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Pairing symmetry in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$

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Abstract. – Although the pairing symmetry of the high-T_c superconductors is widely accepted to be $d_{x^2-y^2}$, measurements in apparent contradiction with this picture have been reported in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ and attributed to s-wave symmetry or complex mixtures of s-wave and d-wave. To clarify this issue, we have measured the transport properties of asymmetric 45° [100]/[110] $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ bicrystal Josephson junctions, a geometry sensitive to the pairing symmetry. All samples investigated show complicated but polarity-symmetric modulation of their critical currents with magnetic field, providing unambiguous, clear evidence for a predominant $d_{x^2-y^2}$ pairing symmetry at $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ interfaces.

The controversy on the pairing symmetry of unconventional superconductors is ongoing. This topic attracts considerable attention because the symmetry of the superconducting order parameter is a check for theories of the pairing mechanism. It is furthermore a key property for the design and performance of superconducting devices and even of high-power applications, such as superconducting cables. So far, the clearest information on the order parameter symmetry at sample surfaces or interfaces in the cuprates has been provided by phase-sensitive experiments, which find that the symmetry in $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2Ca_1Cu_2O_{8+x}$, $Tl_2Ba_2CuO_6$, $HgBa_2CuO_6$, and now also in the electron doped superconductors $Nd_{2-x}Ce_xCuO_4$ and $Pr_{2-x}Ce_xCuO_4$, is dominated by a $d_{x^2-y^2}$ component [1–12]. The phase-sensitive experiments provide only limited information on the order parameter symmetry of the bulk, which has been proposed by Müller to be s-wave while having d-wave–dominated interfaces [13].

Whereas for $YBa_2Cu_3O_{7-\delta}$ all experimental evidence in favor of a dominating conventional pairing state at sample surfaces or interfaces has collapsed, the symmetry in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ continues to be debated. This is surprising, because $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ is one of the best-investigated high-temperature superconductors, as it is well suited for fundamental studies of high-temperature superconductivity and furthermore is valuable for applications. Consequently, over many years numerous measurements have been performed to determine the symmetry of the superconducting order parameter of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$.

One class of such experiments measured the gap anisotropy [14–17] by angular resolved photoemission spectroscopy (ARPES). Most of these measurements suggested a $d_{x^2-y^2}$-wave symmetry. Unsensitive to the phase of the order parameter, ARPES can unfortunately not discriminate between anisotropic s-wave and d-wave order parameters.

In a second set of experiments, the Josephson current of c-axis $Bi_2Sr_2Ca_1Cu_2O_{8+x}$/Pb junctions was analyzed [18–20]. Finite dc-Josephson currents seen in these experiments suggested the existence of a small s-wave component, which could not be attributed to the orthorhombicity of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$. Measurements of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$/Ag/Pb proximity effect junctions did not reveal such a supercurrent and therefore in those studies a finite s-wave component was not reported [19].

The clearest results concerning the $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ pairing symmetry were obtained by searching with scanning SQUID microscopy in tricrystalline samples for half magnetic-flux quanta [8, 20, 21]. In these phase-sensitive experiments, half flux quanta were indeed observed. Because their generation requires phase changes of the order parameter by π, the half flux quanta provided strong evidence for a dominating $d_{x^2-y^2}$-wave component.

It was therefore a surprise when the results of critical-current measurements of c-axis twist bicrystal junctions were published [22–24]. These bulk bicrystals were fabricated by sintering two $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ single crystals together. Remarkably, the critical currents of the junctions, which were reported to be atomically perfect, equalled the c-axis critical currents of the single crystals and did not vary with the twist angle. This was reported to be surprising because the d-wave pairing symmetry had been expected to reduce the critical current of misaligned twist bicrystals. Consequently, these data were presented to be consistent only with an order parameter dominated by an isotropic s-wave component, excluding a $d_{x^2-y^2}$ component [25, 26]. On the other hand, related experiments measuring current flow across junctions formed by crossed $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ whiskers recently revealed the expected angle-dependent critical current [27].

To clarify the pairing symmetry of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$, we present an independent set of phase-sensitive measurements. For this, an experimental technique was selected that differs completely from the scanning SQUID/tricrystal approach and is not affected by any potential problems which could be of concern for studies of bulk samples with low-current-density c-axis junctions. These requirements are fulfilled by measurements of the dependence of the critical current I_c on an applied magnetic field H of faceted asymmetric 45° [100]/[110] bicrystal junctions (see fig. 1). If at least in the vicinity of the grain boundary the pairing symmetry is s-wave dominated, the $I_c(H)$-characteristic will be that of a conventional Josephson junction with an inhomogeneous critical-current density. Conversely, in case the symmetry is determined by a d-wave component, an anomalous $I_c(H)$ pattern is expected, caused by grain boundary faceting and the d-wave symmetry [4]. Faceted [100]/[110] grain boundaries in superconductors with d-wave pairing symmetry are composed of a mixed array of facets forming standard junctions and facets which are biased by a π-phase difference. Across the facets with π-phase shift, the Josephson current is flowing in the direction opposite to the direction of the current crossing standard facets. This results in $I_c(H)$-dependencies that are unambiguously characterized by critical currents that are much smaller in zero applied fields than in specific, well-defined, finite fields. In case a 45° [100]/[110] boundary shows an anomalous $I_c(H)$ characteristic, it has to be concluded that the pairing symmetry is dominated by a d-wave component.

Anomalous $I_c(H)$-patterns have already been found to provide clear evidence for a d-symmetry in $YBa_2Cu_3O_{7-\delta}$ [4]. They have also been utilized successfully to provide an upper

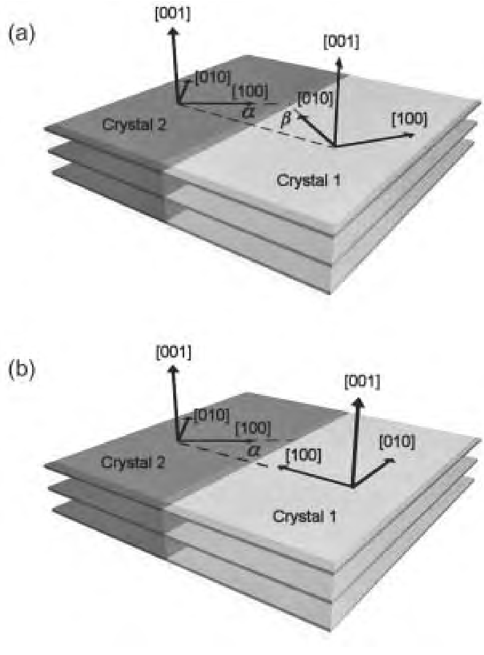

Fig. 1 – Schematic drawing to clarify the crystallographic orientations of the bicrystalline orientations used. A [100]/[110] boundary with $\alpha = \beta$ is termed a symmetric grain boundary, if $\alpha \neq \beta$ it is referred to as asymmetric grain boundary configuration. In the extreme asymmetric case, $\beta = 0$ as shown in (b).

bound to possible admixtures of subdominant order parameter components to the d-wave order parameter of $YBa_2Cu_3O_{7-\delta}$ for a range of dopant elements and concentrations [28].

To perform such measurements, two types of bicrystalline $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ films were grown. The first set was reactively rf-magnetron sputtered from a single target on asymmetric $45 \pm 1°$ ([100]/[110]) and on symmetric $45 \pm 1°$ ([100]/[110]) $SrTiO_3$ bicrystalline substrates. The second type of film was grown with layer-by-layer Molecular Beam Epitaxy (MBE) on an asymmetric $45 \pm 1°$ ([100]/[110]) $SrTiO_3$ bicrystalline substrate. The MBE process yields atomically flat films on the bicrystalline substrate whose epitaxy is monitored during growth with RHEED.

The misorientation of the substrates was verified by Laue backscattering. The rf-sputtered films, 250 nm thick, were deposited at a rate of 0.3 Å/s in a 300 mTorr oxygen-rich atmosphere (O_2 to Ar concentration ratio = 7), with the substrate holder temperature maintained at 755 °C. After deposition, these samples were cooled under the processing conditions to obtain nearly optimally doped samples. The MBE films, 100 nm thick, were deposited layer-by-layer in a 8×10^{-6} Torr pure ozone atmosphere with the substrate heated to 720 °C. These samples were cooled rapidly down to 500 °C over one minute with the ozone pressure halved every 30 °C. More details on the rf-sputter and MBE deposition techniques have been described previously in [29] and [30], respectively. The c-axis orientation and single phase of the sputtered films were confirmed using X-ray diffraction yielding spectra showing only $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ $(00l)$ reflections. The epitaxial growth was confirmed by X-ray diffraction Φ-scans of the substrate and of the films, where only two sets of off-reflections, corresponding to the bicrystalline substrates are obtained (see also the AFM-image, fig. 2). The orienta-

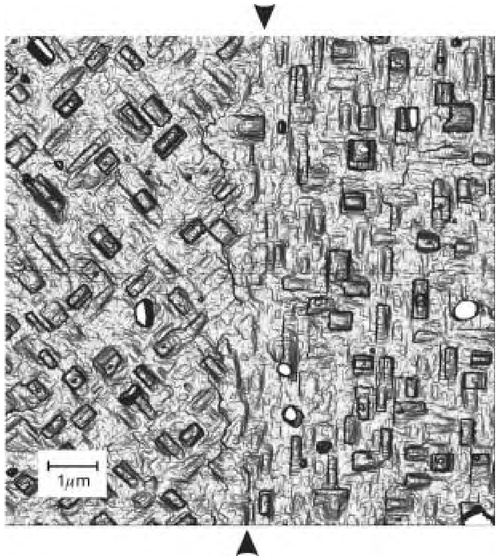

Fig. 2 – AFM image of an asymmetric $45 \pm 1^\circ$ bicrystalline $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ junction. The height of the growth islands is about 10 nm. The image shows that the grain boundary (indicated by the arrows) is meandering on a length scale of several hundred nanometers.

tion and epitaxial growth for the MBE films were monitored *in situ* during growth using RHEED resulting in well-characterized atomically flat films. The critical temperature T_{c0} of the sputtered and MBE films are 79 K and 77 K, respectively.

To study the microstructure of the boundaries, scanning force microscopy (AFM) measurements were performed on the *rf*-sputtered films. The images were taken with a Nanoscope IIIa AFM in the tapping mode. These studies showed that the film surface had a low density of precipitates only. As expected, the AFM investigations revealed clear faceting of the grain boundaries (see fig. 2). As in $YBa_2Cu_3O_{7-\delta}$, the faceting is caused by the formation of growth islands and occurs over a length scale of 10–100 nm. Due to the layered microstructure of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$, along parts of its length the grain boundary line is difficult to discern precisely. The samples were patterned by optical photolithography and Ar-ion-milling to form 4 μm wide superconducting bridges straddling the grain boundaries of the sputtered films and 30 μm wide bridges on the MBE film. Each bridge contains a Josephson junction formed naturally at the grain boundary. The current-voltage ($I(V)$) characteristics of the junctions were measured in four-point configurations. During the measurements, magnetic field was applied to the grain boundary junction perpendicular to the film surface. The measurements were performed with a low-noise setup in a magnetically shielded room. The critical currents of the junctions formed from the sputtered films were determined from the $I(V)$-curves using a voltage criterion of 2 μV, the results being insensitive to the voltage criterion. A feedback technique was used on the MBE junction to measure the critical current using a lock-in to fix the differential conductance of the $I(V)$-curves. This method was used to quickly measure many diffraction patterns at many different temperatures.

As was expected, because of the small irreversibility field of $Bi_2Sr_2Ca_1Cu_2O_{8+x}$, the $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ bicrystals were found to be more susceptible to trapping and thermally activated magnetic flux as compared to $YBa_2Cu_3O_{7-\delta}$ bicrystals fabricated as reference samples. Because measurements at elevated temperatures or in large magnetic fields could not be

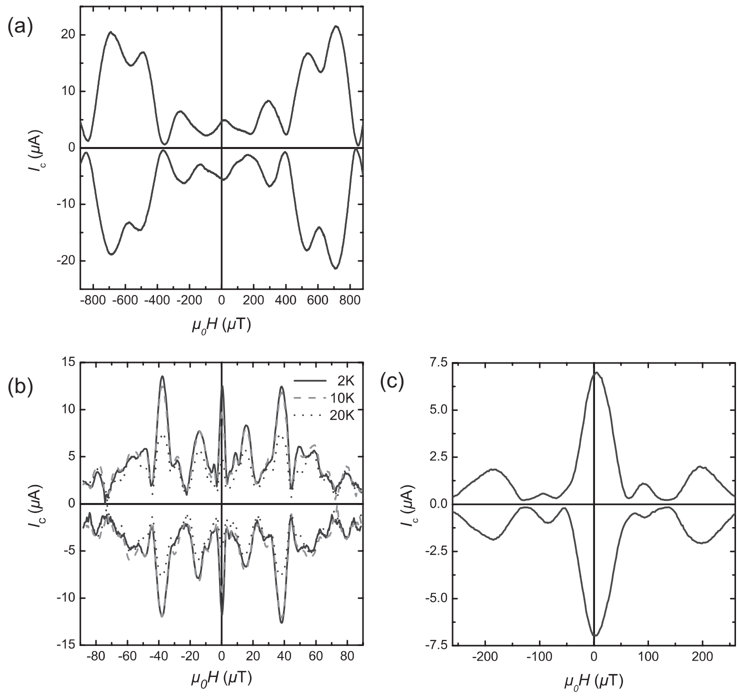

Fig. 3 – $I_c(H)$-characteristics of 45° grain boundary junctions in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ films: (a) asymmetric boundaries from sputtered films, and (b) asymmetric boundaries from MBE-grown films, and (c) symmetric boundaries from sputtered films.

performed without flux trapping, all data were taken at low temperatures ($T < 0.3T_c$) with magnetic fields not exceeding 1 mT.

For all measurements on the 45° [100]/[110] bicrystals, comprising four samples and twenty Josephson junctions, anomalous Fraunhofer patterns were observed. Representative patterns are shown for the sputtered films (fig. 3(a)) and MBE films (fig. 3(b)). The almost perfect symmetry of the $I_c(H)$-characteristic with respect to $H = 0$ and for both current polarities indicates that the influence of trapped magnetic-flux quanta or possible spurious background magnetic fields is negligible. It is pointed out that the differences in the absolute value of the applied magnetic field reflect the differences of the junction widths of the samples. In the temperature range explored, the modulation pattern is furthermore independent of temperature. We note that the MBE-grown films exhibit a narrow critical-current peak at zero field, which we attribute to a second-order Josephson tunneling contribution expected for flat junctions in which the first-order term largely cancels in this geometry [31]. The control measurements on the symmetric $45 \pm 1°$ grain boundaries showed $I_c(H)$-patterns of inhomogeneous but conventional junctions (fig. 3(c)).

These patterns resemble in all respects the $I_c(H)$-characteristics of $YBa_2Cu_3O_{7-\delta}$ bicrystals as shown by Hilgenkamp and Mannhart in ref. [32]. The patterns can only be explained by the presence of a dominant $d_{x^2-y^2}$ pairing state in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$. As is the case for the experiments of Tsuei and Li [8, 24], the symmetry information is only provided directly for the interface layer near the grain boundary. Thus, these results confirm the tricrystal experiments on $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ [8].

Our experimental results contradict the standard interpretation of the I_c-measurements of the c-axis twist Josephson junction studies by Li *et al.* [24]. We find it likely, however, that those measurements which analyze the current flow in c-direction are influenced by atomic layers at the interface with a relatively large s-wave components, which may cause the small, misorientation independent critical currents measured [33]. This layer may form due to intrinsic reasons, as shown by recent STM studies, which observed this effect when tunneling directly into the Cu-O layer [34]. This layer may also be caused by impurities. Because in the work presented in ref. [23, 24] the crystals are handled in air prior to their joining, their surface may react with water, carbon dioxide and other environmental compounds. During sintering of these surfaces, the resulting reaction products create defects at the tunnel junctions which we expect to influence the properties of the junctions, while being invisible in TEM. In addition, it seems possible in at least some studies of bulk samples that self-field effects or very small intragrain critical-current densities prohibit the measurement of the true grain boundary critical currents [32, 35].

In summary, by measuring the $I_c(H)$-characteristic of asymmetric 45° grain boundaries, unambiguous evidence for a d-wave pairing symmetry in $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ interfaces has been established.

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