Possible Phase-Sensitive Tests of Pairing Symmetry in Pnictide Superconductors

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The discovery of the new class of pnictide superconductors has engendered a controversy about their pairing symmetry, with proposals ranging from an extended s wave or "$s_{\pm}$" symmetry to nodal or nodeless d-wave symmetry to still more exotic order parameters such as p wave. In this Letter, building on the earlier, similar work performed for the cuprates, we propose several phase-sensitive Josephson interferometry experiments, each of which may allow resolution of the issue.

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Identification of order parameter symmetry is one of the first tasks one faces upon discovery of a new superconductor. Historically, methods of determining order parameter symmetry have fallen into two classes [1]: techniques which are sensitive to the *magnitude* of the order parameter, and techniques which are sensitive to the *phase*. Most of the magnitude sensitive techniques are ultimately concerned with the presence of Fermi surface nodes. Integrated probes include, e.g., specific heat or London penetration depth. The first experimental technique to yield detailed information about the momentum dependence of the order parameter was angle-resolved photoemission spectroscopy (for a review, see Ref. [2]), or ARPES, which demonstrated the substantial gap anisotropy in the high-T_c cuprates.

None of these tests, however, is a "smoking gun" ultimately capable of unequivocally determining the order parameter structure. For this one also requires a phase-sensitive test, such as the Josephson interferometry [3] or tricrystal junctions [4]. Such tests, as originally proposed by Geshkenbein *et al* [5], Rice and Sigrist [6], and Leggett [3] provided compelling evidence for d-wave superconductivity in the cuprates [1], effectively ending a controversy of several years, and have been also used to address p wave superconductivity in Sr_2RuO_4 [7].

We now consider such a test of order parameter symmetry in the pnictide superconductors. There are now dozens of superconductors in this family, with superconducting transition temperatures T_c as high as 57 K. Band structure calculations and ARPES data indicate that these materials contain disjoint Fermi surfaces, as illustrated in Figure 1, with a hole pocket centered around (0,0) and electron pockets at (π, π) and related points.

Despite this effort, the pnictide gap symmetry remains unknown. A potential gap function presently receiving much consideration is the "$s_{\pm}$" state [8], in which the order parameter changes sign from the hole to electron Fermi surfaces, but is roughly constant on each Fermi surface, with no nodes.

Three phase-sensitive experiments have been performed on the pnictides. The first is the observation in inelastic neutron scattering (INS) measurements on $Ba_{0.6}K_{0.4}Fe_2As_2$ [9] of a resonance peak centered at $\mathbf{Q} = (\pi, \pi)$ that appears below T_c. This effect has been well-studied in connection to the cuprates [10], and in pnictides it had been predicted theoretically for the $s_{\pm}$ states because of the change in order parameter sign [8,11,12] over the vector $\mathbf{Q}$. More recently, an ab-corner-junction experiment was performed [13] on $BaFe_{1.8}Co_{0.2}As_2$, which found no evidence for a phase shift between the a and b directions, suggesting that the d-wave symmetry observed in the cuprates is not present in this material. Similarly, Zhang *et al* [14] fabricated c-axis Josephson junctions between a conventional superconductor and $Ba_{1-x}K_xFe_2As_2$ and observed Josephson coupling, suggestive of an s wave state, but not providing clear evidence for the $s_{\pm}$ state itself.

In this paper we propose direct phase-sensitive tests, based on Josephson interferometry, that may provide

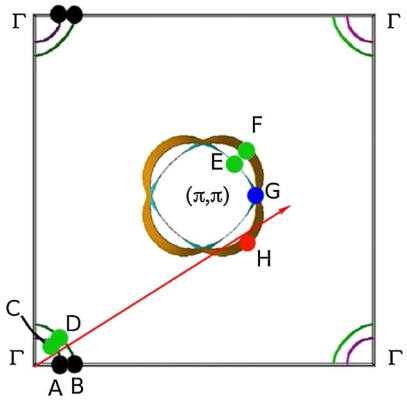

FIG. 1 (color online). A view of the calculated Fermi surface geometry in a superconducting pnictide $LaFeAsO_{0.9}F_{0.1}$, with hole (Γ) and electron pockets (π, π) indicated. For a thick barrier the black circles represent the Fermi surface states which dominate the (100) current, while the green circles represent the states which dominate the (110) current. A possible intermediate angle, where the electron surface may dominate the current, is shown by the arrow. Greek characters represent standard BZ points, while Roman characters refer to the adjacent circles whose wave function character is given in Table I.

strong evidence for an $s_\pm$ state, if existent. The proposal is based on an adaptation of the cuprate ''corner-junction'' experiments.

We briefly review the theory of corner junctions and their application to the cuprates and Sr_2RuO_4. In a corner junction, the Josephson current is allowed to flow from two separate faces of a single crystal of unconventional superconductor. A junction usually preferentially samples current oriented along the normal to the interface. By measuring the critical current flow as a function of magnetic field, one can determine the phase difference between the two directions sampled. Such experiments were enormously successful in determining the pairing symmetry in the high-temperature cuprates [3], and have been also applied to Sr_2RuO_4 [7].

One key to these experiments has been the existence of symmetry constraints dictating a particular phase difference for specific crystallographic directions. In d-wave superconductors, the phase must change by π upon a 90° rotation, while in p wave materials upon a 180° rotation. For an $s_\pm$ state, as presumed in the pnictides, the situation is more complicated. The a and b directions are strictly equivalent. One has to look for two *inequivalent* directions such that one will be quantitatively dominated by hole and the other by electron bands. In the simplest approximation of a specular (infinitely thin) barrier and constant matrix elements this amounts to comparing the number of conductivity channels for each direction, given by the DOS-weighted average of the corresponding Fermi velocity, e.g., $n_z = \langle N(E_F) v_{Fz} \rangle$ [15]. Unfortunately, one realizes right away that in the e-doped compounds transport in all directions (including c) is dominated by the e-pocket [8] (cf. Fig. 1), and in the hole doped by holes (Fig. 4, dark red). Thus, phase-sensitive experiments do not at first appear to be feasible for detecting an $s_\pm$ state in the pnictides.

This is however no longer true for a barrier of an appreciable thickness. While for a specular barrier, all wave vectors from all Fermi surfaces contribute to the current, regardless of tunneling direction, for a thick-barrier electrons tunneling normally to the interface have an exponentially big advantage over those with a finite momentum parallel to the interface, $k_\parallel \neq 0$. For instance, the tunneling probability $T_{\mathbf{k}}$ for a simple vacuum barrier can be expressed as [16]

$$T_{\mathbf{k}} = \frac{4m_0^2\hbar^2K^2v_Lv_R}{\hbar^2m_0^2K^2(v_L+v_R)^2 + (\hbar^2K^2+m_0^2v_L^2)(\hbar^2K^2+m_0^2v_R^2)\sinh^2(dK)}.$$

Here m_0 is the electron mass, $v_{L,R}$ are the Fermi velocity projections on the tunneling directions, d is the width of the barrier, and the quasimomentum of the evanescent wave function in the barrier, iK, is, from energy conservation,

$$K = \sqrt{k_\parallel^2 + 2(U-E)m_0},$$

where U is the barrier height. The above formula is an immediate asymmetric generalization of the textbook result [17]. This formula does not account for the variation of the tunneling matrix elements due to the symmetry of actual electronic states, which, as discussed later, may be important.

So let us for now focus on thick barriers. Note that a thick barrier need not have very low transparency: the transparency is defined by both height (which may be low) and thickness, while the filtering properties are defined by the thickness only.

Obviously, for tunneling along the (100) direction the hole transport will fully dominate, as the electron Fermi surfaces will have a huge $k_\parallel$ of approximately π/a, with a the lattice constant, and will be exponentially suppressed. So, for a thick low barrier the (100) Josephson current will be dominated by the hole states, while for the (110) direction both holes and electrons will contribute (all Fermi surfaces will have points with $k_\parallel = 0$; cf. Fig. 1).

However, as is well known in the theory of spin-polarized tunneling, occasionally tunneling from the zone center ($k_\parallel = 0$) is forbidden by symmetry and the current proceeds through ''hot spots'' with some finite $k_\parallel$ and is correspondingly suppressed [16]. This depends critically upon the character of the wave functions on the Fermi surface, for the corresponding k direction. So let us see how the symmetry of the wave function, based on the density-functional theory (DFT) calculations [18], will affect the tunneling matrix elements in pnictides for different directions.

Some calculated orbital characters are listed in Table I. First of all, we observe that for the (100) direction two hole bands contribute (points C and D). They have wave functions of primarily xz/yz character, with considerable admixture of z^2 and xy states. (This is allowed because despite a tetragonal symmetry the $z = 0$ plane is not a mirror plane in the real space). The xz/yz orbitals are odd with respect to $z \to -z$ reflection, so one can expect tunneling from these orbitals to be suppressed for a thick vacuum (and most other) barriers. Thus the Josephson current for the holes will be mostly controlled by the relative admixture of the z^2 character, and, except for the 100 direction (because the xy orbital is odd with respect to $x \to -x$), of

TABLE I. First-principles orbital band character from Fig. 1.

	Wave function character						
Point	A	B	C	D	E	F	G
xz/yz	0.879	0.717	1.0	0.724	0.921	0.003	0.869
x^2-y^2	0.0	0.0	0.0	0.0	0.079	0.997	0.130
z^2	0.121	0.0	0.0	0.069	0.0	0.0	0.001
xy	0.0	0.282	0.0	0.207	0.0	0.0	0.0

the xy character. On the other hand, the electron pockets are mostly made up by the xz/yz and $x^2 - y^2$ character. Again due to their parity neither of these orbital can tunnel exactly at direction (110) (because $x^2 - y^2$ is odd with respect to the $x \rightarrow y$ reflection). Thus in both (100) and (110) directions the current will be dominated by holes.

But all is not lost. For an in-plane direction deviating from (110) by an angle α, the tunneling from the hole pocket xz/yz orbitals will still be suppressed, while that from the electron pocket $x^2 - y^2$ orbital will only be weakened by a factor of $\sin^2 2\alpha$. The maximum α at which the electron Fermi surface still crosses the $k_{\|} = 0$ line in the Brillouin zone corresponds to the line $\Gamma H'$ in Fig. 1; for the 10% e doping, as shown in the Figure, the $\alpha_{\max} \approx 15°$, $\sin^2(2\alpha_{\max}) \approx 1/4$. Of course, exactly at $\alpha_{\max}$ the Fermi velocity has nearly zero normal component so that the optimal α is close to $\alpha_{\max}$ but smaller. An estimate [19] tells us that the optimal α is about $(3/4)\alpha_{\max}$ and that the Fermi velocity factor for that α suppresses the current by a factor of 2, roughly. The total factor is $(v_\perp/v)\sin^2(2\alpha_{\rm opt}) \approx 0.1$. From the Table I, we can estimate the corresponding factor for tunneling from the hole bands to be 0.2–0.3 (adding up the xy and the z^2 and accounting for the angular dependence). However, the Fermi velocity (from the first-principles calculations) is greater near the electron-surface H point than the hole-surface D point by a factor of approximately 2.5, so the overall factors are roughly equal.

According to this rough estimate, the holes and electrons contribute equally to the near-(110) current, making problematic the observation of a Josephson π-contact pair. However, all the estimates above are very crude, order of magnitude estimates that neglect a number of factors, such as the possibility of a larger superconducting gap for the electron Fermi surface or, most importantly, detailed (unknown) characteristics of the contact. We conclude that there is still some chance of observing a π phase shift in this experiment, and this geometry is still worth pursuing. Importantly, we can say that the optimal angle between the two interfaces should be ~30–35°. In addition, a more strongly electron-doped pnictide would tend to enlarge both the electron/hole Fermi velocity ratio and angle $\alpha_{\max}$, increasing the chance of the electron Fermi surface dominating the near-(110) current.

Fortunately, one can think of some more promising designs. Indeed, let us consider a corner-junction experiment where the (100) junction is a thick-barrier contact (which as we just discussed, is dominated by the h pockets), and the second contact is a (010) or a (001) *specular*-barrier junction. As discussed in the beginning, either of these last contacts in an electron-doped material will be dominated by the e pockets, thus providing the desired π shift. A possible geometry is illustrated in Fig. 2, if the $s_\pm$ state is present.

The point is that, unlike in the cuprates and Sr_2RuO_4, directional selection is not sufficient to select the appropriate region of Fermi surface to sample to uncover a π phase shift. One must use additional selection means, here given by the use of different barrier characteristics in different directions.

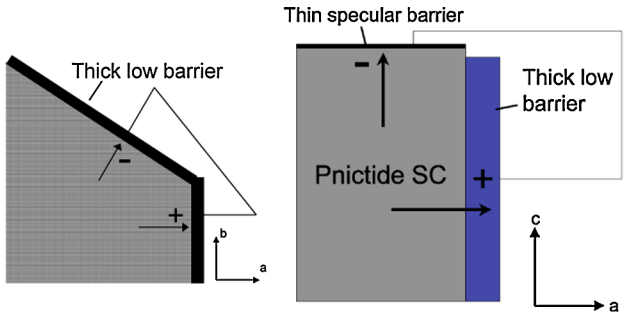

FIG. 2 (color online). A schematic view of tunneling geometry for two possible experiments: left, a (100) -near-(110) orientation, right, an ac orientation with specular and thick barriers as indicated.

Regarding the width and height of the nonspecular potential barrier, the key consideration is that the electron FS be suppressed greatly without a comparable suppression of the hole FS. For a moderate barrier height $U - E = 0.25$ eV (which would require a barrier made out of a small-gap semiconductor, $E_g \sim 0.5$ eV) a barrier of width 20 Å would only suppress the holelike Fermi surface by roughly a factor of 9 ($\sinh^2 1.8$), while suppressing the electron Fermi surface by a factor of $\sinh^2 20 \sim 10^{16}$. We implicitly assume a substantially electron-doped pnictide, so that specular transport is governed uniquely by the electron Fermi surface.

A possible disadvantage of the proposed experiment is that it requires a rather fine control over the interface properties. However, there is yet another possibility of designing a two-junction experiment with a π shift. This requires, however, a bicrystal as shown in Fig. 3. We propose to grow epitaxially a bicrystal of a hole-doped ($Ba_{1-x}K_xFe_2As_2$) and an electron-doped ($BaFe_{2(1-x)}Co_{2x}As_2$) materials. As discussed above, the doping enhances the size and Fermi velocity of the respective Fermi surfaces, and the conductance is dominated by the hole or electron Fermi surface, correspondingly. The only remaining problem is to ensure the proper phase coherence, that is, that the holes in both crystals have the same phase, and the electrons the same, but opposite to that of the holes.

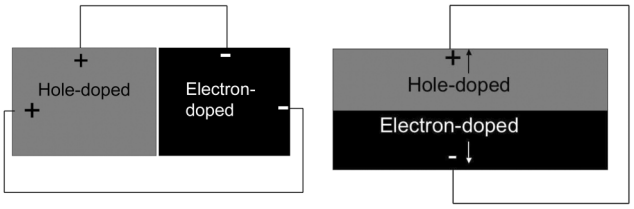

FIG. 3. A schematic view of the tunneling geometry for the proposed bicrystal experiments. Left: an ab-plane orientation with two possible lead orientations; right: a c-axis orientation.

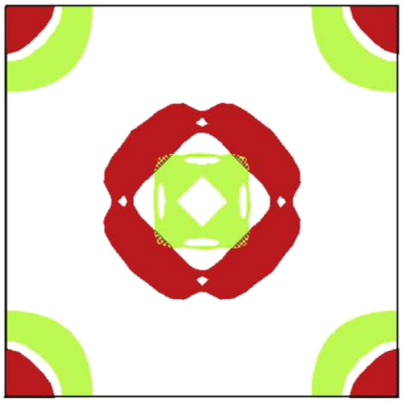

FIG. 4 (color online). A first-principles calculation of the *ab*-plane projected three dimensional Fermi surfaces of $Ba_{0.6}K_{0.4}Fe_2As_2$ (green/gray) and $BaFe_{1.6}Co_{0.4}As_2$ (red/black).

In case of an epitaxial (coherent) interface the parallel wave vector, $k_{\|}$, is conserved through the interface, and the way to ensure that the *h*-*h* and *e*-*e* currents are much larger than the *e*-*h* and *h*-*e* current is to ensure that the overlap of the FS projections onto the interface plane is maximal for the *e*-*e* and *h*-*h* overlaps, as opposed to the *e*-*h* overlap. Obviously, this condition is satisfied in a bicrystal with a (100) interface—there is no *e*-*h* overlap at all, and the *e*-*e* and *h*-*h* overlaps are nearly maximal possible. Unfortunately, growing an epitaxial (100) interface may be very difficult.

On the other hand, growing a (001), or "*c*-axis" interface is much more natural. Let us consider the FS overlaps in this case. Figure 4 plots the projections of the calculated [18] Fermi surfaces of $BaFe_{1.6}Co_{0.4}As_2$ (dark red) and $Ba_{0.6}K_{0.4}Fe_2As_2$ (light green). In this figure the three-dimensional Fermi surfaces have been telescoped onto the basal plane, so that what one sees is the extent of the Fermi surface in the planar direction across all wave vectors. The doping levels of $\pm 20\%$ were chosen because this is the "critical" spread at which the direct overlap of the *e*-FSs nearly disappears. At any smaller spread there is either direct *e*-*e* overlap or both *e*-*e* and *h*-*h* overlaps. Obviously, there is no *e*-*h* overlap and *e*-*h* transport requires substantial nonconservation of the parallel momentum.

In conclusion, we have proposed several phase-sensitive Josephson tests of the ostensible $s_{\pm}$ order parameter symmetry in the superconducting pnictides. The first design involves *ab*-plane corner junctions with angles smaller than 90°, the second either *ab* or *ac* 90° junctions, prepared in such a way that one junction barrier is thin (specular) and the other thick, and the third, probably the most promising one, uses epitaxially grown hole- and electron-doped bicrystals in a sandwich orientation. We await the results of such Josephson tunneling experiments with great interest.

There are several unknowns complicating observation of the interferometric effect proposed. As opposed to *d*- or *p* wave pairing, the π shift here is not a qualitative, symmetry determined effect, but a quantitative one, based upon favorable relations for tunneling probabilities for different bands. While we have taken into account some major factors, accurate calculations of the said probabilities are not possible. Interface properies may greatly affect them.

For these reasons the arguments given above should be considered in the following light: if a π phase shift between the electron and hole Fermi surfaces is observed in any of the proposed geometries, this would be extremely strong evidence for an $s_{\pm}$ state; unfortunately, the lack of observation of such a shift in any given experiment cannot be taken as similarly strong evidence against such a state.

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[18] We used the linear augmented plane wave method (LAPW) in the virtual crystal approximation, as discussed in Ref. [8]. So far experimental evidence has been favorable to the DFT calcultions. It is generally believed that up to a moderate renormalization of the bandwidth, DFT correctly describes the overall nature and character of the electronic bands in pnictides. It is worth noting that the evidence so far is still incomplete and there remain open questions as regards fine details of the band structure. These details, however, remain beyond the scope of our semiquantitative discussion.
[19] We assumed an elliptical electronlike FS of eccentricity 0.17, as merited by Fig. 1, and simply maximized the factor $|\mathbf{v}_F \cdot \mathbf{n}|\sin^2(2\alpha)$, with $\mathbf{n}$ the tunneling normal.