron-like FS is positive, and the one for hole-like FS is negative, with ±0.5° angular resolution) is about 4.3% (±1.2%) of the whole Brillouin zone, in agreement with the nominal bulk electron concentration of 5% per Fe atom. The α and γ, δ bands can be connected fairly well by the Q = (π, π) AF wavevector to allow inelastic interband scattering. Even though AF fluctuations in this material were reported to be much weaker than in other pnictides, our results are qualitatively similar to that reported on other Fe-based superconductors, supporting inter-FS scattering over the near-nested FS as an important ingredient to superconductivity.

Figure 3 shows the temperature dependence of the SC coherent peaks and the SC gaps for the α and γ, δ bands. The symmetrized EDCs at $k_F$ measured at different temperatures are plotted in Fig. 3(a) and 3(b). Assuming particle-hole symmetry, this procedure allows us to approximately remove the effect of the Fermi-Dirac function. We define the SC gap value $\Delta(T)$ as half the distance between the two SC coherent peaks in the symmetrized EDCs. Sharp coherent peaks are seen at low
normalized coherent area given by

\[ \alpha \]

location is indicated as p1 and p2 in Fig. 1d, for the

FIG. 3: (color online) (a), (b) Temperature dependence of

\[ T \]

observation of a shoulder within SC gap in Ba

\[ T \]

peak vanishes. The observation of SC coherence above

fills up and disappears at the same temperature as the

[11], whose origin is still debated, we observe no shoulder

slightly above

\[ T \]

slightly different from the bulk, is slightly higher than in

the peak vanishes, as illustrated in Fig. 3(c). The ex-

tracted gap sizes and coherent peak linewidths for the

hole and electron bands are shown in Fig. 3(d) and 3(e),

respectively. We observe that the gaps change little with

increasing temperature and persist even above \( T_c \). The

linewidth (\( \Gamma \), defined as half width at half maximum),

which is proportional to the scattering rate, also changes

little with temperature. On the other hand, the nor-

malized coherent weight, defined as the integrated area

\[ Z_A = \int A_{\text{coh}}(\omega) d\omega / \int A(\omega) d\omega \]

as following the same procedure as in the earlier work for the cuprates [23, 20], has a strong temperature dependence. As temperature increases, \( Z_A \) decreases and approaches zero at \( T_c \). This unusual temperature evolution is different from the “gap-closing” behavior of a conventional BCS superconductor, and is similar to what has been observed in the under-
doped cuprates [24], suggesting unconventional supercon-
ductivity in this pnictide superconductor.

temperature, with a peak-peak distance of \( \sim 13 \) meV.

With increasing temperature, the coherent peak intensity
decreases steadily and becomes vanishingly small

slightly above \( T_c \). In contrast to previously reported ob-

servation of a shoulder within SC gap in Ba$_{0.68}$K$_{0.4}$Fe$_2$As$_2$
[11], whose origin is still debated, we observe no shoulder

here. The gapped region between the coherent peaks also

fills up and disappears at the same temperature as the

peak vanishes. The observation of SC coherence above

\( T_c \) is possibly due to the existence of a pseudogap with a
crossover temperature (\( T^* \)) about 5–10 K above \( T_c \). An

alternative scenario is that the transition temperature at

the surface, where the mobile Na concentration could be

slightly different from the bulk, is slightly higher than in

the bulk, or the presence of SC fluctuations above \( T_c \).

For a more quantitative analysis of the temperature

evolution of the SC gap, we used the formula suggested by

Norman et al. describing the self-energy \( \Sigma(k,\omega) \) of quasi-

particles in the SC state [24]:

\[ \Sigma(k,\omega) = -i\Gamma + \Delta^2/[(\omega + i0^+) + \epsilon(k)] \]

where \( \Delta \) is the gap size and \( \Gamma \) the single par-

ticle scattering rate simplified as \( \omega \)-independent. The

absence of shoulder within the SC gap allows us to perform

reliable fits as compared to Ba$_{0.68}$K$_{0.4}$Fe$_2$As$_2$. Assuming

a polynomial background, this function fits the spectral

lineshape remarkably well at different temperatures until

the peak vanishes, as illustrated in Fig. 3(c). The ex-

tracted gap sizes and coherent peak linewidths for the

hole and electron bands are shown in Fig. 3(d) and 3(e),

respectively. We observe that the gaps change little with

increasing temperature and persist even above \( T_c \). The

linewidth (\( \Gamma \), defined as half width at half maximum),

which is proportional to the scattering rate, also changes

little with temperature. On the other hand, the nor-

malized coherent weight, defined as the integrated area

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doped cuprates [24], suggesting unconventional supercon-
ductivity in this pnictide superconductor.

FIG. 4: (color online) (a) EDCs of the \( \alpha \) band along the (0,0)–

\(-\pi,\pi\) direction in the SC state \( (T = 4 \) K), (b),(c) EDCs

along the \( \alpha \) and \( \gamma(\delta) \) FSs, respectively. (d) Typical EDC at

\( k_F \) for NaFe$_{0.05}$Co$_{0.05}$As \( \alpha \) band at \( T = 8 \) K. The red curve is

an anti-nodal EDC of optimally-doped Ba$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ at

\( T \ll T_c \). [23], showing the well known peak-dip-hump struc-
ture. (e) Extracted gap size from EDCs along the FSs, plotted

in polar coordinates with respect to their FS center. The

color of the dots refer to the color of the EDCs in (b). Solid

symbols correspond to additional extracted values while blue

circles are obtained by symmetry operations. Black lines are

\( \Delta(s_{\pm}) = \Delta_0 |\cos k_x \cos k_y| \) fits, with \( \Delta_0 = 6.8 \) meV. (f) Same

as (e) but for the \( \gamma(\delta) \) band. The color scale refers to (c).

Black and cyan lines are \( \Delta(s_{\pm}) \) fits with \( \Delta_0 = 6.5 \) meV.

The symmetry of the SC order parameter is arg-

uaably the most important information in understanding

the SC mechanism of a superconductor. Thus we

have performed high-resolution measurements of the \( k-
dependence of the SC gap for the α and γ(δ) bands. One example is given in Fig. 4(a), which shows the EDCs across \( k_F \) of the α band in the SC state (\( T = 4 \) K). The band disperses toward \( E_F \) and starts to bend back at \( k_F \), with the minimum gap situating at \( \sim 6 - 7 \) meV below \( E_F \). Similar behavior was observed for the electron-like γ(δ) bands. We also observed a kink in the band dispersion at \( \omega \sim 11 \) meV, which could be due to a coupling between electrons and a collective mode \( \xi \). EDCs at various \( k_F \) along the α and γ(δ) FSs are plotted in Figs. 4(b) and (c), respectively. Here we compare the spectral lineshape of NaFe\(_{0.95}\)Co\(_{0.5}\)As and the cuprate Ba\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\). The spectrum of the pnictide (α band) shown in Fig. 4(d) has a sharp quasiparticle peak at the gap edge followed by a broad peak which is due to an extra band below the α band. The cuprate has a similar peak-dip-hump structure near \( (\pi, 0) \) and \( (\pi, \pi) \) bands. A similar value is obtained for the α band in NaFe\(_{0.95}\)Co\(_{0.5}\)As compound with the same crystal structure as LiFeAs. Another possibility is the higher mobility of the Li atoms on the surface as compared to Na, which may lead to a different stoichiometry at the surface. In addition, the leading edge shift may likely underestimate the SC gap size, which would in turn yield a smaller \( 2\Delta/k_BT_c \) ratio. Our observation of the large \( 2\Delta/k_BT_c \) ratio and the unusual temperature dependence of the SC gap in NaFe\(_{0.95}\)Co\(_{0.5}\)As strongly suggest unconventional superconductivity in this material.

We acknowledge useful discussions with Ziqiang Wang, Jiangping Hu and Weiqiang Yu. The experiment was supported by the grants from NSF, MOST and CAS of China, and JSPS, JST-TRIP, JST-CREST, MEXT of Japan. The Synchrotron Radiation Center, WI is supported by NSF of US.

[1] Yoichi Kamihara et al. JACS, 130(11):3296, 2008.
[2] A. V. Chubukov et al. Phys. Rev. B, 78:134512, 2008.
[3] S. Raghu et al. Phys. Rev. B, 77:220503, 2008.
[4] M. Dagoher et al. Phys. Rev. Lett. 101:237004, 2008.
[5] P. Szabo et al. Phys. Rev. B, 79:012503, 2009.
[6] K. Hashimoto et al. Phys. Rev. B, 81:220501, 2010.
[7] Y. Nakai et al. Phys. Rev. B, 81:020503, 2010.
[8] C. W. Hicks et al. Phys. Rev. Lett., 103:127003, 2009.
[9] J.-P. Reid et al. Phys. Rev. B, 82:064501, 2010.
[10] L. Malone et al. Phys. Rev. B, 79:140501, 2009.
[11] H. Ding et al. Europhys. Lett., 83:47001, 2008.
[12] H. Fujita et al. Chin. Phys. Lett., 25:3761, 2008.
[13] K. Nakayama et al. arXiv:0907.0763v1, 2010.
[14] T. Kondo et al. Phys. Rev. Lett., 101:147003, 2008.
[15] Shiliang Li et al. Phys. Rev. B, 80:020504, 2009.
[16] S. Borisenko et al. Phys. Rev. Lett., 105:067002, 2010.
[17] D. S. Inosov et al. Phys. Rev. Lett., 104:187001, 2010.
[18] R. Skupnek et al. Phys. Rev. B, 79:054511, 2009.
[19] G.-F. Chen et al. Chin. Phys. Lett., 25:3403, 2008.
[20] K. Kusakabe et al. J. Phys. Soc. Jpn., 78:124712, 2009.
[21] K. Terashima et al. PNAS, 106:7330, 2009.
[22] I. Mazin et al. Phys. Rev. Lett., 101:057003, 2008.
[23] K. Kuroki et al. Phys. Rev. Lett., 101:087004, 2008.
[24] M. Norman et al. Phys. Rev. B, 75:110503, 1998.
[25] H. Ding et al. Phys. Rev. Lett., 87:227001, 2001.
[26] D. L. Feng et al. Science, 289:277, 2000.
[27] P. Richard et al. Phys. Rev. Lett., 102:047003, 2009.
[28] S. H. Pan et al. Nature(London), 413:282, 2001.
[29] Kangjun Seo et al. Phys. Rev. Lett., 101:206404, 2008.
[30] K Nakayama et al. Europhys. Lett., 6(6):7002, 2009.