PHYSICAL REVIEW B VOLUME 57, NUMBER 2 1 JANUARY 1998-II

Origin of the zero-bias conductance peaks observed ubiquitously in high-T_c superconductors

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(Received 24 October 1996; revised manuscript received 28 May 1997)

The midgap surface states predicted previously to exist on non-$\{n0m\}$ surfaces of $d_{x_a^2-x_b^2}$-wave superconductors (SC's) can be extended to midgap interface states (MIS's), which exist at almost all interfaces between grains of such SC's of different principal axes orientations. They can give rise to a zero-bias conductance peak (ZBCP) in quasiparticle tunneling along any axis as shown in our model calculation. When the counterelectrode is a low-T_c SC, its gap is shown to appear as a dip at the center of the (broadened) ZBCP. These and other results support the proposal that such MIS's are responsible for most if not all of the ZBCP's observed ubiquitously in tunneling experiments performed on high-T_c SC's. [S0163-1829(98)04301-X]

Zero-bias conductance peaks (ZBCP's, also known as conductance zero-bias anomalies) have been ubiquitously (but not universally) observed in quasiparticle tunneling experiments performed in various ways on various kinds of high-T_c superconductor (HTSC) samples.[1–21] The high-T_c materials used include at least Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O[$22(n-1)n$]- (with $n=1-3$), and Tl-Ba-Ca-Cu-O(2212)-class compounds (with and without doping), as either ceramic or polycrystalline samples, or epitaxial thin films which are $\{100\}$, $\{001\}$, and $\{103\}$ oriented, etc. Some films contain mixtures of several orientations (such as $\{110\}$ and $\{013\}$). The materials used for counterelectrodes include Pt, Au, Ag, Cu, W, Mo, In, Pb, Pb-Bi, Nb, etc., with at least the last four materials used both above and below their respective superconducting transition temperatures. In some experiments, the electrode and the counterelectrode are both HTSC's.[13,15,17,18] The tunneling barriers were in some cases natural barriers formed with or without exposure of the samples to air, and in some cases artificial barriers made of such materials as Y_2O_3, AlO_x, MgO, CeO_2, and $PrBa_2Cu_3O_7$, etc. The tunneling geometries included the conventional planar type, point contact, ramp type, break junction, broken-film-edge junction, squeezable-electron-tunneling junction, and scanning tunneling microscopy (STM), etc. However, when single-crystal samples were studied, ZBCP's were often not observed (cf. for example, Refs. 22–25 and perhaps also Ref. 26), but there seemed to be also exceptions.[2,5,6,15,20] When a ZBCP was observed, some saw it only when it was not a c-axes tunneling,[16,27] but others seemed to see it in c-axis tunneling as well.[2,6,8,9,11,12,15,17,20] The heights and widths of the ZBCP's observed varied greatly. When the counterelectrode used was a low-T_c SC, the ZBCP's were generally observed to contain a center dip, which deepened to become a range of null conductance at very low temperatures, thereby clearly reflecting the energy gap of the counterelectrode.[3,10–12,16,20] When a magnetic field was applied (while the counterelectrode was normal), some researchers saw in different samples or at different parts of the same sample three types of responses:[28] (i) a ''Zeeman splitting'' of the ZBCP, with a large field-dependent g factor;[1,16] (ii) a broadening of the ZBCP, which might correspond to a very weak splitting; and (iii) a shift away from zero bias (which sometimes was also observed in zero magnetic field,[28,19] and is therefore more likely caused by the surface condition than the applied field. For a possible explanation, see below.) Some also reported not seeing any magnetic-field dependence at all.[1,6]

Many mechanisms have been proposed for explaining the observed ZBCP's; some require both electrodes to be superconducting, such as (i) supercurrent leakage;[4,13,17] and (ii) phase diffusion.[1,13] Other mechanisms proposed, which allow the counterelectrode to be normal, include: (iii) Josephson tunneling from a proximity-induced superconducting region in the counterelectrode into the HTSC electrode;[1,3,8,10] (iv) Tunneling from the counterelectrode into a normal region which was proposed to exist in the HTSC electrode near the tunneling barrier;[1,10,29] and (v) Magnetic and Kondo scatterings due to magnetic impurities in the barrier or on the surface of the sample, i.e., the Applebaum-Anderson mechanism;[1,16,19,20] etc.

None of the the mechanisms metioned above are truly satisfactory: Mechanisms (i) and (ii) are practically ruled out by the fact that ZBCP's are also observed with normal counterelectrodes. Mechanism (iii) cannot account for the behavior in the observed ZBCP when the counterelectrode goes superconducting as a low-T_c SC, or when both electrodes are high-T_c superconductors, It is also difficult to see why proximity-induced superconductivity could occur in a normal counterelectrode in the weak tunneling limit. Mechanism (iv) has the difficulty of explaining why a peak structure should occur at zero voltage, as is already noted in Ref. 10. As for mechanism (v), one would have to conclude that the magnetic or Kondo impurities must exist generically in all high-T_c materials, and not in any extrinsic barriers or in the counterelectrodes. Thus Cu atoms in a different valence state is a likely candidate. A correlation discovered recently between observing ZBCP and d-wave-like characteristics in the high-T_c electrode favors in some way this mechanism[21] than the others mentioned above. However, it probably favors even more a mechanism discussed below. Besides, mechanisms (i)–(iii) and (iv) have not explained why a low-T_c superconducting gap can appear as a dip at the center of the ZBCP, and none of these mechanisms can explain why ZBCP's are much less likely observed in single-crystal samples, whereas the mechanism discussed below can explain both of these two points, as we shall show. Also, Kashiwaya *et al.*[28] have noted that mechanism (iv) cannot explain the third type of magnetic-field effect they observed. This point does not pose any difficulty to the mechanism discussed below either. (See below.)

Three years ago, the author noted the possibility of an intrinsic mechanism for the observed ZBCP's in HTSC's.[30,31] The fundamental concept invoked is that an Andreev reflection can sense the phase or sign of a superconducting order parameter. Thus two consecutive Andreev reflections by the same quasiparticle, separated by any mechanism to change its momentum, such as a specular reflection at a surface, can allow a quasiparticle to compare the phase or sign of the order parameter at two different points of the Fermi surface (if coherence is maintained throughout the processes), and to thereby distinguish superconducting order parameters of different symmetries. One important consequence of this concept is that on a non-$\{n0m\}$ surface of a $d_{x_a^2-x_b^2}$-wave SC (where $\{n0m\}$ includes $\{100\}$ and $\{001\}$), there must exist a sizable area density of quasiparticle states that are all of zero energy (relative to the Fermi energy), independent of their different transverse momenta along the surface (and therefore can be called ''*dispersionless*''), as long as corrections of the order of Δ^2/ε_F or smaller are neglected (i.e., in the WKBJ approximation).[32] As has been pointed out in Ref. 30, one of the many interesting and important consequences of these midgap surface states (MSS's) is that they can give rise to a ZBCP in quasiparticle tunneling. Following this suggestion, Tanaka *et al.*[33] and Xu *et al.*[34] subsequently calculated the NIS tunneling spectroscopy of d-wave SC's, using an approach developed by Blonder *et al.*,[35] and assuming a planar tunneling barrier in an $\langle nm0\rangle$ direction other than $\langle 100\rangle$, and indeed confirmed the occurrence of a ZBCP.

However, Tanaka *et al.*[33] have oversimplified the experimental situation by stating that ''the ZBCP's are frequently observed in ab-plane tunneling junctions, and are rarely observed in c-axis-oriented junctions.'' In fact, as we have reviewed above, ZBCP's have been frequently observed in c-axis tunnelings, at least nominally, especially if the samples are only c-axis aligned, but are not single crystals.[3,6,9,11,12,15,21,36] Furthermore, in most ab-plane tunnelings where ZBCP's were observed, the tunnelings were at least nominally observed in the a (or b) direction, which, according to the general conditions for the occurrence of MSS's,[30,31] and the explicit calculations cited above on NIS tunneling,[33,34] is precisely the direction that ZBCP's should not have been observed. These facts strongly suggest that there is still something missing in this proposal for the origin of the ZBCP's. In fact, it was precisely this observation that made the author state very conservatively in Ref. 30 that ''one is very tempted to associate this ZBCP with the midgap states predicted in (Ref. 30), although none of the samples studied have $\{110\}$ surfaces purposedly created in them.'' (According to Ref. 31 and additional simple considerations, $\{110\}$ should be generalized to non-$\{n0m\}$.)

In the present work, it is pointed out first of all that the MSS's can be generalized to midgap interface states (MIS's), each of which has a wave function which is localized, as far as the directions in the ab plane are concerned, within roughly a coherence length from an interface between almost any two d-wave superconducting domains (i.e., grains) of different ab-axes orientations.[37] A model calculation based on the tunneling Hamiltonian approach[39] is then presented, which shows that such MIS's can give rise to a ZBCP in tunneling along the c or a axis.[40] As for tunneling along other directions (into a d-wave sample containing grain boundaries), the tunneling Hamiltonian approach employed here is less reliable, due to the existence of surface effects at the tunneling barrier when the SC is not s wave,[30,31] and one should more appropriately employ the approach of Blonder *et al.*[35] which is, for example, employed in Refs. 33,34. However, the more accurate results obtained with that approach would merely contain additional contributions due to the surface effects at the tunneling barrier, but the contributions to the ZBCP due to the MIS's at the interior grain boundaries should be essentially the same as the ones calculated here with the tunneling Hamiltonian approach. It is therefore reasonable to draw the conclusion based on the present work that the MIS's existing at the grain boundaries can give rise to a ZBCP in tunneling along *any* axis, if only the high-T_c sample is such that some MIS's exist in it and they have finite amplitudes at the tunneling barrier, i.e., the exponentially decaying wave functions of the MIS's in the ab-plane directions away from the grain boundaries must not have already decreased to essentially zero at the tunneling barrier.

Based on the above conclusion, we see then a very strong candidate for explaining most if not all ZBCP's observed in HTSC's, and why the observation of ZBCP is so ubiquitous in non-single-crystal high-T_c samples, but is far less frequent in single-crystal samples. Of course, we do allow the possibility that in some experiments the observed ZBCP's might in part or in total arise from some MSS's, especially in those experiments where true single-crystal samples were studied, or where the samples contained non-$\{n0m\}$-oriented grains relative to the tunneling direction, or when the sample surface was cracked by a tunneling tip, or when the sample surface used for tunneling is known to have pits or protrusions, with facets that are neither $\{100\}$ nor $\{001\}$ oriented, etc. We also do not yet have sufficient evidence to rule out the possibility that some ZBCP's observed might be due to the mechanisms (i)–(v) reviewed above. We only suggest that most of the ZBCP's observed are due to the mechanism discussed here, and that without it, the MSS's alone or the mechanisms (i)–(v) cannot explain all of the ZBCP phenomena observed in high-T_c superconductors. If this suggestion can be confirmed to be true, the implications would be manyfold: (a) It would resolve the question concerning the ubiquitous observation of the ZBCP's in HTSC's; (b) It would provide many additional ways to confirm that the superconducting state in HTSC's is not pure s-wave (isotropic or anisotropic), but is either pure d wave, or is some close kin of it that can also generate the MIS's and the MSS's (See Ref. 30 for some discussion on this point, which applies to MSS's as well as to MIS's); (c) Finally and most importantly, the MIS's, if confirmed to exit in HTSC's, would have many significant consequences on the thermodynamic and transport properties of the non-single-crystal HTSC's, which are in practice more relevant to most large-scale applications than the single-crystal ones. For example, the existence of these MIS's might affect the vortex-pinning and flux-flow dissipation properties of grain boundaries, and it might also be able to cause the superconducting order parameter to become weaker at most grain boundaries,[38] which might explain why most grain boundaries automatically form Josephson junctions. The ''dispersionless'' electrons filling these MIS's could even form an interesting many-body subsystem with some unique physical properties that deserve detailed studies. (See Ref. 30 for some qualitative suggestions, which apply to MSS's as well as to MIS's.)

Unlike the approach of Blonder *et al.*[35] employed in Refs. 33,34, the calculation presented here based on the tunneling Hamiltonian approach[39] allows me to consider also the case when the counterelectrode is a low-T_c SC. It is then found that a center dip appears in the (broadened) ZBCP which becomes a range of zero conductance as the temperature is lowered much below the transition temperature of the counter-electrode, with a width clearly reflecting its energy gap, exactly as observed. These and other results obtained here, we believe, have already lent a strong support to the above suggestion.

The physics of the MSS's is illustrated by the quasiparticle bound-state orbit depicted in Fig. 1(a), where a normal-metal layer of thickness L_N and of zero pair potential have been inserted on the surface of a d-wave SC, whose pair potential is $\Delta(\mathbf{k})$, as has been done in Ref. 30, in order to make the picture easier to understand, but actually this width L_N can be reduced to zero (i.e., this normal-metal layer can be absent; see Ref. 30 and below[41]). As is indicated in this figure, this bound-state orbit is a closed orbit formed with a cyclic sequence of four reflections: an Andreev reflection, a specular reflection, another Andreev reflection, and another specular reflection, with each Andreev reflection changing the quasiparticle from being electronlike of momentum $\mathbf{k}$ (represented by a solid line) to holelike at momentum $-\mathbf{k}$ (represented by a dashed line), or vice versa, and each specular reflection changing its momentum from $(k_x,\mathbf{k}_\perp)$ to $(-k_x,\mathbf{k}_\perp)$, or vice versa, where x denotes the direction perpendicular to the surface, and $\mathbf{k}_\perp \equiv (k_y,k_z)$. Thus if one Andreev reflection is by the pair potential $\Delta(k_x,\mathbf{k}_\perp)$, then the subsequent one is by the pair potential $\Delta(-k_x,\mathbf{k}_\perp)$, or vice versa. If these two pair-potential values are of opposite sign for the given momemtum vector $(k_x,\mathbf{k}_\perp)$ of interest, i.e., if

$$\Delta(k_x,\mathbf{k}_\perp)\Delta(-k_x,\mathbf{k}_\perp)<0 \tag{1}$$

(which is possible at least for some such pairs of momenta, if the SC is $d_{x_a^2-x_b^2}$-wave, and the surface is not $\{n0m\}$, which includes $\{100\}$ and $\{001\}$), then a zero-energy bound state must exist for each such pair of momemtum vectors on the Fermi surface and for each sample surface, as has been shown in Refs. 30,31. (The energy is strictly zero in the WKBJ approximation only.) Since the energy of the resulting branch of excitation is independent of the transverse momentum $\mathbf{k}_\perp$ in the WKBJ approximation, it can be called dispersionless in this approximation. A deep topological reason actually exists to account for the existence of these zero-energy bound states (i.e., the Atiyah-Singer index theorem[42]). Their occurrence is therefore actually independent of the precise x dependence of the pair-potential magnitude near the surface, including having or not having a range of zero values (as long as it remains real for all x in the gauge of vanishing vector potential in the absence of a magnetic field), which explains why the normal-metal layer can be present or absent. [The condition in Eq. (1) then refers in general to the asymptotic values of the pair potential far away from the boundary.] The Andreev reflections are still possible even when a constant pair potential extends all the way to the surface, since (i) at a pair potential step from zero to a finite value, the Andreev reflection actually does not occur at the pair-potential discontinuity, but at roughly a coherence-length inside the SC [which is qualitatively taken into account in Fig. 1(a)], as may be seen from the exponentially decaying amplitudes of the two-component quasiparticle wave function inside the SC for any such bound state; (ii) a constant pair potential extending all the way to the surface may be viewed from an extended-image-method point of view (cf. Ref. 30), in the case when Eq. (1) is satisfied, as a pair potential changing from, say, $\Delta<0$ for $x<0$, to $\Delta=0$ at $x=0$ (where the surface is), and then to $\Delta>0$ for $x>0$. Therefore even without any normal-metal layer, there can

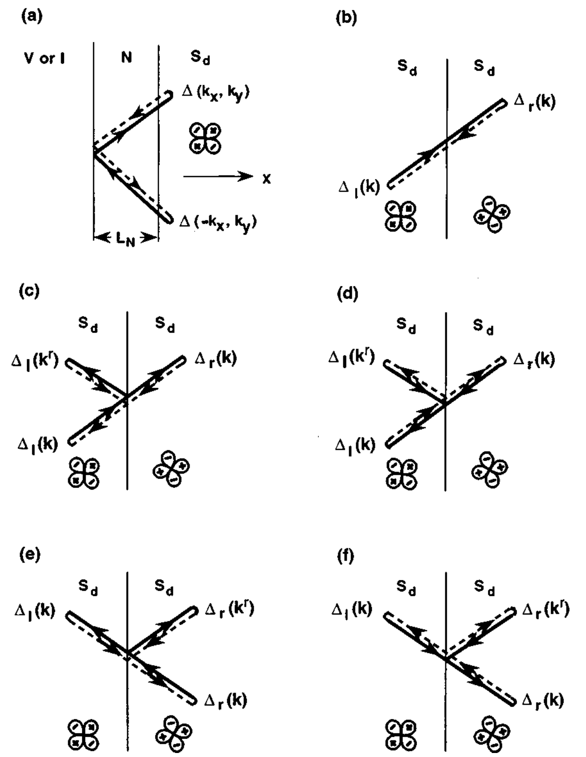

FIG. 1. Orbits of the midgap states under various conditions. (''V or I'' means vacuum or an insulator; ''N'' means a normal metal; and S_d means a d-wave superconductor. $\mathbf{k}^r$ means the reflected $\mathbf{k}$. That is, if $\mathbf{k}=(k_x,k_y)$, then $\mathbf{k}^r=(-k_x,k_y)$. (a) At a sample surface (i.e., the MSS); (b) At an interface between two grains of different principal-axes orientations, assuming $t=1$; (c)–(f) same as (b) but for $t\neq 1$. (c) depicts the orbit of an electron-incident-from-left MIS; (d) depicts the orbit of a hole-incident-from-left MIS; (e) depicts the orbit of an electron-incident-from-right MIS; (f) depicts the orbit of a hole-incident-from-right MIS. Orbits depicted in (b)–(f) are all MIS's.

still be a leftward Andreev reflection on the $x>0$ side, and a rightward one on the $x<0$ side, with the latter being actually the image of the subsequent Andreev reflection in Fig. 1 (a) which occurs on the $x>0$ side.

Now consider a flat interface at $x=0$ of two $d_{x_a^2-x_b^2}$-wave superconducting grains of different principal-axes orientations, each being semi-infinite in size. The pair potentials $\Delta_l(k_x,\mathbf{k}_\perp)$ in the grain on the left (occupying the region $x<0$) and $\Delta_r(k_x,\mathbf{k}_\perp)$ in the grain on the right (occupying the region $x>0$), respectively, can be in general already of different sign for the same momemtum vector $(k_x,\mathbf{k}_\perp)$. Therefore, a zero-energy bound state can already exist at the interface for such a momemtum vector $(k_x,\mathbf{k}_\perp)$, without the need of any mechanism to change the momentum vector between the consecutive Andreev reflections, if only the transmission coefficient at the interface is unity. (See the next paragraph if this is not the case.) Such bound states are the midgap interface states, or MIS's, referred to earlier. The orbit for such a state is depicted in Fig. 1(b), where the transmission probability t at the interface has been assumed to be unity. We have also assumed that the material parameters are the same in the two grains, so that the transmitted momentum is the same as the incident momentum. It is seen to be a closed orbit formed with a cyclic sequence of two reflections: a leftward Andreev reflection on the $x>0$ side, and a rightward Andreev reflection on the $x<0$ side. As far as all directions in the ab plane are concerned, the wave function of this state is localized within roughly a coherence length from either side of the interface.[43]

If the transmission probability t through the interface is not unity, strictly zero-energy bound states at the interface (in the WKBJ approximation) are still possible for a more restricted set of momentum vectors on the Fermi surface, and have orbits shown in Figs. 1(c)–1(f). From these figures, it can be seen that the conditions for the existence of these zero-energy bound states are:

(i) $\Delta_l(k_x,\mathbf{k}_\perp)\Delta_r(k_x,\mathbf{k}_\perp)<0$ and $\Delta_l(k_x,\mathbf{k}_\perp)\Delta_l(-k_x,\mathbf{k}_\perp)<0$, for the MIS orbits depicted in Figs. 1(c) (for $k_x>0$) and 1(d) (for $k_x<0$); or

(ii) $\Delta_l(k_x,\mathbf{k}_\perp)\Delta_r(k_x,\mathbf{k}_\perp)<0$ and $\Delta_r(k_x,\mathbf{k}_\perp)\Delta_r(-k_x,\mathbf{k}_\perp)<0$, for the MIS orbits depicted in Figs. 1(e) (for $k_x<0$) and 1(f) (for $k_x>0$).

We shall call the two types of MIS's depicted in Figs. 1(c) and 1(d) the left-incident MIS's; and the two types of MIS's depicted in Figs. 1(e) and 1(f) the right-incident MIS's. [The state depicted in Fig. 1(c) may be called an electron-incident-from-left MIS; That depicted in Fig. 1(d) may be called a hole-incident-from-left MIS; etc.] In all four types of states, $(k_x,\mathbf{k}_\perp)$ always refers to the momentum of the electron that is transmitted through the interface. It is important to notice that in each of these orbits, there is always a half of it involving the splitting of a quasiparticle orbit into two branches, due to the nonzero probabilities for both transmission and reflection, and a second half involving a time-reversal-like rejoining of two branches into one, so that the orbits can be closed, and the above conditions can be sufficient for generating zero-energy states. Thus this is a different type of bound state made possible by the presence of Andreev reflections on both sides of the interface. (It is important to realize that always a fourth branch is not involved in each of these four types of bound-state orbits for $t<1$, otherwise the conditions for the existence of the MIS's would be too stringent to allow them to be responsible for the ubiquitously observed ZBCP's.)

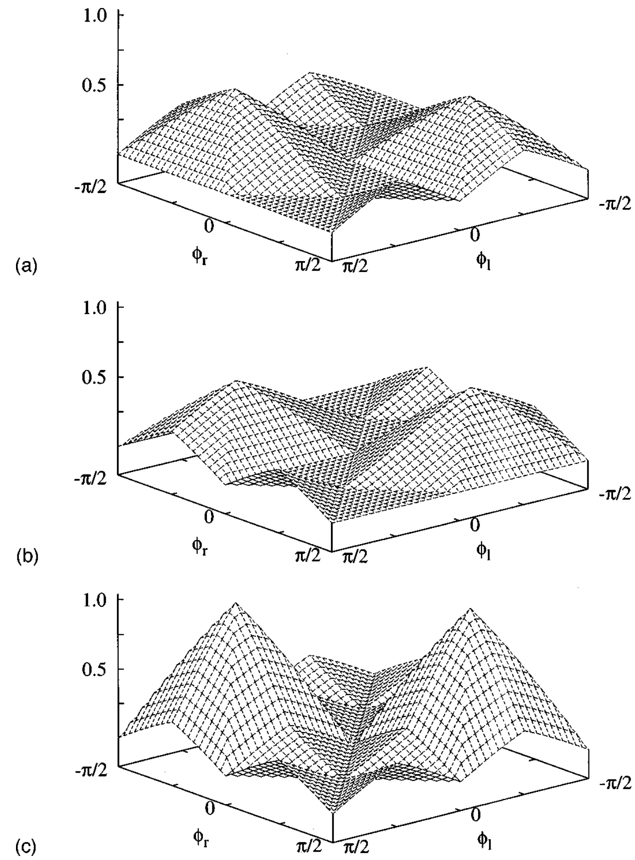

FIG. 2. (a) The calculated area density of left-incident MIS's plotted as a function of ϕ_l and ϕ_r; (b) A similar plot for the right-incident MIS's; (c) A similar plot but including both left- and right-incident MIS's. In (a) or (b), the two equal-height maxima have been normalized to 0.5. In (c), the two equal-height maxima have been normalized to unity.

In Fig. 2(a) we have plotted the area density of the left-incident MIS's, normalized to 0.5 at its two equal-height maxima, as a function of the two angles ϕ_l and ϕ_r, which are the angles made by the a axes of the $d_{x_a^2-x_b^2}$-wave order parameters in the left and right grains, respectively, with the interface normal $\hat{\mathbf{x}}$, assuming that their c axes are given aligned in a direction parallel to the interface. In Fig. 2(b) a similar plot is made for the right-incident MIS's. Then in Fig. 2(c) we have plotted the total area density of all types of MIS's, in the same way, except that the two equal-height maxima are now normalized to unity. This area density, before normalization, is simply the sum of the two area densities plotted normalized in Figs. 2(a) and 2(b). All three plots are t independent, as long as $0<t<1$. Details of the calculation of these area densities will be omitted here, since they are tedious but straightforward, being simply based on the conditions given in (i) and (ii) above. One can see from Fig. 2(c) that this total area density is strictly zero only if $\phi_l=\phi_r$, or $\phi_l+\phi_r=\pm\pi/2$, or $\phi_l=-\phi_r=\pm\pi/2$ (which is actually equivalent to $\phi_l=\phi_r=\pm\pi/2$). [For $t=1$ only the first condition (which includes the third) can lead to zero area density. See below. For $t=0$ the condition would change to "$\phi_l=0$ or $\pm\pi/2$, and $\phi_r=0$ or $\pm\pi/2$," corresponding to having a $\{100\}$ surface for both grains, which can be understood in terms of the analyses of Refs. 30,31, since $t=0$ would mean that the sample has split into two independent semi-infinite halves, each with a surface.] The maxima in Fig. 2(c) are t independent, including $t=0$ and 1, and they always occur at "$\phi_l=\pm\pi/4$ and $\phi_r=\mp\pi/4$." This maximum area density is a factor of 2 larger than the area density of the MSS's on the $\{110\}$ surface of a $d_{x_a^2-x_b^2}$-wave SC, which has been discussed in Ref. 30.

Since the condition for the existence of the MISs in the case of $0<t<1$ is more stringent than the single condition $\Delta_l(k_x,\mathbf{k}_\perp)\Delta_r(k_x,\mathbf{k}_\perp)<0$ for the case of $t=1$, or the condition "$\Delta_l(k_x,\mathbf{k}_\perp)\Delta_l(-k_x,\mathbf{k}_\perp)<0$ or $\Delta_r(k_x,\mathbf{k}_\perp)\Delta_r(-k_x,\mathbf{k}_\perp)<0$" for $t=0$, I think that the "MIS's" for some momentum vectors on the Fermi surface when $t=1$ or 0 will no longer have zero energy when $0<t<1$, but will shift away from zero energy by an amount depending on t (or the reflection probability r), at the interface. This point needs to be more thoroughly investigated in the future. For the present purpose the more important fact is that there is still a finite area density of zero-energy states (in the WKBJ approximation) for *any* $0<t<1$, except when ϕ_l and ϕ_r satisfy one of the conditions given above, which represent a set of measure zero only. Although the result given in Fig. 2(c) is only valid for the case when the two grains are c-axis aligned, it is not difficult to see that qualitatively similar results can be obtained even when the two grains are not so aligned. (But pure tilt of the c axes in the two grains relative to each other without, also, misalignment of both the a and b axes in the two grains, are not sufficient.) Whereas more studies are needed for these cases, it can be concluded now that MIS's should exist at almost all reasonably flat grain boundaries of HTSC's (in the scale of the very short coherence length of such materials), if only they are d wave, and not s wave (isotropic or anisotropic) [other waves can be similarly analyzed to see whether they can also give rise to MIS's], although the area density of such MIS's will vary, depending on the symmetry of the superconducting order parameter, and the orientations of the two grains relative to the interface normal.

Let us now assume $t=1$ from this point on for simplicity,[44] and concentrate on demonstrating that these MIS's can be observed in quasiparticle tunneling in the form of a ZBCP, and how this ZBCP, if broadened to a finite width by, say, interface roughness or impurity scatterings, can, in the case when the counterelectrode is a low-T_c superconductor, exhibit its energy gap in the form of a center dip, as has been already observed by many research groups.

We begin with a tunneling Hamiltonian written in real space in order to allow for a spatially inhomogeneous electrode containing two grains:

$$\hat{\mathcal{H}}(t)=\hat{\mathcal{H}}_1+\hat{\mathcal{H}}_2+\hat{\mathcal{H}}_T(t), \tag{2}$$

$$\hat{\mathcal{H}}_T(t)=v_0[\mathcal{T}\psi^\dagger_{1\alpha}(\mathbf{R})\psi_{2\alpha}(\mathbf{R})+\mathcal{T}^*\psi^\dagger_{2\alpha}(\mathbf{R})\psi_{1\alpha}(\mathbf{R})]e^{\eta t}, \tag{3}$$

where t denotes time, η is a positive infinitesimal, $\hat{\mathcal{H}}_1$ is the Hamiltonian of the counterelectrode, which is assumed to be either a uniform normal metal, or a uniform low-T_c s-wave SC, and $\hat{\mathcal{H}}_2$ is the BCS Hamiltonian of the electrode, which is assumed to contain two c-axis-aligned ($\parallel\hat{\mathbf{z}}$) grains (named l and r) occupying the regions $-L_l<x<0$ and $0<x<L_r$, respectively, with the orientaions of their $d_{x_a^2-x_b^2}$-wave order-parameters described by the two angles ϕ_l and ϕ_r already defined. A periodic boundary condition has been assumed in the x direction for calculational convenience, which implies that the electrode considered actually contains two interfaces (i.e., grain boundaries), with one located at $x=0$, and the other located at $x=L_r$ $(=-L_l)$. The constant $\mathcal{T}$ is a tunneling matrix element, and it has been assumed that tunneling occurs only within a very small volume element v_0 around a spatial point $\mathbf{R}$, but later an ensemble average will be performed, on the results for the tunneling current, with respect to $\mathbf{R}$ over the whole electrode volume (mainly over the range $-L_l<x<L_r$), so that the results will not depend on the local amplitudes of the various contributing quasiparticle states. The result then no longer corresponds to the measurements of any single particular tunneling experiment, but rather to an ensemble average of them which probe different points of the sample uniformly. The fact that such averaged results can show the existence of a ZBCP clearly proves that some individual tunneling experiment can see a ZBCP. In fact, it proves that some local experiment(s) must be able to see it with an even larger amplitude than is found here, and some other experiment(s) will see it with a smaller amplitude, or not see it at all.

Applying an approach developed by Ambegaokar and Baratoff,[45] the following formula is obtained for the tunneling current through $\mathbf{R}$:

$$\begin{aligned} I_{\mathbf{R}}(t)=&(e/\hbar^2)v_0^2|\mathcal{T}|^2\\ &\times\sum_\alpha\int_{-\infty}^{t}dt'\{G^>_{2\alpha}(\mathbf{R}t,\mathbf{R}t')G^<_{1\alpha}(\mathbf{R}t',\mathbf{R}t)\\ &-G^<_{2\alpha}(\mathbf{R}t,\mathbf{R}t')G^>_{1\alpha}(\mathbf{R}t',\mathbf{R}t)+(t\leftrightarrow t')\}e^{\eta t'}, \end{aligned} \tag{4}$$

where we have kept only the normal terms (i.e., the quasiparticle tunneling terms), and have left Josephson tunneling for a separate consideration. The Green functions $G^>_\alpha((x,x')\equiv -i\langle\psi_\alpha(x)\psi^\dagger_\alpha(x')\rangle_0$ and $G^<_\alpha((x,x')\equiv +i\langle\psi^\dagger_\alpha(x')\psi_\alpha(x)\rangle_0$ may be expressed in terms of the Bogoliubov amplitudes $[u_n(\mathbf{r}),v_n(\mathbf{r})]$ using the Bogoliubov-Valatin transformation[46] $\psi_\uparrow(\mathbf{r})=\Sigma_{\epsilon_n>0}[\gamma_{n\uparrow}u_n(\mathbf{r})-\gamma^\dagger_{n\downarrow}v^*_n(\mathbf{r})]$ and $\psi_\downarrow(\mathbf{r})=\Sigma_{\epsilon_n>0}[\gamma_{n\downarrow}u_n(\mathbf{r})+\gamma^\dagger_{n\uparrow}v^*_n(\mathbf{r})]$. The results are

$$\begin{aligned} G^>_\alpha(x,x')=&-i\sum_{\epsilon_n>0}\{[1-f(E_n)]u_n(\mathbf{r})u^*_n(\mathbf{r}')e^{-iE_n(t-t')/\hbar}\\ &+f(E_n)v^*_n(\mathbf{r})v_n(\mathbf{r}')e^{iE_n(t-t')/\hbar}\}\\ &\times e^{-i(\mu+e\phi)(t-t')/\hbar}, \end{aligned} \tag{5}$$

$$G^{<}_{\alpha}(x,x')=+i\sum_{\epsilon_n>0}\{f(E_n)u_n(\mathbf{r})u^*_n(\mathbf{r}')e^{-iE_n(t-t')/\hbar}$$
$$+[1-f(E_n)]v^*_n(\mathbf{r})v_n(\mathbf{r}')e^{iE_n(t-t')/\hbar}\}$$
$$\times e^{-i(\mu+e\phi)(t-t')/\hbar} \tag{6}$$

(for either side of the junction). Combining the above results, we obtain

$$I_{\mathbf{R}}(V)=(4\pi e/\hbar^2)v_0^2|\mathcal{T}|^2$$
$$\times\sum_{n,m}[f(E_n)-f(E_m)]|u_{n1}(\mathbf{R})|^2|u_{m2}(\mathbf{R})|^2$$
$$\times\delta(E_n-E_m+eV), \tag{7}$$

where now the sum over n and m is over both the positive and the negative energy states, and $f(E)\equiv 1/(e^{E/k_BT}+1)$ is the Fermi function, k_B is the Boltzmann constant, and T is the temperature. If the counterelectrode is a uniform normal metal or a uniform low-T_c s-wave SC, then this $I_{\mathbf{R}}$ averaged with respect to $\mathbf{R}$ over the whole volumn of the electrode will no longer depend on the Bogoliubov amplitudes. For both cases, we recover the following familiar formula, but now for the $\mathbf{R}$-averaged, normalized tunneling current $\widetilde{I}\equiv\langle I_{\mathbf{R}}\rangle_{\mathbf{R}}/(G_{nn}\Delta_0/e)$, (where G_{nn} is the tunneling conductance when both electrodes are normal, and Δ_0 is the maximum gap of the electrode):

$$\widetilde{I}(v)=\int_{-\infty}^{\infty}dE\mathcal{N}_1(E-eV)\mathcal{N}_2(E)[f(E-eV)-f(E)], \tag{8}$$

where E is in units of Δ_0, and the total densities of states of the two electrodes, $\mathcal{N}_1(E)$ and $\mathcal{N}_2(E)$, are normalized by their respective normal-state values (i.e., to unity at large E).

To calculate the total density of states of the electrode, $\mathcal{N}_2(E)$, the Bogoliubov equations for the two-grained system are solved in the WKBJ approximation, as in Ref. 30. The pair potentials in the two grains (assumed constant in each grain[47]) have been written as $\Delta_{l,r}=\Delta_0\cos(2(\phi-\phi_{l,r}))$, where it has been assumed that the common c axis of both grains is in the z direction, and $k_y=k_F\sin\phi$, so that $-\pi/2\leqslant\phi<\pi/2$. In the WKBJ approximation, and for $t=1$, the Bogoliubov amplitudes $[u(\mathbf{r}),v(\mathbf{r})]$ have the form $\exp[i(k_{x0}x+k_yy+k_zz)][\widetilde{u}(x),\widetilde{v}(x)]$, where $k_{x0}^2+k_y^2=k_F^2$ under the assumption of a cylindrical Fermi surface. The solutions for the slowly varying envelope functions $[\widetilde{u}(x),\widetilde{v}(x)]$ in the two grains are as in Ref. 30. Matching only the values of $[\widetilde{u}_n(x),\widetilde{v}_n(x)]$ at the interface, not their derivatives in this approximation, the following eigencondition is obtained for $|E_n|>|\Delta_l|,|\Delta_r|$:

$$\frac{\cos(k_{1R}L_r)\cos(k_{1l}L_l)-\cos(k_{x0}(L_l+L_r))}{\sin(k_{1R}L_r)\sin(k_{1l}L_l)}$$
$$=\frac{E_n^2-\Delta_r\Delta_l}{\sqrt{E_n^2-\Delta_l^2}\sqrt{E_n^2-\Delta_r^2}}, \tag{9}$$

where $k_{1(l,r)}\equiv m\sqrt{E_n^2-\Delta_{(l,r)}^2}/|k_{x0}|$. Equation (9) may be analytically continued to $|E_n|$ below $|\Delta_l|$ and/or $|\Delta_r|$. In particular, it can then be shown that $E_n=0$ is a solution in the limit of $L_l,L_r\to\infty$ (actually two solutions, one for each interface), if and only if $\Delta_l(k_{x0},k_y)\Delta_r(k_{x0},k_y)<0$, as we have already pointed out in the introduction.

These eigenequations have been solved by a numerical iteration method assuming $\phi_l=\pi/4$, and $\phi_r=0$. A relatively small size in the x direction has been considered, viz., $L_l=10\xi_0$ and $L_r=20\xi_0$, where $\xi_0\equiv\hbar v_F/\Delta_0$. In order to reduce the size-quantization effects, we have given an artificial linewidth $\Gamma=0.05\Delta_0$ to each energy level. This changed a discrete set of eigenenergies for a given ϕ to a (partial) density of states for the given ϕ. In Figs. 3(a)–3(d), plots of such partial density of states for $\phi=\pm 3\pi/8$ and $\pm 3\pi/16$ are given as examples. Note the appearance of a MIS peak for $3\pi/8$ and $\phi=-3\pi/16$, but not for $\phi=-3\pi/8$ and $3\pi/16$, which is exactly as expected for the present choice of ϕ_l and ϕ_r. (Note that each midgap peak is actually formed with two midgap states slightly split apart, due to the existence of two interfaces at a finite separation from each other. Note also how the two midgap states of each midgap peak are formed at the expense of a state from one of the gap edges of the two grains, and another state of the corresponding negative energy. This is particularly clear when Figs. 3(c) and 3(d) are compared, where the discreteness of the energy spectrum just above the lower gap is more obvious.) To calculate the total density of states for all ϕ, we use

$$\sum_{k_y}=\frac{L_y}{2\pi}\int_{-k_F}^{k_F}dk_y=\frac{k_FL_y}{2\pi}\int_{-\pi/2}^{\pi/2}d\phi\cos\phi \tag{10}$$

and another factor of 2 for the two possible signs of k_{x0}. The range $-\pi/2\leqslant\phi\leqslant\pi/2$ has been replaced by 33 equally spaced values, but the two end points are singular (in the sense of zero times infinity), and have been omitted. This is a contained source of error for the part of the density of states at $E\neq 0$, due to the ''continuum'' states, but it does not affect the ZBCP which has no contribution from $\phi=\pm\pi/2$, so it has not been corrected (as is the error due to the discretization of ϕ). These problems will be faced when quantitatively more accurate results are needed for comparison with data. (Note that the WKBJ approximation is not valid at $\phi=\pm\pi/2$, where $k_{x0}=0$.) The thus obtained total density of states for the electrode is used in Eq. (8) to calculate the tunneling current and the tunneling conductance $G\equiv dI/dV$ at several temperatures. Figure 4 shows the so-calculated tunneling conductance at $k_BT/\Delta_0=$ 0.01, 0.05, and 0.10, for the case when the counterelectrode is normal. The curve at $k_BT/\Delta_0=0.01$ basically reflects the total density of states of the electrode, since this temperature is already much lower than the artificially chosen linewidth of the levels. (Size quantization in both grains of the electrode gives the somewhat irregular oscillations.) A ZBCP is clearly visible in this curve. [Its size relative to the rest of the conductance at $E\neq 0$ is not universal, but can be larger or smaller in an actual tunneling experiment, since the interface density can be different in different samples, and the particular average of $I_{\mathbf{R}}$ corresponding to a particular experiment can sample more or less of the interface region(s).] At $k_BT/\Delta_0=0.05$ the ZBCP is seen to be much reduced, without its apparent width changed visibly. At $k_BT/\Delta_0=0.10$ the ZBCP is found to have disappeared. This is perhaps due to the combined ef-

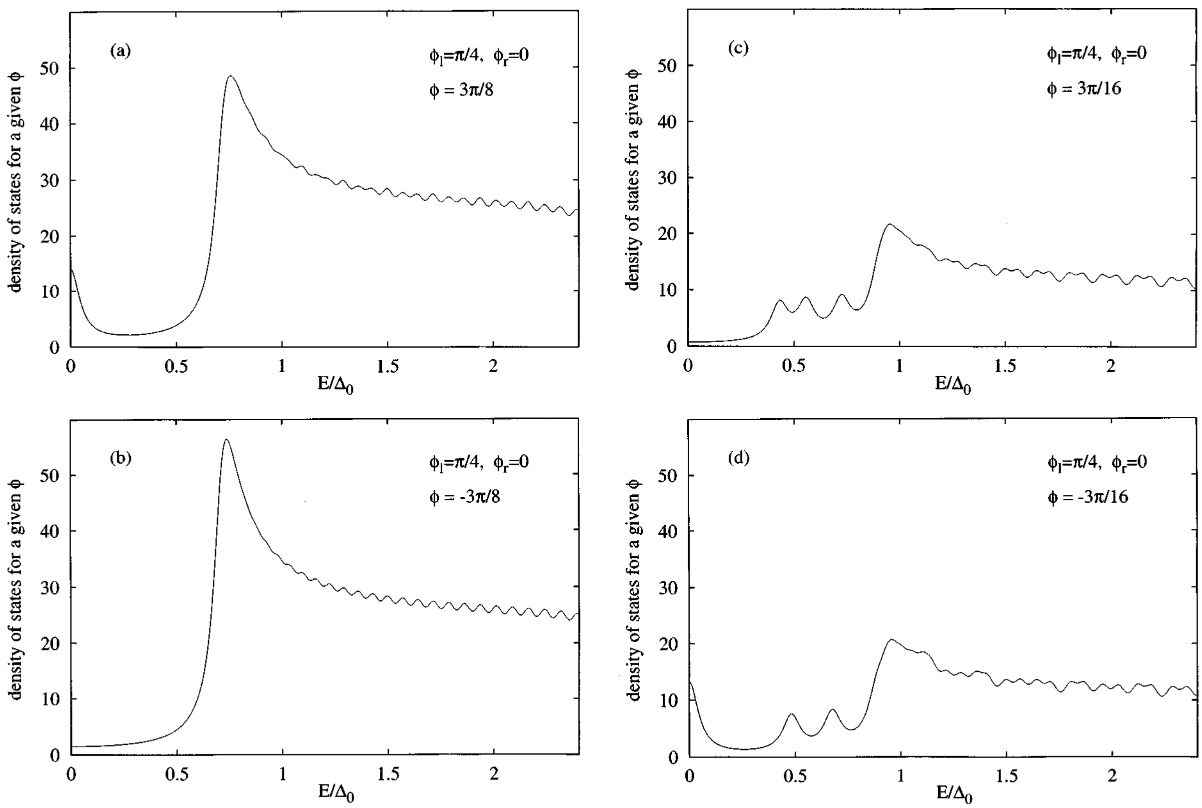

FIG. 3. Calculated (partial) density of states for a given ϕ. (a) $\phi=3\pi/8$; (b) $\phi=-3\pi/8$; (c) $\phi=3\pi/16$; (d) $\phi=-3\pi/16$.

fects of the broadening of the ZBCP, the reduction of its height, and the rising conductance due to the continuum states near $E=0$. (This ''disappearance temperature'' is not universal either.)

Figure 5 shows the corresponding results on the tunneling conductance for the case when the counterelectrode is a low-T_c s-wave SC. Its gap Δ_s is assumed to be equal to $0.10\Delta_0$ for all three temperatures considered. They therefore do not correspond to a fixed material for the counterelectrode, in which case its gap would change with temperature. Instead, these curves purport to show how a given gap of the counterelectrode exhibits itself in the tunneling conductance at different temperatures. We see that at $k_BT\ll\Delta_s$ the ZBCP is much taller than the corresponding peak at the same T for $\Delta_s=0$, but with a deep center dip to a range of nearly zero conductance, thus clearly exhibiting the gap of the counterelectrode. This is exactly the behavior observed experimentally by Geerk *et al.*,[3] for example, who used a moderate magnetic field to suppress the superconductivity in a Pb counterelectrode, without changing appreciably any of the other parameters of the system. (See in particular Fig. 2 in this reference.) As the temperature is raised the ZBCP becomes lower, and its center dip becomes shallower. This is also as observed by many experimenters. Even at $k_BT=\Delta_s(=0.10\Delta_0)$, when, as shown in Fig. 4, a normal counterelectrode at the same T already no longer sees a ZBCP, the low-T_c superconducting counterelectrode still

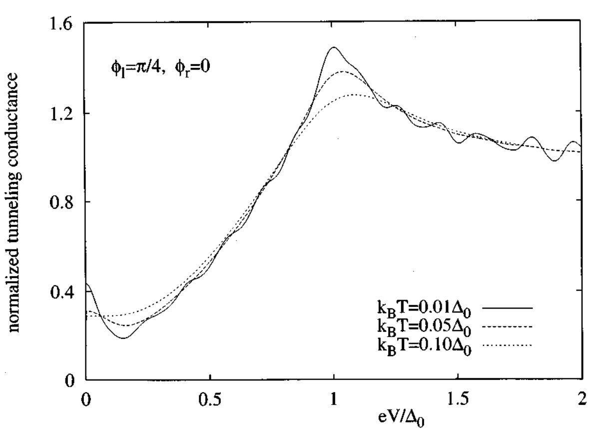

FIG. 4. Calculated tip-location-averaged tunneling conductance between a normal metal and a $d_{x_a^2-x_b^2}$-wave superconductor containing two grains, assuming $\phi_l=\pi/4$ and $\phi_r=0$, at three temperatures.

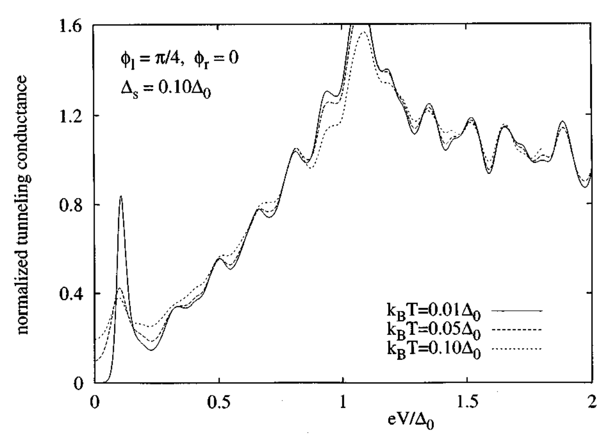

FIG. 5. Calculated tip-location-averaged tunneling conductance between a low-T_c superconductor (with a given gap $\Delta_s=0.10\Delta_0$) and a $d_{x_a^2-x_b^2}$-wave superconductor containing two grains, assuming $\phi_l=\pi/4$ and $\phi_r=0$, at three temperatures.

sees a small ZBCP with a small center dip. My understanding of these results is that the double-peaked density of states of a low-T_c superconducting counterelectrode can give a better resolution in resolving the structure in the density of states of the electrode. (The size quantization oscillations are stronger in these curves than in Fig. 4 for the same reason.) Figure 5 also shows that the width of the ZBCP is not visibly broadened as $k_B T/\Delta_0$ is increased from 0.01 to 0.10. (Recall that we have taken $\Gamma = 0.05\Delta_0$.) This sub-thermal temperature dependence is also consistent with observations,[18] at least qualitatively, but it is difficult to make quantitative comparisons at the present stage, due to the fact that when at least one electrode is inhomogeneous, different tunneling setups can measure very different convolutions of the quasiparticle density of states and wave functions of the two electrodes, and therefore one must know a lot of details about a particular tunneling experiment in such a case, before one can model it quantitatively. However, the subthermal temperature dependence of the width of the ZBCP is expected in the present framework since the distribution function inside a narrow peak in the density of states located at $E=0$ cannot change much with temperature.

Qualitatively, we can make another remark which should be helpful for understanding the very complex behavior of tunneling conductance of HTSC's. We first note that whenever a MIS is formed with momentum $(k_{x0},\mathbf{k}_\perp)$, it is formed by pulling half a state from the bottom of the positive-energy continuum, at energy $\min_{l,r}|\Delta_{l,r}(k_{x0},\mathbf{k}_\perp)|$, and half a state from the top of the negative-energy continuum, at energy $-\min_{l,r}|\Delta_{l,r}(k_{x0},\mathbf{k}_\perp)|$, as is clearly shown in Figs. 3(a)–3(d). The gap $\min_{l,r}|\Delta_{l,r}(k_{x0},\mathbf{k}_\perp)|$ is necessarily smaller than the maximum gap Δ_0, but larger than zero. Thus if the system has formed a large number of MIS's at various ϕ_l, ϕ_r, and ϕ, then the part of the density of states resulting from the continuum states can be substantially suppressed in the regions between 0 and $\pm\Delta_0$, perhaps changing it from V shaped, like that predicted for a bulk single-crystal d-wave SC, toward U shaped, and therefore making it look closer to that of an s-wave superconductor. Then if the tunneling probe is so localized as to not see the MIS's contributions, it could then see a bulk density of states of the electrode that looks almost like that of an s-wave SC, when the electrode is actually a d-wave SC. This could explain the puzzle that some tunneling experiments (using normal-metal probes) performed on some HTSC samples have shown a nearly-s-wave-like density of states,[48] whereas other tunneling experiments performed on high-quality single-crystal HTSC samples clearly revealed a d-wave-like density of states,[49] and many other experimental results now support the conclusion that all hole-doped HT cuprate SC's are d-wave SC's.[50]

As for the magnetic-field effects, the following remarks can be made: Since the grain boundaries are inside a superconductor, the applied magnetic field may or may not be able to reach the MIS's localized near them due to possible screening. When it does not, of course, no magnetic-field effects can be observed. When it does, a Zeeman splitting of the ZBCP is expected. But the magnetic-field reaching the MIS's may be weaker than the applied field, and be temperature and/or field dependent, due to screening effects, or stronger, and be temperature and/or field dependent, due to concentration of the magnetic field in the regions of the sample where superconductivity is weaker, all depending on whether the magnetic field can penetrate into the sample or not. This might explain the very diverse magnetic-field effects observed, including the very strange g factor when the Zeeman splitting is observed. (The shifts of the ZBCP's away from zero sometimes observed may be due to the fact that the superconducting order parameter is not pure d-wave near some part of the sample boundaries due to some surface effects. The results found in Ref. 31 indicate that in such a case the midgap states can shift away from zero energy.) A possible test of this explanation of the magnetic-field effect is to use a thick film sample with many aligned grain boundaries, all perpendicular to the film and parallel to each other, and then to see whether the observed magnetic-field effects would depend on the relative orientation of the applied field and the grain boundaries. Penetration should be easy with the field applied parallel to the grain boundaries, and Zeeman splitting should be observed in this case. Penetration should be confined to the surface only, if the field is applied perpendicular to the grain boundaries, and at most a weak broadening of the ZBCP should be observed if the film is thick in comparison with the penetration depth. (No directional dependence should be observed if the film thickness is in the opposite limit.)

Another direct test of the present explanation of the observed ZBCP's is to use one of those bi- or tricrystal samples with known locations for grain boundaries, and then to use a scanning tunneling probe to see a ZBCP appear and then disappear when one scans across a grain boundary in zero field. In situations where an applied magnetic field can penetrate into the sample and reach the MIS's, the predictions made in Ref. 30 concerning the existence of a saturation magnetic moment in association with the MSS's should also apply to the MIS's, and a direct superconducting quantum interference device measurement of this saturation moment, or possibly a magneto-optic probe of it, might provide another test of the existence of the MIS's. For several other related predictions, see the discussions in Ref. 30, which apply to MIS's as well as to MSS's, if only the applied magnetic field can reach the MIS's.

Summary: (i) It has been shown here that a sizable area density of midgap quasiparticle bound states exist at almost all interfaces between different $d_{x_a^2-x_b^2}$-wave superconducting grains of different principal-axes orientations, and they all have zero energy in the WKBJ approximation (which neglects Δ_0^2/ε_F with respect to unity), in spite of their different transverse momenta along the interface; (ii) These midgap interface states (MIS's), perhaps sometimes together with the midgap surface states (MSS's) predicted by the author previously,[30,31] are very likely responsible for most, if not all, of the zero-bias (tunneling) conductance peaks (ZBCP's) that have been ubiquitously observed in high-T_c superconductors (HTSC's); (iii) A model study presented here shows that the MIS's can give rise to a ZBCP in tunneling along any direction including the a and c directions; (iv) If the counterelectrode is a low-T_c s-wave SC, its gap is shown to appear as a center dip in the ZBCP (if broadened by surface, interface, and/or bulk scatterings), as observed; (v) The width of the calculated ZBCP shows a subthermal temperature dependence, in qualitative agreement with observations; (vi) The calculated ZBCP at a given temperature is much taller if the counterelectrode is a low-T_c s-wave SC, than if it is a normal metal, assuming that all other parameters have the same values, in good agreement with experimental observations. (vii) The very complex magnetic-field effects observed might also find explanations within this framework; (viii) Some predictions have been made for testing this explanation of the observed ZBCPs.

In this work we have assumed that there is no additional overall phase difference ϕ across an interface other than 0 or π (which can be absorbed into a redefinition of the a and b axes). The question whether frustration effects might cause $\phi \neq 0$ or π for most interfaces may be raised. The works of Yip[51] and Tanaka and Kashiwaya[44] can be cited to point out that ϕ may have an equilibrium value ϕ_0 other than 0 and π if t is sufficiently close to unity, and for some choices of the grain orientations on the two sides of the interface, without the help of frustration. Whereas the arguments in these latter works appeared quite elegant, they are nevertheless, in my view, flawed. In Yip's argument, when ϕ_0 is not equal to 0 or π, electrons in one part of the Fermi surface will be steadily pumped from one side of the interface into the other side, whereas electrons in the remaining part of the Fermi surface will be steadily pumped in the opposite direction, so on either side of the interface, a relaxation process seems to be needed to move electrons from the oversupplied part of the Fermi surface back to the depleted part. Can this be a nondissipative process? Until the physics involved in this process can be made more clear, and the predictions based =on it directly confirmed experimentally, this prediction of Yip and Tanaka and Kashiwaya should not yet be taken as fact, and used to reject other ideas. As a matter of fact, according to them, this prediction of ϕ_0 not equal to 0 or π can occur only in a certain temperature range, for special combinations of the grain orientations on the two sides of the interface, and with high transmissivity across the interface. Thus it should not be able to completely prevent the occurrence of the MIS's, but it could reduce their number.

As for the frustration effect, it can indeed induce the existence of half-quantum flux lines at the line joints of an *odd* number of π junctions,[52] with a localized distribution of magnetic induction at each such line joint, extending a distance of the order of the Josephson penetration depth into each interface meeting there,[53] but if the interfaces are all much wider than this penetration depth in the directions away from such line joints, then most part of them will remain with ϕ equal to 0 or π. Quantitatively the presence of these spontaneously generated half-quantum fluxes will surely modify the $I(V)$ and $G(V)$ characteristics, including the height of the ZBCP, but I doubt that it can completely nullify the mechanism proposed here for the generation of ZBCP's, or even to shift them to finite energy, especially since only roughly half of the line joints can be frustrated, if the grain orientations are random. I believe the fact that ZBCP's are ubiquitously observed without such a shift supports my view.

Recently several experimental and theoretical works have become known to the author, which can shed additional light on this subject: On the experimental side, unambiguous ZBCP's have been observed on grain-boundary junctions of Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, and La-Sr-Cu-O,[54] but were still interpreted in terms of spin-flip and Kondo-type scatterings. ZBCP's were also clearly observed on {110} surfaces of single crystals of Y-Ba-Cu-O using low-temperature STM;[55] on high-quality (103)-oriented Y-Ba-Cu-O films using Pb counterelectrodes;[56] and in Pb/Bi-Sr-Ca-Cu-O single crystal ab-plane planar junctions;[57] all interpreted in terms of the MSS's. When a densely-packed, 1, 12-diaminododecane monolayer was spontaneously adsorbed on the (103)-oriented Y-Ba-Cu-O film, and probed with a Cu counterelectrode, the ZBCP was found to split in zero magnetic field below ~7 K,[58] which is interpreted in terms of the MSS's split by a spontaneous time-reversal-symmetry breaking at the surface due to the induction of a subdominant order parameter at the Y-Ba-Cu-O surface. For a bulk order parameter breaking time-reversal symmetry, Yang and I have previously shown[31] that such a splitting should occur. Theories showing that it can also occur spontaneously at a non-{100} surface have been recently advanced. (See below.)

On the theoretical side, surface roughness effects on the MSS's have been analyzed by Matsumoto and Shiba,[32] and by Yamada *et al.*[59] The existence of the MIS's has been shown to alter the formula for the critical current of a d-wave-superconductor Josephson junction and its temperature dependence.[60] The possibility of the coexistence of order parameters of different symmetries near a non-{100} surface at sufficiently low temperatures were raised, through a self-consistent study of the gap equation,[61,62] which can explain the observed splitting of the ZBCP noted in the previous paragraph. Also, tunneling $I(V)$ characteristics between two d-wave superconductors were studied, taking properly into account the midgap states contributions;[63] corrections to the MSS energies were found when deviation of the Fermi surface from a circular symmetry in the ab plane is taken into account.[64]

This work was partially supported by the Texas Center for Superconductivity at the University of Houston.

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[32] This order analysis of the correction to the WKBJ approximation is based on the approximation that the Fermi surface has a circular symmetry in the ab plane. If one goes beyond this approximation, and allows the Fermi surface to only have a square or lower symmetry (for high T_c materials with a tetragonal or lower symmetry, respectively), then the correction can be nominally of the order of Δ_0, but is still small, if the deviation from a circular Fermi surface in the ab plane is small. [cf., M. Matsumoto and H. Shiba J. Phys. Soc. Jpn. **64**, 1703 (1995).] To understand this point, we note that the WKBJ approximation is valid only if the Hamiltonian does not have a discontinuity of the order of ε_F (but it can have a discontinuity of the order of Δ_0). For surface states on a non-$\{110\}$ surface, when the Fermi surface is not circular, such a large discontinuity becomes obvious, if one views the surface state with the generalized image method discussed in Ref. 30. In fact, shift of the surface state energy away from midgap by an amount of the order of Δ_0 can even occur on the $\{110\}$ surface, if the Fermi surface has lower than square symmetry in the ab plane.

[33] (a) Y. Tanaka and S. Kashiwaya, Phys. Rev. Lett. **74**, 3451 (1995); (b) S. Kashiwaya, Y. Tanaka, M. Koyanagi, H. Takashima, and K. Kajimura, Phys. Rev. B **51**, 1350 (1995); and other references by these authors.

[34] J.-H. Xu, J. H. Miller, and C. S. Ting, Phys. Rev. B **53**, 3604 (1996).

[35] G. E. Blonder, M. Tinkham, and T. M. Klapwidjk, Phys. Rev. B **25**, 4515 (1982).

[36] Q. Chen and K.-W. Ng, Phys. Rev. B **45**, 2569 (1992).

[37] A preliminary report of this idea has been made in C.-R. Hu, Bull. Am. Phys. Soc. **40**, 789 (1995).

[38] Self-consistent investigations of the position dependence of a d-wave order parameter near a non-$\{100\}$-surface have been performed by several groups [see, for example, Y. Nagato and K. Nagai, Phys. Rev. B **51**, 16 254 (1995); L. J. Buchholtz, M. Palumbo, and D. Rainer, J. Low Temp. Phys. **101**, 1079 (1995); **101**, 1099 (1995)], indicating a suppression of the order parameter at a non-$\{100\}$ surface. It is worth noting that such suppressions of the order parameter are due to the existence of the MSS's, which is always accompanied by a reduction of the local density of states at nonzero energies below and near the maximum gap.

[39] J. Bardeen, Phys. Rev. Lett. **6**, 57 (1961); **9**, 147 (1962); M. H. Cohen, L. M. Falicov, and J. C. Phillips, *ibid.* **8**, 316 (1963); B. D. Josephson, Phys. Lett. **1**, 251 (1962).

[40] Preliminary reports of this calculation have been made in (i) C.-R. Hu, Bull. Am. Phys. Soc. **41**, 361 (1996); (ii) C.-R. Hu, *Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials and Applications,* Houston, Texas, (World Scientific, Singapore, 1996), p. 551.

[41] There appeared a misunderstanding in the literature on the content of Ref. 30 as to whether the normal-metal layer is required or not (cf., for example, Ref. 33). Actually, Ref. 30 has stated clearly that the normal-metal layer can be present or absent. The existence of the MS's require only a suitable surface, and that the SC is d wave or some other non-s-wave. Another confusion is whether Ref. 30 proposed a possibility to analyze the tunneling spectra in HTSC's by the proximity effect. It did not propose that, since the proximity effect is not essential for the occurrence of the MSS's. It should be stressed that the midgap states are not merely ''Andreev bound states,'' since the latter can also occur at nonzero energies in the WKBJ approximation, but then they would not have a topological origin, and would not depend only on the sign part of the gap function. In addition, the main conclusion in Ref. 33 that the midgap states occurring at a non-$\{100\}$ interface between a $d_{x^2-y^2}$-wave superconductor and *an insulator* can give rise to a ZBCP in quasiparticle tunneling is in agreement with the earlier results of Ref. 30, although the present author does not find that the explanation of the observed ZBCP's can be made in terms of such MSS's alone. In fact, as noted already in Ref. 30, midgap states, being topological in nature, can also occur in many other situations besides a non-$\{n0m\}$ surface. The MIS's discussed here are just another relatively more important realization of that general statement.

[42] M. F. Atiya, V. K. Patodi, and I. M. Singer, Proc. Cambridge Philos. Soc. **77**, 43 (1975).

[43] In the WKBJ approximation, this wave function has a slowly varying envelope which is a simple exponential decay on either side of the interface in the scale of the coherence length, with an abrupt change of slope at the interface. This discontinuity of slope would be removed if the calculation is carried out beyond this approximation, but the change would only occur within roughly a Fermi wavelength on either side of the interface, and would be extremely small.

[44] Actual interfaces most likely have $0<t<1$, but I can assume $t=1$ here, for the only goal of this calculation is to prove in principle that MIS's can give rise to ZBCP's in quasiparticle tunneling along any axis. I have shown already that the area density of MIS's, with energies showing no shift away from midgap in the WKBJ approximation, is finite for all $0<t<1$, albeit lower than that for $t=1$ by a finite fraction. Thus their difference is important only for a quantitative account of the heights of the observed ZBCP's, which is very difficult anyway, since such heights would depend on the total interface area in the sample, as well as the precise orientations of all the grains. Y. Tanaka and S. Kashiwaya, in a theory of the Josephson effect in d-wave superconductors [Phys. Rev. B **53**, R11 957 (1996)] have calculated an F function at imaginary frequencies for arbitrary t. This F function, if analytically continued to real frequency, would contain all information about the MIS's. Whereas they did realize the importance of the signs of the products $\Delta_L(\theta_+)\Delta_L(\theta_-)$, $\Delta_R(\theta_+)\Delta_R(\theta_-)$, and $\Delta_L(\theta_+)\Delta_R(\theta_+)$ in giving rise to MIS's, they obtained the precise combinations of these sign conditions for the existence of the MIS's only for $\alpha=-\beta$, corresponding to $\phi_l=-\phi_r$ in our notation, which is not satisfied in most grain boundaries. If all three products have to be negative for the existence of the MIS's for general values of α and β, most grain boundaries would not have MIS's. So it is not apparent from their work how *easily* MIS's can be obtained, which is crucial for the present argument.

[45] V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. **10**, 486 (1963).

[46] P. G. de Gennes, *Superconductivity of Metals and Alloys* (transl. by P. A. Pincus) (Benjamin, New York, 1966), p. 140.

[47] We have neglected a possible position dependence of the order parameter near the interface, which should exist if the order parameter is solved self-consistently, as has been done near a non-{100} surface by several groups (Ref. 38). This is not a serious neglect here, however, if only the order parameter remains to be pure d-wave everywhere and with a constant phase, since our only goal here is to explain the origin of the ZBCP's in terms of the MIS's, whose existence is *topological* (in the WKBJ approximation), and is therefore independent of any such x dependence of the order parameter. It should be stressed that if our goal were to obtain a quantitative explanation of the whole measured $I(V)$ or $G(V)$ curves, then this neglect would be a serious mistake.

[48] See, for example, Ref. 24.

[49] See, for example, Refs. 25 and 26.

[50] See, for example, the following recent review articles: (i) R. C. Dynes, Solid State Commun. **92**, 53 (1994); (ii) J. R. Schrieffer, *ibid.* **92**, 129 (1994); (iii) D. J. Scalapino, Phys. Rep. **250**, 329 (1995).

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[64] M. E. Zhitomirsky, M. B. Walker, and P. Pairor, Bull. Am. Phys. Soc. **42**, 606 (1997).