Strong electron pairing at the iron $3d_{xz,yz}$ orbitals in hole-doped BaFe$_2$As$_2$ superconductors revealed by angle-resolved photoemission spectroscopy

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Using the angle-resolved photoemission spectroscopy (ARPES) with resolution of all three components of electron momentum and electronic states symmetry, we explicate the electronic structure of hole-doped BaFe$_2$As$_2$, and show that widely discussed nesting and dimensionality of Fermi surface (FS) sheets have no immediate relation to the superconducting pairing in iron-based superconductors. Alternatively a clear correlation between the orbital character of the electronic states and their propensity to superconductivity is observed: The magnitude of the superconducting gap maximizes at 10 meV exclusively for iron $3d_{xz,yz}$ orbitals, while for others drops to 3 meV. Presented results imply that the relation between superconducting and magnetostuctural transitions goes beyond simple competition for FS, and demonstrate importance of orbital physics in iron superconductors.

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I. INTRODUCTION

The theory of unconventional superconductivity is far from being completed, and a lot of effort is devoted to the search for principal features responsible for efficient electron pairing. The field of iron-based superconductors offers broad opportunities for research owing to an availability of a large variety of relevant compounds in the form of high quality crystals $^{[1,2]}$, which suggests that the progress in understanding of unconventional superconductivity is likely to be achieved with these materials. While existing theoretical models do not provide decent descriptions for the observable properties of iron superconductors, several phenomenological tendencies closely related to superconductivity are already established: Presence of the electronic states with a large difference in superconducting gap magnitude, often a two-gap behavior $^{[3–6]}$, gap-to-$T_c$ ratios much higher that the universal BCS value $^{[3,4,7]}$, and correlation of $T_c$ with anion height $^{[8]}$.

A phenomenological approach requires a large amount of input data and therefore is usually applied to a set of materials. A large diversity of electronic states at the Fermi level, found in Ba$_{1-x}$K$_x$Fe$_2$As$_2$, originally was an obstacle on the way to complete understanding of the underlying electronic structure $^{[9–12]}$. At a closer look such variety of electronic states turned out to be a blessing, allowing for detailed studies of the response of different states to the superconducting transition within the same material. Below we use angle-resolved photoemission spectroscopy (ARPES) with variable photon energy and light polarization to investigate the electronic structure of hole-doped BaFe$_2$As$_2$. Matching of the measured three-dimensional momentum distribution of the superconducting gap with corresponding dependence of the orbital character of the electronic states, reveals a clear correlation between these two properties. Namely, the magnitude of the superconducting gap is maximal only for iron $3d_{xz,yz}$ orbitals, while for other orbitals it drops by up to three times, implying the importance of $3d_{xz,yz}$ states for superconductivity. The same orbitals were found to be important for magnetostuctural transition $^{[13–16]}$, which suggests that a theory of superconductivity in iron-based superconductors should account also for the magnetic ordering.

II. EXPERIMENTAL DETAILS

Below we report ARPES measurements, carried out at the 1º-APEX end station at BESSY II synchrotron in Berlin (Helmholtz-Zentrum für Materialien und Energie) on the single crystals of optimally doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $T_c = 38$ K. Growth details and characterization results are available in Refs. $^{[5,17,18]}$. All presented data were taken from optimally doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$, except for the data in Figs. 2(c) and 2(d) and 7(e)–7(g), which were recorded from the optimally doped Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ with $T_c = 34$ K $^{[6,19]}$.

III. EXPERIMENTAL RESULTS

The superconducting gap in BKFA was studied by means of various experimental techniques $^{[4,5]}$, and the vast majority of the results can be interpreted in terms of the presence of a comparable amount of electronic states gapped with a large gap ($\Delta_{large} = 10–11$ meV) and with a small gap ($\Delta_{small} < 4$ meV). The in-plane momentum dependence of the superconducting gap, determined in early ARPES studies, is as follows: The large gap is located on all parts of the FS except for the outer holelike FS sheet around the $\Gamma$ point $^{[11,20,21]}$. Though the crystal structure of iron-based superconductors of interest is layered, and electronic states at the Fermi level are formed...
FIG. 1. (Color online) $k_z$-dependent superconducting gap at holelike Fermi surface sheets centered at the $(k_x = 0, k_y = 0)$ point in optimally doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$. (a) Energy-momentum cut, passing through the $(k_x = 0, k_y = 0)$ point and capturing spectrum around Fermi crossings of $\Gamma$ FS sheets, recorded at $h\nu$ ranging from 13 to 93 eV (vertical and horizontal polarizations for 33 eV). As discussed in the main text, the two nearly degenerate inner $\Gamma$ barrels are often not resolved. All three $\Gamma$ barrels are clearly resolved at excitation energies around the value of $h\nu = 33.5$ eV. Red dashed lines are guides to the eye, located at 0 and 10 meV binding energy. (b) Integrated energy distribution curves (IEDC) fitted to the Dynes function. Inset shows IEDCs for the outer $\Gamma$ barrel at 25 and 27 eV, color coding is preserved. (c) Values of the superconducting gaps at $\Gamma$ barrels as a function of $h\nu$. Underlying fitting curves are described in Ref. [23]. Taking into account that $k_z$-dependence of the gap is observed only for the inner $\Gamma$ barrels and there it possesses large flat regions, the two-gap model still can be sufficient for satisfactory interpretation of many experimental results.
mainly by the atomic orbitals of the iron planes, studying the
dependence of the electronic spectrum on the out-of-plane
momentum leads to quite interesting observations.

The resolution of the electronic spectra along the out-of-
plane momentum is achieved in photoemission experiments
via the variation of the energy of the incoming photons [22].
Figure 1(a) shows an energy-momentum cut capturing the
Fermi crossings of the inner and outer Γ FS sheets, imaged
with excitation energies in the range from 13 to 90 eV. The
values of the superconducting gap were determined from the
fit of the integrated energy distribution curves (IEDCs) to
the Dynes function [20,24,25]. IEDCs and fitting curves are
shown in Fig. 1(b). Upon analysis of ARPES spectra of the
BKFA one unavoidably encounters a problem of additional,
previously surface-related, contributions to the signal. This
issue is discussed in the Appendix, here we only note that
fitting the data allowed us to single out the relevant values
for the gap. The derived hν dependence is shown in Fig. 1(c).
The gap on the inner Γ barrel varies from maximal value of
10.5 ± 0.5 meV, observable for hν = 13, 25, 45 eV, to
the minimal value of 4.5 meV at hν = 33.5 eV. At photon
energies close to 33 eV it is possible to clearly resolve two
components of the inner Γ barrel as separate features in the
spectra [see Figs. 1(a) and 5]; at 33 eV the gaps for the Γ
barrels are 3.5 meV for the outer one, 4.5 meV for the second,
and 5.5 meV for the innermost. It is important to note that the
variation of the gap discussed here is also observed in the peak
positions of single energy distribution curves from the raw
data (see Appendix). The used fitting procedure is chosen as
a primary tool as it allows for determination of the gap values
with enhanced precision.

Δ_{large}(hν) is quasiperiodical, shows large flat regions with
magnitude close to maximal, and rather steeply decreases to
the minimum and steeply increases back to flats, which is
particularly well illustrated by the cusp around 33.5 eV. The
intensity distribution in the FS map also shows rather fast
variations at 33.5, 60, and 93 eV, and regions with rather
smooth variation of the signal in between. Interestingly, there
is a rather transparent connection of such hν dependence of
the photoemission signal to the k, dependence of the electronic
states at the Fermi level in the band structure calculation: As
seen in Fig. 6, there is a band at (k_x = 0, k_y = 0) which is far
above the Fermi level at k_z = 0 and comes down and starts
to interact with two d_{xz,yz}-derived holelike bands in a rather
narrow region around k_z = π. The gap on the outer Γ barrel,
Δ_{small}(hν), remains 3.5 ± 0.5 meV for the whole range of different
k values [Fig. 1(c)], i.e., is essentially k independent. This
behavior is inline with the absence of k dependence of the
electronic states, forming the outer Γ barrel (see Fig. 6).

Next we identify the orbital composition of the electronic
states at the Fermi level by matching the bands, observed in the
ARPES spectra of hole-doped BaFe_2As_2, to the bands
obtained in the band structure calculations. The origin of
the holelike bands in the Brillouin zone (BZ) center is clear—the outermost barrel corresponds to the band formed
prevalently of iron 3d_{xy} orbitals, while two inner barrels consist of combinations of 3d_{xz} and 3d_{yz} orbitals [7,11,20,26,27].
The situation with the propeller-shaped bands, observed by
ARPES at the BZ corner, seems to be more tricky—original FS,
derived in band structure calculations, does not contain
this feature [9]. On the other hand, in the calculations there
is a band, situated below the Fermi level, with dispersion
rather similar to the one observed experimentally for the
band supporting propeller FS sheets (see Figs. 2 and 6).
Therefore, we employ an additional tool for identification of
the electronic states—analysis of spectra, recorded with
differently polarized incoming light. The grounds for such
analysis stem from symmetry considerations: Based on the
symmetry of the electronic wave function in the crystal and
polarization direction of the incoming light, it is possible to
show that the matrix element of photoemission is zero for
certain experimental conditions.

Let us now consider the electronic states along the ΓX line. Figure 2(a) shows the results of calculations for this
direction. We will now concentrate on the band, plotted in red;
this band is composed of d_{yz} orbitals [28]. Figures 2(c) and
2(d) show ARPES spectra, recorded in the same ΓX direction
with light polarizations perpendicular [Fig. 2(c)] and parallel
[Fig. 2(d)] to the ΓX. One of the most prominent changes,
observed upon switching polarization, is complete vanishing
of the band, which was the brightest in Fig. 2(c) and possesses
dispersion very similar to the just discussed red band from the
calculations. Remarkably, the d_{yz} orbital is odd with respect
to the reflection in the plane containing ΓX and the direction
to the detector, and therefore (due to mentioned symmetry
reasons) should yield zero intensity when excited by the light
polarized along ΓX. This implies that not only does the d_{yz}
band in the calculation possess the dispersion similar to the
dispersion of the propeller bands, derived from ARPES, but
also the strong polarization dependence, observed in ARPES,
is fully consistent with the one expected in theory. Figure 2(b)
shows the calculated band dispersions, which are shifted in
order to fit the ARPES spectra.

The last tile in the complete definition of the three-
dimensional electronic structure at the Fermi level is the gap
at the propellerlike bands at the BZ corner. The variations of
the gap magnitude on the propellers were not observed when
changing hν, implying that the gap magnitude on the propeller
remains ~10 meV for all values of k_z, in accord with previous
reports [26,27] and with little k dependence of the correspond-

IV. DISCUSSION

Now, with exhaustive information on the distribution of the
superconducting gap and orbital composition of the electronic
states at the Fermi level at hand (Fig. 3), we see that there is a
strong correlation of these two parameters. Namely, the gap is
large for those and only for those states which originate purely
from d_{xz,yz} atomic orbitals. Indeed: (i) the gap is 3.5 meV
for the outer Γ barrel, composed of d_{xy} orbitals; (ii) the gap is
10 meV for the propellers, composed of d_{xz,yz} orbitals; (iii) for
the inner Γ barrels the gap reaches 10.5 meV around k_z = 0,
where the electronic states originate from d_{xz,yz}, and drops to
5.5 meV at k_z = π, where an admixture of d_{xy} appears;
(iv) additionally, in the Appendix evidence is presented for the
3 meV gap at extra iron 3d_{xz,yz-π} band, barely reaching the
Fermi level (results are summarized in Table I).

The relation between the magnitude of the superconducting
gap and orbital composition of the electronic state, established
here on the example of hole-doped BaFe$_2$As$_2$, holds, at least partially, also for other iron-based superconductors, isoelectronically substituted BaFe$_{2-2x}$P$_{2x}$, and undoped LiFeAs, NaFeAs, and FeTe$_{1-x}$Se$_x$ [29–34], though a thorough analysis of this issue has not been performed. An indirect conformation for orbital dependence of the superconducting gap comes from ubiquitous observation of multigap behavior in iron-based superconductors [3–6] and a superconductivity-induced suppression of an absorption band [35]. Additionally, some theoretical approaches consider orbital character as an important prerequisite for a description of the superconducting and magnetic states in iron arsenides [15,16], and indicate that dominant attractive interaction occurs among the electronic states originating from $d_{x^2-y^2}$ orbitals [16].

![Graph showing band dispersion and polarization](image1)

**FIG. 2.** (Color online) Comparison of the calculated band dispersion, to the band dispersion, extracted from ARPES data. (a) The calculated band dispersion. (b) The band dispersion, extracted from ARPES data, presented in (c) and (d). (c) Energy-momentum cut, passing through the ($k_x = 0, k_y = 0$) point, recorded at 70 eV using horizontal light polarization. (d) Same cut, recorded with vertical polarization. Data recorded from the optimally doped Ba$_{1-x}$Na$_x$Fe$_2$As$_2$.

![Graph showing superconducting gap and orbital composition](image2)

**FIG. 3.** (Color online) Three-dimensional distribution of the superconducting gap and orbital composition of the electronic states at the Fermi level. (a) Distribution of the superconducting gap (plotted as height) and distribution of the orbital composition for the states at the Fermi level (shown in color: $d_{x^2-y^2}$—red, $d_{xy}$—green, $d_{x^2-y^2}$ with admixture of other orbitals—orange) as function of $k_x$ and $k_y$ at constant $k_z = 0$. (b) The same, only for $k_z = \pi$. (c) Same distributions as function of in-plane momentum, directed along BZ diagonal and $k_z$. Note unambiguous correlation between the orbital composition and superconducting gap magnitude.
The special role of iron $3d_{xz,yz}$ orbitals was also noticed in ARPES studies of the magnetostructural transition in the undoped and underdoped Ba-122 iron arsenides [13], implying that electronic states, which are affected most strongly by the magnetic ordering, appear to bear the largest gap in the superconducting state. An important role of orbital degrees of freedom in parent compounds was also derived from neutron measurements [14]. This means that relation between superconductivity and magnetism in iron-based superconductors is more intimate than between phases just competing for the Fermi surface.

V. CONCLUSIONS

In summary, the momentum distribution of the superconducting gap was found substantially three dimensional and rather nontrivial. Such momentum dependence of the superconducting gap is not predicted in simple models, where the pairing strength is determined by conventional Fermi surface nesting, dimensionality of Fermi surface sheets, etc. Alternatively a strong variation of the gap over the Fermi surface and distinct correlation of the gap magnitude with the orbital composition were established; in particular, the superconducting gap magnitude for the electronic states, derived from iron $3d_{xz,yz}$ orbitals, is much higher than for other states.

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APPENDIX

1. Extraction of the superconducting gap magnitude from simple peak position

In Fig. 4 we adduce the gap estimation from spectra by means of peak position measurements in EDC. As an example the photon energies of 27, 33, 50, 60, and 80 eV were chosen. These photon energies correspond to the alternating $k_F$ regions with maximal and minimal gap. The peak positions, related to the outer, middle, and inner bands are summarized in Table II. For most excitation energies two inner $\Gamma$ barrels are nearly degenerate and therefore are not resolved in the spectra. At the same time it would be possible to notice if they

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had substantially different gaps. For \( k_z \), for which it was not possible to determine the gap value for the middle component of the \( \Gamma \) barrel separately, it is nearly equal to the gap given for the inner \( \Gamma \) barrel in Table II. Thus, analysis of the peak position in single EDCs clearly confirms the presence of deep minima in the gap function at \( k_z = \pi, Z \) point. Generally the fitting gives more accurate results, but we understand that it is also important to emphasize that the discussed effect is already seen in the raw data.

2. Spectral weight, related to \( 3d_{3z^2-r^2} \) electronic states at \( (k_x = 0,k_y = 0) \)

Apart from the mentioned three bands, forming quasi-two-dimensional holelike FS sheets in the center of BZ, there is also a rather diffuse intensity below the Fermi level, centered at about 100 meV binding energy [see, e.g., Figs. 5(b), 5(d), and 2(e)]. In the band structure calculations there is a good candidate to account for this intensity—a band, formed by iron \( 3d_{3z^2-r^2} \) orbitals strongly hybridized with As \( p_z \) states [see Figs. 6(c) and 2]. This band has been noticed in previous ARPES experiments on BKFA [26] and rather extensively mapped for the case of KFe\(_2\)As\(_2\) [36]. Figures 5(a) and 5(b) show the same energy-momentum cut, passing through the \( (k_x = 0,k_y = 0) \) point, recorded with \( h\nu = 33 \) eV and different polarizations of the incoming light. The electronic states of interest produce much photoemission intensity for the case of horizontal polarization [see Fig. 5(b)] and are almost invisible in the vertical polarization [Fig. 5(a)]. Figure 5(c) shows the EDCs at momentum \( (k_x = 0,k_y = 0) \) for data presented in Figs. 5(a) and 5(b). Not only do the electronic states at higher binding energies yield more intensity when switching polarization from vertical to horizontal, but also some additional intensity appears at the Fermi level, as shown by arrows in Fig. 5(c), implying that at least some spectral weight, related to this \( 3d_{3z^2-r^2} \) band, reaches Fermi level due to self-energy broadening of and crossing the Fermi level at some \( k_z \) values. In Fig. 5(d) we show an energy-momentum cut, recorded at 1 K with \( h\nu = 34 \) eV. One can notice two stripes close to the Fermi level at \( (k_x = 0,k_y = 0) \): The one at higher binding energy is related to the fusion of Bogoliubov dispersion branches, observed before in BKFA [7], while the second stripe in closer vicinity to the Fermi level remained unnoticed before. In order to better visualize this spectral feature we present EDC from \( (k_x = 0,k_y = 0) \) point in Fig. 5(e). The arrows indicate the peaks—coming from the fusion of bogoliubons and the second newly detected peak. We propose that the second peak stems from a small superconducting gap opened at the electronic states discussed above, originating from a lower-lying band with \( 3d_{3z^2-r^2} \) character. From a fit to Dynes function we have determined that the magnitude of this superconducting gap is about 3 meV. Alternatively this new feature may originate from the spectral weight, related to the upper Bogoliubov dispersion branch. Though such interpretation does not explain the observed polarization dependence [Figs. 5(a) and 5(b)] and according to simulations (not shown) requires rather large pair-breaking scattering in order to partially fill the superconducting gap, we cannot rule it out at the present stage.

3. Results of band structure calculations

The calculated band structure of undoped BaFe\(_2\)As\(_2\) is presented in Fig. 6. The electronic states at the Fermi level are formed almost entirely of iron \( 3d \) orbitals. Figures 6(a)–6(d) present band dispersion with superimposed circles, denoting the weight of the atomiclike states in the decomposition of the wave functions. Figure 6(e) presents the isoenergetic contours, obtained by cutting the calculated band dispersion at 250 meV below the Fermi level. The similarity of the four holelike elongated ellipses at the BZ corner to the propellers, observed in FS maps, measured by ARPES, hints that the calculated and measured band structures can be matched if one slightly shifts and bends the bands. An important remark that is to be done here is that for denoting the orbital composition of the bands we use the reference frame with \( x \) and \( y \) axes directed along the diagonals of a two-dimensional Fe\(_2\)As\(_2\) unit cell, and \( z \) directed perpendicular to the iron-arsenic layers (to avoid confusion: momentum components \( k_x \) and \( k_y \) are directed parallel to the boundaries of the Fe\(_2\)As\(_2\) unit cell). The dispersion of the spectral weight near the BZ corner in the energy-momentum cut [see Fig. 2(c)] in turn reminds

**FIG. 5.** (Color online) Observation of the additional spectral weight presumably related to the iron \( 3d_{3z^2-r^2} \) orbitals at the Fermi level and superconducting gap on it for optimally doped Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\). (a) Energy-momentum cut, passing through the \( (k_x = 0,k_y = 0) \) point, recorded with \( h\nu = 33 \) meV and vertical polarization of the incoming light. (b) The same cut, recorded with horizontal polarization. (c) EDCs directly from \( (k_x = 0,k_y = 0) \) point recorded with horizontal and vertical polarizations. Comparison of EDCs recorded at different polarization suggests that spectral weight originating from three-dimensional electronic states, seen in spectrum as rather smeared intensity [see (b)], reaches the Fermi level. (d) Energy-momentum cut, passing through the \( \Gamma \) point. (e) \( \Gamma \)-EDC reveals two peaks near the Fermi level: One at binding energy about 17 meV corresponds to the observed in this compound “fusion of bogoliubons” [7], while the one closer to the Fermi level corresponds to the superconducting gap with magnitude about 3 meV.
the dispersion of the $3d_{xz,yz}$ band, situated right below the bottom of the electronlike pockets in the calculation [see Fig. 6(b)]. Another characteristic feature of the calculated band structure is a strongly three-dimensional band at ($k_z = 0, k_y = 0$) coming from high above the Fermi level as a function of $k_z$ and starting to interact with two $3d_{xz,yz}$ bands at $k_z$ values of about $\pi \pm \pi/4$ [see Figs. 6(a)–6(d)]. As already mentioned above, such behavior is consistent with rather abrupt variation of many characteristics of the photoemission spectrum in the vicinity of some values of $h\nu$ and no considerable variation for large regions in between. An independent confirmation that peculiar $h\nu$ values of 33.5, 60, and 93 eV correspond to the $Z$ point comes from the fitting of the $h\nu$ dependence of the superconducting gap [23]. The detailed dependence of the electronic states of the calculated band structure on $k_z$ is shown in Fig. 6(g): At ($k_x = 0, k_z = 0$) the interaction of the quasi-two-dimensional bands, supporting $\Gamma$ FS sheets, with the mentioned band, coming from higher energies, results
in the onset of the \( k_z \) dispersion and variation of the orbital composition at \( k_z = \pi \).

The matrix element of a transition from an initial state \( u_i \) to a final state \( u_f \) upon action of the electromagnetic field of the incoming light can be written as

\[
\int u^*_f(\mathbf{r}) \mathbf{A} \cdot \nabla u_i(\mathbf{r}) d^3\mathbf{r},
\]

(A1)

where integration is performed over the whole coordinate space. Zero matrix element would mean that the transition does not happen, i.e., some particular electronic states do not contribute to the observed photoemission signal. Symmetry considerations reveal many cases when the matrix element is zero, e.g., if there exists such a mirror plane that the integrand is odd with respect to the corresponding reflection, the whole integral is zero. It is particularly convenient to analyze parity with respect to the plane containing both the normal to the sample surface and the momentum of photoelectron flying to the analyzer. Such an analysis has been carried out for ARPES on iron arsenides to identify the bands in the center of BZ, and in particular to resolve two closely located bands [26]. In Figs. 2(c) and 2(d) we have presented a symmetry analysis for the energy-momentum cut passing through the BZ diagonal and cutting through all different FS sheets. For the case of the bands, formed by combination of \( d_{xz,yz} \) orbitals, the orbitals lying in a plane are even with respect to reflection in it, while the ones standing “perpendicular” to the plane are odd. The most prominent difference upon switching polarization occurs for the band, composed of \( d_{xy} \) orbitals (for the orbital character, obtained from the calculation, refer to Figs. 6 and 3(e) in Ref. [28]).

It is still unclear whether the entire propeller-shaped intensity, seen in ARPES (including central small electronlike pocket), can be satisfactorily reproduced by cutting the calculated band structure at the suitable energy level and emulation of the self-energy broadening. Additionally, temperature dependence of ARPES signal from propellers has been observed [9,37], suggesting that appearance of propellerlike structure at the BZ center and propellerlike structure at the BZ corner, illustrating the already mentioned similarity of the electronic structures of sodium- and potassium-doped BaFe\(_2\)As\(_2\) (see also Ref. [19]). The temperature dependence of the cut, passing through the propeller’s blade [pink dashed line in Fig. 7(e)] is presented in Fig. 7(f). The hololek dispersion of the band, supporting the propeller’s blades, is clearly visible. The development of the superconducting gap can be recognized as modification of the spectral function in the vicinity of the Fermi level in Fig. 7(f) and by growth of the prominent coherence peak in the integrated spectrum in Fig. 7(g). Clear observation of the large superconducting gap implies that the propellerlike Fermi surface takes an active part in the superconductivity.

5. Additional component of the photoemission signal from the inner \( \Gamma \) barrel

Already in first studies of the superconducting gap in BKFA an additional component of the inner \( \Gamma \) barrel was noticed and attributed to the nonsuperconducting part of the photoemission spectrum [11,20]. More recent experiments have shown that this feature is not entirely nonsuperconducting, but bears a reduced superconducting gap of 3–7 meV [26,39]. To investigate this issue more thoroughly we have performed time-dependent measurements of the intensity distribution in the vicinity of the Fermi level in the superconducting state. Figures 8(a)–8(d) show two equivalent spectra taken from the same cleaved sample surface soon after cleavage and on the next day. An aged sample surface obviously exhibits a prominent nonsuperconducting (or bearing very small gap) component, while for the freshly cleaved surface the secondary component is gapped with a \( \sim 6 \) meV gap, and therefore is not that prominent, merging visually with the peak from the \( \sim 11 \) meV gap. Interestingly, both in case of aged and fresh surfaces, the large gap remains the same, \( \sim 11 \) meV, i.e., it is robust with respect to surface degradation. The inner \( \Gamma \) barrel is double walled, so generally one might expect an additional feature at this location in the Brillouin zone: Each of these two nearly degenerate bands might bear different superconducting gaps. However, such explanation for two distinct gaps in this momentum region faces the following difficulties: (i) The two inner \( \Gamma \) barrels are highly degenerate and have virtually the same orbital composition of the wave functions, therefore it seems unlikely that they that they bear gaps of such different magnitudes (6 vs 10.5 meV), and (ii) one of the gaps almost completely vanishes with time, while the other remains unchanged, also implying different origin of the two neighboring features, while the impact of surface data is taken into account upon fitting the data [38], and the magnitude of the reduced gap can be extracted separately. In Fig. 7(c) are shown temperature dependencies for the gap magnitude on the outer \( \Gamma \) barrel, two unresolved inner \( \Gamma \) barrels, and surface component of the inner \( \Gamma \) barrels. Thus, both the small gap on the outer \( \Gamma \) barrel and the large gap on the inner \( \Gamma \) barrels emerge upon entering the superconducting state, and consequently are unambiguously related to the superconductivity.
FIG. 7. (Color online) (a) Sequence of temperature-dependent measurements, performed on Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with $T_c$ of 38 K, for the energy-momentum cut, passing through the $\Gamma$ barrels in the range of 1–43 K. The emergence of superconducting gap shows up as appearance of the “beaks” at Fermi crossings of both inner and outer $\Gamma$ barrels. (b) Temperature dependence of the IEDC, referring to the inner $\Gamma$ barrel, integrated in the range shown in the inset. The spectrum above $T_c$ is nothing but Fermi step, while the coherence peak starts to grow at superconductivity onset. (c) Same as (b), only for the outer $\Gamma$ barrel. (d) Temperature dependence of the superconducting gaps, derived from fit of integrated EDC to Dynes function. (e)–(g) Present data, taken from Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ with $T_c$ = 34 K. (e) Fermi surface map. (f) Temperature dependence of the energy-momentum cut passing through the center of the propeller’s blade, as shown by a dashed line in (e). (g) Temperature dependence of the integrated EDC, revealing the appearance of prominent coherence peak below $T_c$.

degradation on the two components of the inner $\Gamma$ barrel is expected to be very similar, as they both are composed of the same iron $d_{xz,yz}$ orbitals. A more plausible explanation is that the spectral feature with reduced gap corresponds to the photoemission signal from the topmost surface layer, and consequently, should be filtered out when speaking of the bulk gap structure.

Figures 8(e) and 8(f) show two spectra, taken in the very same conditions from the same cleave even with no adjustment of sample position. The difference between these two spectra is due to surface degradation, related to the residual pressure in the measuring chamber. Visually presence of a component with reduced gap is seen as a “hat” on top of the feature bearing a large gap [see Figs. 8(e) and 8(f)]. The difference between spectra in Figs. 8(e) and 8(f) is that this hat is shifted more towards the Fermi level, i.e., further from the feature with the robust large gap. Figure 8(g) shows a detailed analysis of the near-$k_F$ EDC for data presented in Figs. 8(e) and 8(f). The peak in the EDC is fitted to two Lorentzians, also shown in Fig. 8(g) below the data. Remarkably, the difference in the fits for more and less degraded spectra is only in the shift of the Lorentzian, located at the lower binding energy to even lower; at the same time the position of the Lorentzian at higher binding energy and relative weights of Lorentzians remain unchanged. This allows us to conclude that the main effect of surface degradation is in further closing of the reduced gap.

To get some quantitative estimate of the residual pressure effect on the surface degradation, we have performed a time-dependent measurements of the same spectrum capturing $\Gamma$ barrels [Fig. 8(h)]. The residual pressure was 1.3 $\times$ 10$^{-10}$ mbar, and time interval between consequent measurement, shown in Fig. 8(h), was 12.5 min. In Fig. 8(i) we plot the temperature dependence for positions of the leading edge midpoints of the inner and outer $\Gamma$ barrels.
FIG. 8. (Color online) Deterioration of the sample surface with time after cleavage results in reduction of the gap in the surface-related part of the photoemission spectrum. At the same time another bulk component of the signal exhibits a robust time-independent gap value. (a) Energy-momentum cut, passing through the $\Gamma$ point, recorded soon after cleavage. (b) EDC, integrated around the Fermi crossing of the inner $\Gamma$ barrel, as indicated in (a). (c) The same cut, recorded from the same cleave after more than 25 h. (d) Corresponding EDC. (e)–(g) A different data set, where (e) and (f) represent signals from less and more deteriorated surfaces, respectively. (g) Near-\textit{k-F} EDCs after deconvolution together with fits to two Lorentzians. The peak corresponding to bulk signal remains unchanged, while the peak corresponding to the surface signal with reduced gap shifts towards Fermi level. (h) Third data set: Time evolution of the similar cut, passing through the $\Gamma$ barrels, recorded immediately after cleavage at residue pressure in the measuring chamber of $1.3 \times 10^{-10}$ mbar and using a Janis ST400 cryomanipulator. (i) Time dependence of the leading edge position (LEG) for the outer (gray circles) and inner (blue crosses) $\Gamma$ barrels. All data recorded from optimally doped $\text{Ba}_1\text{K}_x\text{Fe}_2\text{As}_2$.

The time evolution for the inner $\Gamma$ barrel shows exponential behavior with a time constant of approximately 1 h. The same temperature dependence for the outer $\Gamma$ barrel shows a small decrease instead of an expected small increase due to onset of different effects (variation of intensity distribution, broadening of spectral features, etc.) influencing the leading edge midpoint position.

We emphasize once more that the large superconducting gap on the inner $\Gamma$ barrel is a robust property of the ARPES spectra of optimally doped BKFA, while the reduced gap is strongly dependent on the experimental conditions, and most likely is related to the surface. It is worthwhile noting that in the case of ARPES experiments on LiFeAs no additional components of the signal with reduced gap has been noticed and the spectra generally deteriorate less with time passed after cleaving [29,40]. The reason is that, in contrast to 122 iron arsenides, LiFeAs has a natural cleavage plain and topmost superconducting Fe-As layer appears to be covered with a whole Li layer.

Presence of two components in the spectra—the one with a reduced gap value, dependent on the surface quality, and the other with a large robust gap—imply that the observed
spectra represent a superposition of a signal coming from the topmost surface layer and a signal from the deeper subsurface layers. The fact that the difference between the surface and subsurface signal mainly consists in the gap values, while no or only little difference in the band dispersion was detected, suggests that surface effects do not critically alter the dispersion relation in Ba$_1$-$\alpha$K$_2$Fe$_2$As$_2$. Together with matching Hall and ARPES measurements [37] and with observation of the large superconducting gap opening at $T_c$ [Fig. 7(f)], it gives good substantiation for the bulk origin of the propellerlike Fermi surface and its active role in superconductivity.

[19] The electronic structures of K- and Na-doped BaFe$_2$As$_2$ are very similar. ARPES spectra of both compounds are characterized by propellerlike FS at the BZ corner, three hololeike bands at the BZ center—all of very close size, similar magnitude and momentum distribution of the superconducting gap including similar $k_z$ dependence [partially published in S. Aswartham et al., Phys. Rev. B 85, 224520 (2012)]. Possible differences between Ba$_1$-$\alpha$K$_2$Fe$_2$As$_2$ and Ba$_1$-$\alpha$Na$_2$Fe$_2$As$_2$ are insignificant for the analysis presented here.
[21] Though generally we consider essentially three-dimensional electronic structure of BKFA in this paper, for the hololeike sheets in the BZ center we will use the notation of “Γ barrels,” stemming from two-dimensional terminology. We will also sometimes refer to the “inner” and “outer” Γ barrels, implying that splitting of the two inner FS sheets is not principal for particular considerations.
[23] The fitting curves, used for approximation of the excitation energy dependence of the superconducting gap magnitudes on the Γ barrels in Fig. 1(d), are $\Delta_{\text{ang}}(h\nu) = 10.5 - 5 \sin^2[0.5 \cdot 6.7 \sqrt{h\nu + 7.6}]$, $\Delta_{\text{ang}}(h\nu) = 10.5 - 6 \sin^2[0.5 \cdot 6.7 \sqrt{h\nu + 7.6}]$, and $\Delta_{\text{ang}}(h\nu) = 3.5$. Apart from the value of 7.6 eV for the inner potential, from fitting of the data we can infer that the peculiar points in the $h\nu$ dependence correspond to the $k_z = \pi$, i.e., $Z$ point in the three-dimensional BZ. The deviation of the model from experimental data at photon energies below 20 eV is expected from break down of the free electron approximation for the final state.
[24] The integration is performed in a momentum range sufficient to collect most of spectral weight, referring to the chosen Fermi crossing. An example is given in Fig. S7.
[34] The behavior of the superconducting gap, suggesting presence of the gap nodes along $k_z$, was found for the case of $\text{BaFe}_2\text{As}_2-x\text{P}_x$ [33]. The $k_z$ dependence of the gap is very reminiscent of the one observed for $\text{Ba}_1-x\text{K}_x\text{Fe}_2\text{As}_2$, only with a deeper minimum at $Z$ point. This is perfectly consistent with the orbital dependence of the gap proposed here: In $\text{BaFe}_2\text{As}_2-x\text{P}_x$, the electronic states at $\Gamma$ point exhibit stronger dependence on $k_z$.
[38] Though the shape of the spectrum below $T_c$ exhibits significant deviations from the BCS behavior, in particular due to prominent effects of a mode scattering [7] [P. Richard, T. Sato, K. Nakayama, S. Souma, T. Takahashi, Y.-M. Xu, G. F. Chen, J. L. Luo, N. L. Wang, and H. Ding, Phys. Rev. Lett. 102, 047003 (2009)], the values of the gap, extracted from the fit of the data to the Dynes function are still reasonable quantitative characteristics of the superconducting state. More detailed investigation of the spectrum shape is the matter of future studies.