Surface State Effects in High-T_c Superconductors

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Under appropriate conditions a band of electronic surface states may exist on the topmost CuO_2 layer of a high-T_c superconductor. This layer can then have higher T_c and energy gap values than the bulk. The surface band vanishes at the k_x, k_y points in the Brillouin zone where the bulk bands touch. Such surface states can cause tunneling results to depend upon the method and the geometry, and alter the interpretation of photoemission measurements of the energy gap. Both experiments are consistent with s-wave order parameter symmetry in high-T_c materials.

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Recently, there has been a substantial controversy regarding the orbital symmetry of the superconducting order parameter (OP) $\Delta(\mathbf{k})$ in the high transition temperature (T_c) superconductors such as $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) and $YBa_2Cu_3O_{7-\delta}$ (YBCO). A number of experiments on these materials were interpreted in terms of $\Delta(\mathbf{k})$ having a $d_{x^2-y^2}$ symmetry such as $\Delta_0(k_x^2 - k_y^2)$, with nodes for $k_x = \pm k_y$. Among these are the photoemission experiments of Shen *et al.* [1], the corner SQUID and Josephson junction experiments of Wollman *et al.* [2], and the penetration depth λ measurements of Hardy *et al.* [3], for which $\lambda_{ab}(T)$ was found to be nearly linear in the temperature T for $T \ll T_c$. In addition, some workers [4–8] have interpreted the different tunneling behaviors observed in point contact, break junction, and junction measurements on the same and on different sample surfaces as evidence for a d-wave, or node-containing OP.

On the other hand, very recent c axis [9] and grain boundary [10] Josephson tunneling experiments, plus $\mathbf{H} \perp \hat{\mathbf{c}}$ torque measurements [11] were found to be consistent with an isotropic or s-wave OP, $\Delta(\mathbf{k}) = \Delta_0$, or possibly with an anisotropic but nodeless OP, such as $s + id$. It would thus be useful to reconcile all of the above experiments under the *same* theory. In a separate comment, one of us [12] has offered an alternative s-wave explanation of the corner SQUID and junction experiment [2], suggesting that demagnetization effects associated with the sample corners may be responsible for the observed effects. While several other $\lambda_{ab}(T)$ measurements suggested a nonlinear low-T behavior, we [13] have used the bulk version of the model presented here to obtain *quantitative* fits with the linear low-T $\lambda_{ab}(T)$ data of [3]. In this Letter, we offer a possible s-wave explanation for the photoemission [1] and tunneling experiments [4–8,14], based upon the possible presence of electronic surface states. Hence, we suggest that our model may explain all of the data presently available.

The model consists of alternating superconducting (S) and normal (N) layers, coupled by the proximity effect. The top layer is superconducting, and is connected to the next N layer by the hopping strength J_1. The N layer is connected to the S layer in the next unit cell by J_2. The sequence repeats *ad infinitum* inwards. The quasiparticles are assumed to move freely within the layers. In YBCO, the top layer is either an insulating BaO or a disordered CuO chain layer, and is neglected. There are three conducting layers per unit cell, with the two CuO_2 layers acting as an S layer, and the CuO layer (except the partial layer on the surface) acting as an N layer. In BSCCO, the top BiO layer is insulating (or semiconducting), the CuO_2 double layers per half unit cell act as an S layer, the BiO double layers per half unit cell comprise an N layer, and we neglect the unit cell doubling. Hence, in both YBCO and BSCCO, the top conducting layer is assumed to be an S layer, and our model is relevant.

In this model, a band of surface states forms readily if the top layer is electronically isolated [15], i.e., $J_1 < J_2$. In this event, the top S layer can have a significantly *larger* energy gap than the bulk. Such behavior is in marked contrast with the *suppression* of T_c and the OP at the surface in Ginzburg-Landau (GL) calculations [16], and differs significantly from the very weak surface T_c enhancement found for isotropic materials [17]. In neither [16] nor [17] were surface states discussed, and the GL approach cannot describe an energy gap. Hence, this is the *first* treatment of the relevance of surface states to the energy gap of layered superconductors.

The model Hamiltonian is $H = H_0 + V$, where the band energy term is

$$H_0 = \sum_{\mathbf{k}\sigma}\sum_{j=1}^{\infty}\sum_{n=1}^{2}\xi_0(\mathbf{k})\psi^{\dagger}_{jn\sigma}(\mathbf{k})\psi_{jn\sigma}(\mathbf{k}) + \sum_{j\mathbf{k}\sigma}\Big[J_1\psi^{\dagger}_{j1\sigma}(\mathbf{k})\psi_{j2\sigma}(\mathbf{k}) + J_2\psi^{\dagger}_{j2\sigma}(\mathbf{k})\psi_{j+1,1\sigma}(\mathbf{k}) + \text{H.c.}\Big], \quad (1)$$

$\xi_0(\mathbf{k}) = \mathbf{k}^2/2m_0 - E_F$, $\mathbf{k} = (k_x, k_y)$, E_F is the Fermi energy, σ is the spin index, $n = 1, 2$ is the layer index

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within a unit cell, and the sum on j is over all unit cells normal to the planes. We choose units in which $\hbar = k_B = 1$. The interaction term is

$$V = -\frac{1}{2}\sum_{j\sigma}\sum_{\mathbf{k}\mathbf{k}'}\lambda_0\psi^\dagger_{j1\sigma}(\mathbf{k})\psi^\dagger_{j1,-\sigma}(-\mathbf{k}) \times \psi_{j1,-\sigma}(-\mathbf{k}')\psi_{j1\sigma}(\mathbf{k}'), \quad (2)$$

where only the S layers have the pair coupling strength λ_0, which is cut off at energies differing from E_F by $\omega_\parallel$. The interaction V leads to s-wave intralayer pairing, although the main effect under discussion is independent of the pairing symmetry. This model is an extension to $J_1 \neq J_2$ of the S-N model studied by Abrikosov [18].

The bulk properties of this model were described elsewhere [19]. Both T_c and Δ_0 of the S layers decrease with increasing hopping, due to interband pair breaking. The density-of-states (DOS) curve has a double peak structure. The inner peaks correspond to the OP in the band representation, while the positions of the outer peaks are determined by a combination of the OP and the c-axis band dispersion.

The quasiparticle Green's function matrix elements are defined in the familiar way:

$$G_{jn,j'n'}(\mathbf{k},\tau-\tau') = -\left\langle T\left[\psi_{jn\sigma}(\mathbf{k},\tau)\psi^\dagger_{j'n'\sigma}(\mathbf{k},\tau')\right]\right\rangle,$$
$$F_{jn,j'n'}(\mathbf{k},\tau-\tau') = \left\langle T[\psi_{jn\sigma}(\mathbf{k},\tau)\psi_{j'n',-\sigma}(-\mathbf{k},\tau')]\right\rangle, \quad (3)$$

where $\langle\cdots\rangle$ denotes a thermal average, and the spin indices are suppressed. We define the jth S layer order parameter Δ_j in terms of the Matsubara frequencies ν,

$$\Delta_j = \lambda_0 T\sum_\nu\sum_{\mathbf{k}} F_{j1,j1}(\mathbf{k},\nu), \quad (4)$$

which can be taken to be real. The inverse of the Green's function matrix has the form

$$\hat{G}^{-1}(\mathbf{k},\nu) = \begin{pmatrix} \hat{K}_{11} & \hat{K}_{21} & 0 & 0 & 0 & \cdots \\ \hat{K}_{12} & \hat{K}_{22} & \hat{K}_{32} & 0 & 0 & \cdots \\ 0 & \hat{K}_{23} & \hat{K}_{33} & \hat{K}_{43} & 0 & \cdots \\ 0 & 0 & \hat{K}_{34} & \hat{K}_{44} & \hat{K}_{54} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}, \quad (5a)$$

where the $\hat{K}_{jj'}$ are the 4×4 matrices defined by

$$\hat{K}_{jj} = \begin{pmatrix} i\nu-\xi_0(\mathbf{k}) & -J_1 & \Delta_j & 0 \\ -J_1 & i\nu-\xi_0(\mathbf{k}) & 0 & 0 \\ \Delta_j & 0 & i\nu+\xi_0(\mathbf{k}) & J_1 \\ 0 & 0 & J_1 & i\nu+\xi_0(\mathbf{k}) \end{pmatrix} \quad (5b)$$

and

$$\hat{K}_{j,j+1} = \hat{K}^T_{j+1,j} = \begin{pmatrix} 0 & -J_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & J_2 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (5c)$$

In the normal state where $\Delta_j = 0$ for all j, the inversion of the Green's function matrix involves some straightforward algebra. The quasiparticle band energies in the infinite system are given by $\xi_0(\mathbf{k}) \pm \epsilon_\perp(k_z)$, where $\epsilon_\perp(k_z) = [J_1^2 + J_2^2 + 2J_1J_2\cos k_z s]^{1/2}$, s is the thickness of the unit cell, and k_z is the quasiparticle wave vector along the c direction. In the semi-infinite system a band of surface states exists at $k_z s = \pi + i\kappa$ if $J_1 < J_2$, where $\kappa = \ln(J_2/J_1)$. This surface band has $\epsilon_\perp(k_z) = 0$, and thus intersects the Fermi energy on a circular cylinder in the middle of the two sheets of corrugated cylindrical Fermi surfaces. The surface states have the charge density $\rho_{j1} = r^{-2j}[r^2 - 1]$, where $r = J_2/J_1$, on the S layer of the jth cell, and zero charge density on the N layers, $\rho_{j2} = 0$. The surface states do not form under the opposite condition, i.e., $J_1 \geq J_2$. In real materials one finds closely spaced CuO_2 bands separated by a band gap. Since in the two band model the band gap is given by $2|J_1 - J_2|$, we need $J_1 \neq J_2$ to simulate the situation.

The matrix inversion problem in the superconducting state is hampered by the fact that the Δ_j's are expected to be unequal. To render the calculation tractable, we make a local approximation such that in deriving the gap equation for the jth cell, we approximate all OP's by Δ_j. The rationale of this procedure is that the OP of each layer is affected mainly by the electronic structure of that layer and less so by the two adjacent N layers. The much reduced effects of the more distant S layers are treated approximately.

The gap equation for the jth layer derived this way is

$$\Delta_j = \lambda_0\int_0^{\omega_\parallel}\tanh\frac{\omega}{2T}\,d\omega\int_{-\infty}^{\infty}d\xi_0 \times\int_{-\pi/s}^{\pi/s}\frac{s\,dk_z}{2\pi}N_j(k_z)\frac{[\omega^2-\xi_0^2]\Delta_j}{D_j}, \quad (6a)$$

$$D_j = (\omega^2-\xi_0^2)^2 - 2\epsilon_\perp^2(\omega^2+\xi_0^2) + \epsilon_\perp^4 - |\Delta_j|^2(\omega^2-\xi_0^2), \quad (6b)$$

where $N_j(k_z)$ is the normal state DOS of the S layer in the jth unit cell in the neighborhood of k_z, given by

$$N_j(k_z) = N(0)\frac{2[J_1\sin jk_z s + J_2\sin(j-1)k_z s]^2}{\epsilon_\perp^2(k_z)}. \quad (6c)$$

The integral over ξ_0 in Eq. (6a) can be done analytically. The equations have been solved at $T = 0$ and the results are shown in Fig. 1. The top S layer OP Δ_1 is significantly larger than the bulk OP Δ_{bulk} when the hopping strengths are comparable to T_c. The OP Δ_2 of the S layer in the next cell is not very different from Δ_{bulk}. Beyond the second unit cell, the surface effect is negligible. The fact that Δ_1 is larger than Δ_{bulk} is consistent with the top layer having a higher transition temperature T_{c1} than the bulk T_c, a result which we obtain from Eq. (6a) without the local approximation. This effect has negligible consequences in bulk measurements on bulk samples, but may affect results on thin samples or surface-sensitive measurements on bulk materials.

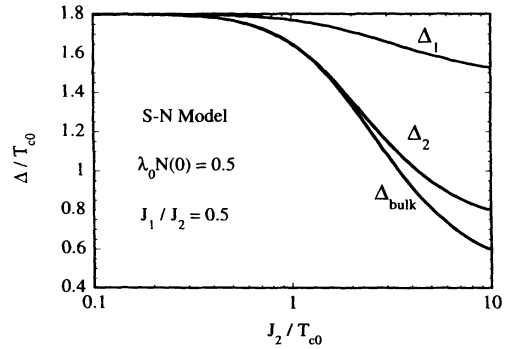

FIG. 1. The energy gap of the top two S layers and the bulk energy gap for the model in Fig. 1 plotted as functions of hopping strengths.

The DOS of the nth layer in the jth unit cell at $T = 0$ is given by

$$N_{jn}(\omega) = \frac{1}{\pi} \sum_{\mathbf{k}} \mathrm{Im} G_{jn,jn}(\mathbf{k}, \nu)|_{\nu \to -i\omega + \delta}, \qquad (7)$$

where $\delta = 0^+$. In Fig. 2 we compare the top layer DOS with that of the bulk superconductor. Figure 2(a) shows the bulk DOS, i.e., $N_{j1}(\omega) + N_{j2}(\omega)$ for $j \to \infty$. This curve has the double peak structure discussed previously [19]. Figure 2(b) is the DOS of the top layer, $N_{11}(\omega)$, which has only one set of peaks at a much larger gap value. There is only a hint of the bulk DOS in the background, indicating that the top layer is effectively isolated from the rest of the system, and justifying the local approximation. We also performed similar calculations for $J_1 \geq J_2$, for which there is no surface band, and found that Δ_1 is only slightly enhanced and the DOS is indistinguishable from that of a bulk superconductor.

The presence of surface states can greatly affect the observed tunneling measurements of the gap, depending upon the type of junction and the tunneling surface geometry. With point contact tunneling along the a, b axes, tunneling into the bulk S and N layers leads to a fairly accurate measurement of the bulk tunneling DOS, as pictured in Fig. 2(a). With point contact tunneling with the tip along the c axis, different results are expected. Such differences are most pronounced when the tip is near a crystal growth seam the height of one c-axis unit cell. In this case, it is likely that the tunneling current is predominantly within the top S layer (perpendicular to the c axis), being dominated by surface state effects, with a resulting DOS curve resembling that in Fig. 2(b). With junction tunneling along the c axis, the barrier often reacts chemically with the top surfaces (e.g., removing oxygen), destroying the surface state. Thus, junction tunneling along both the a, b and c-axis directions should give similar bulklike DOS results, *provided* that good junctions can be prepared and the tunneling current penetrates more than a unit cell depth. Break junction

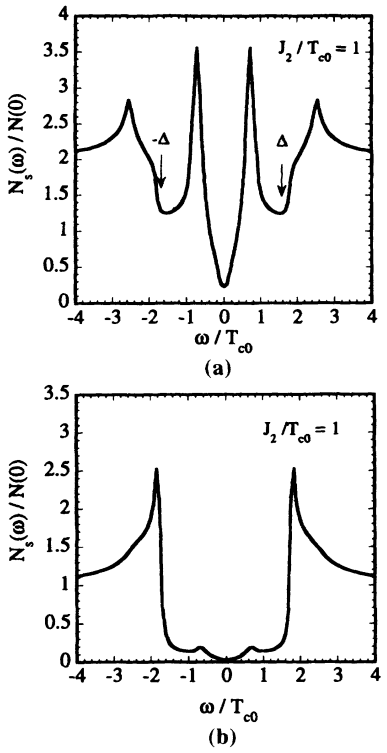

FIG. 2. The bulk (a) and the surface (b) density of states in the ground state of the two-layer SN model for a specific set of hopping strengths $J_1/T_{c0} = 0.5$ and $J_2/T_{c0} = 1$.

results along the c axis would be sensitive to surface states, whereas those along the a, b axes would not.

Both point contact and junction tunneling experiments have been reported for BSCCO in the c direction. The junction tunneling results of Tao *et al.* [4] reveal a gap at approximately 40 meV, in agreement with the (a, b)-plane tunneling result, 35 meV, reported by Chen and Ng [5]. Both papers show tunneling characteristics with V-shaped bottoms. The point contact result reported by Hasegawa *et al.* [6] shows tunneling curves with flat bottoms and gap values in excess of 50 meV, close to the value of 55 meV obtained by Mandrus *et al.* [7] with an (a, b)-axis break junction. Those authors did not observe any c-axis break junction gap structure, but that may be a feature of the cleaved Bi-O surface layer on each junction half. The situation with YBCO is quite similar. The junction tunneling data of Gurvitch *et al.* [8] revealed a gaplike, temperature-dependent feature at 4–5 meV. Point contact tunneling [6] gave a gap of roughly 15 meV. The contrast in shapes of the tunneling curves is similar to but more pronounced than that in BSCCO. These different tunneling results are consistent with our model of s-wave superconductivity with surface states.

We have also solved the one S layer per unit cell problem and found that no surface band can exist. There should thus be no difference between the surface and bulk

DOS, and both are BCS-like for intralayer s-wave pairing. This is an agreement with the recent point contact tunneling measurements on $HgBa_2CuO_{4+\delta}$ by Chen *et al.* [14].

Photoemission experiments are also vulnerable to surface state effects. In these experiments one does not see the gap directly, but infers the existence of a gap by a shift of the peak as one traverses T_c. In this case, a surface band, because of its much larger energy gap, tends to dominate the observed shift. Pickett *et al.* [20] have shown that for YBCO the normal state bulk energy band dispersion along the c axis depends upon k_x and k_y. Gofron [21] was able to observe two bands near E_F close to the Y-S and X-S directions, but not along the Γ-S direction. Such two-band Fermi surfaces were predicted [22] in a calculation of the electronic structure of BSCCO, both with and without mixing of the Bi-O bands with the CuO_2 bands, and observed experimentally [23] in that material, and interpreted in terms of a lack of band mixing. In both theory and the experiment, the CuO_2 bands *touch each other along the* Γ-X *and* Γ-Y *lines,* due to the high crystal symmetry of these directions. At these points, the spectral weight of the surface band *vanishes.* Figure 3 shows a possible manifestation of this electronic structure, in which J_1 and J_2 are functions of k_x, k_y such that $J_1(\mathbf{k}) = J_2 - J'|\cos k_x a - \cos k_y a|$, with $J' > 0$ so that $J_1(\mathbf{k}) < J_2$ over the 2D Brillouin zone except at four points where they are equal. At these points the two bulk bands and their Fermi surfaces touch at $k_z = \pi/s$, and the spectral weight of the surface states vanishes, as in [1,21–23]. Hence, the apparent vanishing of the gap at these points in BSCCO [1] is consistent with the vanishing of the spectral weight of the surface states in an s-wave superconductor. The fact that the apparent anisotropy disappears once the surface is contaminated [1] also suggests that the entire effect is linked to the surface band rather than the bulk band.

In conclusion, both the variety of tunneling results and the apparent gap anisotropy observed with photoemission on high-T_c superconductors are *consistent* with s-wave superconductivity, provided that one takes the surface states into account. We would urge similar experiments be performed on $HgBa_2CuO_{4+\delta}$, for which there is only one CuO_2-derived band and no normal layers [24], and hence such surface states are not expected.

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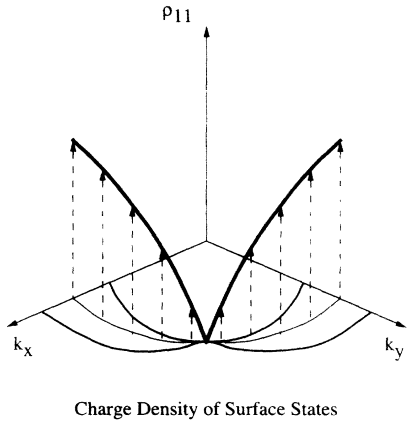

FIG. 3. The distribution of the surface state charge density on the top layer of a model system where the hopping integrals are dependent on k_x, k_y such that $J_1 = J_2$ at a set of points in the 2D Brillouin zone. The surface state vanishes at these points.

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