# Broken Particle-Hole Symmetry at Atomically Flat *a*-Axis $YBa_2Cu_3O_{7-\delta}$ Interfaces

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We have studied quasiparticle tunneling into atomically flat *a*-axis films of $YBa_2Cu_3O_{7-\delta}$ and $DyBa_2Cu_3O_{7-\delta}$ through epitaxial $CaTiO_3$ barriers. The junction heterostructures were grown by oxide molecular beam epitaxy and were carefully optimized using *in situ* monitoring techniques, resulting in unprecedented crystalline perfection of the superconductor-insulator interface. Below $T_c$, the tunneling conductance shows the evolution of a large unexpected asymmetrical feature near zero-bias. This is evidence that superconducting YBCO crystals, atomically truncated along the lobe direction with a titanate layer, have intrinsically broken particle-hole symmetry over macroscopically large areas.

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Tunneling into superconductors probes the electronic structure of quasiparticle (QP) excitations. According to the Bogoliubov description in conventional BCS theory, at the Fermi energy QPs are made up of electrons and holes with equal weight. Tunneling electrons into or out of the superconductor reveals the hole and particle content of the excitations, and in the absence of magnetism produces particle/hole (*p-h*) symmetric conductance spectra. For this reason, broken *p-h* symmetry in the local QP density of states (DOS) near impurities [1,2] and vortices [3,4] in cuprates has provided some of the most detailed experimental data on intrinsic magnetism in these superconductors [5,6]. Experimentally, impurity-induced DOS perturbations behave counterintuitively. For example, local DOS behavior near nominally nonmagnetic Zn in $Bi_2Sr_2CaCu_2O_{8+\delta}$ [1] has been explained by the Kondo effect [7,8] while nominally magnetic Ni causes less order parameter disruption than Zn [2]. Similarly, chain oxygen vacancies in $YBa_2Cu_3O_{7-\delta}$ (YBCO) cause strong resonances in the local DOS distributed in energy throughout the gap [9] and reveal magnetic character of the vacancy-Cu complex. These experiments play a crucial role in theoretical discussions of cuprates [10,11] and point to the utility of studying the electronic behavior of new defect structures. They have been possible only on *c*-axis surfaces of single crystals (cold-cleaved *in situ*). Study of the DOS of other surfaces [such as an abruptly truncated (100) crystal] and defect structures (such as a linear impurity array) requires either *in situ* vacuum tunneling into the as-grown surface or epitaxial stabilization of the defect structure by a suitable tunnel barrier.

In this Letter, we report *p-h* asymmetric conductance spectra tunneling into an atomically flat (100) YBCO surface through a nonmagnetic insulator, and we propose this asymmetry is caused by the underlying magnetism of the cuprate states. The barrier is a heteroepitaxial $CaTiO_3$ film, and Fig. 1 shows the arrangement of Cu-O planes and chains at the interface in this geometry; it is the precise truncation of the lattice at this plane that leads to our new results. We find a large particle-hole asymmetry in the subgap DOS in the superconducting state. We attribute these modifications of the DOS to QP scattering at the interface which behaves as a linear array of impurities. We have measured both the temperature and doping dependence of the asymmetry, and find it is strongest at optimal doping and weakens with underdoping, disappearing as the critical temperature $T_c \rightarrow 50$ K.

The tunnel junctions were fabricated from normal-metal–insulator–superconductor (NIS) trilayer films grown by ozone assisted molecular beam epitaxy, which has demonstrated excellent control of atomic layering of transition metal perovskites [12]. We used *in situ* reflection high-energy electron diffraction (RHEED) to characterize the surface crystal structure and morphology during film and heteroepitaxial barrier growth. (100) orientation of 200 nm thick YBCO and DyBCO films is accomplished by the self-template technique [13] on carefully prepared (100) $SrTiO_3$ substrates [14]. After YBCO deposition [Fig. 2(a)], the RHEED specular spot

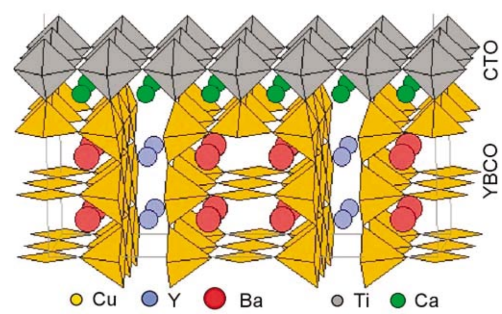


FIG. 1 (color online). Schematic crystal structure at the (100) YBCO/CTO interface, showing oxygen coordination of Cu and Ti atoms. O atoms are present at the vertices of each polyhedron. Note the fivefold coordination of chain Cu at the interface instead of fourfold in the bulk, and alignment of $TiO_3$ octahedron along the truncated $CuO_2$ plane edges.

  

(SS) intensity was equal to that of the starting substrate, and the third and first-order spots were comparable in intensity, with no reconstruction or other spots visible. These characteristics indicate that the surface was very close to an ideally truncated (100) crystal. *Ex situ* atomic force microscopy of YBCO films grown with identical RHEED showed rms roughness <4 Å over many $mm^2$, and asymmetric x-ray diffraction reciprocal space maps showed pure $a$-axis orientation and pseudomorphic growth up to 200 nm [15]. Directly following the cuprate growth, an insulating barrier of precisely 4, 5, or 6 unit cells of $CaTiO_3$ (CTO) was deposited. The CTO grew two-dimensionally and pseudomorphically, showing one SS oscillation/monolayer. The third-order spots disappeared within two CTO layers [Figs. 2(b) and 2(c)], and the SS was completely recovered by five layers [Fig. 2(d)]. Taken together, these features indicate uniform barrier coverage. Doping was controlled via a predetermined cooling procedure [16], followed by *in situ* Au counter electrode deposition.

The NIS trilayers were patterned into vertical mesa junctions with areas of 50–1000 $\mu m^2$. For this study we fabricated junctions ranging from near optimal ($T_c = 83$ K) to moderately underdoped ($T_c = 55$ K). The surface $T_c$, determined by the initial appearance of the gap structure described below, and bulk $T_c$, determined by transport on the film underneath, agree to within a few degrees. This is strong supporting evidence that the surface DOS sampled by tunneling is not marred by extrinsic effects (disorder or oxygen loss) and that the drastically altered superconductivity seen in the DOS is entirely due to the abrupt (100) termination.

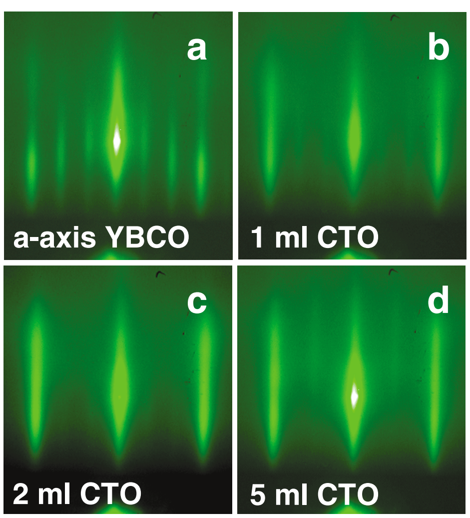


FIG. 2 (color online). RHEED images during trilayer deposition. (a) After 2000 Å YBCO; one-third order spots are due to the self-assembled $c$-axis structure lying in the plane of the film. The $a$-axis films are $b$-$c$ twinned, with domain sizes ~100 nm inferred from linewidths of diffraction maxima. (b)–(d) Diffraction during barrier growth.

Differential conductance $G(V)$ measurements identify tunneling as the dominant transport mechanism. $G(0)$ has a weakly insulating $T$ dependence from 300 to 100 K (decreasing less than a factor of 2) and below $T_c$, $G(100\ \mathrm{mV})$ is nearly $T$ independent. Moreover $G(0)$ scales linearly with junction area and exponentially with barrier thickness (a factor of 12 per titanate layer, at fixed doping). In addition, well into the normal state, $G(V)$ has the general form of a shifted parabola with minimum at $\approx +20$ mV for all junctions [Fig. 3]. This is consistent with elastic tunneling between metals of different work functions, resulting in a trapezoidal barrier profile [17]. Estimates of barrier thickness and height by fitting $G(V)$ at 100 K as in Ref. [17] are reasonable compared to other perovskite junctions with titanate barriers we have grown [18]. Fit thicknesses are within 25% of the nominal, and barrier heights for electron tunneling in the ~40 junctions presented here are $800 \pm 250$ meV (YBCO) and $205 \pm 120$ meV (Au).

The most important new result reported here is the unusual low bias ($|V| \leq 50$ mV) behavior of $G(V)$ below $T_c$. At negative bias, corresponding to tunneling of QPs from cuprate states with mostly particlelike character ("occupied" states) into empty Au states, $G(V)$ acquires a gaplike feature that reflects the onset of superconductivity. At $T \ll T_c$, near optimal doping the filled-state DOS [Figs. 3(a) and 4, normalized] shows a coherence peak near $-25$ meV whose energy is independent of $T$, and a "peak-dip-hump" feature. This behavior is in good quantitative agreement with angle-resolved photoemission data on untwinned, optimally doped $c$-axis YBCO

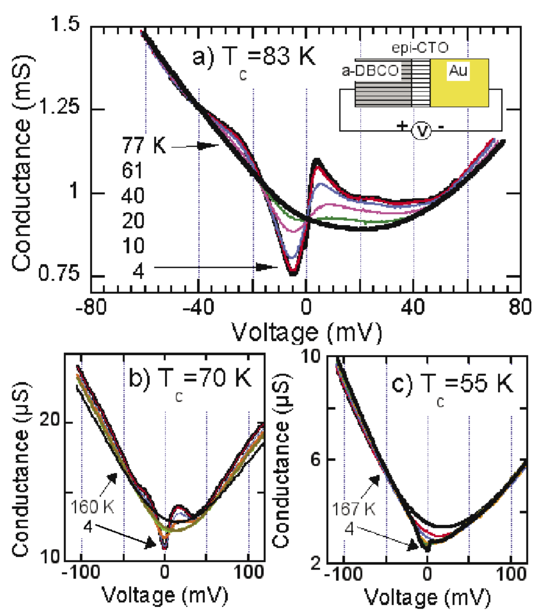


FIG. 3 (color online). (a)–(c) Raw conductance data for three NIS junctions with different underdopings, showing temperature evolution of the gap structure for occupied state DOS and filling in of empty-state DOS for $T < T_c$. $P$-$h$ asymmetry is strongest at highest $T_c$.

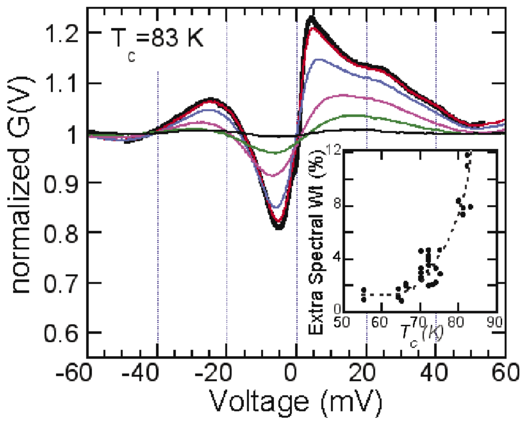


FIG. 4 (color online). Normalized $G(V)$ data for junction of Fig. 3(a). The inset shows extra spectral weight at $T = 4$ K in empty-state DOS versus $T_c$ for all junctions (filled-state DOS is conserved). The extra spectral weight decreases with decreasing $T_c$, disappearing as $T_c \rightarrow 50$ K.

at the $(\pi, 0)$ point in the Brillouin zone [19]. STM or STS on optimally doped $c$-axis YBCO has also shown a $T$-independent coherence peak energy [20]. Integrating the normalized $\int_{-60\,\mathrm{mV}}^{0} G(T, V)dV$, DOS is conserved as expected (to normalization error, $\leq 2\%$).

In stark contrast, $G(V)$ for positive bias shows an unexpected and dramatic steplike increase just above $V = 0$ where a "gap" is expected by symmetry. This bias corresponds to electrons tunneling from the gold into cuprate states with mostly holelike character. For $V > 0$, the integrated "empty" state DOS is not conserved; data near optimal doping [Fig. 4] show 12% more states at low $T$ as compared to the normal state. This clearly demonstrates the breaking of symmetry between particle-like and holelike DOS at this interface in the superconducting state. The extra spectral weight decreases linearly in $T$ (not shown), vanishing at $T_c$. Samples with lower $T_c$ show less pronounced asymmetry [Figs. 3(b) and 3(c)]. This extra spectral weight can be used to quantify the strength of symmetry breaking at different doping, and is summarized for all junctions in Fig. 4 (inset). We emphasize that *every* epitaxial junction with pure $a$-axis orientation we have measured shows extra states only above the chemical potential and inside the gap, with occupied state DOS conserved. The $G(V)$ curves are also relatively insensitive to magnetic fields up to 7 Tesla (parallel or perpendicular to the surface) at any voltage, including low bias. This rules out an explanation involving collectively generated interfacial currents, such as when the splitting of a zero-bias conductance peak increases in field [21].

Thus, we conclude that this steplike DOS asymmetry, seen only below $T_c$, is a robust and intrinsic feature of YBCO crystals atomically truncated along a lobe direction by an epitaxial CTO layer. This behavior is in marked contrast to all tunneling data on $c$-axis, (110) or rough (100) surfaces, with or without impurities or defects, in that here $p$-$h$ asymmetry is a *global* (averaged) property of the atomically flat surface. We contrast this with symmetric DOS seen at (110) and rough (100) YBCO surfaces [22] showing a large zero-bias conductance peak (ZBCP) attributed to Andreev bound states (ABS) [23]. For flat lobe-facing surfaces the ABS model predicts $p$-$h$ symmetric DOS and no ZBCP. Flat (100) YBCO surfaces with amorphous barriers have shown a ZBCP [24] attributed to the nonspecular interface. We also contrast our results with small sloping backgrounds in $G(V)$ outside the gap in STM spectra of $c$-axis Bi-2212 [25] in which coherence peaks and subgap $G$ are nearly symmetric about $V = 0$.

Two aspects of our data merit particular attention: (i) the low bias asymmetry appearing only in the superconducting DOS, and its doping dependence, and (ii) the large residual subgap conductance seen in $G(V)$: the subgap conductance never vanishes, even at $T \ll T_c$; at most it falls to $\sim$80% of $G(0)|_{T=T_c}$. As for (ii), we note that all planar cuprate NIS junctions ($a$-$b$ plane and $c$ axis) in the literature show similar or larger subgap $G$ [26], and its origin is not understood. It is often ascribed to weakened superconductivity at the surface, intrinsically or due to disorder. In our case it persists despite the fact that the interface epitaxy was carefully optimized and that tunneling (with a narrow forward cone estimated $\leq 25°$) probes QP states near antinodes where the energy gap is fully formed and $G(0)|_{T=0}$ should approach zero.

Regarding (i), two qualitative scenarios based on how the plane and chain DOS are perturbed by local defects may be relevant to our data. Our low bias asymmetry may be compared to asymmetric resonances observed in the local DOS at Cu sites next to a Ni impurity [2] or in individual YBCO chains [9], both of which can show substantial $p$-$h$ asymmetry but yield nearly symmetric DOS when averaged over large ($>100 \times 100$ Å$^2$) areas [27]. That is, extra spectral weight in empty-state DOS at one site is compensated for by extra weight in filled-state DOS at other sites. In our geometry, the interface consists of one-dimensional $CuO_2$ plane edges, as well as interleaved $CuO_{1-\delta}$ chains [Fig. 1]. The truncation of the $CuO_2$ plane with a row of $TiO_3$ octahedra may perturb the QP DOS at the Cu site in a manner analogous to that seen experimentally [2] around a Ni defect and predicted theoretically [28,29]. It is precisely into these sites that tunneling occurs and, because of the translational symmetry of the interface (all sites are equivalent), the asymmetry in the tunneling DOS would no longer disappear upon averaging over the interface.

Similarly, a perturbation of the chain-derived DOS at the interface may arise from a different oxygen coordination of chain Cu atoms next to the titanate. In unperturbed chains, $s$-wave pairing is induced by proximity to superconducting planes, and $p$-$h$ asymmetric resonances along chains in $YBCO_{6.97}$ seen by STM or STS [9] imply a magnetic character for the scattering defects. A theory of these resonances [11] may be relevant here, assuming perturbed surface chains remain superconducting by proximity in the $a$-axis geometry and represent a tunneling channel comparable in strength to plane edges. Scattering resonances in this model may contribute to a large residual subgap $G$, or to $p$-$h$ asymmetric DOS, or both, depending on the sign and distribution of the scalar component $U_0$ of the impurity potential (notation of Ref. [11]) characterizing the defects. A distribution with large $U_0$ would lead to nonzero residual $G$. If all defects are identical (e.g., chain O vacancies), they likely produce $U_0$ of a definite sign, and thus lead to $p$-$h$ asymmetry on top of residual $G$. This may explain the doping dependence of both the residual subgap $G$ and the $p$-$h$ asymmetry seen here: as the defect density increases, bound states begin to interfere, gradually washing out the asymmetry and further filling in the gap [30].

To conclude, we have performed the first systematic study of $a$-axis tunneling into atomically flat YBCO with an epitaxial titanate barrier. We observe a remarkable subgap asymmetry of the QP DOS in the superconducting state, which we interpret as a consequence of the termination of the cuprate crystal at the boundary. Since the interface is regular and homogeneous, this result provides a clear test for theories of high $T_c$ superconductivity.

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