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 (GBJs) fabricated from the high temperature superconductors (HTS) YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO), Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO), La$_{1.85}$Sr$_{0.15}$CuO$_4$ (LSCO) and Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-δ}$ (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 which 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.

There is strong evidence that the superconducting order parameter (OP) in the HTS has a dominating d-wave symmetry. 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 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 ZBCP has been predicted originating from mid-gap surface (interface) states or zero energy bound states (ZES) at the Fermi level. 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 a 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 (LTSTS) and planar type junctions. We note that the ZBCP is sensitive to surface roughness making it difficult to distinguish between the directions in the plane.

Initially, the ZBCP in the tunneling spectra of HTS junctions has been explained within the Appelbaum-Anderson (AA) model 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 and a phase with broken time-reversal symmetry. In such state the Andreev bound states shift to finite energies resulting in a splitting of the ZBCP even in zero magnetic field. 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 GBJs, in this report we present a comprehensive analysis of the ZBCP for different materials including YBCO (60 K-phase and 90 K-phase), BSCCO, LSCO, and NCCO. We emphasize that for YBCO, BSCCO and LSCO the OP is considered to have a dominating d-wave component, whereas for NCCO the dominating component most likely is a s-wave as suggested by several experiments. Therefore, if ZES are the origin of the observed ZBCP, such 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. 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 artefact of the finite surface roughness of the HTS electrode. In our experiments we used well defined [001] tilt HTS-GBJs fabricated on bicrystal substrates [2]. 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 GBJs which has been discussed both in terms of ZES [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-GBJs. There are several advantages of using GBJs. Firstly, 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. Secondly, the tunneling direction for [001] tilt GBJs is along the ab-plane. Thirdly, 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 GBJs 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 GBJs has been described in detail elsewhere [24,22]. 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.

![FIG. 1. Differential conductance vs. voltage for a 36.8° [001] tilt LSCO-GBJ between 4 and 23 K.](image1)

![FIG. 2. Normalized conductance vs. normalized voltage of [001] tilt GBJs 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.](image2)

In Fig. 2 the normalized tunneling conductance, $G/G_n$, of GBJs 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 $\Delta_0$, in contrast to the BCS-theory. See for example the calculations in reference [3]. It is evident from Fig. 2 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 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 an s-wave superconductor, only a gap structure but never a ZBCP is observed as demonstrated by Fig. 3b.

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 one expects $G_3(V,T) \propto \ln[E_0/(|eV| + k_B T)]$, where $E_0$ is a cut-off energy. Applying a magnetic field the Zeeman splitting of the impurity levels causes a dip of width $2\delta = 2g\mu_B H$ due to a reduction of $G_2$. Here, $g$ is the $g$-factor and $\mu_B$ the Bohr magneton. Furthermore, in an applied field the Kondo peak is split into three peaks separated by $2\delta$ 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 $2\delta = 2g\mu_B H$ that increases as $H$, i.e. $\delta/H = g\mu_B \simeq 0.12$ meV/T for $g \simeq 2$. This is in clear contradiction to our results, which show both much larger absolute values of $\delta/H$ up to more than 2 meV/T and a strong increase of $\delta/H$ with decreasing $H$, in agreement with other data reported in literature [10,12]. 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 a \( s \)-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. For example, for a surface to \( a \)-axis orientation of 20°, \( G(0,T)/G_a(0) \) was predicted to decrease about \( \propto 1/T \) \([3]\) 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. \([11]\) and experimentally observed by Covington et al. \([16]\). 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 mK for LSCO and 4.2 K for YBCO similar to other experiments \([\beta]\). 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 \([\beta]\). This is the reason why the observed behavior of \( \delta \) 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 GBJs can be used for probing the symmetry of the order parameter in HTS. The tunneling spectra of \([001]\) tilt GBJs 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 HTS. The existence of ZES represents a 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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