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Spatially continuous zero-bias conductance peak on (110) $YBa_2Cu_3O_{7-\delta}$ surfaces

L. Alff,* H. Takashima, S. Kashiwaya, N. Terada, and H. Ihara
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

Y. Tanaka
Niigata University, Ikarashi, Niigata 950-21, Japan

M. Koyanagi and K. Kajimura
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

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We report the observation of a pronounced high zero-bias conductance peak (ZBCP) in the conductance spectra of (110)-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin-film surfaces by low-temperature scanning tunneling microscopy/spectroscopy at 4.2 K. On films with very low surface roughness, both the superconducting gap structure and the ZBCP could be clearly observed in the spectra and neither depended on the measurement position or on the distance between the tunneling tip and the sample surface. This result is in agreement with the recent theoretical prediction of the formation of bound states on surfaces of d-wave superconductors that lead to a ZBCP with a maximum for (110)-oriented surfaces. [S0163-1829(97)50922-2]

A zero-bias conductance peak (ZBCP) has been observed in the conductance spectra of a wide variety of junctions with at least one electrode being a high-temperature superconductor (HTS).[1–5] Since many experiments suggest strongly a d-wave order-parameter symmetry for the oxide HTS's, interest in the relation between the pairing type and the conductance spectra has risen. Recently, it has been shown that the d-wave order-parameter symmetry leads to the formation of zero-energy states at surfaces and interfaces due to the sign change in the pair potential.[6] For $d_{x^2-y^2}$-wave symmetry the presence of these bound states leads to a ZBCP in the conductance spectra in superconductor–insulator–normal metal (SIN) junctions. This peak depends on the surface orientation being maximum for (110)-oriented surfaces.[7–10] The advantage of measuring the conductance spectra on the surface of a HTS by low-temperature scanning tunneling microscopy and spectroscopy (LTSTM/S) is the high spatial resolution due to the small diameter of the junction.[11] Several groups have performed LTSTS measurements using HTS samples with different crystal orientations.[3,12–14] However, the results are still not uniform, probably because the model assumption of perfectly flat interfaces or surfaces may not always be realized in experiments. It has been suggested that surface roughness weakens the bound states, and may even lead to a ZBCP on a-axis and c-axis oriented surfaces.[15–17] In this paper, we report a spatially resolved observation of a continuous ZBCP on high-quality (110)-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films.

A very important requirement for the reliable measurement of conductance spectra on the surface of a HTS is a high sample surface quality. Reproducible samples with atomically flat surfaces and not degraded electronic surface states are indispensable for obtaining spectra with consistent properties at different measurement locations on the sample surface. A detailed description of our fabrication process and of the sample characterization will be given elsewhere.[18] Briefly, the thin films were sputtered on chemically etched $SrTiO_3$ substrates using a self-template method and pure oxygen plasma. Typical values of the critical temperature, T_c, were between 75 and 82 K. The alignment of the c axis in the substrate plane was found to be over 95%. Reflection high energy electron diffraction (RHEED) analysis confirmed the absence of possible (103)/(013) phase components in the surface layers. The surface roughness of the samples was characterized by atomic force microscopy (AFM) at room temperature. The films grown on HCl-etched $SrTiO_3$ substrates were found to have a very flat surface with some isolated pit and mountain structures. In large parts of the sample surface, the roughness was well below 1 nm, and no structures could be resolved within the z resolution of our experimental equipment. Macroscopical corrugations[14] probably due to (103)/(013) growth[19] or crack formation, as frequently found in (110) $YBa_2Cu_3O_{7-\delta}$ films, were not observed for our samples. Furthermore, in the LTSTS measurements the portion of semiconducting spectra was insignificantly small, indicating high surface quality and stability of the surface electronic states, despite an air-exposure time of about 30 min.

The experimental setup of our LTSTM/S system has been described elsewhere.[20] In brief, the tunneling current between the superconductor surface and a platinum tip was observed for various bias voltages, here between 40 mV and 200 mV. The current was always set to 1 nA at the respective bias voltage. This effectively realized a SIN point contact with a very small diameter and resistance typically of the order of 0.1 GΩ. The samples were cooled down to 4.2 K using helium as a heat exchange gas. The results of LTSTS measurements can considerably depend on the place of measurement and the bias voltage, due to strongly inhomogeneous surface quality and tip-surface interactions, respectively. Therefore, we established as criterion *sine qua non* for reliable data that the spectra do not depend on the measurement position or the tip-sample distance, as postulated elsewhere in order to achieve vacuum tunneling.[21] With the apparent work function $\phi_A \equiv (\hbar^2/8m)(d \ln I/ds)^2$, where

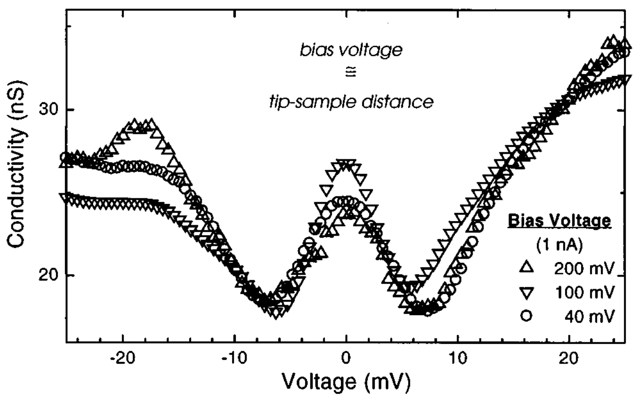

FIG. 1. Conductance spectra on the surface of (110)-oriented $YBa_2Cu_3O_{7-\delta}$ films for different bias voltages at 1 nA. The different bias voltages correspond to different tip-sample distances. The conductivity values for 200 and 100 mV were adjusted to the values for 40 mV.

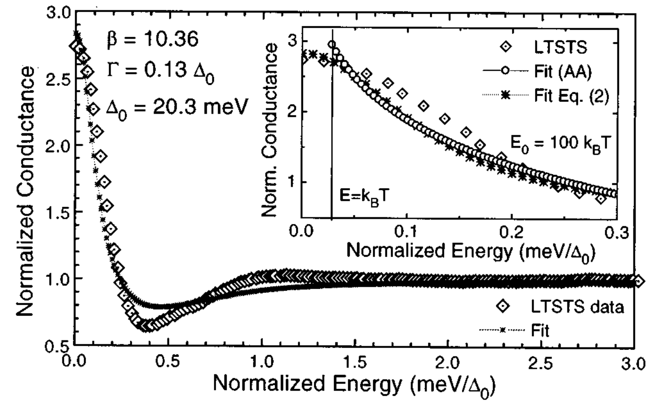

FIG. 2. Normalized conductance vs normalized energy of a SIN junction measured by LTSTS. The experimental data is represented by dotted diamonds, a fit according to Eq. (2) is shown as stars. In the inset a comparison with the Anderson-Appelbaum model is shown.

s is the tip-sample distance and *I* the tunneling current, typical values for ϕ_A were about 0.1 eV. For comparison, Edwards *et al.* obtained about 1 eV for *in situ* cleaved $YBa_2Cu_3O_{7-\delta}$ single crystals, where a higher surface quality is expected.[22]

In Fig. 1 the dependence of the as-measured tunneling spectra on the bias voltage is shown. The current was set to 1 nA at the respective bias voltage by changing the distance between tip and sample. Thus, an increased bias voltage corresponds to a larger tip-sample distance. The zero-bias conductance and the gap structure did not depend significantly on the tip-sample distance. This result indicates that the tunneling current did not stem from possible tip-sample interactions. Note the spectra do not depend on the place of measurement. During automatic line scans and after a new tip approach on a different surface location inside an arbitrarily chosen square with a 160 nm length of a side, the spectra showed no change. Each sample was measured only once and the spectra were taken prior to the topographic measurements in order to avoid sample surface and/or tip damage.

A typical measured conductance spectra is shown in the main part of Fig. 2, represented by the dotted diamonds. Here, the numerical derivative, dI/dV, of a measured current-voltage characteristic was normalized by its linear background conductance and plotted versus energy normalized by the energy gap, Δ_0. For $|eV|>|\Delta_0|$ a linear background conductance was observed. Such linear backgrounds have been observed for various types of SIN junctions and have been attributed to strong inelastic tunneling processes.[23] However, since the data in the literature is diverging, a more detailed background analysis is still required. For example, sometimes an asymmetry in the background conductance was found that is not understood at present.

The normalized conductance was highest at an energy where one would expect the superconducting gap, sloping down to a minimum at about 0.4 times the normalized energy. For our films, the value of Δ_0 was around 20 meV. Thus, for $2\Delta_0/k_BT_c$ a value of about 5.8 was obtained, typical for high-temperature superconductors.[24] Approaching zero energy, a large ZBCP with a peak height of 2.5–3.5 times the value of the conductance at Δ_0 was always observed. The peak had a full width at half maximum of about 0.4 times the energy gap.

In Fig. 3 the spatial variation of the conductance is shown in a three-dimensional plot. Here, the conductance spectra of 51 different measurement sites equidistantly located in a scan range of 160 nm are displayed, measured with a current of 1 nA at 100 mV bias voltage. Without exception, all spectra show a pronounced ZBCP. Before and after the LTSTS scan shown in the upper part of Fig. 3, a topographic image along the scan line was taken. These measurements are displayed in the lower part of Fig. 3, which shows a constant sample tilt of about 3° and a very low surface roughness—results which reinforce our previous AFM measurement. Even though we were not able to detect atomical

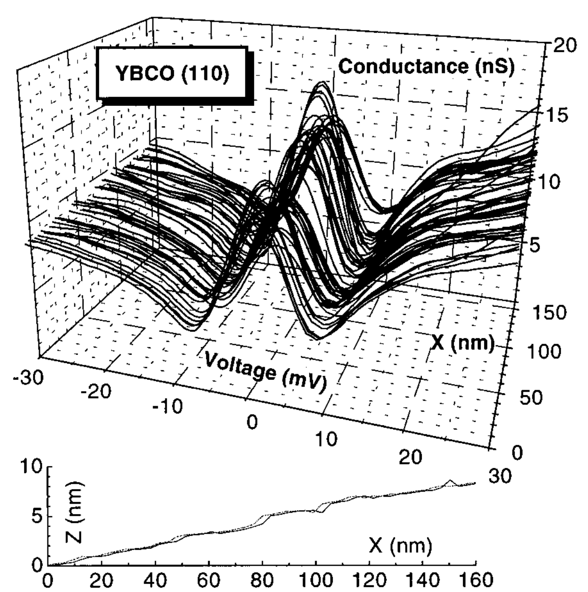

FIG. 3. Spatial variation of the conductance spectra measured in a line scan of 160 nm length. The lower image shows topographic data taken before and after the scan along the same line.

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corrugations on the (110)-oriented surface, the smoothness of the topographical data is consistent with the spatial uniformity of Δ_0 and the continuous ZBCP in the scan range. This is an observation of a spatially resolved *continuous* ZBCP on a (110)-oriented HTS surface. The changes in the height of the ZBCP at some locations may be attributed to small changes in the surface quality and roughness that are expected to influence the zero-bias conductance peak.[15,16] We conclude from this data that the ZBCP is an *intrinsic* feature of the spectra obtained on a (110) $YBa_2Cu_3O_{7-\delta}$ surface. We suggest that there are three main obstacles in observing a ZBCP in practice: inhomogeneous electronic surface states leading to a high percentage of semiconducting spectra, deviations from the crystal orientation [as might occur if (103)/(013) growth is predominant], and surface roughness. Only if all these conditions are dealt with is a continuous observation of the ZBCP possible. We note in addition that the same continuous ZBCP is found when the scan range is arbitrarily reduced, until it reaches 10 Å, i.e., the spacing of the measurement points is about 0.2 Å.

Some groups[2,4,5,25] have tried to explain the ZBCP as originating from inelastic spin-flip scattering of electrons tunneling through the barrier. A corresponding theory has been formulated for NIN junctions in the Anderson-Appelbaum model.[26,27] This model postulates the existence of isolated localized magnetic states with arbitrarily directed magnetic moments allowing exchange scattering. For interfaces of superconducting junctions, the maximum density of localized states as candidates for the paramagnetic scattering centers has been estimated, for both Nb junctions with amorphous silicon barriers[28] and HTS,[29] to be about $10^{20}/\mathrm{cm}^3$ eV. Assuming this value also holds for the surface states, less than one state per eV would be found in a cube of 2 nm side length. Thus, within the Anderson-Appelbaum model one would expect LTSTS—with its clearly higher spatial resolution—to observe isolated spin states giving a ZBCP with no ZBCP in between. The measurement of a continuous ZBCP is therefore contradictory to this model. In addition, the assumption of paramagnetic states associated with the copper atoms is not consistent with the antiferromagnetic ground state in a HTS.

Quantitatively, the Anderson-Appelbaum model predicts a logarithmic behavior of the zero-bias conductance, G, in approximation for the energy above the noise energy given by k_BT:

$$G(V,T)\propto \ln\left(\frac{E_0}{|eV|+k_BT}\right). \tag{1}$$

Here, E_0 is a cutoff energy for the densities of states; the Fermi energy is taken to be zero. As shown in the inset of Fig. 2, we observed deviation from this predicted logarithmic behavior, especially in the case of low energy due to negative curvature. Using the unapproximated formula resulted in fact in worsening the fit. Thus, both the qualitative and the quantitative comparison with this theory give evidence against the assumption of magnetic impurity states on the surface of HTS's. We note in addition that Andreev tunneling can be excluded as an explanation of the origin of the ZBCP as well, for it can only be expected for junctions in the low-resistance regime.[8,30]

As for the formation of midgap states in interfaces due to the d-wave symmetry in a HTS,[6] recently a crystal-orientation-dependent behavior of the zero-bias conductance in tunneling spectroscopy was predicted.[7] For $d_{x^2-y^2}$-wave superconductors, the zero-bias conductance is supposed to be maximal for a (110) surface. The observation of a spatially continuous ZBCP on the surface of high-quality (110) $YBa_2Cu_3O_{7-\delta}$ thin films is in natural agreement with this theory.

In the low-conductance limit for large barrier height junctions, the total tunneling conductance spectra, $\sigma_T(E)$, is calculated[10] as

$$\sigma_T(E)\approx \frac{\int_{-\pi/2}^{\pi/2}\sigma_N\rho_S(E)\,d\theta}{\int_{-\pi/2}^{\pi/2}\sigma_N\,d\theta}. \tag{2}$$

Here, θ is the incident angle of electrons with respect to the SI interface, ρ_S is the surface density of states of an insulator/d-wave superconductor interface, and σ_N is the conductance of a NIN junction. We assume that σ_N is a Gaussian function giving the probability distribution of tunneling electrons, $e^{-\beta\theta^2}$, in k space. The factor β depends on the experimental situation, e.g., the tip diameter. Interactions between the tip and the sample surface or tip damage result in large β values, i.e., small distribution in momentum space. To calculate ρ_S, a lifetime broadening factor Γ is incorporated into ρ_S as an imaginary part of the energy E, according to Dynes.[31] The best fit we could obtain is shown in Fig. 2, which set Γ to $0.123\times\Delta_0$ and β to 10.36. A small Γ and a small β both seem to be reasonable in the case of a junction with a small diameter so we can conclude that tip-sample interactions may be negligible. While the peak height can be easily fitted, this is not the case for the depth of the dip and the slope for voltages right below the energy gap. Reasons for this deviation may be the neglect of self-consistency in calculating the energy gap and additional inelastic tunneling processes. However, the qualitative behavior of the superconducting gap structure and the ZBCP can be naturally explained within this theory by using only Eq. (2). Additional experimental evidence supporting our given interpretation is the finding that tunneling spectra of most of the c-axis oriented junctions reported so far almost never showed a ZBCP. The measurement of conductance spectra on a-axis oriented thin films revealed a strongly reduced appearance of the ZBCP (Ref. 32) as expected for $d_{x^2-y^2}$-wave symmetry. Furthermore, a comparison with the electron doped s-wave superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-y}$, where no ZBCP was observed for (100)-, (001)-, or (110)-oriented single crystals,[32] also proves that the ZBCP is related to the symmetry of the pairing state and not, for example, to the presence of localized states associated with the copper-oxygen planes. Due to the symmetry-dependent behavior of the spectra, LTSTS can be used as a powerful tool to probe the pairing symmetry of superconductors.

In conclusion, we give strong experimental evidence that the origin of the zero-bias conductance peak is *intrinsic* to high-temperature superconductors due to their *d*-wave order-parameter symmetry, and that this symmetry leads to the formation of midgap surface states with zero-energy level. As predicted, the maximum ZBCP is found on (110)-oriented surfaces and the ZBCP can be measured continuously. Paramagnetic surface states acting as scattering centers for Kondo-type scattering can be excluded as an explanation for the ZBCP.

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*Electronic address: lalff@colorix.ph2.uni-koeln.de. Permanent address: Universität zu Köln, II. Physikalisches Institut, Lehrstuhl für Angewandte Physik, Zülpicherstrasse 77, D-50 937 Köln, Germany.

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