Observation of bound surface states in grain-boundary junctions of high-temperature superconductors

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We have performed a detailed study of the tunneling spectra of bicrystal grain-boundary junctions (GBJ's) fabricated from the high-temperature superconductors (HTS) $YBa_2Cu_3O_{7-\delta}$ (YBCO), $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO), $La_{1.85}Sr_{0.15}CuO_4$ (LSCO), and $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO). In all experiments the tunneling direction was along the CuO_2 planes. With the exception of NCCO, for all materials a pronounced zero bias conductance peak (ZBCP) was observed that decreases with increasing temperature and disappears at the critical temperature. These results can be explained by the presence of a dominating *d*-wave symmetry of the order parameter resulting in the formation of zero-energy Andreev bound states at surfaces and interfaces of HTS. The absence of a ZBCP for NCCO is consistent with a dominating *s*-wave symmetry of the pair potential in this material. The observed nonlinear shift of spectral weight to finite energies by applying a magnetic field is in qualitative agreement with recent theoretical predictions. [S0163-1829(98)08441-0]

There is strong evidence that the superconducting order parameter (OP) in the high-temperature superconductors (HTS) has a dominating *d*-wave symmetry.[1,2] For this pairing symmetry there is a π-phase shift of the OP in orthogonal *k*-space directions resulting in a positive and negative sign of the pair potential in those directions. This also means that there are directions with nodes of the pair potential, e.g., for a pure $d_{x^2-y^2}$ symmetry, the nodes are along the [110] direction in the CuO_2 plane. For the tunneling spectra of junctions employing HTS electrode materials with a *d*-wave symmetry of the OP, a pronounced zero bias conductance peak (ZBCP) has been predicted originating from midgap surface (interface) states or zero-energy bound states (ZES) at the Fermi level.[3–8] The physical reason for these states originates from the fact that quasiparticles incident and reflecting from the surface, propagate through different order-parameter fields, which leads to Andreev reflection. The constructive interference between incident and Andreev-reflected quasiparticles results in bound states. Stable ZES are formed if the scattering induces a change in sign of the OP. For a $d_{x^2-y^2}$-wave symmetry such sign change and, hence, the presence of ZES is possible for all surfaces parallel to the *c* axis except for those with the lobe directions perpendicular to the surface, whereas for an *s*-wave symmetry no ZES are possible. The spectral weight of the ZES for a $d_{x^2-y^2}$-wave symmetry depends on the orientation of the surface with respect to the crystal axis. The maximum spectral weight is expected for a (110) surface and, hence, a maximum ZBCP is expected for tunneling in the direction of the nodal lines, i.e., the [110] direction. This has been observed recently using low-temperature scanning tunneling spectroscopy[9] and planar-type junctions.[10] We note that the ZBCP is sensitive to surface roughness making it difficult to distinguish between the directions in the plane.[11–13]

Initially, the ZBCP in the tunneling spectra of HTS junctions has been explained within the Appelbaum-Anderson (AA) model[14] due to the presence of a large density of magnetic scattering centers at the surface of the junction electrodes. However, the AA model predicts a ZBCP that is not expected to disappear at a certain temperature and to split *linearly* with increasing applied magnetic field. Furthermore, it has been suggested recently that the surface of *d*-wave superconductors might show spontaneously generated surface currents[11,15] and a phase with broken time-reversal symmetry.[16] In such state the Andreev bound states shift to finite energies resulting in a splitting of the ZBCP even in zero magnetic field.[16] Applying a magnetic field results in a further splitting of the ZBCP. However, in contrast to the AA-model prediction this splitting is predicted to increase *nonlinearly* with applied field. In order to clarify these issues experimentally and to rule out competing explanations for the origin of the ZBCP in grain-boundary junctions (GBJ's), in this paper we present a comprehensive analysis of the ZBCP for different materials including $YBa_2Cu_3O_{7-\delta}$

(YBCO) (60-K phase and 90-K phase), $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO), $La_{1.85}Sr_{0.15}CuO_4$ (LSCO), and $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO). We emphasize that for YBCO, BSCCO, and LSCO the OP is considered to have a dominating *d*-wave component,[17] whereas for NCCO the dominating component most likely is an *s*-wave as suggested by several experiments.[18–21] Therefore, if ZES are the origin of the observed ZBCP, such a peak should be present only for the *d*-wave but not for the *s*-wave material. As shown below, for NCCO indeed no ZBCP is observed, giving strong evidence for the ZES scenario and ruling out the magnetic interface scattering model. Our data also show a nonlinear evolution of the shift of spectral weight to higher energies with increasing magnetic field.

Up to now in several experiments a ZBCP has been observed in junctions where only a single electrode was based on a cuprate superconductor.[9,10,21–25] Many more experiments with the tunneling direction along the *c*-axis have been performed, where a ZBCP due to ZES is expected only as an artifact of the finite surface roughness of the HTS electrode. In our experiments we used well-defined [001] tilt HTS GBJ's fabricated on bicrystal substrates.[26] It has been shown recently that the quasiparticle transport mechanism in these junctions is dominated by elastic, resonant tunneling via localized states making them suitable for spectroscopic studies.[27–30] A pronounced ZBCP has been observed in the tunneling conductance of these GBJ's which has been discussed both in terms of ZES (Ref. 30) and the presence of magnetic scattering centers at the grain boundary.[29] In this report, we clearly show that the former analysis can be applied for the HTS GBJ's. There are several advantages of using GBJ's. First, these junctions are formed by two HTS electrodes and can be fabricated easily from different HTS materials.[26,30] Employing *intrinsic* interfaces less problems arise from contamination due to *ex situ* processing of the samples. Second, the tunneling direction for [001] tilt GBJ's is along the *ab*-plane. Third, the direction of tunneling within the *ab*-plane can be varied by varying the misorientation angle of the bicrystal substrate, although the faceting of the grain boundary always results in an averaging over a finite range of angles.[31] In this context, we note that an exact quantitative description of effects related to the faceting is not yet available.

The GBJ's studied in our experiments were prepared on symmetrical [001] tilt $SrTiO_3$ bicrystals with 24° or 36.8° misorientation angles. The fabrication and characterization of the GBJ's has been described in detail elsewhere.[26,32] The measurements of the current-voltage $[I(V)]$ and conductance vs voltage $[G(V)=dI(V)/dV]$ characteristics were performed in a standard four-lead arrangement.

Figure 1 shows a set of typical $G(V)$ curves obtained for LSCO GBJ's. The critical temperature T_c of the LSCO electrodes was about 24 K. Very similar curves (see Fig. 2) have been measured for oxygen-deficient YBCO ($T_c \approx 60$ K), BSCCO ($T_c \approx 80$ K) (Refs. 29 and 30), and fully oxygenated YBCO ($T_c \approx 90$ K). At voltages above the gap voltage of the electrode material the $G(V)$ curves show a temperature-independent conductance that has an about parabolic shape and can be modeled by the influence of the applied voltage on the shape of the tunneling barrier.[29] Below the gap voltage a reduced conductance due to a reduced density of states

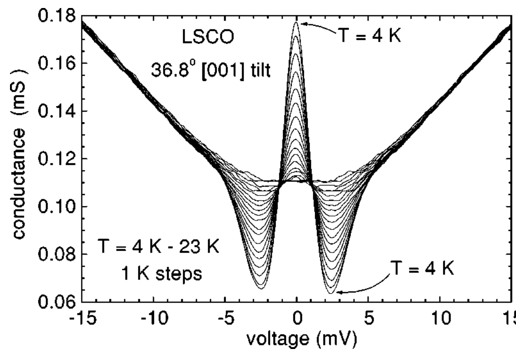

FIG. 1. Differential conductance vs voltage for a 36.8° [001] tilt LSCO GBJ between 4 and 23 K.

is observed. With increasing temperature the conductance increases approaching the normal-state curve $G_n(V)$ with T approaching T_c. The height of the ZBCP decreases with increasing temperature and vanishes at $T=T_c$. For most samples over a considerable temperature range the decrease follows a $1/T$ dependence. The temperature evolution of the $G(V)$ curves clearly demonstrates that the superconducting state is being probed. This proof is important with respect to the interpretation of the ZBCP in terms of Andreev bound states. The $G(V)$ curves also show that the parabolic background conductance $G_n(V)$ is a normal-state effect, which in the following is eliminated by normalizing $G(V)$ to $G_n(V)$.

In Fig. 2 the normalized tunneling conductance G/G_n of GBJ's fabricated from YBCO, BSCCO, LSCO, and NCCO ($T_c \approx 24$ K) is plotted versus the voltage normalized to the gap voltage V_g. Here, $V_g=25$, 20, 15, 6, and 6 meV was used for BSCCO, YBCO (90-K phase), YBCO (60-K phase), LSCO, and NCCO, respectively. In first approximation eV_g can be considered to be close to the gap energy Δ_0, in contrast to the BCS theory. See for example the calculations in Ref. 5. It is evident from Fig. 2(a) that YBCO, BSCCO, and LSCO, for which the OP is considered to have a dominating *d*-wave component, qualitatively show the same behavior. A clear gap structure with reduced density of states is observed in combination with a ZBCP. For BSCCO and YBCO-90 the

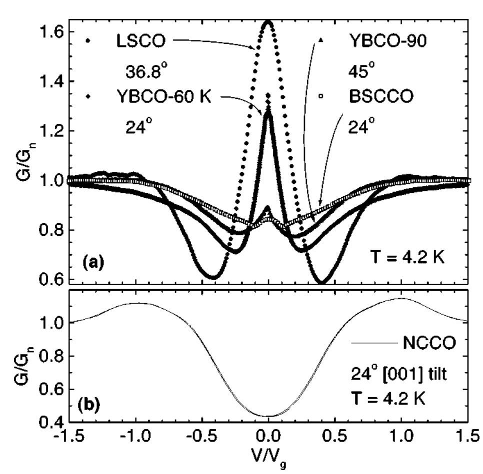

FIG. 2. Normalized conductance vs normalized voltage of [001] tilt GBJ's formed by YBCO (90- and 60-K phase), BSCCO, and LSCO at $T=4.2$ K. In (b) the same dependence is shown for a NCCO GBJ.

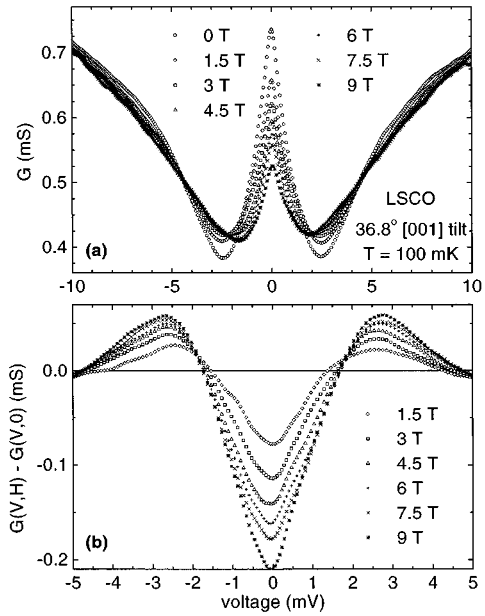

FIG. 3. (a) Magnetic-field dependence of the ZBCP at 100 mK for a [001] tilt LSCO GBJ. In (b), $G(V,H)$-$G(V,0)$ is plotted for the same sample. The applied magnetic fields ranged between 1 and 9 T (1.5 T steps).

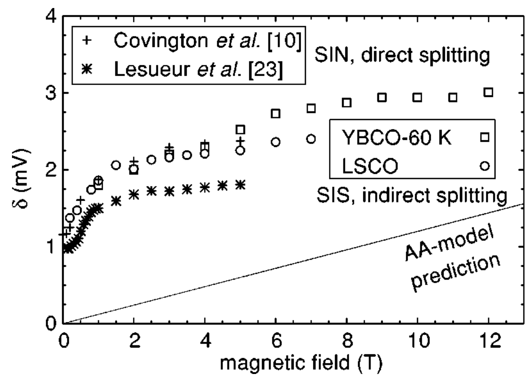

FIG. 4. Splitting δ of the $G(V,H)$-$G(V,0)$ curves vs applied magnetic field of a 36.8° [001] tilt LSCO GBJ at $T=100$ mK and a 24° [001] tilt YBCO GBJ at $T=4.2$ K. Also shown are data for the *direct* splitting in $G(V,H)$ of superconductor-insulator-normal metal (SIN) junctions from literature.

ZBCP is reduced in height as compared to YBCO-60 and LSCO. The reason for this reduction is not clear at present. However, considering the dependence of the ZBCP on the degree of faceting of the grain boundary, which determines the amount of averaging over the in-plane crystal directions, this observation is not surprising. In contrast, for NCCO, which is considered to be a *s*-wave superconductor, only a gap structure but never a ZBCP is observed as demonstrated by Fig. 2(b).

We also measured the dependence of the ZBCP on a magnetic field H applied parallel to the grain-boundary plane. A typical result is shown in Fig. 3. The applied magnetic field reduces the spectral weight at zero energy and shifts it to finite energies that increase with increasing field. As shown in Fig. 3(b) this results in a split peak structure of the difference curve $G(V,H)$-$G(V,0)$ where the distance between the peaks is defined as 2δ. We emphasize that so far we could not directly observe the splitting in the $G(V)$ curve down to $T=100$ mK, where the thermal smearing amounts to only a few 10 μeV. In Fig. 4, δ is plotted versus H for a LSCO GBJ at 100 mK and a YBCO GBJ at 4.2 K together with data of the *direct* split in $G(H)$ taken from literature. Clearly, δ does not vary linearly with H as predicted by the AA model. For all investigated samples δ increases slower than linearly and tends to saturate at high fields in agreement with results published recently.[10]

We first will discuss our experimental findings in terms of the AA model.[14] For tunneling across a barrier containing localized spins beyond a contribution G_1 due to direct tunneling without interaction with the spins there are two further contributions G_2 and G_3 to the total conductivity. The first (G_2) is related to tunneling involving a spin exchange and the latter (G_3) to Kondo-type scattering. According to the AA model[14] one expects $G_3(V,T)\propto\ln[E_0/(|eV|+k_BT)]$, where E_0 is a cutoff energy. Applying a magnetic field the Zeemann splitting of the impurity levels causes a dip of width $2\delta=2g\mu_BH$ due to a reduction of G_2. Here, g is the g factor and μ_B the Bohr magneton. Furthermore, in an applied field the Kondo peak is split into three peaks separated by δ with the zero bias peak completely suppressed. This results in a peak of $G(V,H)$-$G(V,0)$ at $eV=\pm\delta$. The AA model predicts a peak-to-peak width $2\delta=2g\mu_BH$ that increases $\propto H$, i.e., $\delta/H=g\mu_B\simeq0.12$ meV/T for $g\simeq2$. This is in clear contradiction to our results, which show both much larger absolute values of δ/H up to more than 2 meV/T and a strong increase of δ/H with decreasing H, in agreement with other data reported in literature.[10,23] Furthermore, for all YBCO, BSCCO, and LSCO samples the ZBCP always disappeared just at T_c, which is significantly different for the different materials. This is very difficult to be explained within the AA model, which predicts the ZBCP to decrease with increasing T but not to disappear at a specific temperature. Finally, within the AA model the absence of the ZBCP for NCCO would imply the absence of magnetic scatterers for this material. Supposing that magnetic scatterers at grain boundaries result from oxygen loss and the formation of magnetic Cu^{2+} ions, the basic difference between NCCO and the other materials is difficult to understand.

We now turn to the Andreev bound-state model. As discussed above, in this model the ZBCP arises from bound states formed by the constructive interference of quasiparticles that propagate through different order-parameter fields incident and reflecting from the surface of the junction electrode. ZES are formed if the scattering induces a change in sign of the OP. Hence, ZES are not possible for an *s*-wave symmetry of the OP. However, in the case of a dominating $d_{x^2-y^2}$ symmetry of the OP, at all surfaces parallel to the c axis ZES are formed except for the surfaces exactly perpendicular to the *a*- or *b*-axis direction. Hence, the ZES model naturally accounts for the observation that a ZBCP is observed only for YBCO, BSCCO, and LSCO, which most likely have a dominating *d*-wave component of the OP, whereas it is absent for NCCO, which is supposed to have a dominating *s*-wave OP. The ZES model also qualitatively accounts for the increase of the height of the ZBCP with decreasing temperature and the nonlinear shift of the peak spectral weight to finite voltages with increasing magnetic field.[13,16,33,34] For example, for a surface to *a*-axis orientation of 20°, $G(0,T)/G_n(0)$ was predicted to decrease about $\propto 1/T$ (Ref. 13) in fair agreement with our data. A detailed quantitative analysis of our experimental data still is not possible, since no prediction of the exact T and H dependence of the ZBCP is available taking into account the angle averaging due to the faceting of the grain boundaries.

We finally would like to address the possibility of a surface state with broken time reversal symmetry as predicted by Fogelström *et al.*[16] and experimentally observed by Covington *et al.*[10] In this case the ZBCP is expected to split in zero magnetic field. Such splitting has not been observed directly in our experiments down to temperatures of 100 K for LSCO and 4.2 K for YBCO similar to other experiments.[35] A possible reason for this observation may be the considerable faceting of the grain-boundary plane together with impurity scattering that suppresses the field splitting of the ZBCP.[34] This is the reason why the observed behavior of δ vs H does not provide definitive evidence for a subdominant *s*-wave OP and time-reversal symmetry breaking at the grain-boundary interface. This issue has to be clarified by future experimental and theoretical work taking into account the grain-boundary faceting and impurity scattering.

In conclusion, it has been shown that quasiparticle tunneling in GBJ's can be used for probing the symmetry of the order parameter in a HTS. The tunneling spectra of [001] tilt GBJ's formed by YBCO, BSCCO, and LSCO were found to always show a ZBCP while such peak is absent for NCCO. The height of the ZBCP decreases with increasing temperature and disappears at T_c. These observations are not compatible with the assumption of tunneling involving magnetic impurities as described by the AA model, but can naturally be explained by the presence of zero-energy Andreev bound states at surfaces of a HTS. The existence of ZES represents further proof that the order parameter of YBCO, BSCCO, and LSCO changes sign on the Fermi surface and most likely has a dominating *d*-wave component. The tunneling data of NCCO is consistent with an anisotropic *s*-wave symmetry of the pair potential in the electron-doped HTS. The evolution of the ZBCP with varying applied magnetic field and temperature can be qualitatively described within the *d*-wave scenario.

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