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Experimental evidence for a small s-wave component in the order parameter of underdoped $YBa_2Cu_3O_{6+x}$

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Abstract. – We report conductance measurements in underdoped $YBa_2Cu_3O_{6+x}$ tunneling junctions of the ramp type, oriented along different directions in the ab plane. We find that the $d_{x^2-y^2}$-wave gap is suppressed in the region near the node, but has a non-zero value of $\Delta = 2.5 \pm 0.3$ mV at the node. This result supports the existence of a sub-dominant is component in the order parameter of underdoped $YBa_2Cu_3O_{6+x}$.

Many experiments to date have demonstrated that the dominant symmetry of the order parameter in the high-temperature superconductors (HTSC) is the $d_{x^2-y^2}$-wave in nature [1–4]. Especially useful are the phase-sensitive tests of the pairing symmetry which involve corner and edge junctions on single crystals [1] and tricrystal and tetracrystal junctions [2]. In addition, tunneling experiments in the ab plane along the main axes and along the nodes which show a gap structure and a zero-bias peak (ZBP), respectively, are also consistent with a $d_{x^2-y^2}$-wave symmetry of the order parameter [3–5]. Some experiments, however, reveal sub-dominant components of the order parameter in the HTSC. These components, having an s, is or id_{xy} symmetry, are responsible for the observed splitting of the ZBP [5–7], and for the appearance of spontaneous magnetization which was found during the transition to superconductivity of the HTSC samples [8]. While the phase-sensitive experiments did prove that the order parameter changes sign as $\cos(2\theta)$, where θ is the in-plane angle, the exact angular dependence of the gap energy was actually never determined directly in YBCO. In BSCO 2212, however, angle-resolved photoemission ARPES measurements were performed, but while in one case a pure $d_{x^2-y^2}$-wave symmetry was found [9], in another study by the same group, a clear deviation was observed with an extended node region [10]. Given the somewhat low-energy resolution in ARPES, in the present study we measure with high resolution the full angular dependence of the energy gap in $YBa_2Cu_3O_{6+x}$ (YBCO)-based ramp-type (or edge) junctions. We find a modified $d_{x^2-y^2}$-wave gap behavior with extended node region and a non-zero gap at the node.

We prepare underdoped YBCO-based ramp-type junctions with Fe-doped YBCO barriers by a multi-step process, where the epitaxial thin-film layers are prepared by laser ablation deposition, patterning is done by waterless deep UV photolithography, and etching by Ar-ion

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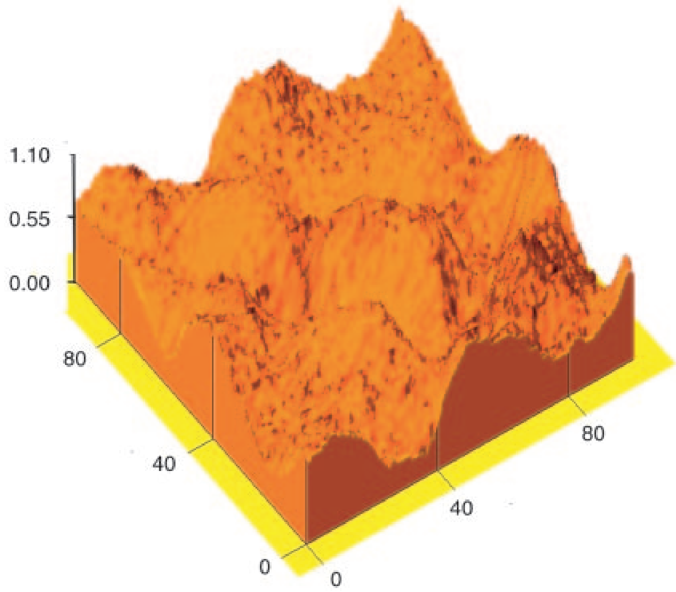

Fig. 1 – AFM image of a typical exposed ramp of an YBCO base electrode near one junction.

milling [11]. We used the same $YBa_2Fe_{0.45}Cu_{2.55}O_{6+x}$ (YBFeCO) barrier as before [11], but patterned the 10 junctions on the (100) $SrTiO_3$ wafer each in a different direction (θ) in the *ab* plane of the films. Three separate milling steps of the base electrode were used, each time patterning only one group of $\theta \pm 15°$ junctions while protecting the others with a copper shadow mask. This was done in order to obtain quite similar ramp angles of $\sim 35 \pm 5°$ in all the 10 junctions on the wafer. The thickness of the base and cover electrodes was 90 nm, while the barrier thickness on different wafers ranged between 15 and 22 nm. The width of each ramp-type junction was $4\,\mu$m. A gold layer was deposited on top of the cover electrode and patterned to produce the 4×10 contact pads for the 4-probe transport measurements. Figure 1 shows an atomic-force microscope image of a typical exposed ramp of the YBCO base electrode in one of our junctions. Clearly, the ramp morphology is quite uniform laterally and rough on a scale of less than one unit cell height (< 1 nm). This shows that the interface in our junctions is smooth on the same scale which is smaller than a coherence length ξ, and has a well-defined crystallographic orientation. Thus, our angular-dependent results are hardly affected by faceting and averaging over this small interface roughness.

Figure 2 shows the resistance *vs.* temperature of 10 junctions on a wafer with a barrier thickness of 22 nm. The oxygen annealing process produced underdoped YBCO electrodes which become superconducting at 50–55 K [11]. The resistance of the junctions goes through a minimum between 20 and 40 K, and increases at lower temperature. At 5 K, the junction resistances R_N are between 20 and 130 Ω. The increasing resistance with decreasing temperature at low temperatures is due to localization in the YBFeCO barrier [11]. Since the epitaxial films of the electrodes are twinned, we should ideally have equal R_N values for the junctions along the 0° and 90° directions, but we actually find $R_N(90°) \cong 2 \times R_N(0°) \cong 130\,\Omega$. We also observe that the R_N values of the 30°, 45° and 60° junctions are the lowest and equal to $\sim$ 20–25 Ω. This last result can be due to the lower Fermi velocity in the node region. Further work is needed to understand these R_N results.

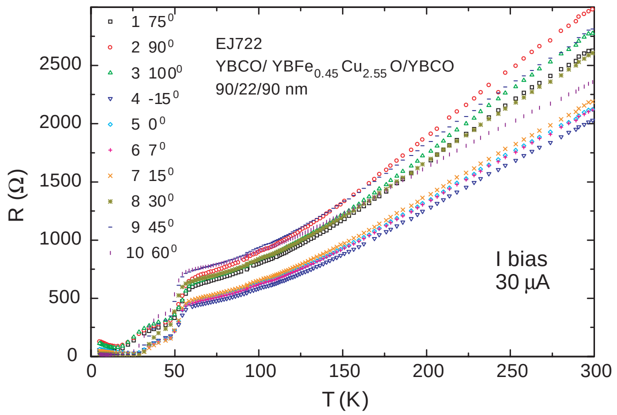

Fig. 2 – Resistance *vs.* temperature of the 10 junctions on the wafer.

Figure 3 presents the main results of the present study, namely the conductivity normalized to the high bias values of the 10 junctions on the wafer. One can observe a clear angular dependence which can be separated into two main groups. One group is that with the angles near the node (30°, 45° and 60°), and the other group including all other angles. The second group shows a characteristic d-wave gap structure, with 2Δ in between 30 and 50 mV, while the first group shows a broad Andreev enhancement of the conductivity. In addition to the Andreev enhancement, the first group shows a gap structure with values of 2Δ in the range of $\cong$ 5–7 mV, and a set of regular peaks and dips at higher voltages which can be due to either Tomasch or McMillan-Rowell oscillations [11, 12]. The appearance of these geometrical resonances is indicative of the high quality and good uniformity of the interfaces

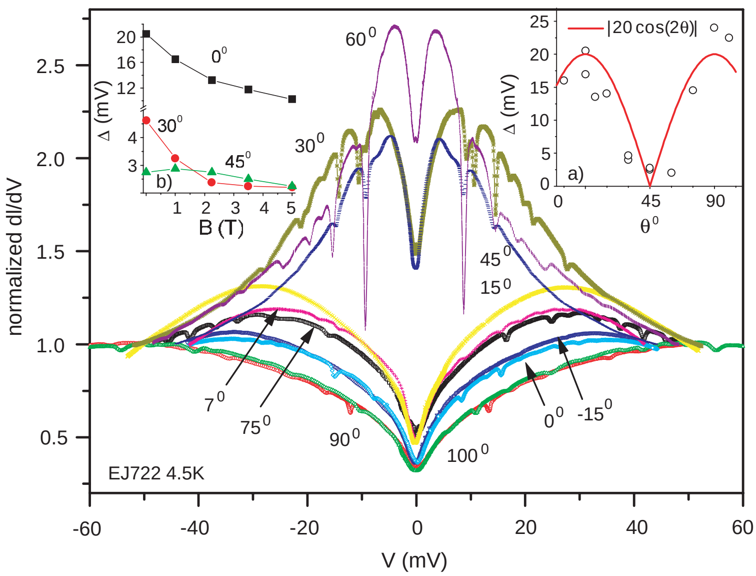

Fig. 3 – Normalized conductivity *vs.* voltage bias. Inset a) gives the angular dependence of the peak-to-peak gap parameter and inset b) the magnetic-field dependence of some gaps.

in our junctions (see also fig. 1). Note that these sharp dips are not due to switching effects [13], since the I-V curves here are *not* hysteretic and the dips disappear at magnetic fields of 1-2 T. As a first approximation, we determine the measured tunneling gap Δ of our SIS junctions as the peak-to-peak voltage difference divided by 4. The resulting $\Delta(\theta)$ is shown in inset a) of fig. 3 together with $\Delta_0|\cos(2\theta)|$, where $\Delta_0 = 20\,\mathrm{mV}$. The dominant nature of a $d_{x^2-y^2}$-wave symmetry is clearly seen. The scatter in the data can be estimated from the difference between the $\Delta(0°) = 17$–$20.5\,\mathrm{mV}$ and $\Delta(90°) = 24\,\mathrm{mV}$ values which in principle should be equal due to the fact that the films are heavily twinned. This yields a relative error of about $\pm 10\%$. This relative size of error is similar for all our data. Therefore, the measured gap value at $\theta = 45°$ of $2.5 \pm 0.3\,\mathrm{mV}$ is clearly non-zero as one would expect for a pure $d_{x^2-y^2}$-wave superconductor. This seems to imply the existence of an additional sub-dominant component to the order parameter.

One may argue that the observation of a finite gap at the node is due to nano-facets, roughening of the interface, or to quasi-particle tunneling along directions close to that of the node (finite tunneling cone). To check this, we have used the BTK model adapted to anisotropic superconductors to simulate the finite cone effect on the conductance in the pure d-wave case [14]. We found that the pure d results with and without the angular distribution of the cone are very similar (see fig. 4), thus faceting does not play a significant role here. Actually, the observed $\Delta(30°)$ value of $4.6\,\mathrm{mV}$ and $\Delta(60°)$ of $2\,\mathrm{mV}$ are 2–5 times smaller than $20\cos(2\theta)$ at 30° (10 mV). Note that the small value of the observed $\Delta(60°) = 2\,\mathrm{mV}$ gap at $V = 2\Delta = 4\,\mathrm{mV}$ in fig. 3 is apparently underestimated due to the huge negative dip in the conductivity of the 60° junction at 9 mV. Moreover, the observation of sharp and strong geometrical resonances also supports the scenario in which tunneling in our ramp-type junctions is quite directional, with a very small angular spread. Figure 3, thus, shows an extended small-gap region in the vicinity of the $d_{x^2-y^2}$-wave node at $\theta = 45° \pm 15°$, which cannot result from a pure $d_{x^2-y^2}$-wave symmetry. ARPES measurements show a similar extended node region in heavily underdoped BSCO 2212 with T_c of 10 K [10], but also near optimal doping the measured gap values near the node region seem to be below $\Delta_0\cos(2\theta)$ within the resolution of this method [9]. Our result is consistent with the coexistence of a dominant but modified $d_{x^2-y^2}$-wave gap, and a sub-dominant gap with an s or is symmetry. While an s-wave component in the pair potential would give rise to asymmetries between the 0° and 90° gaps, and the 30° and 60° gaps, as we seemingly observed here, we find it hard to accept that this scenario is possible in our heavily twinned YBCO films. Also, since there is evidence for a pair potential component with a broken time reversal symmetry that gives rise to a splitting of the zero-bias peak in the conductivity [6,7], the is-wave scenario is more likely. An id_{xy}-wave scenario was invoked by Carmi *et al.* to explain their spontaneous-magnetization results [8], but this scenario does *not* produce a gap structure at low bias at the node in the calculated conductivity with a barrier strength Z of ≈ 1 [14]. We are thus left with the is symmetry as the most likely one for the sub-dominant component of the order parameter. The only experiment we know of that attempted to measure the gap anisotropy in ramp-type junctions is that of Iguchi *et al.* who measured SN junctions of YBCO and Ag [15]. Their high-transparency junctions (low Z) showed clear zero-bias peaks with increased intensity at the node, and some gap and sub-gap structures. Their results however, show no clear angular dependence of the gap.

To double check our conclusion regarding $d + is$ symmetry in YBCO, we measured the conductivity of the 0°, 30° and 45° junctions in a magnetic field normal to the wafer. The resulting gap dependencies on magnetic field are plotted in inset b) of fig. 3. We find that the gap suppression in a magnetic field in the junction along the main axis is distinctly different from the one along the node. While the former is faster and leads to a gap value of about $0.5\Delta_0$

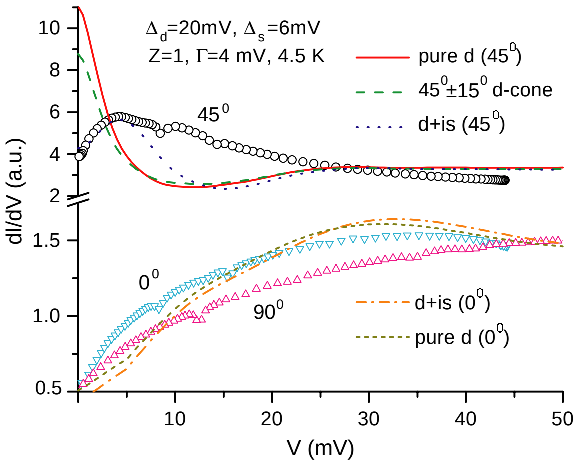

Fig. 4 – Measured conductivity (symbols) and model fitting (lines) of a few junctions.

at 5 T, the latter is much slower and shows a gap of $\sim 0.8\Delta_{45}$ at 5 T. The gap suppression of the 30° junction is crossing over from the faster to the slower behavior at about 2 T. These results thus show the different nature of the gap along the axis and along the node, and support our interpretation concerning the coexistence of the *is* component in the order parameter. It is tempting at this point to make a conjecture that if the faster magnetic suppression of the gap is due to the *d*-wave nature of the order parameter, then the slower magnetic suppression along the node must point out to an *s*-wave component rather than to a d_{xy} one. We know of no theory that predicts the behavior of the gap in an underdoped *d*-wave superconductor under magnetic fields, that can help us resolve this issue at the present time.

Figure 4 shows the data of fig. 3 in the directions of the main axes and the node together with typical good theoretical fits to the Tanaka and Kashiwaya model [14]. The calculated curves were averaged over ϕ, the phase difference between the superconducting electrodes, and carried out with a broadening parameter of $\Gamma = 0.2\Delta_d$. One can see that, while the tunneling data at 0° and 90° can be fitted reasonably well by this model, the 45° data could not. The addition of an *is* component helped to fit the 45° data at low bias, but at higher voltages no satisfactory fit could be obtained. The apparent problem with this model is that it shifts an excessive amount of density of states from higher voltages to the zero-bias peak. This leads to a depletion of the density of states in the 10 to 20 mV range, which is not observed in the measured conductivity curve along the node. We, thus, conclude that further theoretical modeling of the anisotropic conductivity in *d*-wave superconductors is needed.

Conductivity measurements *vs.* temperature were carried out on all junctions also at 15, 35, 50 and 60 K. At 15 K, the results are quite similar to those of fig. 3 but with somewhat more smeared-out features, while at 35 K all curves show a smooth and enhanced Andreev conductivity with no tunneling signature. At 50 K, some small Andreev features are left, whereas at 60 K (above T_c of the electrodes, see fig. 2) only flat conductivity curves are obtained up to ~ 300 mV bias. The conductivity curves of the 45° and 30° junctions were measured more systematically as a function of temperature, in order to trace the small energy gap behavior. The results of the 45° junction are given in fig. 5 (main panel), together with the gap values $\Delta(T)$ inferred from the peak-to-peak distances (inset). Up to about 12 K the gap values are almost temperature independent. At higher temperatures, the gap fills up and decreases with temperature, but somewhat faster than one would expect from a BCS

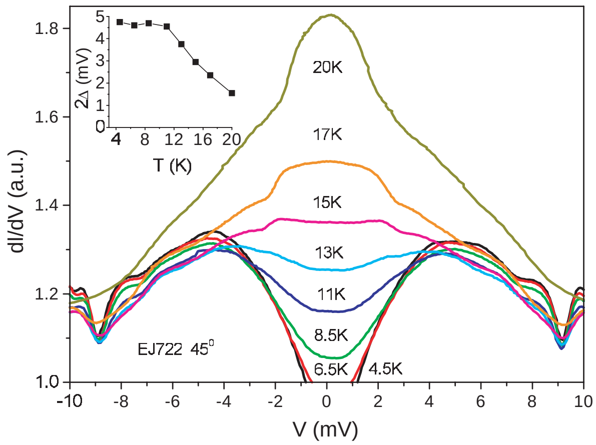

Fig. 5 – Temperature-dependent conductivity of the 45° junction (main panel), and the gap *vs.* temperature (inset).

behavior. The tunneling conductance curve crosses over to a zero-bias peak behavior with increasing temperature, while the junction resistance up to 25 K is almost constant and equal to $\sim 20\,\Omega$. As a result, the clear gap peaks at low temperatures are masked to a certain extent by this Andreev bound-states peak and only a knee-like feature is left. The 60° junction was also measured *vs.* temperature, but the gap peak was smeared already at about 11 K, thus preventing us from measuring any temperature dependence. The results of fig. 5 lend further support to the interpretation of the observed peaks in fig. 3 in the vicinity of the node as due to real gap structures.

Since our results are obtained in underdoped YBCO junctions with Fe-doped YBCO barrier, it is possible that magnetic scattering plays a role in the measured conductance. To check this, we are currently studying ramp-type junctions with Ca-doped electrodes (which also allow access to the overdoped regime) and non-magnetic Ga-doped YBCO barrier. Note that with the present Fe-doped barrier, SIS (tunneling) response is obtained only in the underdoped regime, while in the optimally doped regime an SNS or SS′S response is found [11]. Our ramp-type junctions with thinner barriers of 15 and 19 nm thickness had generally lower normal resistances R_N of about 1–10 Ω at 5 K as compared to the 20–130 Ω for the 22 nm junctions (see fig. 2). As a result we observed in many of them at 5 K strong zero-bias peaks, more Andreev enhancement, less tunneling-like behavior, and even critical current in some cases. Preliminary results show that the angular dependence of the integrated conductivity under the zero-bias peaks behaves approximately as $\sin(2\theta)$. Finally, we note that many groups measured the angular dependence of the critical current $I_c(\theta)$ in grain boundary junctions [16–19]. In their results, however, the symmetry of the order parameter was masked, since the different junctions had different barrier strength (Z) that originated in defects and lattice mismatch at the interface. This leads to an exponential decrease of I_c *vs.* θ. In our all epitaxial ramp-type junction, the artificial barrier layer determines, at least in principle, the *same* Z for *all* junction orientations. The fact that the observed normal resistance is not the same for all junctions indicates that the interface resistance contributes a certain spread in the actual Z values. Nevertheless, the spread in the Z values here is smaller than in the case of the grain boundary junctions and thus the observed features reflect more reliably the symmetry of the order parameter.

In conclusion, our results demonstrate the existence of a modified d-wave order parameter in underdoped YBCO, with extended node regions, and a sub-dominant is component whose value is about one tenth of the main gap.

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