Time-reversal symmetry-breaking superconductivity

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We study time-reversal symmetry-breaking superconductivity with $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_\alpha$ ($\alpha=s$ or d_{xy}) symmetries. It is shown that the behavior of such superconductors could be *qualitatively* different depending on the minor component (α) and its phase at lower temperatures. It is argued that such *qualitatively different* behaviors in thermal as well as in angular dependences could be a *source* of consequences in transport and Josephson physics. Orthorhombicity is found to be a strong mechanism for the mixed phase (in the case of $\alpha=s$). We show that due to electron correlation the order parameter is more like a pure $d_{x^2-y^2}$ symmetry near optimum doping. [S0163-1829(99)05102-4]

During the last several years, a great deal of effort has been devoted to determine the symmetry of the superconducting order parameter (SCOP) of high-T_c cuprate superconductors.[1] While there is a strong concensus both from experiments and theory that the symmetry of the SCOP in the cuprates could be $d_{x^2-y^2}$ type; recent studies provide increasing evidence that the pairing symmetry may be an admixture with a minor component, like s, d_{xy} with predominant $d_{x^2-y^2}$ symmetry. The pairing symmetry provides clues to identify a pairing mechanism which is essential for the development of the theory of high-temperature superconductivity in cuprates, and still remains a challenge after a decade of its discovery.

Several different types of measurements which are sensitive to the phase of $\Delta(k)$ indicate a significant mixing of s-wave components with $d_{x^2-y^2}$ symmetry. For example, c-axis Josephson tunneling studies on junctions consisting of a conventional s-wave superconductor (Pb) and twinned or untwinned single crystals of Y-Ba-Cu-O indicate that the SCOP of Y-Ba-Cu-O has mixed $d\pm s$ (or $d\pm \mathrm{i}s$) symmetry.[2,3] Recently, a class of c-axis Josephson tunneling experiments were reported by Kouznetsov *et al.*,[4] in which a conventional superconductor (Pb) was deposited across a single twin boundary of a Y-Ba-Cu-O single crystal. There measurements of critical current as a function of the magnitude and angle of a magnetic field applied in the plane of the junction provides a direct evidence for mixed d- and s-wave pairing in Y-Ba-Cu-O. A series of high-resolution measurements on thermal conductivity (κ) in $Bi_2Sr_2CaCu_2O_8$ by Krishana *et al.*[5] show that the κ at low temperature becomes field independent above a temperature-dependent kink field $H_k(T)$. This remarkable result indicates a phase transition separating a low-field state where the thermal conductivity decreases with increasing field and a high-field one where it is insensitive to the applied magnetic field. The authors argue that this phase transition is not related to the vortex lattice because of the temperature dependence of the field $H_k(T)$ (which is roughly proportional to T^2) as well as its magnitude. Instead, they suggest a field-induced electronic transition leading to a sudden vanishing of the quasiparticle contribution to the heat current. Possible scenarios would be the induction of a minor $e^{i\theta}\Delta_\alpha$ ($\alpha=d_{xy}$ or s) component with $d_{x^2-y^2}$ symmetry with application of a weak field. A similar conclusion may also be obtained based on the results of an angle-resolved phtoemission spectroscopy (ARPES) experiment by J. Ma *et al.*,[6] in which a temperature-dependent gap anisotropy in the oxygen-annealed $Bi_2Sr_2CaCuO_{8+x}$ compound was found. The measured gaps along both high-symmetry directions (Γ-M, i.e., Cu-O bond direction in real space and Γ-X, i.e., diagonal to the Cu-O bond) are nonzero at lower temperatures and their ratio is strongly temperature dependent. This observed feature cannot be explained within a simple d-wave scenario (but is consistent with $d_{x^2-y^2}+e^{i\theta}\alpha$ scenario) and has been taken as a signature of a two-component order parameter, $d_{x^2-y^2}$-type close to T_c, and a mixture of both s and d otherwise.[7] However, surprisingly enough, the experimental result[6] has never been reproduced by any other equivalent experiments. In Josephson physics, it was found[8] that the current-phase relationship depends on the mutual orientation of the two coupled superconductors and their interface (the induced minor component then would be associated with any arbitrary phase, θ). This property is the basis of all the phase-sensitive experiments probing SCOP. Therefore, motivated by strong experimental evidences of a mixed order-parameter symmetry in high-T_c cuprates we present basic behaviors of superconductors with mixed order-parameter symmetries such as $d+e^{i\theta}\alpha$, $\alpha=s$, d_{xy}, which is characterized by a local breakdown of time-reversal symmetry. Clear evidence will emerge that the time-reversal superconductivity at lower temperatures gives rise to *unusual* behaviors depending on α and its phase.

Assuming a well-defined quasiparticle picture in the superconducting (SC) state, the free energy of a superconductor with arbitrary pairing symmetry may be written as

$$F_{k,k'}=-\frac{1}{\beta}\sum_{k,p=\pm}\ln(1+e^{-p\beta E_k})+\frac{|\Delta_k|^2}{V_{kk'}}, \tag{1}$$

where $E_k=\sqrt{(\epsilon_k-\mu)^2+|\Delta_k|^2}$ are the energy eigenvalues of a Hamiltonian that describes superconductivity. It is generally believed that a single-band Hubbard model contains the essential ingredients to describe Cu-O planes where transport processes takes place. Therefore, our model Hamiltonian reads as

$$\mathcal{H}=H_{\mathrm{HUB}}+H_{\mathrm{PAIR}}, \tag{2}$$

$$H_{\rm HUB}=\sum_{ij\sigma} t_{ij}c^{\dagger}_{i\sigma}c_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow}-\mu\sum_{i\sigma} n_{i\sigma}, \quad (3)$$

$$H_{\rm PAIR}=\sum_{kk'} V_{kk'}c^{\dagger}_{k\uparrow}c^{\dagger}_{-k\downarrow}c_{-k'\downarrow}c_{k'\uparrow}, \quad (4)$$

where the notations have their usual meanings.

Treatment of the Hubbard on-site correlation is a known problem. We use the slave-boson theory of Kotliar and Ruckenstein[9] in which the Hubbard model has a solution for any filling and any value of repulsion. The slave-boson formulation of Kotliar and Ruckenstein[9] introduces four auxilliary boson fields corresponding to the occupancy of a site, namely empty (e_i), doubly occupied (d_i), singly occupied $(p_{i\sigma}/p_{i-\sigma})$ with spin $\pm\sigma$, respectively. In terms of the slave-boson field operators the single-band Hubbard model takes the form

$$H_{\rm HUB}=\sum_{ij,\sigma} t_{ij}z^{\dagger}_{i\sigma}c^{\dagger}_{i\sigma}c_{j\sigma}z_{j\sigma}+U\sum_{i} d^{\dagger}_{i}d_{i}-\mu\sum_{i\sigma} c^{\dagger}_{i\sigma}c_{i\sigma}$$
$$+\sum_{i}\lambda_i\left(1-e^{\dagger}_ie_i-d^{\dagger}_id_i-\sum_{\sigma} p^{\dagger}_{i\sigma}p_{i\sigma}\right)$$
$$+\sum_{i\sigma}\lambda'_{i\sigma}(c^{\dagger}_{i\sigma}c_{i\sigma}-d^{\dagger}_id_i-p^{\dagger}_{i\sigma}p_{i\sigma}), \quad (5)$$

where

$$z_{i\sigma}=(1-d^{\dagger}_id_i-p^{\dagger}_{i\sigma}p_{i\sigma})^{-1/2}(e^{\dagger}_ip_{i\sigma}+p^{\dagger}_{i-\sigma}d_i)$$
$$\times(1-e^{\dagger}_ie_i-p^{\dagger}_{i-\sigma}p_{i-\sigma})^{-1/2}$$

and the boson field operators are not independent of each other but are constrained by the requirements of completeness and local charge conservation at a site, hence the fourth and fifth terms are added in the Hamiltonian with the help of Lagrange multipliers (λ_i and λ'_i). The values of the boson field operators and Lagrange multipliers are determined by minimizing the free energy in the saddle-point approximation. This approximation diagonalizes the U term whereas renormalizes the hopping term as $\tilde{q}t_{ij}$ with $\tilde{q}=z^{\dagger}z$; $\tilde{q}$ usually being complicated function of u $(=U/U_c)$, dopant concentration (δ), and $x(=e+d)$ carries the necessary information of electron correlation. In this approach solutions are obtained for the paramagnatic state for all values of u and band fillings[7] that reproduce the correct Brinkman-Rice result for the metal-insulator transition (U_c) at half-filling.

As a consequence the total Hamiltonian (2) takes the form

$$\mathcal{H}=\sum_{k\sigma} (\tilde{q}\epsilon_k-\mu)c^{\dagger}_{k\sigma}c_{k\sigma}+\sum_{kk'} \tilde{q}^2V_{kk'}c^{\dagger}_{k\uparrow}c^{\dagger}_{-k\downarrow}c_{-k'\downarrow}c_{k'\uparrow}$$
$$+\ \text{bosonic terms}, \quad (6)$$

where the band dispersion $\epsilon_k=\Sigma_{i=1}^{5}C_i\eta_i(k)$ are obtained from the angle-resolved photoemission spectroscopy (ARPES) results[10] on $Bi_2Sr_2CaCuO_8$. In deriving Hamiltonian (6) fluctuations of the bose-field operators are *not* considered [a consequence of on-site correlation has shown up in Eq. (6) as $\epsilon_k\rightarrow\tilde{q}\epsilon_k$ and $V_{kk'}\rightarrow\tilde{V}_{kk'}=\tilde{q}^2V_{kk'}$].

A mean-field superconducting (SC) order parameter $\Delta^{\star}(k)=\Sigma_{k'}\tilde{V}_{kk'}\langle c^{\dagger}_{k'\uparrow}c^{\dagger}_{-k'\downarrow}\rangle$ allows us to solve the Hamiltonian (6) exactly to find the energy eigenvalues E_k and hence minimization of the free energy (1) (i.e., $\partial F_{k,k'}/\partial\Delta_k=0$) will result in the superconducting (SC) gap equation as

$$\Delta_k=\sum_{k'} \tilde{V}_{kk'}\frac{\Delta_{k'}}{2E_{k'}}\tanh\left(\frac{\beta E_{k'}}{2}\right), \quad (7)$$

where the pairing potential $V_{kk'}$ for a two-component order parameter with a separable form and the corresponding gap functions are obtained as

$$V_{kk'}=\sum_{j=0}^{1} V_jf^j_kf^j_{k'} \ \text{ and } \ \Delta_k=\sum_{j=0}^{1} e^{j(i\theta)}\Delta_jf^j_k. \quad (8)$$

For a mixed $d_{x^2-y^2}-d_{xy}$ symmetry, $V_{0(1)}\equiv V_{d_{x^2-y^2}}$ $(V_{d_{xy}})$ and $f^{0(1)}_k\equiv\cos k_x-\beta'\cos k_y(2\sin k_x\sin k_y)$ and the corresponding gap amplitudes are $\Delta_{0(1)}\equiv\Delta_{d_{x^2-y^2}}(\Delta_{d_{xy}})(\beta'\leqslant1$ corresponds to orthogonal or tetragonal symmetry). Similarly for a mixed $d_{x^2-y^2}-s$ symmetry, $V_1\equiv V_s$, $f^1_k\equiv$const and $\Delta_1\equiv\Delta_s$. Substituting Eq. (8) in Eq. (7) the gap equations for different components can be separated out as

$$\Delta_j=\sum_{k} V_j\frac{\Delta_jf^{j\,2}_k}{2E_k}\tanh\left(\frac{\beta E_k}{2}\right). \quad (9)$$

The two coupled gap equations (9), a number conserving equation to fix chemical potential (μ), and a sixth-order algebric equation in $x(=e+d)$ (to get correct values of $\tilde{q}$ for any value of u,δ) are solved self-consistently for a fixed cutoff parameter $\Omega_c=500$ K around the Fermi level beyond which SC pairing does not exist.

In Figs. 1(a) and 1(b) phase diagrams of superconductors with $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\alpha$ where $\alpha=\Delta_{xy}(k)$ (a) and $=\Delta_s$ (b) are obtained for a fixed band filling $\rho=0.80$ and in a tetragonal square lattice. The phase diagrams comprise the amplitudes of pair condensates, evaluated at 5 K, in different channels as a function of the ratio $\gamma=V_{d_{x^2-y^2}}/V_\alpha$. The minor components α appear at the same value of γ irrespective of the phase θ in the predominant $d_{x^2-y^2}$ phase. But the rate of growth of the minor component is different depending on θ. For $\theta=0$, i.e., for a real order parameter with (a) $d_{x^2-y^2}+d_{xy}$ or (b) $d_{x^2-y^2}+s$-wave symmetry, both the minor as well as the $d_{x^2-y^2}$ component increases with a decrease in γ, thereby inducing each other. In the case of $d+s$ symmetry this phenomena is very pronounced. However, for any finite $\theta(\neq0)$ the $d_{x^2-y^2}$ component is suppressed with the enhancement in the isotropic s component at some values of γ depending on θ resulting in a pure s-wave phase. This feature is absent in the $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_{xy}(k)$ scenario.

For $\pi/2<\theta<0$, the minor component has two parts, real and complex (thereby giving rise to the most probable mixing), that couples to the $d_{x^2-y^2}$. A close look at Fig. 1 therefore, would suggest that the mixing of a minor real s or d_{xy} component will stabilize the $d_{x^2-y^2}$ symmetry, whereas inclusion of a complex minor component s wave tends to suppress the $d_{x^2-y^2}$ gap. The d_{xy} minor component with a complex phase has hardly any influence on the $d_{x^2-y^2}$ symmetry. These *qualitatively different* behaviors in different classes of

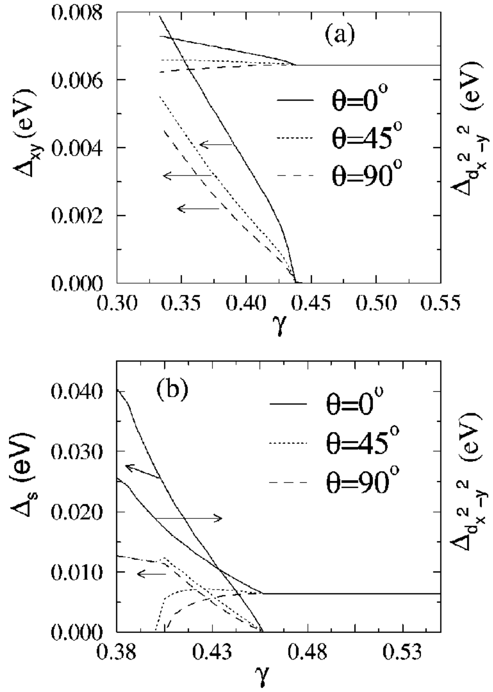

FIG. 1. Phase diagrams of superconductors with (a) $\Delta_k=\Delta_{x^2-y^2}(k)\ +e^{i\theta}\Delta_{xy}(k)$ and (b) $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_s$ symmetries. Amplitudes of the $d_{x^2-y^2}$, d_{xy}-, and s-wave pairing condensates (at 5 K) are plotted as a function of the ratio of pairing strengths in the respective channels, $\gamma=V_{d_{x^2-y^2}}/V_{d_{xy}}$ for $u=0.4$. Note the *qualitative difference* in (a) and (b); the onset of the s-wave component influences the $d_{x^2-y^2}$ amplitude very strongly (suppresses or enhances depending on the phase θ) whereas the onset of the d_{xy} component has no influence on the $d_{x^2-y^2}$ amplitude except for the $d_{x^2-y^2}+d_{xy}$ phase.

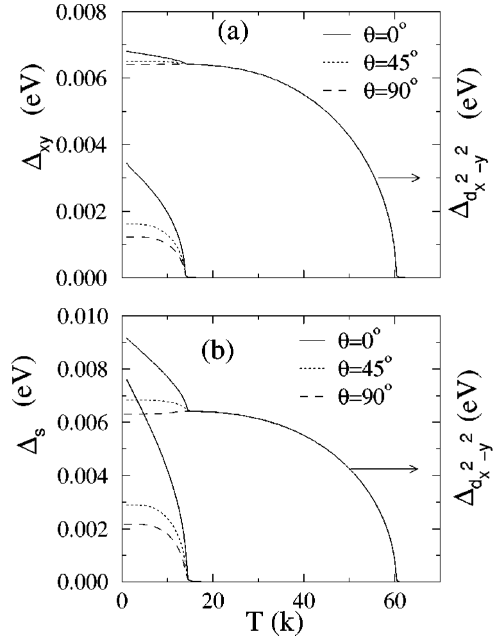

FIG. 2. Thermal behavior of superconductors with (a) $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_{xy}(k)$ ($\gamma=0.195$) and (b) $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_s$ ($\gamma=0.18$) symmetries for various values of θ ($u=0.4$). The minor (s or d_{xy}) components, although having the *same* T_c, their thermal growth inside the d component is *qualitatively* different. Consequently, the predominant d component is influenced (e.g., further stabilized for $\theta=0$ and suppressed for $\theta=90$) very *differently*.

mixed order-parameter symmetries are also responsible for so, with respect to thermal dependency.

It is evident from Figs. 2(a) and 2(b) (for $\rho=0.8$) that at lower temperatures the minor component plays a significant role to the predominant d wave. For example, when the minor component mixes with the d wave with a real coefficient (i.e., $\theta=0$), the minor component has a very fast growth with lowering in temperature and it always *induces* the d-wave component by further stabilizing it. On the other hand, mixing of the minor component with a complex coefficient (i.e., $\theta=90°$) suppresses the d-wave component when the minor component is s wave and has no effect when the same is d_{xy}. These behaviors are *bound* to have immense influence on thermodynamic quantities which are sensitive to the thermal gradient of the SC gap. For instance, the specific heat will then have two jumps, at T_c and at $T_c^{\alpha}<T_c$ where the minor component (α) vanishes and the nature of the *second* jump can be very different depending on the phase θ providing the signature of a true *second* transition below T_c.[11]

In Figs. 3(a) and 3(b) we present the angular correlation between the amplitudes of different channels evaluated at 5 K and $\rho=0.8$. For any finite mixing of the minor component with the $d_{x^2-y^2}$ wave thus produces states that spontaneously break time-reversal symmetry. A further interesting point to note is that with small orthorhombicity $\beta'=0.98$ (in the lattice as well), the s component gets enhanced largely (curves with solid circle symbol), whereas the change in the d component with orthorhombicity is rather dependent on θ. For example, the predominant d component increases with orthorhombicity for $0<\theta<0.22\pi$ or $1.78\pi<\theta<2\pi$ and decreases otherwise [both cases being small, cf. Fig. 3(a)]. The corresponding changes in $\Delta_{d_{xy}}$ and the associated change in $\Delta_{d_{x^2-y^2}}$ are negligibly small [cf. Fig. 3(b)] for such orthorhombicity. Therefore, orthorhombicity could be an intrinsic mechanism for d and s mixing (with an arbitrary phase between them), the $d+s$ state being the most favorable.

In Figs. 4(a) and 4(b) we demonstrate the role of electron correlation on mixed pairing symmetry. It is shown that the minor component is always minimum at the optimum doping and is suppressed largely due to electron correlation, explaining the features observed in the ARPES experiment.[12] This is based on the study of the amplitudes of the different components for the case of $\theta=\pi/2$ (i.e., the $d+is$ state) and for fixed $T_c^{\alpha}=45$ K at $u=0$ as a function of density ρ ($=1-\delta$). The amplitudes are normalized with respect to the value of the d component at optimum doping (the d wave also gets suppressed with u but at a slower rate). Note, the electronic correlation suppresses the minor component very largely close to half-filling, whereas it hardly has any effect at lower densities (the d-wave boundary shrinks a bit). Also, this behavior with density is similar for any other arbitrary value of θ.[11] Apparently, therefore, close to the optimium doping the order parameter will be more pure $d_{x^2-y^2}$ like. Furthermore, no mixing is found within a wide range of densities between the d wave with other probable minor components like $s_{x^2+y^2}$,s_{xy} (e.g., these components have maxima at $\rho\sim0$).

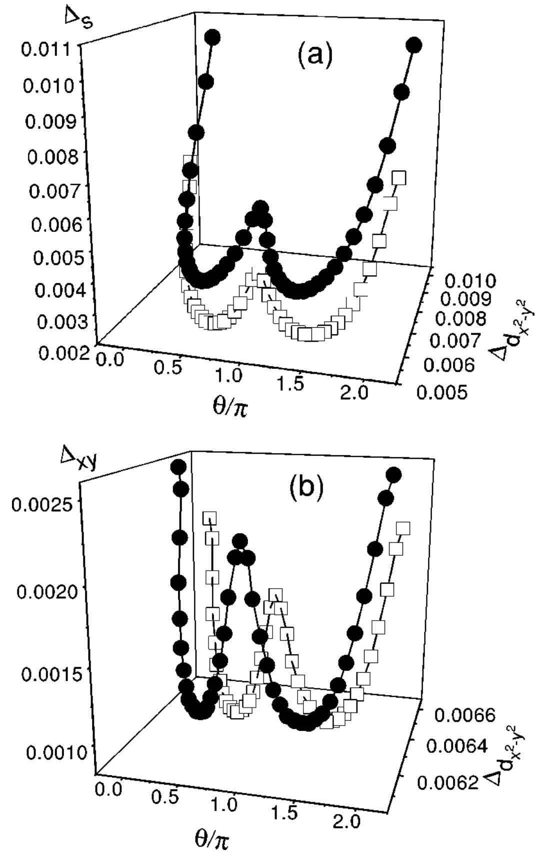

FIG. 3. Amplitudes of the $d_{x^2-y^2}$ and the minor gap (a) s or (b) d_{xy} as a function of the phase of the minor component (for $u=0.4$ and $T_c^{\alpha}=14$ K). The curves with solid circles represent the orthorhombic phase with $\beta'=0.98$ whereas the curves with open squares correspond to the tetragonal lattice.

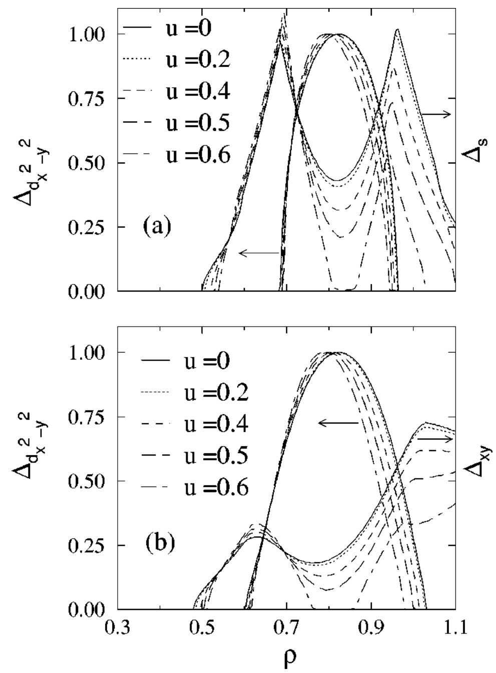

FIG. 4. Amplitudes of different components of (a) $\Delta_k=\Delta_{x^2-y^2}(k)+i\Delta_s$ and (b) $\Delta_k=\Delta_{x^2-y^2}(k)+i\Delta_{xy}$ superconductors at 5 K. The minor (s or d_{xy}) component at $u=0$ has $T_c^{\alpha}(0)=45$ K. The electron correlation minimizes the mixing of the minor component at optimum doping.

Therefore, we have presented basic consequences of time-reversal symmetry-breaking superconductivity. It is demonstrated that mixing of a minor component at lower temperatures can give rise to *unusual* thermal behaviors depending on the nature of the minor component as well as the phase associated with it. In the *fully gapped* phase at lower temperatures, as described by the $\Delta_k=\Delta_{x^2-y^2}(k)+e^{i\theta}\Delta_{\alpha}$ scenario, the number of quasiparticles will be exponentially small and hence will contribute negligibly small to thermal conductivity (and in any other transport properties). This scenario therefore can justify the experimental observation by Krishana *et al.*,[5,7] This scenario also has a strong potential to have a natural explanation for the experimental observation[4] as discussed earlier, because mixing of a minor component (s or d_{xy}) with a predominant $d_{x^2-y^2}$ wave would change sign across the twin boundary (hence the situation is described in Fig. 3), yielding a dramatically different angular dependence.

In particular, this study provides a significant understanding of the nature of the thermodynamic transition to a gapped or coherent phase from an ungapped or incoherent phase.[13] We also pointed out the shuttle role of electronic correlation with number density prohibiting the mixing of the minor component at optimum doping.

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