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Robustness of the midgap states predicted to exist on a {110} surface of a $d_{x_a^2-x_b^2}$-wave superconductor

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It was shown recently that a sizable areal density of midgap states exists on a {110} surface of a $d_{x_a^2-x_b^2}$-wave superconductor [C.-R. Hu, Phys. Rev. Lett. **72**, 1526 (1994)]. Here we study how these midgap states are affected if (i) the surface is not exactly {110}; (ii) the crystalline structure is slightly orthorhombic; (iii) and (iv): the order parameter is not a pure d wave, but is $s+id_{x_a^2-x_b^2}$ and $d_{x_a^2-x_b^2}+id_{x_a x_b}$, respectively. We find that for cases (i) and (ii), the midgap surface states still exist but with reduced areal density. For case (iii), all surface-state energies are found to shift away from midgap to $\pm|\Delta_s|$. For case (iv), the surface states exist on both {110} and {100} surfaces (and on surfaces of all other orientations) but with a **k**-dependent energy shift from midgap.

The nature of the pairing order parameter in cuprate high-T_c superconductors has attracted considerable attention recently.[1] Many theoretical model studies[2] and experiments[3–7] have suggested that it has $d_{x_a^2-x_b^2}$-wave symmetry defined relative to the a and b axes of the CuO_2 planes. Although the d-wave pairing seems to be consistent with a number of independent experimental measurements, such as the penetration depth,[8] the microwave conductivity,[9] the electronic Raman scattering,[10] and the NMR,[11–13] etc., other possibilities have not been excluded. In fact, the anisotropic s-wave pairing can also account for almost all of these experimental measurements[14] (or at least makes the interpretations controversial). Therefore, it is highly desirable to come up with ways to determine directly the sign of the order parameter. Among several proposals, one of the authors (C.R.H.) has recently shown[15] that a sizable areal density of midgap surface states (i.e., surface states with essentially zero energy relative to the Fermi surface) exists on a {110} surface of a $d_{x_a^2-x_b^2}$-wave superconductor. Such midgap states would not occur in similar conditions if the superconductor is s wave, whether isotropic or anisotropic, and therefore can be taken as a clear signature of d-wave superconductivity. These midgap states have many observable consequences, including in particular the novel consequence of a giant surface magnetic moment as discussed in Ref. 15. They therefore can provide a particularly promising way to experimentally distinguish $d_{x_a^2-x_b^2}$-wave superconductivity from other types of order-parameter symmetry. Whereas the midgap surface states have been predicted to exist under the ideal condition of a pure $d_{x_a^2-x_b^2}$-wave superconductor with a {110} surface, it is natural to ask how robust are these midgap states with respect to various types of deviations from this ideal condition. In this paper we study the following four types of deviations: (i) The surface is not exactly a {110} plane, but has a surface normal which makes an arbitrary angle θ with the [100] direction (or its equivalent) in the ab plane; (ii) the compound structure is slightly orthorhombic rather than being exactly tetragonal, thus the order parameter cannot be naturally a pure $d_{x_a^2-x_b^2}$ wave. Then we consider two often proposed deviations of the order-parameter symmetry from a pure d wave,[16,17] namely, (iii) $s+id_{x_a^2-x_b^2}$ (or $s+id$ for short), and (iv) $d_{x_a^2-x_b^2}+id_{x_a x_b}$ (or $d+id'$ for short).

As in Ref. 15, we consider a semi-infinite superconductor located at $x>0$, with a planar free boundary at $x=0$, which, for some cases considered below, is no longer a {110} surface of the crystal. But we assume that the z direction is always along the c axis of the crystal. For simplicity, we adopt the assumption used in Ref. 15 that the gap-function or pair-potential order parameter has the form

$$\Delta(\mathbf{k},\mathbf{r})=\Delta(\mathbf{k})\Theta(x),$$

where $\Theta(x)$ is a Heaviside step function, which means that we neglect the effect of any possible distortion of the order parameter near the surface.

The beginning part of our analysis leading to an eigenequation for the elementary excitations is essentially the same as that in Ref. 15, except that here we wish to take into account that $\Delta(\mathbf{k})$ is in general complex. Thus the Δ in Eqs. (2b) and (4b) of Ref. 15 should be replaced by Δ^*, the complex conjugate of Δ. Then we obtain the following eigenequation for the bound-state elementary excitations, for which $|\epsilon_n(\mathbf{k}_F)|<|\Delta(\mathbf{k}_F)|$, where $\epsilon_n(\mathbf{k}_F)$ denotes the energy of the nth elementary excitation characterized by a momentum $\mathbf{k}_F\equiv(k_{x0},k_y,k_z)$ on the Fermi surface, and a weak-coupling WKBJ approximation has been employed:

$$\frac{\Delta(k_{x0})}{\epsilon_n-i\sqrt{|\Delta(k_{x0})|^2-\epsilon_n^2}}=\frac{\Delta(-k_{x0})}{\epsilon_n+i\sqrt{|\Delta(-k_{x0})|^2-\epsilon_n^2}}, \quad (1)$$

where $\Delta(\pm k_{x0}) \equiv \Delta(\pm k_{x0}, k_y, k_z)$. It is easy to see from this equation that for a $d_{x_a^2-x_b^2}$-wave superconductor with a {110} surface, there is one zero-energy surface state for each allowed $\mathbf{k}_F$ (and spin), because in this case $\Delta(\pm k_{x0}) \propto \pm k_{x0}k_y$. Therefore, a sizable areal density of the midgap surface states is obtained, which is $k_F^2/2\pi$ for a spherical Fermi surface and $2k_F/\pi c$ for a cylindrical Fermi surface, where c is the average distance between neighboring conducting planes. We now proceed to study the four deviations from this ideal condition as listed in the introduction:

(i) Consider first a pure $d_{x_a^2-x_b^2}$-wave superconductor in the region $x>0$, with a planar free surface at $x=0$, where the x axis is in the direction which makes an arbitrary value θ with the a axis in the ab plane of the crystal. [For $\theta=\pi/4$ the free surface is the {110} surface considered in Ref. 15.] In this case, the pure d-wave order parameter $\Delta(\mathbf{k}_F)=\Delta_0(\hat{k}_a^2-\hat{k}_b^2)$, with Δ_0 a constant, and $\hat{\mathbf{k}} \equiv \mathbf{k}_F/k_F$, becomes

$$\Delta_0 \cos 2\theta(\hat{k}_x^2-\hat{k}_y^2) - \Delta_0 \sin 2\theta(2\hat{k}_x\hat{k}_y) \tag{2}$$

in our chosen coordinate system. This means that an intrinsic $d_{x_a^2-x_b^2}$-wave superconductor generally has a $d_{x^2-y^2}+d_{xy}$ order-parameter structure relative to a general coordinate system. (Conversely a $d_{x^2-y^2}+d_{xy}$ order parameter in some coordinate system with a real ratio of its two components can be transformed to a pure $d_{x^2-y^2}$ wave in a suitable coordinate system.) Before we study the possible surface states for the order parameter given by Eq. (2), we first prove a general theorem for a *real* superconducting order parameter (up to any unimportant constant overall phase factor):

Theorem: For a "real" order parameter $\Delta(k_{x0})$ (as defined above): (a) Eq. (1) has no nonzero energy solutions inside the gap; (b) Eq. (1) has a zero energy solution for a given $\mathbf{k}_F$ (and spin) if and only if

$$\Delta(k_{x0})\Delta(-k_{x0})<0. \tag{3}$$

Note that the ratio of $|\Delta(k_{x0})|$ and $|\Delta(-k_{x0})|$ is arbitrary in this theorem.

This Theorem can be proved as follows: Since the order parameter is "real," the (complex) eigenequation (1) can be shown to be equivalent to the following two real equations:

$$[\Delta(k_{x0})-\Delta(-k_{x0})]\epsilon_n=0, \tag{4}$$

$$\Delta(k_{x0})\sqrt{\Delta^2(-k_{x0})-\epsilon_n^2}+\Delta(-k_{x0})\sqrt{\Delta^2(k_{x0})-\epsilon_n^2}=0. \tag{5}$$

Suppose there exist a nonzero energy solution, then we must have

$$\Delta(k_{x0})=\Delta(-k_{x0}),$$

$$\sqrt{\Delta^2(-k_{x0})-\epsilon_n^2}=-\sqrt{\Delta^2(k_{x0})-\epsilon_n^2}.$$

The only solutions of these equations are $\epsilon_n=\pm|\Delta(k_{x0})|$ and $\Delta(k_{x0})=\Delta(-k_{x0})$, which must be rejected because they are not inside the gap. [For $|\epsilon_n|\geq|\Delta(k_{x0})|$ Eq. (1) is not valid.] This proves part (a) of the Theorem. Part (b) of the Theorem can be easily proved by simply setting ϵ_n equal to zero. Then Eq. (4) becomes automatically satisfied, whereas Eq. (5) leads to Eq. (3) as a necessary condition. On the other hand, it follows trivially from Eq. (1) that Eq. (3) is also a sufficient condition for the existence of a zero energy solution. The Theorem is therefore proved.

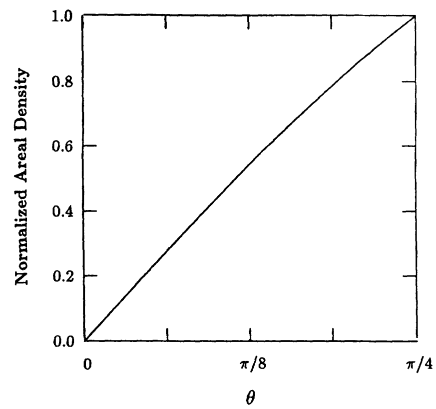

FIG. 1. The θ dependence of the normalized areal density of the midgap surface states given by Eqs. (6) and (7).

As is pointed out in Ref. 15, for a $d_{x_a^2-x_b^2}$-wave superconductor with a {110} surface, practically all wave vectors on the Fermi surface contribute to the midgap states. (One might have to exclude those k_{x0}'s which are very close to zero or k_F, since then the gap is so small that one cannot comfortably talk about bound states in the presence of any slight bit of smearing of the levels due to impurity or other types of scattering.) When the surface is not exactly a {110} surface, as can be seen from the above Theorem, only those $\mathbf{k}_F$'s which satisfy the condition (3) contribute to the midgap states, therefore one can expect that the areal density of the midgap states will be reduced in this case. By enforcing Eq. (3) we obtain the following inequality:

$$4[1+(\tan 2\theta)^2]\hat{k}_y^4-4[1+(\tan 2\theta)^2]\hat{k}_y^2+1<0.$$

This inequality holds only when

$$\sqrt{a_-}<\hat{k}_y<\sqrt{a_+} \quad \text{and} \quad -\sqrt{a_+}<\hat{k}_y<-\sqrt{a_-},$$

where

$$a_\pm=\tfrac{1}{2}(1\pm|\sin 2\theta|). \tag{6}$$

Therefore the areal density of the midgap states normalized to that of the {110} surface is

$$\sqrt{a_+}-\sqrt{a_-}. \tag{7}$$

In Fig. 1 we have plotted this normalized areal density of the midgap states as a function of the angle θ. It clearly shows that the areal density of the midgap states reaches its maximum at $\theta=\pi/4$ and minimum (=0) at $\theta=0$. We therefore find that the midgap surface states do not exist only if the surface is exactly {100}.

(ii) The second situation that we consider here arises directly from the lattice structure of the cuprate compounds. When we write the $d_{x_a^2-x_b^2}$ order parameter as $\Delta_0(\hat{k}_a^2-\hat{k}_b^2)$, we have made an implicit assumption that the compound is

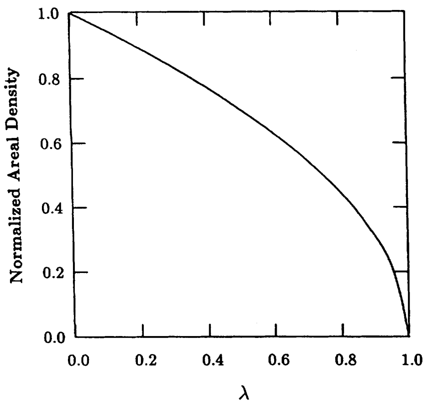

FIG. 2. The λ dependence of the normalized areal density of the midgap surface states given by Eq. (9).

in the tetragonal phase, which has a symmetry between the a and b axes. However, in the actual situation, the material often has a small orthorhombic distortion. The symmetry between the a and b axes is then weakly broken. As a result, one expects that the pure $d_{x_a^2-x_b^2}$-wave order parameter $\Delta_0(\hat{k}_a^2-\hat{k}_b^2)$ for the tetragonal structure would change in general to

$$\Delta_0(1+\lambda)\hat{k}_a^2-\Delta_0(1-\lambda)\hat{k}_b^2=\Delta_0(\hat{k}_a^2-\hat{k}_b^2)+\lambda\Delta_0$$

for the orthorhombic structure, where λ is a real parameter. Therefore there exists a small (in general extended) s-wave component in the order parameter. To study the effect of this change alone we assume the surface normal of the superconductor be still at 45° with the [100] direction in the ab plane, and only let the order parameter be changed as given above. The order parameter on the Fermi surface will then have the form

$$\lambda\Delta_0-\Delta_0(2\hat{k}_x\hat{k}_y) \tag{8}$$

in our chosen coordinate system. Since this order parameter is real, the Theorem proved above can also be applied here. Therefore, the midgap states are the only bound states within the gap (assuming that the pair-potential order parameter is not drastically suppressed near the surface). Again the areal density of these midgap states is determined by the range of $\mathbf{k}_F$ which satisfies the condition in Eq. (3), which leads to the following equation:

$$4\hat{k}_y^4-4\hat{k}_y^2+\lambda^2<0.$$

Thus only those $\hat{k}_y$'s in the range

$$(1-\sqrt{1-\lambda^2})/2<\hat{k}_y^2<(1+\sqrt{1-\lambda^2})/2$$

can give rise to midgap states. It follows that the areal density of the midgap states is reduced in this case from that of a pure $d_{x_a^2-x_b^2}$-wave superconductor by the factor

$$\sqrt{(1+\sqrt{1-\lambda^2})/2}-\sqrt{(1-\sqrt{1-\lambda^2})/2} \tag{9}$$

if $\lambda^2\leqslant 1$, whereas no midgap states exist at all if $\lambda^2>1$. This result is illustrated in Fig. 2. It is easy to understand why no midgap states exists if $\lambda^2>1$: The order parameter should be more appropriately identified as extended s wave rather than extended d wave if $\lambda^2>1$, since the order parameter does not change sign at all on the whole Fermi surface. (The physical values of $|\lambda|$ are expected to be much smaller than unity if the order-parameter symmetry deviates from a pure d wave because of the orthorhombic distortion of the crystalline structure *only*.) When the surface is not exactly at 45° with the a axis, although we have not exactly analyzed this case here, we can expect that the areal density of the midgap states for a given λ is further reduced from that of the case studied here.

(iii) Next we consider the order-parameter symmetry[16] $s+id$ for which the order parameter has the form $\Delta_s+i\Delta_d(\hat{k}_a^2-\hat{k}_b^2)$ with real Δ_s and Δ_d. To study the effect of this change alone, we assume that the crystalline structure is still tetragonal and the surface is still {110}. Then the order parameter on the Fermi surface can be written as

$$\Delta(\mathbf{k}_F)=\Delta_s-i\Delta_d(2\hat{k}_x\hat{k}_y) \tag{10}$$

in our coordinate system. Equation (1) is then satisfied if

$$\Delta_d(2\hat{k}_x\hat{k}_y)\epsilon_n=\Delta_s\sqrt{\Delta_s^2+4\Delta_d^2\hat{k}_x^2\hat{k}_y^2-\epsilon_n^2},$$

which leads to the following solution for each $\mathbf{k}$:

$$\epsilon_n=\Delta_s\mathrm{sgn}(\Delta_d\hat{k}_x\hat{k}_y).$$

Without loss of generality, we can assume $\Delta_d>0$ and $\hat{k}_x=k_{x0}/k_F>0$. Therefore, each positive $\hat{k}_y$ contributes a surface bound state at energy Δ_s, whereas each negative $\hat{k}_y$ contributes a surface bound state at energy $-\Delta_s$ (for either sign of Δ_s). The areal densities of the surface bound states at energy $\pm\Delta_s$ are both equal to half of that for $\Delta_s=0$ at zero energy. This is an extremely interesting result, since it implies that all occupied surface states at $T=0$ (with energy below the Fermi energy) have momenta along y having the same sign. (But those associated with two parallel surfaces will be opposite and cancel, as may be seen by rotating our solution about $\hat{\mathbf{z}}$ by π.) Experimental consequences of this result will be investigated in detail in future works.

(iv) Finally we study the order-parameter symmetry[17] $d+id'$ for which the order parameter has the form $\Delta_1(\hat{k}_a^2-\hat{k}_b^2)+i\Delta_2(2\hat{k}_a\hat{k}_b)$ with real Δ_1 and Δ_2. As in case (iii) we assume that the crystal structure is tetragonal. We shall consider two special orientations of the surface only. The first one is a {110} surface. In this case, the order parameter on the Fermi surface is equal to

$$-\Delta_1(2\hat{k}_x\hat{k}_y)+i\Delta_2(\hat{k}_x^2-\hat{k}_y^2) \tag{11}$$

in the present coordinate system, and the eigenequation (1) reduces to

$$\Delta_1(2\hat{k}_x\hat{k}_y)\epsilon_n=-\Delta_2(\hat{k}_x^2-\hat{k}_y^2)\times\sqrt{[\Delta_1(2\hat{k}_x\hat{k}_y)]^2+[\Delta_2(\hat{k}_x^2-\hat{k}_y^2)]^2-\epsilon_n^2},$$

the solution of which is

$$\epsilon_n=-\Delta_2(\hat{k}_x^2-\hat{k}_y^2)\mathrm{sgn}(\Delta_1\hat{k}_x\hat{k}_y),$$

which always lies inside the gap (which is located between $\mp\sqrt{[\Delta_1(2\hat{k}_x\hat{k}_y)]^2+[\Delta_2(\hat{k}_x^2-\hat{k}_y^2)]^2}$).

In contrast to the previous cases, these surface states are dispersive (i.e., having **k**-dependent energies). Therefore the midgap-state peak is spread into a flat distribution of a finite width which is equal to $2|\Delta_2|$. To observe them clearly one might need to perform **k**-specific measurements unless Δ_2 is very small.

The second special orientation of the surface that we consider here is a $\{100\}$ surface. In this case the order parameter has the form

$$\Delta_1(\hat{k}_x^2-\hat{k}_y^2)+i\Delta_2(2\hat{k}_x\hat{k}_y),$$

and the bound surface states have energies

$$\epsilon_n=-\Delta_1(\hat{k}_x^2-\hat{k}_y^2)\mathrm{sgn}(\Delta_2\hat{k}_x\hat{k}_y).$$

The midgap-state peak is again spread into a flat distribution of a finite width which is now equal to $2|\Delta_1|$. To clearly observe these states in a non-**k**-specific measurement one now needs Δ_1 to be very small. Even though we have not presented results for surfaces with normals in other directions in the ab plane, it should be obvious that bound surface states also exist and are dispersive for those cases.

In conclusion, we have found that the midgap surface states obtained for a pure $d_{x_a^2-x_b^2}$ superconductor with a $\{110\}$ surface are rather robust against deviations from this ideal condition, including the surface orientation being not exactly $\{110\}$, and the lattice having a slight orthorhombic distortion. When the order parameter has a $s+id_{x_a^2-x_b^2}$ symmetry, instead of being a pure d wave, we still find a sizable areal density of surface states on the $\{110\}$ surface, but at energies $\pm\Delta_s$ where Δ_s is the s component of the order parameter. When the order parameter has a $d_{x_a^2-x_b^2}+id_{x_ax_b}$ symmetry, surface states can exist on all surfaces, but are dispersive which makes them more difficult to observe. (For example, no giant surface magnetic moment would be implied by the existence of them unless the magnitude of one of the order parameter component is very small.) Finally, we remark that unlike the conclusions of Ref. 15, the conclusions obtained here are not all insensitive to the spatial dependence of the order parameter near the surface. But it is safe to say that if only the order parameter is not drastically suppressed near the surface, the results obtained here are at least semiquantitatively valid.

Note added in proof: Recently, we received an unpublished paper by M. Matsumoto and H. Shiba, which mainly studies the effects of surface roughness on the midgap states, but its conclusions overlaped somewhat with those for the situation (i) studied here.

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