Electronic band structure and momentum dependence of the superconducting gap in Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ from angle-resolved photoemission spectroscopy


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Electronic structure of newly synthesized single crystals of calcium iron arsenide doped with sodium with $T_c$ ranging from 33 to 14 K has been determined by angle-resolved photoemission spectroscopy (ARPES). The measured band dispersion is in general agreement with theoretical calculations, nonetheless implies absence of Fermi-surface nesting at an antiferromagnetic vector. A clearly developing below $T_c$ strongly band-dependant superconducting gap has been revealed for samples with various doping levels. The BCS ratio for optimal doping, $2\Delta/k_B T_c = 5.5$, is substantially smaller than the numbers observed for related compounds.

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Iron-based high-temperature superconductors form an increasingly growing subject for investigation. Unlike other types of high-temperature superconductors, iron-based compounds can be synthesized in the form of various crystals, exhibiting a large variety of electronic band structures, magnetic properties, superconducting order parameters, and electronic properties in general. On the other hand, experimental difficulties, connected to the limitations of each particular technique, and the complexity of the electronic interactions in iron-based materials hinder accurate and precise determination of the electronic structure in many cases. Thus, despite such abundance of possible forms of iron-based superconductors, the electronic spectrum, including both electronic band structure and superconducting gap function, has been thoroughly addressed experimentally only for hole-doped BaFe$_2$As$_2$ (Refs. 4–9) and LiFeAs. Available information at hand is still insufficient to tell which features are generic to all iron-based high $T_c$ s and responsible for the effective electron pairing.

Here we report detailed studies of the electronic structure of newly synthesized large single crystals of Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ (CNFA), with doping level $x$ up to 0.7 and $T_c$ between 14 and 33 K. Angle-resolved photoemission spectroscopy (ARPES) measurements were performed at 1$^3$ end station at BESSY II synchrotron in Berlin. The sample surface was prepared by cleaving, and was shown to be highly suitable for ARPES experiments: sharp spectral features and a pronounced superconducting transition at nominal $T_c$ were observed, offering the possibility for detailed studies of the electronic band structure and superconducting gap distribution with high resolution.

The Fermi surface (FS) of CNFA consists of a propeller-shaped structure at the Brillouin zone (BZ) corner, like other hole-doped 122 compounds, and holelike FS sheets at the BZ center of increased size [see Figs. 1(a) and 1(b)]. Figure 1(c) shows cuts through the photoemission intensity distribution at different binding energies, and the holelike nature of the propeller’s blades is confirmed by the increase of their size with binding energy. Figures 1(d) and 1(e) show an energy-momentum cut, passing close to the high-symmetry $\Gamma X$ line. Dispersion of the holelike bands supporting $\Gamma$ barrels and propeller blades is seen. Panel 1(f) shows the band dispersion, obtained for CaFe$_2$As$_2$ theoretically. Band structure calculations were performed using the linear muffin-tin orbital (LMTO) method for the experimental crystal structure of Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ with $x = 0.5$. The effect of doping by 0.5 hole per Fe on the bands was accounted for by a rigid-band shift.

The revealed electronic band structure of CNFA is generally similar to the electronic structure of the well studied Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (BKFA). Differences between the band dispersions of CNFA and BKFA can be described in the following way: (i) the sizes of the holelike $\Gamma$ barrels are increased, in accordance with higher level of hole doping; (ii) both outer and inner $\Gamma$ barrels are more squarish; (iii) splitting between the outer and inner $\Gamma$ barrels is larger; (iv) the electron pocket is larger, and the propeller blades are smaller; (v) the electronic states at $(k_x = 0, k_y = 0)$, presumably originating from $3z^2 - r^2$ orbitals, are located closer to the Fermi level. Additionally a seeming splitting of the outer $\Gamma$ barrel is observed for CNFA, while no such effect has been observed in the spectra of BKFA, where the outer $\Gamma$ barrel appears as the sharpest feature. The latter discrepancy between CNFA and BKFA spectra is perfectly explained by the band-structure calculations: although calculated band structures of CaFe$_2$As$_2$ (CFA) and BaFe$_2$As$_2$ (BFA) are very similar, there are important differences caused by stronger interlayer coupling in CFA. In particular, the top of a Fe $d_{3z^2 - r^2}$ band at the Z point, which in BFA lies below the Fermi level, shifts above the top of a two-dimensional $d_{x^2}$ band. As a consequence, at the Z point the outmost holelike FS is formed by the strongly dispersing $d_{3z^2 - r^2}$ band. Thus comparison to theoretical band structure allows us to identify the inner $\Gamma$ barrel as originating from $d_{x^2}$ orbitals of iron, the outer $\Gamma$ barrel as $d_{xy}$, and the propeller as mainly $d_{x^2 - y^2}$ (see also Ref. 8). Without in-depth analysis we estimate band...
FIG. 1. (Color online) (a) and (b) Fermi-surface maps of Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ with $x = 0.68 \pm 0.04$ and $T_c = 33$ K, recorded at 40 and 80 eV excitation energy ($h\nu$) respectively. (c) Cuts through photoemission intensity distribution at different binding energies reveal holelike nature of the propellers blades, recorded at $h\nu = 80$ eV. Energy-momentum cut passing close to $\Gamma X$ line recorded with 90 eV-horizontally (d) and-vertically (e) polarized light. (f) Theoretical band dispersion.

renormalization for CNFA as 2.5–3, which is close to other iron arsenides.$^{4,8,9}$

Figure 2 shows temperature-dependent measurements, revealing the opening of the superconducting gap in the photoemission spectra. The energy-momentum cut, shown in Fig. 2(a), captures Fermi crossings of the inner and outer $\Gamma$ barrels. The bending of the band dispersion is seen for both outer and inner $\Gamma$ barrels with a stronger effect for the latter. Figure 2(b) shows the temperature dependence of the partial density of states, exhibiting growth of the coherence peak below $T_c$. Partial density of states for the inner band measured at 1 K is shown in the Fig. 2(c) with a fit to the Dynes function.$^{7,19}$ Fitting yields a gap value of 7.8 meV. Corresponding analysis for the outer band yields a gap magnitude of 2.3 meV (d). A noticeable nonsuperconducting component is present in the photoemission spectra, similar to the case of the hole-doped BaFe$_2$As$_2$.4,7,8

Figure 2(e) shows energy-momentum cuts recorded at $h\nu = 25$ eV along $\Gamma X$ and $\Gamma \Gamma$ directions. While there is virtually no difference between these directions for the gap on the inner $\Gamma$ barrel, the back-bending dispersion, which is a signature of a gap, at the outer $\Gamma$ barrel is substantially more pronounced for the $\Gamma \Gamma$ direction. Further analysis of $k_F$ energy distribution curves (EDCs) [see Figs. 2(f) and 2(g)] shows that the spectrum for the $\Gamma \Gamma$ direction is shifted further from the Fermi level, as compared to $\Gamma X$, suggesting that the superconducting gap at the outer $\Gamma$ barrel is anisotropic with minima along the Brillouin-zone diagonal, $\Gamma X$ line. Though this anisotropy is rather weak and generally is within error bars of experiment, several data sets indicate that it is as described
FIG. 2. (Color online) (a) Temperature dependence of the energy-momentum cut passing through the Γ point for the sample with $T_c = 33$ K. (b) Temperature dependence of the partial density of states, i.e., integrated energy distribution curves (IEDCs). (c) Gap size, extracted from fit IEDC to Dynes function, equals 7.8 meV for the two $xz/yz$ inner Γ barrels. (d) A similar analysis for the $xy$ outer Γ barrel results in the gap magnitude of 2.3 meV. (e) Energy-momentum cuts along ΓΓ and ΓX. (f) and (g) $k_F$ EDC for the outer and inner Γ barrels at ΓΓ and ΓX. (h) Temperature dependence of the spectra recorded from $X$ pocket. (i) $61$-K spectrum divided by Fermi function. (j) Temperature dependence of IEDC from $X$ pocket. (k) $k_F$ EDC for inner Γ barrel and propeller’s blade. (l) Momentum dependence of the superconducting gap in Ca$_{1-x}$Na$_x$Fe$_2$As$_2$.

above: for the outer Γ FS sheet the gap is smaller along ΓX and the modulation magnitude is comparable to the gap size, as opposed to the inner Γ FS sheet, for which the modulation is much smaller than the gap size itself.

Figure 2(h) shows the temperature dependence of the electronlike $X$ pocket. Flattening of the spectrum top below $T_c$ indicates opening of the superconducting gap here. Figure 2(i) shows a high-temperature spectrum of the $X$ pocket divided by the Fermi function, clearly confirming the electronlike nature of these FS sheets. Even better the onset of superconductivity is seen in Fig. 2(j), where the partial DOS for the $X$ pocket is presented: the peak grows below $T_c$ and the leading edge shifts towards higher binding energies. Spectra, taken from the inner Γ barrel and propeller blades at the same conditions, indicate a uniform gap for the entire propeller structure [see Fig. 2(k)]. Additionally the electronic states of the above-mentioned 3$z^2-1$ band at $(k_x, k_y) = (0, 0)$ exhibit a clearly noticeable response to the superconducting transition with a gap comparable to the one found for the outer Γ barrel. The in-plane momentum dependence of the superconducting gap is summarized in Fig. 2(l). The found in CNFA momentum distribution of the superconducting gap is
FIG. 3. (Color online) (a) Temperature dependence of an energy-momentum cut passing through the $\Gamma$ point for Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ sample with $T_c = 14$ K. (b) Temperature dependence of the partial density of states for the inner $\Gamma$ barrel. (c) The same for the outer $\Gamma$ barrel. (d) and (e) Data at 1 K and fits to Dynes function for inner and outer $\Gamma$ barrels respectively. The derived gap sizes are 3.5 for the inner and 1.9 meV for the outer $\Gamma$ barrels.

very similar to the one that has been observed in BKFA$^{7,8}$ except for the suggested large relative variation of the gap function for the outer $\Gamma$ barrel. The dependence of the gap on the out-of-plane electron momentum has been also measured, and is generally similar to those previously reported for BKFA$^3$ and BaFe$_2$As$_{2−x}$P$_{x}$.$^{20}$ sharp minima in the gap as a function of $k_z$ occur at the $Z$ point, where the $d_{x^2−y^2}$ band interacts with $d_{3z^2−r^2}$ bands of $\Gamma$ barrels. The gap-to-$T_c$ ratio, found here for CNFA, $2\Delta_{\text{max}}/k_BT_c = 5.5$, clearly exceeds the universal BCS value, however is substantially smaller than the values
inner and outer the superconducting gap are equal to 3.5 and 1.9 meV for the states fitted with a Dynes function. The derived values for able compounds, Ba$_{1-x}$Fe$_2$As$_2$ (Ref. 8), optimally doped ($T_c = 34$ K) and underdoped ($T_c = 33$ K) optimally doped ($T_c = 33$ K) and underdoped ($T_c = 14$ K) Ca$_{1-x}$Na$_x$Fe$_2$As$_2$. Red dots represent maximal gap for the inner $\Gamma$ barrel, blue dots represent outer $\Gamma$ barrel. All values were extracted from ARPES data by fitting partial density of states to Dynes function.

found for other iron-based superconductors. For example, for the related compound BKFA, gap-to-$T_c$ ratios of 6.3, 7.8, and even 9.5 (Ref. 21) were reported. For Sm-1111 with $T_c$ of 52 K, close to the record among iron-based superconductors, $2\Delta_{\text{max}}/k_BT_c$ was found to be 9.22

Additionally we have succeeded to measure the superconducting gap opening for a Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ phase with $T_c$ of 14 K. The temperature dependence of the energy-momentum cut passing through the BZ center is shown in Fig. 3(a).

In conclusion, we have presented investigation of the electronic band dispersion and superconducting gap distribution in a new 122-iron arsenide, Ca$_{1-x}$Na$_x$Fe$_2$As$_2$. The Fermi surface consists of holelike sheets at $\Gamma$ and a propellerlike structure at the X point, therefore excluding the possibility of good nesting. On the other hand, two inner $\Gamma$ barrels and propeller are of comparable sizes, are separated by the ($\pi,\pi$) vector, and all are predominantly composed of iron $3d_{x^2-y^2}$ orbitals, indicating that there are channels for enhanced electron scattering at the antiferromagnetic vector. The superconducting gap is large ($\sim$7.8 meV) for the inner $\Gamma$ barrels and propeller, and small ($\sim$2.3 meV) for the outer $\Gamma$ barrel. Though the gap is mostly uniform within each FS sheet and no indication for gap nodes have been found, there is evidence for in-plane gap minima along the $\Gamma X$ direction for the outer $\Gamma$ barrel, and for a $k_z$-dependent gap with a minimum at the Z point for inner $\Gamma$ barrels. A rather complicated Fermi surface with clear departures from the theoretical calculations is established as a characteristic property of the hole-doped 122-iron arsenides with highest $T_c$s. Momentum dependence of the superconducting gap appears very similar for all studied compounds too, suggesting universality of the pairing mechanism.

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