Arguments and evidence for a node-containing anisotropic *s*-wave gap form in the cuprate superconductors

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Although not widely recognized, there is much evidence suggesting that the superconducting cuprates have an anisotropic *s*-wave type of gap form, a form which is usually so highly anisotropic that it contains gap nodes and regions of opposite sign. This evidence is presented and reviewed. This evidence motivates a search for *s*-wave explanations of the many experiments which seem to require the *d*-wave gap form. *s*- wave explanations are presented here for three of the phase-sensitive Josephson tunnelling experiments, experiments which are widely regarded as some of the most convincing evidence for the x^2-y^2 *d*-wave gap form. A key feature in all of these explanations is orthorhombicity. Although the evidence and reinterpretations of phase-sensitive experiments clearly improve the credibility of the anisotropic-*s* gap form, some important issues are still unsettled and the question of the gap form remains open. An experimental test is proposed.

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I. INTRODUCTION

It is well known that there is much experimental evidence favoring the x^2-y^2 *d*-wave gap form for the hole-doped cuprate superconductors. This evidence has been extensively reviewed,[1] and the majority of these reviews have concluded that the overall evidence is overwhelmingly in favor of this gap form. There is consequently a widespread belief that the *d*-wave gap form is now firmly established. Nevertheless, there is also a lot of evidence suggesting that the cuprates should instead have an *s*-like gap form, a form which is highly anisotropic and which typically has gap nodes and regions of opposite sign. This evidence is generally much less well known, and in our opinion this evidence has been underrated and deserves more serious consideration. Our first goal in this paper is to present and review this evidence. (By *d*-wave or *s*-like, we mean that under a 90° rotation of the tetragonal CuO_2 plane, the gap does or does not change sign, respectively. It has long been known that this *s*-like symmetry—tetragonal A_{1g} symmetry—does not rule out gap nodes.[2]) We must acknowledge that much of our motivation here is to defend a valence-fluctuation pairing mechanism which leads to such an anisotropic-*s* gap form.[3–5] But the gap-form issue has an obvious and fundamental importance which is separate from the question of the specific mechanism. The focus of this paper is on experimental evidence and its interpretation.

In spite of this experimental orientation, a theoretical comment is needed at the outset. This is to counter the popular argument which claims that a large (strongly repulsive) Hubbard *U* interaction must make the pair interaction too repulsive to allow pairing in the *s*-symmetry channel. We must point out that this argument is not conclusive. This ignores the effect of the strong correlations induced by the *U* interaction and also the possible beneficial effect of a strong radial *k* dependence in the pair interaction.[3,5]

There is another reason for presenting this *s*-wave evidence. This is to demonstrate that in spite of the abundance of apparent *d*-wave evidence and the widespread consensus about this, it is nevertheless still reasonable to search for *s*-wave explanations of these data. It is significant here that although some of the *d*-wave evidence seems quite convincing by itself, this is also true for some of the *s*-wave evidence. This situation reveals that these experiments cannot all be taken at face value, and there is still a need for further critical examination. Having thus motivated such a search, we present several *s*-wave explanations we have found. We shall demonstrate that some of the apparently most direct and convincing *d*-wave evidence is at least potentially also consistent with the anisotropic-*s* gap form. This is evidence from three experiments involving phase-sensitive Josephson tunneling: (i) *c*-axis tunneling through a planar junction which straddles a single twin boundary of YBCO ($YBa_2Cu_3O_{7-\delta}$) (Kouznetsov *et al.*[6]), (ii) the Maryland corner superconducting quantum interference device (SQUID) experiment (Mathai *et al.*[7]), and (iii) the high-symmetry *a*-*b*-plane tunneling experiment with a multicrystal of T1-2201 ($Tl_2Ba_2CuO_{6+\delta}$) (Tsuei *et al.*[8]). The key to all of these explanations is orthorhombicity in the crystal structure. These arguments do not disprove the *d*-wave gap form, but they definitely improve the credibility of the anisotropic-*s* form as a reasonable alternative. To distinguish between these possible *d* and *s* forms a specific experimental test is proposed, a test which should be quite feasible.

The type of gap form considered here is

$$\Delta(\theta) \propto (1 + r\cos 4\theta). \tag{1}$$

The angle θ parametrizes the position on the "Fermi circle" as viewed from the enclosed (π,π) point, the angle being measured from a planar Cu-O bond direction. This gap is maximum along the Cu-O bond direction, in agreement with the x^2-y^2 *d*-wave gap form. Assuming $r>1$, this Δ has a pair of nodes near each diagonal or (q,q) direction, for a total of eight gap nodes, and there is also a subsidiary or secondary maximum of negative sign at each diagonal point on the Fermi circle. We do not insist on a precise $\cos 4\theta$ angle dependence. Higher harmonics of the form $\cos 4n\theta$ (n = integer>1) may also contribute,[2] but we assume that they

do not change the gross features. This gap form can be described as ''$s+g$,'' with s being the isotropic component and g labeling the $l=4$ component. Some investigators may call this an ''extended-s'' form, but we avoid that term because this is usually attached to a precise form which is too restrictive for the present context. We shall generally call this the eight-node gap form or the anisotropic-s-wave gap form.

Two experimental consequences follow immediately from this gap form. The first is a subsidiary or ''within the gap'' peak in the one-electron tunneling state density.[2] Such a peak has been observed in several cuprates (as discussed in Sec. II), and furthermore rather indistinct evidence for this feature can often be seen. A second consequence is that the nodes and subsidiary maximum can be removed by sufficient ''dirt'' or disorder in the sample, since disorder tends to angle-average the gap function. More subtle consequences of this gap form are presented in the detailed discussion.

A majority of the experimental studies which have been claimed as evidence for the d-wave gap form are in the *nonphase-sensitive* category, i.e., they do not directly compare the phase of the gap on different parts of the Fermi surface. (We refer here to the many k-integrated or non-k-specific experiments, as contrasted to angle-resolved photoemission. The latter is discussed in the concluding section.) These nonphase-sensitive experiments have in many cases been analyzed in terms of a conventional *isotropic* s-wave gap form, in addition to and as a contrast to analysis in terms of the x^2-y^2 d-wave gap form. In such cases the d-wave assumption has nearly always provided a better fit to the data. It is important here to recognize that the majority of these experiments are really just providing evidence for gap nodes and are *not* specifically indicating a d-wave gap form. The aniso-s gap form (1) can also provide gap nodes if the anisotropy is strong enough, as has long been recognized,[2] but this possibility has unfortunately been very often overlooked. (Even in the relatively few cases where an anisotropic s-wave form has been used in modeling, the possibility of nodes and negative or opposite-sign regions in the gap has typically not been considered.) Thus, with faulty logic, the finding of evidence for gap nodes has often been claimed as evidence for a d-wave gap form. It would be helpful to have more of these gap-node-evidence experiments analyzed also by means of the present gap form. Any such experiments with sufficient resolution to distinguish between these node-containing gap forms would of course be interesting and significant. In Sec. II we argue that some of the conventional tunneling experiments do accomplish this, and there are also some further examples of this class of data which appear to favor the eight-node gap form.[9] A recent analysis of the full temperature dependence of London penetration depth data (for a high-quality fully oxygenated YBCO specimen) has found much better agreement with this eight-node form than for the usual d-wave gap form, and likewise for an analysis of nonlinear Meissner effect data.[10]

In contrast to the data just mentioned, there has been common agreement that the most definitive evidence for the gap form should be *phase-sensitive* data, which can be obtained from Josephson tunneling in a variety of special geometries. We focus on examples of this phase-sensitive data in Secs. III–V. There are of course many other types of data which have been claimed as support for the d-wave gap form, and we shall comment on some of these in the concluding section.

Several other overviews of the s-vs-d issue also argue in favor of an s-wave gap form.[11] These papers present much further information which we do not attempt to cover. Their perspective is somewhat different from the present paper, being rather more skeptical of the validity of the data itself, for the main examples of the apparent d-wave evidence. Here we are more inclined to accept this data, but are instead providing alternative interpretations. Another aspect of our orientation is that we are assuming the gap form to be basically time-reversal invariant, and assuming that any violation of this invariance (e.g., by magnetic impurities) can be safely neglected. This means that we only consider gap forms which are real valued. Evidence for a real-valued (time-reversal invariant) gap form was found in Ref. 7. Although we are not considering the pseudogap here, a comment about this may also be appropriate. We have argued elsewhere (Ref. 5, Sec. 6.4) that the pseudogap phenomena are mostly consequences of the microscopic phase separation observed as ''stripes.'' We are also neglecting this phase separation.

Following the initial submission of this paper, a very significant paper on s vs d has appeared.[10] This presents many arguments for the same type of gap form, Eq. (1) (described there as ''extended s wave''). This work also presents several successful quantitative analyses, including the above-mentioned study of the penetration depth and of its absolute slope $d\lambda_{ab}/dT$ near $T=0$ and of nonlinear Meissner effect data. There are also some significant differences: the attribution of apparent d-wave Josephson tunneling evidence to a difference between surface and bulk gap forms, and a different selection of tunneling features to identify the main and subsidiary gap maxima in YBCO. The views about low I_cR_n values in c-axis tunneling data are also different.

Of course, many other alternatives to the conventional x^2-y^2 d-wave gap form have been suggested. Perhaps the most relevant of these for the present context are (a) the idea of a pair of similar but not identical anisotropic s-like gap forms for the bonding and antibonding bands of a bilayer cuprate model system, with opposite signs for the gaps of these two bands,[12–16] and (b) a related idea which assumes a major role for the gap on the chains of YBCO.[16,17] The former efforts[12–16] were motivated partly by the fact that most of the data concerning cuprate gap symmetry have come from the bilayer materials YBCO and Bi-2212 ($Bi_2Ba_2CaCu_2O_{8+\delta}$), and they were also motivated partly by the so-called π resonance, the resonance at or near 41 meV and at (π,π,π) in the Brillouin zone, found below T_c in inelastic neutron scattering for these same two bilayer materials.[18] It has been argued[15] that this type of gap form (and/or the presence of a major chain contribution with opposite sign[16,17]) can explain the π phase difference found in corner-junction and corner-SQUID tunnelling experiments, the phase difference which is commonly viewed as the signature of the d-wave gap form. Although the lack of gap

nodes weighs against this particular proposal, this is not an essential limitation; the pair of nodeless gap functions could be replaced by eight-node anisotropic-*s* gaps. The essential difference then comes down to the question of whether the bilayer aspect (and/or the chain gap function) is required in order to explain the π phase difference found in the corner tunneling experiments. A related question is whether the pair interaction provides sufficient coupling between quasiparticle pairs on neighboring planes or chains. Our present assumption is that such an interplane (or plane-chain) pair interaction is not significant, and therefore the opposite sign for the gaps of the bonding and antibonding bands does not occur.[19] Whether this can be reconciled with the π resonance remains to be seen (we comment on this in Sec. III). We also assume that there is no major role for the pairing on chains. Many consequences have been suggested for the chain pairing (chain gap function),[20] and significant chain contributions have been demonstrated for the superfluid density[21] and for the specific heat jump.[22] It has been shown, however, that the chain contributions in these experiments can be explained by a proximity effect model, a model without any plane-chain or intrachain pair interaction.[23] The general similarity of monolayer and bilayer cuprates also argues against any major role for plane-plane or plane-chain pair interactions. (The cuprate T_c systematics has been explained in Ref. 4 without a significant interplane pair interaction.)

We also examine the gap-form evidence for *electron-doped* cuprates. This likewise indicates an aniso-*s* gap form, consistent with the previous general concensus, although recent evidence indicates stronger gap anisotropy and sometimes the presence of gap nodes.

In Sec. II we summarize and review the main evidence suggesting an anisotropic-*s* gap form in the hole-doped cuprates. Section III provides anisotropic-*s*-wave explanations for two of the phase-sensitive Josephson tunneling experiments: *c*-axis tunneling through a planar junction which straddles a single YBCO twin boundary[6] and the Maryland corner-SQUID experiment.[7] Section IV describes an experimental test which can distinguish between the *d*-wave and anisotropic-*s*-wave interpretations of these two experiments, and Sec. V shows that the high-symmetry *a*-*b*-plane tunneling experiment with a multicrystal of Tl-2201 (Ref. 8) is not conclusive. Section VI discusses the gap-form evidence for electron-doped cuprates. Concluding remarks are in Sec. VII.

II. EVIDENCE SUGGESTING AN ANISOTROPIC-*s* GAP FORM

We now review the current state of evidence suggesting a strongly anisotropic *s*-like gap form for the hole-doped cuprates. We focus first on the evidence we consider most sound and convincing (in the points numbered below), after which some other possible or at least claimed evidence is discussed. Some of the following arguments have originated from other investigators, some are our previous observations,[3,24] with updates, and there is also some new material.

(1) There are a number of hole-doped cuprates for which distinct inner-gap or within-the-gap features have been seen in tunneling (YBCO, Bi-2212, Bi-2223, Tl-2212, Tl-2223),[25,26] and there are also weak indications of such features in Tl-2201 and Hg-1212.[25] In some of the data for YBCO, Bi-2212, and Bi-2223, the tunneling conductance is actually nonmonotonic (i.e., hook-like) inside the gap, and in Bi-cuprate data the inner peak is sometimes amazingly sharp and prominent.[26] This nonmonotonic feature—i.e., the existence of a local maximum with energy less than the main peak energy—is just what is expected for the anisotropic-*s* case with nodes,[2] whereas this is inconsistent with the common *d*-wave form. (In view of the typical angle-averaging effect of dirt or disorder, we expect that the data which show the strongest or most sharp within-gap structure are the most intrinsic.) In YBCO the inner gap at 4–5 meV could conceivably be due to the CuO chains, but the fact that inner-gap features of nearly the same energy are found in Tl and Hg cuprates makes this chain interpretation unlikely. A curious feature of these data is that the strong within-gap structure has been found mainly in experiments with the conventional planar geometry, i.e., with a macroscopic tunneling area. This structure is generally much weaker in STM (scanning tunneling microscope, i.e., vacuum tunneling) data, and the more recent focus on STM data has therefore tended to minimize this evidence. This dependence on tunneling geometry could be a consequence of the tunneling contributions from the planar oxygen $2p$ components of the band states.[27] Alternatively, this may be due simply to noise and loss of resolution resulting from inadequate stability of the STM tip position. (The STM data do generally look rather noisy.) The inner-gap peaks are especially prominent in some of the data for the bismuth cuprates,[26] and, in fact, broadened remnants of these features can be seen in much of the published tunneling data for Bi-2212. Although this latter aspect of Bi-2212 data is often rather obvious, this has generally been ignored.

(2) For several hole-doped cuprates there is conflicting evidence from ordinary (one-electron) tunneling, some of the conductance data appearing ''*s*-like'' (flat bottomed or U shaped inside the gap) and other data being ''*d*-like'' (V shaped, suggestive of gap nodes).[28,29] This inconsistency can be rationalized in terms of a disorder or other angle-averaging scattering source in some of the junctions. There is actually considerable evidence for this view,[29] which therefore supports the anisotropic-*s* picture. [Theoretical work has shown that surface roughness can also provide significant variability in the tunneling data for a *d*-wave gap, but in this case this variability apparently does not include a flat-bottomed ''*s*-like'' conductance form.[30] On the other hand, in point (7) below a U shape is shown to be explainable by a *d*-wave gap form when tunneling edgewise into the *a*-*b* planes in some directions.] An alternative possibility is that the cuprate surfaces in different *c*-axis junctions may consist of different chemical layers, e.g., a BiO layer versus a CuO_2 layer. [Such a variation of cleavage surface is uncommon in Bi-2212, as shown by the typical uniformity of its photoemission data (although counterexamples are shown in Ref. 30), but this variation may be more common in some other cuprates.] Having different types of surface layers becomes especially significant if some of these lead to surface or bar-

rier states, whose spectrum is generally different from the bulk spectrum.[31] But whether this difference can account for both ''*s*-like'' and ''*d*-like'' conductance plots is unclear.

(3) The rate of depression of T_c by impurity doping or radiation damage was found to be only about one-half of the minimum rate expected for a *d*-wave gap, in YBCO, when the amount of defect scattering is expressed in terms of the residual resistivity.[32,33] Consistent with this, another study found the T_c depression rate to be only one-third of what is expected for a *d*-wave gap.[34] These findings are consistent with an anisotropic-*s* gap, however, because in general this rate is proportional to the anisotropy parameter $[1-(\langle\Delta\rangle^2/\langle\Delta^2\rangle)]$, and for a highly anisotropic *s*-like gap this parameter can still be fairly large.[33] With gap nodes present, a factor of 1/3 is quite reasonable here.[33] A caveat here is the possible importance of anisotropic scattering by the defects. This has been shown to eliminate the *d*-wave discrepancies for both the Pr doping and the radiation damage data on YBCO (data of Ref. 32) if the anisotropic component of the scattering is strong enough and is suitably oriented with respect to the gap anisotropy.[35] But it is doubtful whether the conditions required here are realistic. On the other hand, this evidence against the *d*-wave form is strengthened by another consideration: In nearly all investigations of this type, it has been assumed that the *only* effect of the defects (impurities or radiation damage), if they are nonmagnetic, is to produce potential scattering which tends to angle-average the gap. This ignores the possibility that the defects may also be *directly degrading* the pair interaction, which is *a priori* quite plausible if the pair interaction comes at least partially from special electronic features involving orbital geometry and chemical bonding.[36,37] When this possibility is taken into account the likelihood of a genuine discrepancy from the *d*-wave prediction becomes even stronger. Also, if some such degradation is accepted, the upwards curvature seen in this data can be explained by an anisotropic-*s* gap form.[38]

(4) For YBCO there is a monotonic and strong increase in the isotope shift exponent α when T_c is degraded by doping, with α appearing to approach the BCS value (0.5) as $T_c \rightarrow 0$.[39] This is consistent with the expectation of some new or unconventional pairing mechanism in the cuprates, *provided* that this mechanism is acting together with the conventional phonon mechanism *in the same pairing symmetry channel* (*s*-wave-like symmetry).[40] It is significant here that the data show no sign of a discontinuity as a function of doping—the discontinuity that one would expect if there were a transition between *d*-wave and *s*-wave pairing.[39]

(5) In Raman scattering for highly overdoped Bi-2212 and Tl-2201, in the superconducting state, the energies of the electronic continuum peaks for the three symmetry channels (A_{1g}, B_{1g}, B_{2g}) are found to essentially coincide.[41] This is very different from the corresponding data for less hole doping. This channel-independence feature implies a fairly isotropic gap. (This feature has also been found for the electron-doped material $Nd_{2-x}Ce_xCuO_4$,[42] the cuprate for which there is much independent evidence of a nodeless and rather isotropic gap.[43]) Furthermore, for both compounds the apparent gap ratio $2\Delta/k_BT_c$ has declined considerably from its value at optimum doping. Both of these aspects suggest a strong reduction of the gap anisotropy by angle averaging due to scattering.[44] (The signal interpreted as Δ typically represents the *maximum* of the anisotropic gap, rather than its average, so that angle averaging should reduce this Δ. See the tunneling state densities plotted in Ref. 2.)

(6) Consistent with the previous point, angle-resolved photoemission spectroscopy (ARPES) data on highly overdoped Bi-2212 ($T_c = 60$ K) have shown clear evidence of a gap at the 45° or (q,q) position on the Fermi surface.[45] Besides showing a shift of the intensity midpoint, this data also presents an intensity peak below T_c. The latter is similar to the well-known peak at the Fermi surface near the *M* points [(1,0) points with respect to the Cu-O bond directions], and in further similarity there is also a slight dip beyond this (q,q) peak, at twice the binding energy of this peak. (This is data taken in the Γ-*Y* direction, parallel to the superlattice distortion, so there should be no problem here from the satellite bands generated by the superlattice.) This finite gap is just at the point where the x^2-y^2 gap form demands a gap node, independent of the orthorhombic distortion which is found in this material. (See Sec. V concerning the distortion in Bi-2212.)

(7) Data from Josephson tunneling perpendicular to the *c* axis, in a systematic series of YBCO bicrystal junctions with different mismatch angles, show better agreement with the eight-node aniso-*s* gap form than with the *d*-wave form.[46] Earlier data of this type also led to this conclusion.[47]

(8) There is also interesting data on one-electron tunneling edgewise into the *a*-*b* planes (perpendicular to the *c* axis) in Bi-2212.[48] Single crystals were cut with a razor blade to produce surfaces perpendicular to the [100] direction (the Cu-O bond direction), to the [110] or 45° direction, and also to a variety of angles between these directions, and a scanning tunneling microscope was used to obtain vacuum tunneling into each of these cut surfaces. Data were taken at many points on each surface, and, perhaps surprisingly, in each case a generally good consistency was found. (One might have expected a stepped break structure, giving a bimodal or more complex variation in the data.) The tunneling differential conductance (dI/dV) taken rather near the [100] direction (at 9° and at 19° from this direction) was strongly U shaped, indicating an essentially complete gap within the cone of *k* states which contribute strongly to these tunnelling currents. At larger angles (27°, 35°, and 38°) a kink appeared at zero voltage, and the data became progressively more V shaped, thus signaling a node within the cone of significant *k* states. This is qualitatively what one would expect for the x^2-y^2 *d*-wave gap form, and the authors interpreted their data as evidence for this gap form. But for the tunneling along the 45° or [110] direction, the data reverted back to a nearly U-shaped form, with only a weak kink (*V* component) at zero voltage. (In this respect it resembles the 27° data.) Taken at face value, this result suggests a local gap maximum at 45°, with a node roughly half way between 27° and 45°. These 45° data have another interesting feature as well. The peak in this dI/dV plot, which appears to represent a local gap maximum, has an energy which is about half as large as the corresponding peak energy at smaller angles

(e.g., in the 19° data). This ratio of 1/2 agrees with the location of the within-gap feature (sometimes a clear local maximum) found in the Bi-2212 data of point (1) above. (This gap energy ratio is material dependent; for YBCO, this ratio is about 0.25. See a comment on this ratio in Sec. V. Actually, for Bi-2212 we would expect the conductance spectra for tunneling into the *a* and *b* orthorhombic axes to be considerably different from each other, even without the effects of the superlattice; see Sec. V.) The authors interpret their 45° or [110] data differently, however. For these data they appeal to the analysis of Tanaka *et al.*[27] on the effects of surface oxygen atoms, which are assumed to provide the dominant amplitudes for the vacuum tunneling process. But this interpretation is *ad hoc*, because there is no justification for this use of the model of Tanaka *et al.* for the [110] (and also [100]) tunneling while ignoring this special role of oxygens for the tunneling at intermediate angles. (Also, the detailed atomic geometries of the various cut surfaces, in particular the locations or the absences of oxygens at these surfaces, are unknown.) The sharpness of the gap peak at 45°, the fact that its energy is far smaller than the corresponding peak energy at smaller angles, and the energy-ratio consistency with point (1) above all suggest that the interpretation of Tanaka *et al.* is not appropriate here and that the eight-node anisotropic-*s* gap is playing a significant role. This evidence clearly favors the aniso-*s* gap form.

(9) A recent experiment of *c*-axis Josephson tunneling through [001] twist grain boundaries in Bi-2212 has produced the remarkable result that the *critical current is essentially independent of the twist angle*.[49] The junctions in this experiment are of exceptionally high quality, and there is also extensive theoretical analysis.[50,51] A rather weak dependence on the twist angle might be expected for an anisotropic-*s* gap form, because of an effective angle averaging of the gap due to strong in-plane scattering of the electrons or quasiparticles. An obvious source for such strong scattering is the epitaxial mismatch at the *c*-axis grain boundary, but if this were the entire source, one might expect an increase of the critical current for small and especially for vanishing twist angle. Such an increase was not found. (This increase might not be observable, however. Even a miniscule twist could lead to major misregistry of opposing Cu rows over much of the junction area. On the other hand, their *c*-axis bonding tendency might confine this misregistry to limited regions of discommensuration. This issue is separate from the angle dependence of the transfer matrix elements considered in Ref. 51, which also contributed there to a steep drop at small twist angles, in the absence of angle averaging.) Another plausible source for strong in-plane quasiparticle scattering is a thermal effect,[52] which is possible here because these data were taken at the relatively high temperature of $0.9T_c$. (If this is correct, the gap nodes of our assumed eight-node gap form may not persist at temperatures near T_c.) The observed angle independence could therefore be consistent with the aniso-*s* gap form. But it is also quite possible that this angle independence is spurious and is instead the result of a runaway heating effect from the normal contacts for the applied current, since the junction areas were somewhat larger than the current contact areas.[53] This experiment should therefore be repeated with much smaller junction areas.[53] But in spite of this problem, this experiment is still very significant. The effect of such possible heating, as just described, is that the apparent I_c's should all be *lower bounds* for the corresponding true I_c's. The fact that the apparent I_c's (and therefore the true I_c's) remain large for twist angles at and near 45°, with no sign of a decrease in this region, is clearly inconsistent with the *d*-wave gap form, even after considering its orthorhombic distortion, because for a *d* wave the I_c must vanish somewhere in the vicinity of 45°. In fact, examination of the orthorhombic symmetry of Bi-2212 (which differs from that of YBCO; see Sec. V) shows that *any s*-wave component should be precisely orthogonal to the orthorhombically distorted x^2-y^2 form. This experiment therefore leads to the striking conclusion that Bi-2212 has *no* x^2-y^2 *gap component at all*.[50,51] (This result is also in sharp contrast to the case of *a*-*b*-plane bicrystal junctions, for YBCO, where with increasing mismatch angle there is an enormous falloff of the tunneling critical current by factors of $\sim 10^{-3}$–10^{-4} and likewise for the I_cR_n product, by $\sim 10^{-2}$.[54] Those rapid falloffs have, however, been explained by mechanisms that are basically independent of the gap symmetry.[55])

(10) A very recent analysis of the full temperature dependence of the London penetration depth, for a high-quality fully oxygenated YBCO sample, found excellent agreement with the eight-node gap form and clear disagreement with the common *d*-wave gap form.[10] This paper also demonstrated agreement with nonlinear Meissner effect data, for the eight-node gap form.

Most of the evidence just described has not been explained or has not even been considered in the context of the *d*-wave gap form.[56] However, the history of the *s*-vs-*d* controversy has had so many unexpected twists and turns that it would be dangerous to claim any one or any combination of the above arguments as being presently adequate to prove an *s*-wave gap form. We do not make such a claim. But it is certainly clear now that this evidence makes the eight-node *s*-wave gap form a very reasonable candidate which must be seriously considered. In Sec. IV we propose an experiment which would provide an important constraint.

Other data claimed as s-wave evidence. We now discuss several other cases of claimed *s*-wave evidence. These are examples which we consider to have lesser degrees of validity.

There are other *c*-axis Josephson tunneling data for Bi-2212, using more conventional contacts of lead with a silver buffer layer.[57] These junctions have very small I_cR_n products, however, whose average value is only 2.8 μV. (This is 10^{-3} times smaller than estimates of the Ambegaokar-Baratoff[58] type.) Another experiment has used Bi-2212/Au/Nb junctions[59] and produced essentially the same result. On the one hand, the existence of a nonvanishing tunneling current could be argued as evidence for an *s*-wave gap component and, thus, by an argument just mentioned in point (9), as evidence against the x^2-y^2 gap form. But this does not explain the extreme smallness of the I_cR_n's. On the other hand, there is a proposal to explain this in terms of a *d*-wave cuprate gap interacting with the small intrinsic anisotropy of the gap in Pb.[60] This could explain the

Nb result as well, since Nb also has some gap anisotropy, and this would also at least qualitatively explain the smallness of the I_cR_n's. However, the tunneling current formula used in that study has been shown to be incorrect,[51] and it is therefore not clear whether a realistic treatment of this type could explain the observed I_cR_n's. And in any event, the *c*-axis twist data in point (9) is a major obstacle for this proposal. It must also be noted that similarly small I_cR_n's have been observed in *c*-axis tunneling between lead and the electron-doped cuprate $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO),[61] where the gapless (and thus apparently *s*-wave) character of the gap is reasonably well established[43] (but see Sec. VI). The smallness here is especially surprising, and this too is unexplained. [This is in striking contrast to some corresponding data for YBCO, where the orthorhombic symmetry allows an *s* (isotropic) component to coexist with x^2-y^2. As discussed in Sec. III, the I_cR_n products can in this case be quite large, even large enough to suggest that the *s*-wave component may be the dominant one. Nevertheless, there are also tunneling data for YBCO thin films with Pb or Ag/Pb junctions where the observed I_cR_n's were only a few μV,[62] just as in the Bi-2212 and NCCO cases above, so it appears that the thin-film character may somehow be responsible for the just-mentioned NCCO result.] At least two possibilities for reducing I_cR_n have been suggested—the effect of heavy twinning[62] and the proximity effect of having a normal-metal layer next to the insulating barrier layer[63]—but so far there has not been a consistent resolution of the present problems. The significance of these *c*-axis tunneling experiments is therefore unclear.

The so-called π resonance, an inelastic neutron-scattering resonance at or near 41 meV which is found below T_c at the (π,π,π) point in bilayer cuprates (YBCO and Bi-2212),[18] has also led to the suggestion of an *s*-like gap function.[13] This was concluded from an analysis in terms of the conventional RPA (random phase approximation) description of a collective excitation, suitably modified below T_c by inclusion of coherence factors. A key assumption here was that the product $\Delta_k\Delta_{k+Q}$ must be negative for the dominant state pairs $k,k+Q$ near the Fermi surface, in order to obtain a coherence enhancement instead of a near-vanishing coherence factor. This negative-sign feature is commonly assumed in order to explain why this collective mode is found at the k_z zone boundary. In the scenario of Ref. 13 it was therefore deduced that the assumed nodeless *s*-wave gaps of the bonding band and the antibonding band must have opposite signs, consistent with Refs. 12 and 14–16. Adequacy of the *d*-wave gap for this purpose has also been claimed in Ref. 14. This latter conclusion is contrary to Ref. 13 where it was argued that this is inconsistent with the location of this resonance at the k_z zone boundary. But an alternative explanation has been offered for this zone boundary feature, in terms of a stronger nesting for the $k\rightarrow k+Q$ transitions which are interband (bonding band to antibonding band) transitions.[64] This weakens the *s*-wave conclusion of Ref. 13, but it also allows the possibility that the present aniso-*s* gap form, with gap nodes and *without* a sign change between the bonding and antibonding bands, may somehow be consistent with the observed π resonance. The π resonance data and theory are therefore presently inconclusive about the gap form.

There is also a Raman-scattering study of Hg-1223 which claimed to strongly support the eight-node anisotropic-*s* gap form.[65] Two types of evidence were presented. One is a prominent linear-in-ω behavior in the B_{1g} spectrum. The other is a data fit of the peak regions of the B_{1g} and A_{1g} spectra, in which their peak energies were identified with the positive and negative extrema, respectively, of the eight-node gap form. This paper also argued for an energy-magnitude connection between these Raman peaks and features in one-electron tunneling data, for several cuprate materials. But a more recent work from the same group, with more strongly underdoped Hg-1223, showed data of much more conventional form.[66] This latter work therefore concluded that the gap probably has the conventional *d*-wave form. Another work has analyzed the former (Ref. 65) Hg-1223 data in terms of a $d+s$ gap form.[67] Although the data fit is better in some respects, the overall quality of the fit is, in our opinion, not as good as in Ref. 65. [In this context we want to mention a proposal made in Ref. 5 (Sec. 6.3) to interpret the typically rather large difference in the energies of the maxima in the A_{1g} and B_{1g} Raman spectra. It was argued there that the higher energy of the B_{1g} maximum (and part of its breadth as well) is due to a strong but unresolved contribution from the van Hove singularity, which has a finite energy separation from the Fermi energy. (As explained in Ref. 5, the theory of Ref. 3 implies a strong enhancement of the van Hove contribution.) A corrollary is that the extremely large values of the gap ratio $2\Delta/k_BT_c$, which have been deduced from B_{1g} spectra in strongly underdoped samples, are partly spurious.]

There is other evidence which appeared to support an *s*-wave gap form, but which was later found to be invalid for this purpose. This is a Josephson tunneling experiment involving a misoriented hexagonal grain within a thin-film epitaxial crystal of YBCO, where the effect of successively destroying the six junctions along the sides of this hexagon was measured.[68] The problem for this experiment is that the length scale for the individual tunneling segments (hexagon sides) was much larger than the Josephson penetration length, so that spontaneous flux could be generated at the segment ends (the hexagon corners).[69] This flux could therefore effectively compensate for any sign differences in the Josephson couplings of the various tunneling segments, so that a *d*-wave gap form could produce nearly the same critical-current data as an *s*-wave form.

III. CORNER-JUNCTION TUNNELING GEOMETRY

Most of the phase-sensitive Josephson tunneling experiments which seem to demonstrate the *d*-wave gap form have been done with YBCO, a material which is obviously orthorhombic because of its CuO chains. The *electronic* orthorhombicity of this material is known to be quite strong.[70] The distortion of the gap form by this orthorhombicity is commonly described by the addition of an *isotropic s*-wave component to the presumed main x^2-y^2 *d*-wave component: thus, in shorthand notation ''d''$\rightarrow$''$d+s$,'' where this *s* component is subsidiary.

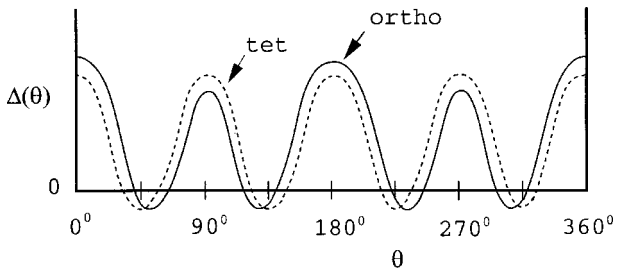

FIG. 1. The eight-node "$s+g$" gap form for a CuO_2 plane. Dashed line: undistorted tetragonal case. Solid line: orthorhombic case for YBCO. Pair k vectors at the Fermi surface are parametrized by θ, their angle position as viewed from (π,π), the center of the holelike Fermi surface.

In contrast, what we are describing as the anisotropic-s gap form, for an ideal tetragonal CuO_2 plane, is "$s+g$," where this s is an isotropic component and g means an $l=4$ (here $\cos 4\theta$) component. With a sufficiently large g component this gap form has eight nodes,[2] as shown by the dashed line in Fig. 1. In common with the usual d-wave form, experiment suggests and the valence-fluctuation theory[3] predicts that this gap is largest along the Cu-O bond directions ($\theta=0°, 90°, 180°, 270°$). [Here θ is an angle parametrizing the k states on the Fermi surface, as viewed from (π, π), the center of the holelike Fermi surface.] The effect of the orthorhombicity in YBCO is now described by adding a *subsidiary* x^2-y^2 d-wave component to produce the form shown by the solid line in Fig. 1. Note the shifts in the angular positions of the nodes and of the most negative points (shifts away from 45° etc.), and also the alternation of stronger and weaker gap maxima along the CuO bond directions.

Consider now what this orthorhombic distortion can do to the tunneling across a twin boundary, assuming the present eight-node gap form. Since the twin boundaries in YBCO are aligned at 45° to the planar Cu-O bonds, the relevant gap-function geometry could be as shown in Fig. 2. The two offset parabolic curves represent the lowest parts of the two gap functions (from the two sides of the twin boundary), and the bell curve represents the relative amplitude for Josephson tunneling of a pair at the Fermi surface, whose k-vector direction is labeled by θ. (The tunneling amplitude is greatest

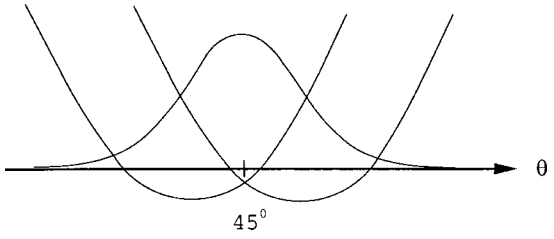

FIG. 2. Possible gap-function geometry for a YBCO twin boundary, showing how π-junction behavior can arise. The offset parabolic curves represent the lowest sections of the gap functions from opposite sides of the twin boundary. The bell curve shows the relative amplitude for Josephson tunneling of a pair at the Fermi surface. Pair k vectors are parametrized by θ as in Fig. 1, where the normal to the twin boundary is at 45°.

for k's aligned with the normal to the twin boundary, marked 45° in the figure.) If the various parameters have suitable values, the dominant k contributions to the tunneling will couple the $-$ to $+$ and $+$ to $-$ regions of the two gap functions, leading to a net "π-junction" (π phase=negative) coupling for the dominant "$s+g$" component of the gap. Just such a π-junction coupling for the s-wave (isotropic) component of YBCO has been demonstrated by c-axis tunneling into Pb, with the junction straddling a single twin boundary.[6] This result has been interpreted[6,71] as evidence for a d-wave-dominant gap form, the "usual" d-wave form distorted by orthorhombicity, but it is now clear that this is not the only reasonable interpretation. (With either interpretation, this experimental result raises the question of why relatively large critical currents, as measured by I_cR_n, were observed in earlier c-axis tunneling experiments with heavily twinned YBCO.[72,73] A plausible answer[73] is that uniaxial stress in the sample can enlarge the domains of one of the twin orientations, at the expense of the other twin orientation, and such a dominance of one twin orientation has in fact been directly observed.[74] On the other hand, for *untwinned* YBCO the corresponding I_cR_n is $\sim$1 mV,[73] which is about 20% of the Ambegaokar-Baratoff value obtained by assuming a conventional s-wave gap.[72,73] This magnitude of I_cR_n is so large that this is even suggestive of a *dominant* s-wave component here, as other investigators have noted. Essentially the same large magnitude of I_cR_n has also been observed in an ingenious geometry of a misoriented grain in a YBCO thin film, which provided a pair of very clean (100)/(001) grain-boundary junctions in series.[75] [This latter paper also has corresponding and quite intriguing data for (110)/(001) junctions. The authors suggest that this is d-wave evidence, but it is actually not clear how this latter data should be interpreted.])

We now consider the effect of these geometric features for the case of a corner-junction tunneling experiment, assuming a heavily twinned sample. The relevant geometry is shown in Fig. 3, where the diagonal stripes represent individual twin domains and the arrows show their a-axis (or possibly b-axis) orientations. [The other superconductor, which wraps around the corner, is Nb (Ref. 7) or Pb (Ref. 76).] The key feature now is the alternation between the stronger and weaker gap maxima, as shown in Fig. 1. These stronger and weaker lobes are symbolized by the larger and smaller bulges along the x and y crystal faces in Fig. 3. Clearly, the positive contributions should dominate along one of these crystal faces and the negative contributions along the other, leading to an apparent phase shift of π between the x and y crystal faces. Subject to some caveats below, this result can explain the experiment of Mathai *et al.*[7] This has been considered one of the most convincing of the d-wave experiments, mainly because a SQUID scanning microscope was used to ensure the absence of trapped flux. In this experiment there was actually a hole at the corner, making this a corner SQUID instead of a corner junction, but this difference does not affect the present argument. (This experiment also demonstrated time-reversal invariance, thus ruling out complex gap forms such as "$d+is$.") The present explanation bears some resemblance to previous s-wave proposals in-

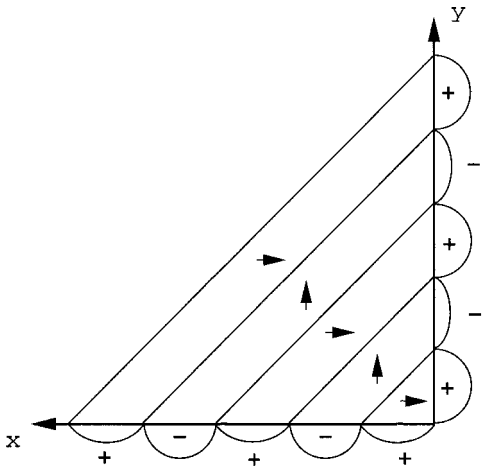

FIG. 3. Effect of twinning in a YBCO corner junction. The diagonal stripes are the individual twin domains, the arrows showing their respective *a* axes (or possibly their *b* axes). The alternating larger and smaller bulges, along the *x* and *y* crystal edges, represent the alternating stronger and weaker positive gap lobes from Fig. 1. The alternating signs come from the π junctions at the twin boundaries.

volving competition between gaps of opposite signs for the different bands (bonding and antibonding bands) of a bilayer[12–16] or of a bilayer plus chain[16,17] system, but in the present case these gaps have the same sign and the bilayer character of YBCO does not play an essential role. The chain gap is also assumed here to be unimportant for symmetry-sensitive experiments. A common defect of these alternative schemes for YBCO is that they have not dealt with the problem of continuity versus sign change of the isotropic *s* component across a twin boundary. As just discussed, and as emphasized in Ref. 71, this issue is very important.

The caveats are the following: (1) We are ignoring the effects of electronic coupling between adjacent CuO_2 planes, as well as such coupling to the chains. (This is appropriate in the context of the valence fluctuation theory, at least to a reasonable first approximation, as explained in Ref. 4. It was shown there that this assumption is compatible with the common and strong dependence of T_c on the number of adjacent CuO_2 planes, which is attributed to changes in the effective electronic parameters controlling the individual CuO_2 planes.) (2) The twin boundary must provide a sufficient barrier to restrict the tunneling amplitude to *k*'s in a not-too-wide angular window around the boundary normal. There is some evidence for a significant barrier here.[77] (3) The strength of the electronic orthorhombicity, specifically here the angular offsets of the minima in Fig. 2, must be within an appropriate range. (4) Scattering from irregularity along the twin boundaries must not be too strong. (5) Any net excess area of one of the twin orientations over the other, due to uniaxial stress, must not be too large. (6) The individual twin domain widths must be smaller than the Josephson penetration length, as discussed in the following section.

In the corner-junction experiment of Wollman *et al.*[76] the various single-crystal samples had widely varying twin densities and even included samples with no twin boundary in the corner-junction region. The Frauenhoffer-like diffraction patterns, for critical current as a function of applied field, were stated to be essentially independent of the twin density. (Nevertheless, a deviation from the ideal diffraction pattern was quite noticeable.) This is clearly a problem for the present picture. There have, however, been two major criticisms of this experiment.[11] One criticism is that a flux line is likely to be trapped at the sample corner, during the cooldown through T_c, because of its ''mirror charge'' attraction to each one of the two crystal edges. There is thus a need for SQUID microscope examination of sharp-cornered single-crystal samples of YBCO to see if such a flux trapping may be the typical behavior. This suspicion also applies to the untwinned single-crystal corner SQUID experiment of Brauner and Ott.[78] The other criticism is the experimental observation[7,79] that self-field effects (arising from junction asymmetry) can produce phase shifts similar to those observed by Wollman *et al.*[76]

IV. PROPOSAL FOR AN EXPERIMENTAL TEST

This interpretation of the corner-junction and corner-SQUID tunneling experiments can be tested. Along the YBCO crystal face, where there is a junction with an s-wave superconductor (Pb), each twin-boundary termination provides a tricrystal junction. According to the present interpretation, if the spacing between the twin boundaries is large enough there should be approximately a half-quantum of spontaneous flux localized around each such tricrystal point, and this flux should be detectable with a SQUID scanning microscope. The criterion to have such regions of relatively large spontaneous flux, of alternating sign, is that the distance between the tricrystal points should be larger than the Josephson penetration length,[69,80] which for the YBCO-Pb junction is probably >1 μm and perhaps ~ 10 μm. (The Josephson penetration length plays the role of an effective averaging distance for the gap behavior along the junction.[69,80]) However, in the only SQUID scanning microscope examination to date for such a tunneling geometry (the experiment of Mathai *et al.*[7]), the typical twin domain width was <1 μm. This experiment did not find such spontaneous flux, in agreement with the expectation for these narrow twin domains. Another reason, however, is the relatively large diameter of the scanning SQUID pickup loop, which was ~ 10 μm. It would thus be worthwhile to do similar SQUID scanning examinations of YBCO corner junctions (or corner SQUID's) having much wider twin domains, with Pb-junction arms long enough to cover several such domains. Actually, such a Pb junction along a *single* YBCO *x* or *y* crystal face should suffice here. According to the common d-wave picture, the dominant d-wave component continues across each twin boundary without change of sign,[6,71,73] and since this is the component which determines the tunneling at the *x* or *y* crystal face, there should thus be no such spontaneous flux. This is a clear difference from the present aniso-*s* prediction. With the present technology of sample preparation and SQUID microscopes, this test should be quite feasible.

V. SYMMETRY OF Tl-2201

A multicrystal (tetracrystal) tunneling experiment by Tsuei, Kirtley, *et al.*[8] (hereafter TK) has the elegant feature of relying *entirely* on symmetry arguments to establish the *d*-wave gap form. This experiment is claimed to be a definitive proof for the *d*-wave gap form—the most definitive of the *d*-wave experiments. An essential feature here is the assumed tetragonality, or *lack* of orthorhombicity, of $Tl_2Ba_2CuO_6$ (Tl-2201), the material which was used. It is recognized that this material can be prepared with either tetragonal or orthorhombic structure, depending on the amount of Cu substitution at the Tl sites and on the amount of excess oxygen.[81,82] The epitaxial film sample of TK was determined to be tetragonal within the resolution limits of a number of different characterization techniques (although some of this evidence was inferred from tests on similar samples).

There is, however, another study, by Willemin, Rossel, *et al.*[83] (hereafter WR) using angle-dependent torque magnetometery, which found that two very similar[84] and also nominally tetragonal (tetragonal at room temperature) epitaxial film samples had *very strong* electronic orthorhombicity in the superconducting state. (These samples had different film thicknesses.) At $T/T_c=0.6$, the ratio $H_{c2}(b)/H_{c2}(a)$, for the H_{c2}'s along the orthorhombic *b* and *a* axes, was found to exceed 1.6. At first sight this result is very surprising and paradoxical. It is unlikely that such a large electronic effect could come from an orthorhombicity which is undetectably small at room temperature and which is temperature independent. As the most likely explanation, the authors suggested that an orthorhombic distortion developed spontaneously in the samples *at low temperature*. Another feature found by the authors provides some independent support for this proposal. The authors tried repeatedly warming their samples above T_c and then cooling and repeating the measurements. It was found that this thermal cycling sometimes shifted the orientation of the anisotropy by 90°. These shifts are consistent with spontaneous distortion, whereas they are probably inconsistent with most of the possible experimental artifacts. We shall now argue that this proposed spontaneous distortion is quite likely the correct explanation, because there is a very reasonable mechanism for this. It follows from this argument, as well as from the WR experiment, that a similar low-temperature orthorhombicity may well have occurred in the experiment of TK.

There is much crystallographic evidence for strong *short-range* (within unit cell) distortion within the thallium-oxygen layers of the thallium cuprates,[81,85,86] which involves *large* in-plane displacements of these ions away from their nominal positions [shifts of ~0.4 Å for O, ~0.3 Å for Tl (Ref. 85)]. These displacements are local adjustments to relieve a mismatch between the chemically preferred planar Tl-O and Cu-O bond lengths: namely, to create shorter (and thus more optimum) planar Tl-O bonds. Unfortunately, lack of long-range order has severely limited the information about this distortion that can be extracted from conventional Bragg diffraction analysis. Analysis of the radial pair distribution function has therefore been very helpful here, by providing constraints on the *correlations* between displacements of nearby ions in the Tl-O plane.[85] This technique has shown that the short Tl-O bonds are linked to provide zigzag Tl-O chains oriented at 45° to the planar Cu-O bond directions, at least over some undetermined short range. According to Ref. 85, the obtained short Tl-O bonds have a length of 2.39 Å, close to the chemically expected 2.28 Å and much shorter than the 2.73 Å length in the undistorted structure. This zigzag chain arrangement is similar to the form of short-range distortion encountered in Bi-2212, where the long-range continuity and near periodicity of the distortion has led to more secure information from Bragg diffraction.[87] Although Bi-2212 has the additional complications of extra oxygen ions and an incommensurate modulation or superstructure, there are analog materials without these complications [$(Bi, Pb)_2(Sr, La)_2CuO_6$ and $(Bi, Pb)_2Sr_2(Ca, Y)Cu_2O_8$], where ''pure'' zigzag chains of this form have been confirmed as the long-range ordered structure.[88] (This peculiar zigzag structure is governed by the feature that the short Tl-O bonds preserve O-Tl-O bond angles of nearly 90°, and similarly for the bismuth analogs.) There is also additional chemical and electronic motivation for this type of structure.[86,89] The radial pair distribution study[85] was actually done on Tl-2212, but this evidence from Tl-2212, Bi-2201, and Bi-2212, together with the bond-length and other chemical motivation,[86,89] now makes this form of distortion highly likely also for Tl-2201, at least on a short-range scale.

At room temperature in the ''tetragonal'' Tl-2201 samples the Tl-O layers have no long range order, whereas *at low temperatures* it is quite possible that the distortions may become organized into long-ranged chains of the type just mentioned, thus providing a macroscopically orthorhombic distortion.[86,90] (Whether this actually occurs, for a particular sample, may depend rather delicately on details such as the type and concentration of defects at the thallium sites—the substitutions or vacancies.) This conclusion is based on analogy to the bismuth cuprates, where there is some evidence for an order-disorder transition far above room temperature and for which a statistical-mechanical model has been developed.[90] It was furthermore argued in that model study that the temperature scale for this transition should be much smaller for the thallium cuprates than for the bismuth cuprates. In the Tl-2201 experiment of WR it appears that the orthorhombicity sets in just at or very near T_c. (This could be an illusion, because the sought-for signal depends on superconductivity and the data shown have been subjected to a subtraction of above-T_c data, but on the other hand the form of the data also suggests onset at T_c.) A near-T_c onset is also supported by the above-mentioned result of thermal cycling. There are also several other experiments indicating structural changes at or quite near T_c.[91,92] In particular, a radial pair-distribution neutron study (of Tl-2212) (Ref. 91) revealed strong buckling in the CuO_2 plane, a distortion which represents tilting of the CuO_6 octahedra (or CuO_5 pyramids, for this material). [Such a tilting distortion is well known to occur in $La_{2-x}(Ba, Sr)_xCuO_4$.[93]] The pattern of this buckling was found to change at or near T_c.

In the present context this ''tilting'' character of the CuO_2-plane distortion has two appealing aspects: (a) This provides a means to coordinate or lock together the distor-

tions in different planes, so as to generate a three-dimensional orthorhombic structure. The Tl displacements can be expected to cause similar displacements of the apical oxygens and vice versa, thus linking the Tl-O plane distortions to the CuO_6 (or CuO_5) tilts, while the tilts coordinate the distortion order on opposite sides of the CuO_2 planes. There is not yet any direct evidence of coordination between adjacent Tl-O planes, but this is probably similar to what is observed in Bi-2212.[87] (b) This tilting allows for a strong orthorhombic distortion *without* requiring changes of the Cu-Cu lattice parameters. In a single crystal such lattice-parameter changes would of course be expected, but in the case of epitaxially pinned films (the TK and WR experiments) it is quite possible that the pinning would not inhibit this form of orthorhombic distortion.

Because the picture we have just described has not been directly confirmed for Tl-2201, we must emphasize the variety of clues that this is based on: chemical bond lengths, crystallographic data, tight-binding band calculations related to chemical valence (doping) considerations,[86,89] analogy to bismuth cuprates, statistical-mechanical modelling,[90] and the anisotropy-orientation shifts resulting from thermal cycling. Furthermore, the development of this picture was quite independent of the WR experiment, and indeed this was done without any concern for the gap symmetry. More low-temperature studies are needed, with examination of the systematic effects of copper substitution on thallium sites and of extra oxygen. (We emphasize again that the realization of this low-temperature orthorhombicity in ''tetragonal'' samples is likely to be sensitive to sample details.) The lack of adequate experiments for Tl-2201 has been due, at least in part, to inadequate sample homogeneity at the time of the above-mentioned experiments.[94]

The net result of this discussion is that, due to the very reasonable possibility of such a strong crystallographic and electronic orthorhombicity developing at low temperature in the TK sample (as strongly suggested by the WR experiment), the symmetry-based experiment of TK is *not* conclusive *d*-wave evidence. The *d*-wave gap form is therefore not proved in this experiment, although it is not disproved either. While one cannot expect an arbitrary aniso-*s* gap form to explain the TK result, it is quite possible that *some* such form may work. This is suggested, for example, by the bicrystal tunnelling experiments in point (7) of Sec. II. (It is noteworthy that the maximum group velocity at the Fermi surface is at or very near where the eight-node gap form is negative, which may therefore enhance the influence of the negative-gap regions.) In a modeling study it would of course be important to determine whether a gap parameter regime can be found that also explains the earlier tricrystal experiment with this material.[95]

In common with the bismuth cuprates, e.g., Bi-2201 and Bi-2212, the orthorhombicity of the thallium compounds differs geometrically from that of YBCO. In the Tl and Bi cuprates the orthorhombic axes are at 45° to the planar Cu-O bonds, instead of being parallel to these bonds. Thus, in the *d*-wave picture, the orthorhombic distortion in these cuprates does not shift the node locations away from their undistorted positions at 45° to the Cu-O bonds. In our *s*-wave picture the nodes remain symmetrically displaced from the 45° and 225° directions by angles $\pm\delta_1$, while they are displaced from the 135° and 315° directions by different shifts of $\pm\delta_2$. This distortion can be qualitatively described by adding a subsidiary *d*-wave component of the *xy* form (instead of x^2-y^2). If this distortion is strong enough, this will remove four of the ''original'' eight nodes. At the same time the displacements ''δ'' of the other four nodes should be enlarged, and the magnitude of the corresponding antinodes (say, at 45° and 225°) should be increased. This latter aspect could be the reason why the within-gap feature of Bi-2212 occurs at a relatively higher energy (about one-half of the gap maximum) than for the other materials in point (1) of Sec. II, where this ratio is generally near 0.25. The nature of any twin boundaries—namely, the appropriate analog of Fig. 2—is unclear, but there is much less tendency for twinning in these materials. This was not a problem in the experiment of WR, where the sample consisted of a single domain.

VI. GAP FORM IN ELECTRON-DOPED CUPRATES

As is well known, there is much evidence for a nodeless and fairly isotropic *s*-like gap in the electron-doped cuprate $Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO).[43] This evidence includes an activated exponential decrease of the penetration depth increment $\Delta\lambda(T)=\lambda(T)-\lambda(0)$ at $T\ll T_c$, Raman evidence for a nearly isotropic gap, and the absence of any zero-bias conduction peak in tunneling data. There are, however, several recent papers which challenge this conclusion for the electron-doped cuprates NCCO and $Pr_{2-x}Ce_xCuO_{4-y}$ (PCCO). We now briefly examine this recent work.

A study of the temperature and magnetic field dependence of λ has found power-law behavior in the H dependence.[96] The authors argued that this indicates gap nodes. But the lowest temperature reached in this study was still rather high—namely, $0.4T_c$—so the validity of this apparent power-law behavior is questionable. On the other hand, there was also an excellent activated exponential fit to $\Delta\lambda(T)$ for $H=0$, from 17 K to the lowest temperature of 7.5 K. (There was also evidence for very little influence from the paramagnetism of the Nd^{3+} ions.)

Two more recent studies[97,98] of the temperature dependence of $\Delta\lambda$, for NCCO and PCCO, also found reasonable consistency with the power-law behavior expected for the *d*-wave gap form. These studies featured better samples, more refined apparatus, and lower temperatures (down to 1.2 and 0.4 K, respectively) than in previous works. But both of these studies also found consistency with the activated exponential form $\Delta\lambda(T)=\lambda(0)[\pi\Delta(0)/k_BT]^{1/2}\exp[-\alpha\Delta(0)/k_BT]$, where α is a constant. In both papers the authors rejected these activated fits as unreasonable, because of conspicuously small values obtained for the parameters $\Delta(0)$ and $\lambda(0)$. We note, however, that for a strongly anisotropic but nodeless gap, the $\Delta(0)$ from such a low-temperature fit would be the *minimum* value occurring in this gap form. The associated $\lambda(0)$ would also be small because, according to this $\Delta\lambda(T)$ formula, it would in effect be characterizing the fraction of the Fermi surface associated with a near-minimum gap. At higher T the $\Delta\lambda(T)$ should rise faster than

this simple activated form, because of the additional contributions from Fermi surface regions with larger gap values. Such a faster rise was indeed seen for both materials. These data are therefore consistent with nodeless but strongly anisotropic gaps in NCCO and PCCO. It appears from this that the anisotropy is stronger in samples of higher quality [the fitted $\Delta(0)$'s are smaller], as should be expected. The PCCO data of Ref. 98 are analyzed in much detail in Ref. 10, showing good consistency with a nodeless but anisotropic gap, and inconsistency with a dirty *d* wave. There are also data on tunneling through bicrystal grain-boundary junctions which indicates strong gap anisotropy in both NCCO and PCCO.[99]

There are also papers which present apparent *d*-wave evidence. By tunneling into the *a*-*b* plane of NCCO, a zero-bias conduction peak has been observed.[100] Such a peak is generally regarded as evidence for bound states due to Andreev reflection and, thus, as evidence for a gap node among the important tunneling *k* vectors (although a contrary mechanism has recently been proposed[101]). Tricrystal experiments have found a half quantum of flux around the three-grain intersection point, for both NCCO and PCCO.[102] This result clearly requires gap nodes. Although this suggests the conventional *d*-wave gap form, it is also quite possible that this can be explained by the eight-node gap form (1). [Encouragement for this can be found in point (7) of Sec. II.] A detailed modeling study is needed here.[103]

The most straightforward and likely possibility to reconcile all of this information is that in all cases the gap has an aniso-*s* form and that the previous general absence of nodes and the near isotropy has been due to angle averaging from poorer sample quality. This possibility is nicely consistent with *s*-wave evidence for the hole-doped cuprates and likewise with evidence[104] for anisotropic *s*-wave gaps in the majority of the other exotic superconductors.

VII. CONCLUDING REMARKS

We have presented evidence for an anisotropic-*s*-wave gap form, with nodes, for the hole-doped cuprates, and we have reviewed the current state of this evidence. The combined weight of this evidence provides strong motivation to search for alternative explanations for the many experiments which appear to require a *d*-wave gap form. We have noted at the outset that most of the non-phase-sensitive experiments can plausibly be accounted for by the nodes in the anisotropic-*s* gap form. Further examination of this data is desirable to see to what extent this data can distinguish between the *d*-wave and the eight-node anisotropic-*s* gap forms. Conventional one-electron planar tunneling is one example which clearly favors the latter form, and other data[9] are suggestive. There are very recent analyses of several examples of such data which clearly favor the aniso-*s* gap form.[10]

We have also presented anisotropic-*s*-wave explanations for three of the phase-sensitive Josephson tunneling experiments. These are experiments which are widely regarded as some of the most convincing *d*-wave evidence. Altogether, these arguments demonstrate that the anisotropic-*s*-wave evidence is stronger and the *d*-wave evidence is weaker than is commonly believed. A specific experimental test has been proposed.

Although there are now alternative explanations for some of the apparently most important *d*-wave evidence, we have obviously not covered all of this evidence. We now consider some of this other evidence.

The data for $|\Delta|$ from angle-resolved photoemission experiments is a serious problem for the present interpretation and, perhaps, the most serious problem. The observed gap minimum at 45° is too sharp: i.e., it shows too much of a V shape, suggesting a *d*-wave rather than an aniso-*s* gap form.[105] And farther away from 45° this data continues to follow the *d*-wave prediction quite well.[105] But there are several possibilities which may be able to explain this. The photoemission data below T_c could be dominated by surface pair states, which might provide this V shape.[11,28,106] Also, a number of recent works argue that these data are complicated by a strong interaction between the ''simple'' quasiparticle state and an accompanying virtual spin fluctuation.[107] It has also been suggested that the variation along the Fermi surface of the quasiparticle peak width may be influencing the ARPES-deduced gap,[108] due to the typical use of the ''leading edge shift'' criterion to determine this gap. Another problem is the one-electron or band-structure effect[109] of the microscopic phase separation found in the stripe picture, since stripes may well be present in the samples used (near optimal doping). [The ARPES data show several similarities to the corresponding data for 2H-$TaSe_2$,[11,110] a material well known for its charge-density-wave (CDW) distortion. The CDW can be viewed as an incipient stripe formation.] Thus, by any of these means, the V-shaped dip may not represent the intrinsic angle variation of $|\Delta|$. A further problem is that the ARPES technique itself has recently been shown to be less straightforward than was generally believed. There are unexpectedly strong matrix element effects,[111] which are so striking that the Fermi surface has appeared to change significantly (from hole to electron topology) when the incident photon energy is changed.[112] There are claims that the earlier-obtained Fermi surface has now been reestablished.[113] However, a more complete resolution of this problem is now recognized to be the existence of a bilayer splitting of the quasiparticle bands in Bi-2212, and a photon energy dependence of the matrix elements that favors the shallower (antibonding) band at lower photon energies ($\sim$22 eV) and the deeper (bonding) band at higher photon energies ($>$30 eV).[114] The implications for the previous $|\Delta|$ data are still unclear. (This bilayer splitting requires a reassessment of other conclusions from ARPES data, such as the abovementioned strong interaction between ''simple'' quasiparticles and an accompanying spin fluctuation or paramagnon.) All of these matters may complicate the determination of $|\Delta|$. Another concern to be dealt with in this context is the ARPES data on highly overdoped Bi-2212,[45] which is clearly contrary to the standard *d*-wave picture [point (6) in Sec. II]. It is also noteworthy that for the single-layer material Bi-2201 the $|\Delta|$ determined by angle-resolved photoemission is strongly U shaped[115] and is even somewhat suggestive of the eight-node anisotropic-*s* gap form.

Another area of much current interest is the systematics of

the zero-bias anomalies in quasiparticle tunneling.[116] These anomalies are attributed to states at the tunneling barrier which arise from sign changes in the gap under Andreev reflection, so these data may also provide evidence for the gap form (but see Ref. 101). So far, most of these data show good consistency with the dominant-*d*-wave type of gap form (see Ref. 101 for exceptions), but the theoretical consequences of the present eight-node form with orthorhombicity have not been investigated. The same can be said for the recently observed spatial modulation of the STM tunneling conductance in the neighborhood of a zinc or nickel impurity in Bi-2212.[117] The possibility of an *s*-wave explanation of the 41-meV π resonance was considered in Sec. III. As noted in Secs. V and VI, there is also a need for modeling of the various tricrystal and related experiments, and furthermore the apparent inconsistencies of $I_c R_n$ for *c*-axis tunneling data (Sec. II) need a consistent explanation. The puzzle of the nonlinear Meissner effect data has, however, now been explained by means of the aniso-*s* gap form.[10]

The difficulties just mentioned must of course be weighed against the problems for the *d*-wave picture, as discussed in Sec. II. Just as a serious *s*-wave proposal must confront the apparent *d*-wave evidence, the *d*-wave proponents should now be expected to deal with the *s*-wave evidence of Sec. II and Ref. 10. The gap form in the hole-doped cuprates has continued to be a slippery problem, but the possibility of a consistent anisotropic-*s* outcome now looks much more reasonable than this has seemed in recent years. The experimental test proposed in Sec. IV should be quite significant.

Finally, we must say that the aniso-*s*-wave picture for the hole-doped cuprates has an appealing consistency with the aniso-*s* conclusion of Sec. VI for electron-doped cuprates. This eliminates the problem of apparently needing different mechanisms for the hole-doped and electron-doped cuprates. This is also nicely consistent with the evidence for anisotropic-*s*-wave gaps in the majority of the other exotic superconductors.[104]

Note added in proof. Evidence for strong gap anisotropy in the electron-doped material NCCO has also been obtained by angle-resolved photoemission.[118]

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