Admixtures to \(d\)-Wave Gap Symmetry in Untwinned \(\text{YBa}_2\text{Cu}_3\text{O}_7\) Superconducting Films Measured by Angle-Resolved Electron Tunneling


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We report on an \(ab\) anisotropy of \(J_{\parallel ab}/J_{\parallel ab} = 1.8\) and \(I_{\parallel ab}/I_{\parallel ab} = 1.2\) in ramp-edge junctions between untwinned \(\text{YBa}_2\text{Cu}_3\text{O}_7\) and \(s\)-wave Nb. For these junctions, the angle \(\theta\) with the \(\text{YBa}_2\text{Cu}_3\text{O}_7\) crystal \(b\) axis is varied as a single parameter. The \(R_{\parallel b}\) dependence presents twofold symmetry. The minima in \(I_{\parallel b}\) at \(\theta \cong 50^\circ\) suggest a real \(s\)-wave subdominant component and negligible \(d_{x^2-y^2}\)-wave or imaginary \(s\)-wave admixtures. The \(I_{\parallel b}\) dependence is well fitted by 83\% \(d_{x^2-y^2}\), 15\% isotropic \(s\), and 2\% anisotropic \(s\)-wave order parameter symmetry, consistent with \(\Delta_b/\Delta_a = 1.5\).

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Phase-sensitive experiments [1,2] and tunnel spectroscopy [3] have provided rich evidence for the sign change of the pair wave function in the crystal \(ab\) plane of high-\(T_c\) superconductors. Insight in the extent of subdominant admixtures to the \(d_{x^2-y^2}\)-wave symmetry is less well established. They are of high importance for the basic understanding of high-\(T_c\) superconductivity and the design of novel \(d\)-wave based Josephson devices, but also for standard high-\(T_c\) junctions. They determine, for instance, the exact position of the nodes and the amount of \(ab\) anisotropy.

In \(\text{YBa}_2\text{Cu}_3\text{O}_7\) strong anisotropy in the electronic structure has been reported, which can be interpreted as an effective mass anisotropy along the \(a\) and \(b\) axes: An elongated vortex shape by scanning tunneling spectroscopy [4] suggests 50\% anisotropy. Sixty percent anisotropy is found in the London penetration depth by far-infrared spectroscopy [5], as well as using \(c\)-axis \(\text{YBa}_2\text{Cu}_3\text{O}_7/\text{Pb}\) Josephson junctions with a magnetic field oriented parallel to the \(a\) or \(b\) axis [6]. Other studies, neutron scattering on flux-line lattices [7] and single-crystal torque measurements [8], indicate a smaller anisotropy of 1.2. Related surface impedance [9] and resistivity measurements [10] demonstrate an anisotropy of \(R_{\parallel ab}/R_{\parallel ab} = 1.5\) to 1.6 and \(\sqrt{\rho_a/\rho_b} = 1.5\), respectively.

Also, implications for the anisotropy of the superconducting gap have been discussed. Raman scattering [11] evidences a real isotropic \(s\)-wave admixture of 5\%; thermal conductivity measurements in a rotating magnetic field [12] place a maximum of 10\% based on the node positions. Angle-resolved photoemission spectroscopy (ARPES) [13] indicates larger \(ab\) anisotropy of \(\Delta_b/\Delta_a = 1.5\). The use of untwinned single crystals is considered crucial in all these studies. However, a clear consensus on subdominant order parameter symmetries is not reached, nor are detailed angle-resolved data in the \(ab\) plane of thin films available, although first attempts on twinned films have been performed [14]. In view of this, we present here new results on the anisotropy, comparing untwinned and twinned \(\text{YBa}_2\text{Cu}_3\text{O}_7\).

In untwinned \(\text{YBa}_2\text{Cu}_3\text{O}_7\) thin films, the usual “random” exchange of the \(a\) and the \(b\) axis is eliminated. This enables to study the electronic properties angle resolved in the \(ab\) plane. The experimental layout is summarized in Fig. 1. Basically, the \(\text{YBa}_2\text{Cu}_3\text{O}_7\) base electrode is patterned into a nearly circular polygon, changing the orientation from side to side by \(5^\circ\). A Au barrier and Nb counterelectrode contact each side. In this way, the angle with respect to the \((010)\) orientation is varied as a single parameter.

First, bilayers of 170 nm \(\text{YBa}_2\text{Cu}_3\text{O}_7\) and 100 nm \(\text{SrTiO}_3\) are grown by pulsed-laser deposition (PLD) on single-crystal \(\text{SrTiO}_3\) substrates. The \(\text{YBa}_2\text{Cu}_3\text{O}_7\) films are optimally doped, with \(T_c \geq 89\) K. Ramps are ion-milled in the bilayers using a photosresist stencil. To assure equivalent ramp quality over 360\°, the sample stage is...
rotated around the substrate normal, while maintaining the angle of incidence of the Ar-ion beam constant at 40° with the substrate plane. The resulting ramp angle with the substrate plane is $0.0011 R$. On a microscopic scale the interfaces may present some faceting, albeit less than in, e.g., grain boundaries. This faceting is not expected to affect the main conclusions of the presented studies.

After removal of the photoresist stencil and a short 90°-incidence ion mill for cleaning purposes, a 5 nm YBa$_2$Cu$_3$O$_7$ interlayer [15] is deposited to prepare an in situ interface to a 30 nm Au barrier formed also by PLD. Then, a 160 nm thick Nb counterelectrode is dc-sputter deposited through a lift-off stencil. Special care is taken to obtain a clean Au/Nb interface by a 50 s rf-plasma etch just before Nb deposition. After lift-off, redundant Au and YBa$_2$Cu$_3$O$_7$ interlayer material is removed by Ar-ion milling. The junctions are 4 μm wide.

The twin behavior of (001)-YBa$_2$Cu$_3$O$_7$ films is influenced by the substrate vicinal angle $\alpha$ and its in-plane orientation $\beta$ [16]. Here, $\alpha$ is defined between the crystallographic and optical substrate normal, and $\beta$ describes the in-plane orientation with respect to the SrTiO$_3$ (100) crystal axis. The degree of twinning can be controlled from completely untwinned to the presence of four ab orientations, varying $\alpha$ from $\sim 1.1^\circ$ to a small vicinal angle ($\sim 0.1^\circ$), where $\beta \equiv 0^\circ$. For $\alpha \equiv 1.1^\circ$, growth with the b axis along the step ledges is induced, and only one crystal orientation is present. On the contrary, four twin orientations are present for small vicinal angle substrates. The twin orientations have pairwise their in-plane diagonal of the YBa$_2$Cu$_3$O$_7$ crystal aligned with each substrate diagonal, so that a and b axes and vice versa are arranged nearly in parallel [16]. After completion of the device, the YBa$_2$Cu$_3$O$_7$ base electrode is examined with x-ray diffraction (XRD). An average of the a and b unit cell dimensions is found for untwinned films (see Table I). For untwinned films, the individual a and b unit cell parameters can be distinguished and are close to single-crystal values. Detailed $hk$ scans of the (034) reflections show four different orientations for YBa$_2$Cu$_3$O$_7$ films grown on small vicinal angle substrates [Fig. 2(a)], associated with the above-mentioned four twin orientations. For films grown on substrates with $\alpha \approx 1.1^\circ$, however, only one orientation is present [Fig. 2(b)].

The XRD and electrical data presented in this Letter correspond to the same samples. Figure 3 presents the electrical characterization of the twinned base-electrode sample [panels (a)–(c)] and the untwinned one [panels (d)–(f) and (h)]. During the measurement, the magnetically shielded sample space reduces background fields below 0.1 μT. Trapped flux in or near the junctions is excluded by systematic $I_c(B)$ measurements, assuring a correctly determined critical current density ($J_c$). The superconducting properties of the Au/Nb bilayer are independent of the orientation. Therefore, $J_c$ depends on the in-plane orientation $\theta$ with respect to the b axis of the YBa$_2$Cu$_3$O$_7$ crystal only, and presents four maxima for both samples, approaching zero in between. This is in agreement with predominant $d_{x^2−y^2}$-wave symmetry of the superconducting wave function in one electrode only, and a cos(2θ) dependence is expected [17]. In closer detail, the nodes of the untwinned YBa$_2$Cu$_3$O$_7$ sample are found at 5° from the diagonal between the a and b axis. This presents direct evidence for a significant real isotropic s-wave admixture. A first estimate for the s-type gap ratio is calculated as $|\cos(2\theta_0)| \equiv 17\%$ for a node angle $\theta_0 = 50^\circ$. For the twinned base electrode, the nodes are found at the diagonal, which is expected if all twin orientations are equally present, and contributions of subdominant components average out to zero.

The suppressed $J_c$ in the nodal direction ($\pm 0.01J_c$) suggests small, if not absent, imaginary admixtures [18], for instance, of the isotropic $is$-wave or $id_{x^2−y^2}$-wave type, which in contrast would lift the nodes. A significant real $d_{x^2−y^2}$-wave admixture is excluded, because this would induce a rotation in the same direction with respect to the crystal of all nodes.

In the untwinned case, the $J_c$ value is 1.8 times larger in the b direction than in the a direction. Preparation effects can be eliminated, since circular symmetry with respect to the substrate normal has been conserved at all phases of the fabrication. The normal-state resistance ($R_n$) is lower along the b axis than along the a axis, and presents a twofold symmetry axis for the untwinned case. Using the angle-resolved values, the anisotropy in the $I_cR_n$ product amounts to $I_cR_n || /I_cR_n \perp \approx 1.22$.

### Table I. Vicinal angle $\alpha$ and its orientation $\beta$ of the SrTiO$_3$ substrates and YBa$_2$Cu$_3$O$_7$ films. The YBa$_2$Cu$_3$O$_7$ data is obtained after device completion.

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>Twinned</th>
<th>Untwinned</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$: $\alpha/\beta$</td>
<td>0.12°/119.0°</td>
<td>1.07°/357.9°</td>
</tr>
<tr>
<td>YBa$_2$Cu$_3$O$_7$: $\alpha/\beta$</td>
<td>0.20°/97.3°</td>
<td>0.75°/346.3°</td>
</tr>
<tr>
<td>a-axis length (Å)</td>
<td>3.866(3)</td>
<td>3.849(6)</td>
</tr>
<tr>
<td>b-axis length (Å)</td>
<td>3.867(4)</td>
<td>3.892(7)</td>
</tr>
<tr>
<td>c-axis length (Å)</td>
<td>11.678(3)</td>
<td>11.703(7)</td>
</tr>
</tbody>
</table>

![FIG. 2](color). Logarithmic contour plots of $hk$ scans near the (034) reflection of YBa$_2$Cu$_3$O$_7$: (a) grown on a small vicinal angle SrTiO$_3$ substrate ($\alpha \approx 0.12^\circ$) and (b) grown on an $\alpha \equiv 1.07^\circ$ and $\beta \equiv −2.1^\circ$ vicinal SrTiO$_3$ substrate. Both scans are measured after device completion.
To estimate the \( I_c R_n \) products in our junctions, we model them as SINS' structures, where S is \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) and I is the \( \text{YBa}_2\text{Cu}_3\text{O}_7/\text{Au} \) interface barrier, which has a much higher resistance than the Au (N) and the Au/Nb (N/S') interface. From independent resistance measurements on our PLD Au (\( \rho_{\text{Au}} \approx 4.6 \mu \Omega \) cm at 4.2 K), the mean free path is \( l_{\text{Au}} \approx 18 \text{ nm} \), and the dirty-limit coherence length is \( \xi_{\text{Au}} \approx 49 \text{ nm} \). Using these values and the \( \text{YBa}_2\text{Cu}_3\text{O}_7/\text{Au} \) interface resistance \( R_{\text{BA}/\text{Au}} \approx 10^{-8} \Omega \text{ cm}^2 \), the transparency at this interface is low: \( \gamma_{\text{BA}/\text{Au}} \approx 440 \), where \( \gamma_{B} = R_{B}/\rho_{\text{Au}} \xi_{\text{Au}} \) [19]. From a small Fermi-velocity mismatch, we estimate the Au/Nb interface transparency to be much larger, \( \gamma_{\text{Au}/\text{Nb}} < 20 \). The electrode separation is \( d_{\text{Au}} = 26 \text{ nm} \) for 30 nm thick Au and ramp angle \( \alpha_{\text{R}} = 30^\circ \). Since \( l_{\text{Au}} < d_{\text{Au}} \) and \( l_{\text{Au}} < \xi_{\text{Au}} \), Au is in the diffusive regime, while \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) is in the clean limit with the anisotropic gap function \( \Delta_y \).

We extend the expression for the supercurrent in diffusive SINS' structures [19] to our case of a low-transparent junction between a clean \( d \)-wave superconductor and a diffusive NS' bilayer. The contribution of midgap Andreev bound states is small in such a junction [20] and can be neglected:

\[
I_c R_n = \frac{1}{N} \int d\phi d\chi \sin(\chi) D \gamma \sin(\Delta \varphi),
\]

\[
\gamma = \frac{2 \pi k_B T}{e} \sum_{n=0}^{\infty} \frac{\Phi \Delta y}{\Phi^2 + \omega_n^2} \sqrt{\alpha^2 + \omega_n^2},
\]

\[
\Phi = \frac{\pi k_B T \xi_{\text{Nb}} \Delta_{\text{Nb}}}{\pi k_B T_{\text{Nb}} + \gamma_{\text{Au}/\text{Nb}} (d_{\text{Au}}/\xi_{\text{Au}}) \Delta_{\text{Nb}}^2 + \omega_n^2},
\]

where \( \chi \) is the angle with the interface normal, and \( N = \int d\phi d\chi \sin(\chi) D \) is the normalization constant. The integration is performed over angles \( \phi = 0 \) to \( 2\pi \), and \( \chi = 0 \) to \( \frac{\pi}{2} \) of a half-sphere of all trajectories: for each junction orientation and ramp angle into account. The barrier transmission coefficient \( D = \cos(\chi) \exp[\kappa(1 - \cos^{-1}(\chi))] \) is in the limit of a small \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) Fermi velocity, where \( \kappa \) describes the tunneling. The sum in Eqs. (2) and (3) is taken over the Matsubara frequencies \( \omega_n = \pi T(n + 1) \). \( \Phi \) is the isotropic proximity-induced gap function in Au. \( \Delta_{\text{Nb}} \) and \( T_{\text{Nb}} \) are the bulk pair potential and the critical temperature of Nb, respectively. The critical current \( I_c \) and the \( I_c R_n \) product should be found by calculating a maximum of \( I_c R_n \) over the phase difference \( \Delta \varphi \) across the junction.

Tunneling along the \( a \) and the \( b \) axis may then be compared theoretically in terms of the ratio \( \Gamma = I_c R_{n||b}/I_c R_{n||a} \). Using Eqs. (1)–(3), it can be shown that, for constant properties of the Nb/Au bilayer, the ratio of the \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) gap for these directions is \( \Delta_{Y||b}/\Delta_{Y||a} \geq 1 \). Therefore, the observed anisotropy of \( \Gamma \approx 1.22 \) represents a lower limit for this gap ratio, which is valid for extremely small ratios \( \Delta_{Y}/\Delta_{\text{Nb}} \ll 0.1 \). For increasing ratio \( \Delta_{Y}/\Delta_{\text{Nb}} \), the value \( \Gamma \approx 1.22 \) requires a rapid increase of \( \Delta_{Y||b}/\Delta_{Y||a} \). In this estimate, \( \Gamma \) depends only on the gap ratios and on the Au/Nb interface transparency.

The anisotropic gap in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) depends on the in-plane angle \( \theta (0 \text{ to } 2\pi) \), and the angle \( \eta (-\frac{\pi}{2} \text{ to } \frac{\pi}{2}) \) with the \( ab \) plane. Various possible symmetry functions exist to describe this gap. Here, we consider the following 3D gap function in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) consisting of a dominant \( d_{x^2-y^2} \)-wave component with an isotropic and an anisotropic \( s \)-wave admixture:

\[
\Delta_{Y} = \Delta_{Y0} \cos^2(\eta) \sum_{l=0}^{2} c_l [\cos^2(\theta) - \sin^2(\theta)]^l.
\]
with the coefficients $c_1 > c_0$, $c_2$ and $c_1 + c_0 + c_2 = 1$. Here $\Delta y_0$ denotes the magnitude of the YBa$_2$Cu$_3$O$_7$ gap at the interface. Consistent with our earlier estimate $\Delta_{y||}/\Delta_{y\perp} > 1.22$, the gap ratio is taken as $\Delta_{y||}/\Delta_{y\perp} \approx 1.5$ in agreement both with the observed node positions and ARPES [13]. With this, the coefficients are found from the fit to the data $c_0 = 0.15$, $c_1 = 0.83$, and $c_2 = 0.02$. Other choices for the gap symmetry functions lead to slightly different numbers but will not alter the basic results of our calculations.

A series of fits is presented in Fig. 3(h): the wider the tunneling cone (smaller $\kappa$), the smaller the width of the oscillations in the $I, R_n(\theta)$ dependence (arrow). The effective YBa$_2$Cu$_3$O$_7$ gap $\Delta_{y_0}$, and $\gamma_{Ba/Nb}$ must then become larger. This dependence is presented in Fig. 3(g). The minimum value $\Delta_{y_0}$ occurs for normal-incidence tunneling $(\lim \kappa \rightarrow \infty)$, so that $\Delta_{y_0} \approx 6.4$ meV. For reasonable $\Delta_{y_0}$ values ($<0.5$ eV), $\gamma_{Ba/Nb}$ varies from 13.6 to about 18. This gives an estimate for the Au/Nb interface resistance: $R_{\text{BA}} \approx 0.36 \pm 0.05$ n$\Omega$ cm$^2$. In contrast to $\gamma_{Ba/Nb}$, it is not possible to give an accurate estimate for the YBa$_2$Cu$_3$O$_7$ gap from our data. Therefore, we choose to fit the data with $\Delta_{y_0} = 44$ meV, $\gamma_{Ba/Nb} = 16.8$ in Figs. 3(c) and 3(f). These are not claimed to be the correct values; the simulation demonstrates, however, that large $\Delta_{y_0}$ may well be consistent with small $I, R_n$ values. For the untwinned case, $\kappa = 18.4$, corresponding to a tunnel cone with a FWHM of 31.0° (cosine term of $D$ not included). For the twinned case, the $I, R_n(\theta)$ dependence is simulated with the same parameters, except for a slightly smaller cone ($\kappa = 26.3$, FWHM = 26.0°), and assuming equal presence of both twin orientations: $\frac{1}{2}(I, R_n(\theta) + I, R_n(\theta + \frac{\pi}{2}))$. The smaller tunnel cone for the twinned case is consistent with higher $R_{\text{BA}}$ and lower $J_\parallel$ values. This may result from a slightly thicker tunnel barrier at the YBa$_2$Cu$_3$O$_7$/Au interface, e.g., due to minor variations in the Au PLD conditions, modifying this interface.

The $R_n(\theta)$ dependence is fitted with an ellipsoidal relation of the conductivity projections along the main crystal directions of the YBa$_2$Cu$_3$O$_7$/Au. Written in terms of the $R_n$ values along these directions, this gives $R_n(\theta) = \sqrt{R_{n||}^2 \cos^2(\theta) + R_{n\perp}^2 \sin^2(\theta)}$. Figure 3(e) shows the result using $R_{n||} = 44$ n$\Omega$ cm$^2$ and $R_{n\perp} = 29$ n$\Omega$ cm$^2$. For the untwinned case, a geometrical average of the conductivities is assumed, $R_n(\theta) = 2/[R_{n||}^{-1}(\theta) + R_{n\perp}^{-1}(\theta + \frac{\pi}{2})]$. The used values in Fig. 3(b) read $R_{n||} = 141$ n$\Omega$ cm$^2$ and $R_{n\perp} = 47$ n$\Omega$ cm$^2$. Although these phenomenological fits are indicative, angle-resolved calculations including aspects of the YBa$_2$Cu$_3$O$_7$ bandstructure and band-bending effects are needed for a detailed understanding. Finally, the $J_\parallel(\theta)$ fits are obtained with the ratios of the $I, R_n(\theta)$ and the $R_n(\theta)$ dependencies, the ensemble of which gives a consistent simulation of the angle-resolved junction properties.

The experimental results support theories based on a two-band model of the chains and planes [21,22] modeled with a symmetric, antisymmetric, and isotropic component. Furthermore, our findings agree with $c$-axis tunneling from two twinned YBa$_2$Cu$_3$O$_7$ grains to a Pb counterelectrode that depends on the magnetic field orientation, [23] and angle-dependence studies on grain boundary junctions [24]. For all high-$T_c$ junctions and circuits, we mark the anisotropy as a possible intrinsic source of their limited reproducibility: both twin orientations may not be uniformly present, yielding an important variation in $J_c$. Control over the crystal orientation then presents a key to improvement. Another important aspect concerns the nodes at 5° from the (110) crystal direction. The best choice for the electrode orientation of devices aiming a $d$-wave induced second harmonic in the current-phase relation, such as $\approx$ SQUIDs based on grain boundary junctions, may therefore deviate from the (110) crystal direction.

In conclusion, an angle-resolved electron tunneling study using Josephson junctions with an untwinned YBa$_2$Cu$_3$O$_7$ base electrode is presented. Evidence for significant in-plane anisotropy in the electronic properties of YBa$_2$Cu$_3$O$_7$ is found.

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