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Electrical Transport Across Grain Boundaries in Bicrystals of $YBa_2Cu_3O_{7\delta}$

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ELECTRICAL TRANSPORT ACROSS GRAIN BOUNDARIES IN BICRYSTALS OF $YBa_2Cu_3O_{7-\delta}$

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The superconducting properties of about 20 bulk-scale flux-grown bicrystals of $YBa_2Cu_3O_{7-\delta}$ have been measured in order to deduce the nature of the coupling across their grain boundaries. Bicrystals with two types of misorientation relationship were studied: (i) θ [001] (C-type) and (ii) 90° [010] plus an additional rotation about the $a_I \parallel c_{II}$ axis (P-type). A general trend for a transition from flux pinning (FP) to Josephson Junction (JJ) to resistive (R) behavior was observed as the misorientation angle increased. However, FP character was observed well into the high-angle regime, in particular, for P-type bicrystals, and JJ behavior was observed at as low as 10° [001]. The J_{ct} values of two bicrystals were increased by a second oxygen anneal. In one case (28° [001] boundary), extended oxygenation produced a change from JJ to mixed JJ/FP behavior, markedly raising the transport critical current density (J_{ct}) at all fields. HRTEM has been performed on two of the same bicrystals which were electromagnetically characterized. A thin second phase layer unobservable by conventional TEM was observed in a resistive boundary, whereas no such phase was detected at a JJ boundary. We conclude that the character of the boundary cannot be predicted either from its misorientation angle or the magnitude of its J_c.

1. INTRODUCTION

Electrical transport across high angle grain boundaries (HAGB) of the 123 compounds has always been difficult. This was shown most explicitly by thin-film bicrystal experiments[1] which showed that only very small crystal misorientations drastically reduced the J_c. From these experiments, it was concluded that the GB acquired a Josephson Junction (JJ) character when the misorientation angle about any of the principal axes exceeded about 5°. This transition from a strongly coupled GB to a weak-linked GB can be useful in SQUID and other electronic devices but it is very undesirable for magnetic field applications, since the field sensitivity of the transport critical current density, $J_{ct}(H)$, is then very strong and $J_{ct}(H)$ falls to low values in fields of a few millitesla at 4.2K.

Our group[2] has investigated electrical transport in bulk-scale flux-grown bicrystals of $YBa_2Cu_3O_{7-\delta}$. Our motivation was to understand the high field transport critical current density and to understand how the specific structure and formation conditions of individual boundaries influence $J_{ct}(H)$. On quite general grounds we would expect such an influence: grain boundaries have structure which depends on the crystallographic misorientation of neighboring grains, the grain boundary plane, chemical segregation and other effects. Indeed, the distribution of [001] misorientations observed for flux-grown $YBa_2Cu_3O_{7-\delta}$ bicrystals was markedly dependent on angle[3], suggesting that the grain boundary energy for some misorientations was significantly lower than for others. In our initial investigations, we found flux pinning (FP), that is non-weak-linked behavior, for both a 14° [001] bicrystal and a 90° [010] bicrystal, for which the ab planes in one crystal are perpendicular to those of the other crystal. Both of these boundaries had significant J_{ct} values out to fields of at least 7T at 77K, the magnitude and field dependence of the J_{ct} being close to that in a similarly grown single crystal. The present paper summarizes recent work on a larger set of similar bicrystals.

2. SAMPLE PREPARATION

The bicrystals were grown by a Cu-O rich flux technique.[4] They were subsequently oxygenated in pure oxygen for various times at 420°C. Four lead electrical contacts were made to the crystals with gold wires and silver epoxy. The misorientation was generally determined from light micrographs of the (001) faces of the crystals. The misorientation angle was determined from the surface twin traces and the (100) crystal faces with an uncertainty of ± 1°. Selected samples were examined by secondary electron channelling and by selected area diffraction in TEM. In agreement with previous studies[5], the c-axes in bicrystals determined to have nominally parallel [001] axes by light microscopy were generally misaligned by less than 3°. Samples for TEM were produced by mechanical grinding to ~ 50 μm and ion thinning (LN_2 cold stage) to electron transparency.

3. OVERVIEW OF THE ELECTROMAGNETIC RESULTS

An overview of the results is shown in the first two columns of Table 1, where the character of the boundary is described as flux pinning (FP), Josephson Junction (JJ) or resistive (R). Some boundaries (Fig. 1) have characteristics which change significantly only for strong fields of several tesla. Others are extremely sensitive to even millitesla magnetic fields (Fig. 2) and some are resistive even down to 4K. It is this $J_{ct}(H)$ characteristic, rather than the magnitude of the zero field J_{ct}, that we use to distinguish the FP from the JJ boundary. We thus categorize the boundary by the mechanism which controls current flow across the boundary.

Table 1 shows the tendency for the character of the boundary to change as the misorientation angle increases. For c-type boundaries (rotations about parallel c axes), evidence for flux pinning character is found well into the high angle regime. JJ behavior was found for c-type bicrystals as low as 10°. Resistive behavior was found in 42° and 45° [001] boundaries. Less information is available on the P-type boundaries for which the misorientation of the c axes of the 2 crystals is 90° (the (001) basal planes of one crystal are perpendicular to the (001) planes of the second). An important conclusion of the data is that the misorientation angle does not suffice to predict the properties. For example, one 10° [001] boundary had FP and one had JJ character

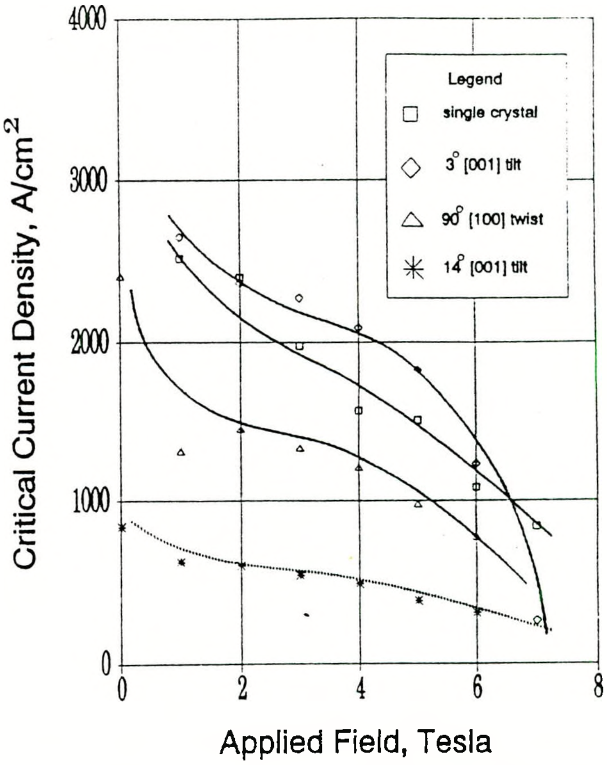


Figure 1. Critical current characteristics at 77K with H//c for bicrystals and one single crystal, all having flux pinning characteristics.

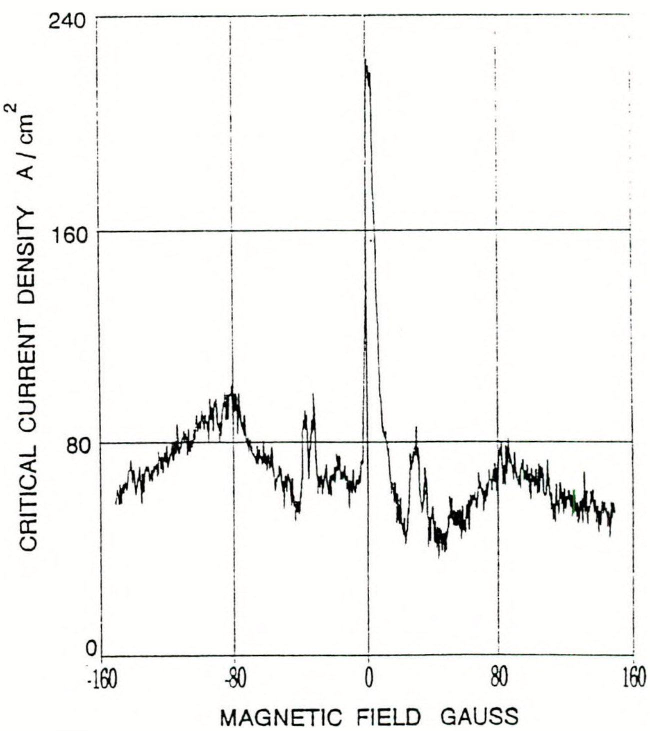


Figure 2. Low field critical current characteristic for 30° [001] tilt (sample C30 boundary).

Table 1.

BICRYSTAL[1]	CHARACTER	T_c (R=0) (K)	J_{ct} (0, 77K) (A/cm^2)	J_{ct} (0, 4.2K) (A/cm^2)	$\rho_n d$ ($\Omega\mu m^2$)	$I_c R_n$ (μV)
C3	FP	93	3000	nm[3]	---	---
C6	FP	95	3300	nm	---	---
C10-1	FP	90.5	1700	nm	---	---
C10-2[4]	JJ → JJ	85.1 → 92	57 → 342	1000 → nm	6.5 → 2.6	14 → 35
C14	FP	92.5	850	nm	---	---
C22...37[2]	FP	90	370	nm	---	---
C22	JJ	84.7	210	4000	0.92	23
C26	JJ	87.3	170	900	1.0	9
C28[4]	JJ → JJ/FP	81.5 → 93	20 → 590	1100 → 4400	10.0 → 2.0	---
C33	JJ	90	269	nm	1.2	---
C40	JJ	32.5	0	273	26.4	98
C43	R	< 4.2K	0	0	16.5	---
C45	R	< 4.2K	0	0	89	---
P3	FP	92.5	1750	nm	---	---
P15-1	FP	89	33	nm	---	---
P15-2	R	< 4.2K	0	0	---	---
RAH[5]	JJ	42	0	14	71.4	10

[1]For C-type bicrystals, the dominant component of the misorientation is a rotation by the angle given in the bicrystal's name about the [001] axis of both crystals. For P-type boundaries, crystal II is first rotated 90° relative to crystal I about a common b-axis, resulting in the $C_{II} \parallel a_I$. Crystal II is further rotated about the C_{II} (a_I) axis by the given angle. For P-type bicrystals, the (001) basal planes of crystal II are always perpendicular to the (001) planes of crystal I.
[2]Flux-pinning current in this multi-crystal must have passed along a path containing either (a) a C24, (b) a C29, (c) a C37 and C29, or (d) a C16, C22, and C37 high-angle boundary. The exact path could not be determined.
[3]nm = not measured
[4]Second figure represents values after a second oxygenation.
[5]RAH is a high-angle bicrystal which has neither the c-type nor the P-type geometry.

and the 28° boundary had its character changed from JJ to mixed JJ/FP by extended oxygenation. Thus, at minimum, the specific local structure and composition are important in determining the electrical characteristics of the boundary.

4. FLUX PINNING CHARACTERISTICS

In order to determine the flux pinning characteristics, it is necessary to measure J_{ct} in magnetic fields, preferably to high fields over a range of temperatures. Figure 3 shows J_{ct}(H) characteristics for the P3 boundary (Table 1) in fields up to 12T and at temperatures from 87 to 40K. Several features of this data are important.

Two orientations of the magnetic field and the crystallographic axes are reported. Figure 3a shows the high H_{c2} orientation (H//ab planes of both crystals) while Fig. 3b shows the situation where H is parallel to the c axis in one crystal and to the ab plane in the second. In this second configuration, J_{ct}(H) should be limited by current transport in the grain having the low H_{c2} (H//c) orientation or by the grain boundary. As Fig. 1 shows, however, there is no evidence for any different character of the bicrystal as compared to the single crystal. Comparing Fig. 3a and 3b, the field dependence of J_{ct} follows what would be predicted from H_{c2}, namely that the high H_{c2} orientation possesses the higher J_{ct}. The absolute magnitudes of J_{ct} are of order 1000-4000 A/cm^2, depending on field and temperature. These values are comparable to those deduced from magnetization measurements on similar single crystals and exhibit the same minimum of J_{ct} in field that we have shown is characteristic of flux pinning by oxygen-deficient regions.[6] The minimum is seen in both magnetic field orientations.

Figure 4 presents an explicit test of the scaling observed across a 6° [001] low angle grain boundary (C6 Table 1). In this case J_{ct}(H) data at 77, 85 and 90K are plotted in reduced units $J_{ct}(H)/J_{ct}(0)$ vs. H/H_{c2}^*, where H_{c2}^* represents the extrapolated field at which J_{ct} tends to zero.

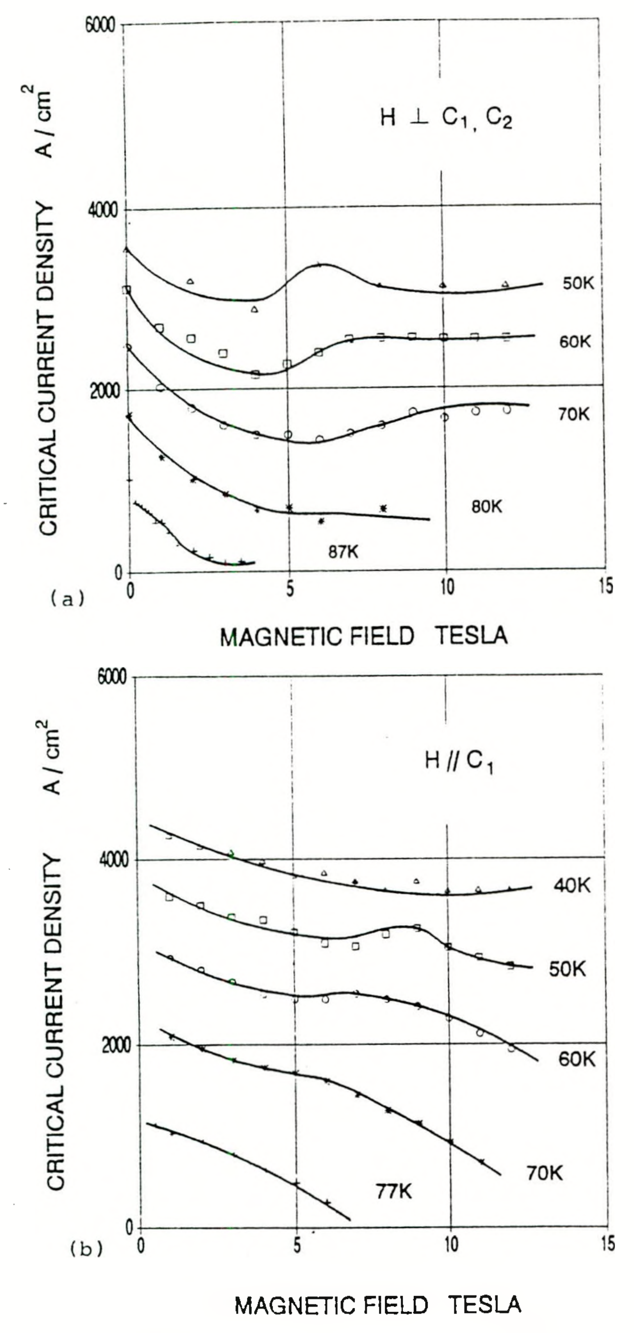


Figure 3. $J_{ct}(H)$ for near 90° [100] twist boundary (sample P3), with the applied field a) parallel to the AB planes of both crystals; and b) perpendicular to the AB planes of one crystal.

In all of the above cases the $J_{ct}(H)$ characteristics have a flux pinning character, whether low-angle (C6, Fig. 4), intermediate angle (C14, Fig. 1) or high angle (P3, Fig. 3). They have J_{ct} values of similar magnitude and exhibit similar $J_{ct}(H)$ characteristics to single crystals.

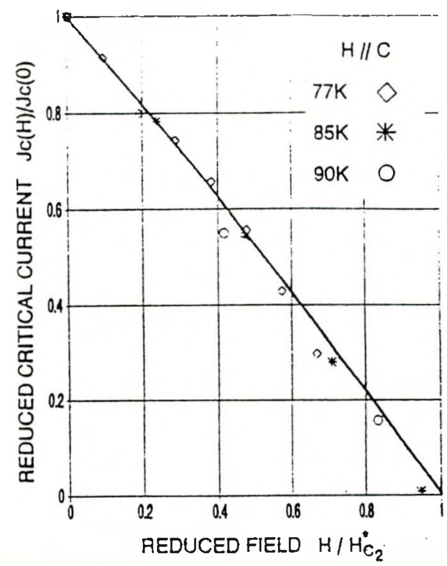


Figure 4. Scaling behavior of $J_{ct}(H)$ for 6° [001] tilt boundary (sample C6).

5. JOSEPHSON JUNCTION CHARACTERISTICS

Detailed data contrasting the different characteristics of the JJ and FP boundaries are collected in Table 1. Their essentially different $J_{ct}(H)$ characteristics have already been contrasted in Fig. 1 and Fig. 2. Here we focus on the magnitudes of the zero field, $J_{ct}(0)$, and then look at the normal state grain boundary resistivity ($\rho_n d$) deduced from the slope of the V-I trace above I_c and the I_cR_n product of the JJ. The data show that there is a definite tendency of the GB to have a depressed T_c in the standard oxygenated state (10 days at 420°C). Sometimes the depression is small (e.g., C10-2 T_c (R=0) = 85K), sometimes very large (RAH T_c (R=0) = 42K). This contrasts with the FP boundaries for which T_c (R=0) was never less than 89K. $J_{ct}(0)$ values always tended to be larger for the FP boundaries (e.g., 1700-1750 A/cm^2 at 77K for C10-1 and P3, as compared to a maximum JJ J_{ct} (0, 77K) of 270 A/cm^2 for the C33 boundary). Some of the JJ boundaries showed a strong increase in J_{ct} at 4.2K (e.g., C22 increased from 210 to 4000 A/cm^2) but 4.2K measurements could not always be made because of frequent burnout of the current contacts at the higher I_c values.

$\rho_n d$ values for the JJ boundaries varied from 0.92 to 71 $\Omega\mu m^2$. The two resistive boundaries had values of 16.5 and 89 $\Omega\mu m^2$. There thus seems to be a continuum of behavior between the JJ and R boundaries. I_cR_n products varied from 9 to 98 μV. This value is much less in all cases than the expected energy gap of order 20 mV.

A different aspect of the continuum behavior was shown when certain bicrystals were re-oxygenated. In the case of the C10-2 boundary, J_{ct} (0, 77K) was raised from 57 to 300 A/cm^2 upon oxygenating for a further 24 hrs at 420°C and $\rho_n d$ was reduced from 6.5 to 2.2 $\Omega\mu m^2$. Thus both the normal state and the superconducting properties depend on the oxygenation condition. The most significant change, however, was seen for the C28 boundary (Fig. 5). As originally tested, it had a low J_{ct} (0, 4.2K) of ~ 1100 A/cm^2 with a very sharp field-induced depression. Further oxygenation of 50 hrs at 420°C both raised J_{ct} and totally changed the $J_{ct}(H)$ characteristic. The J_{ct} fell off much less rapidly in field; J_{ct} was still finite at 7T, 4.2K. The sample was then oxygenated for a further 72 hrs at 420°C and prepared for testing at 7T at 4.2K. J_{ct} then exceeded 10^4 A/cm^2, higher than any previously measured value but the current contacts burned out rendering further testing impractical. We conclude that the effect of the oxygenation was to produce a mixed FP/JJ character in the boundary.

6. MICROSTRUCTURAL EXAMINATION

So far two of the electromagnetically examined bicrystals, C26 having a JJ character and C42 having a resistive behavior, have been thinned for TEM examination. In both cases (Fig. 6), the boundaries were twin matched[6] on both the light microscopy and TEM-scale over a large fraction of their length and they appeared clean of any second phase under conventional diffraction contrast TEM imaging. By HRTEM, however, there appeared a wetting second phase 1-3 nm thick in the C42 resistive boundary. The

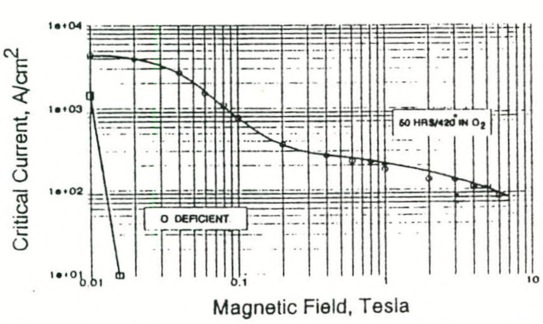
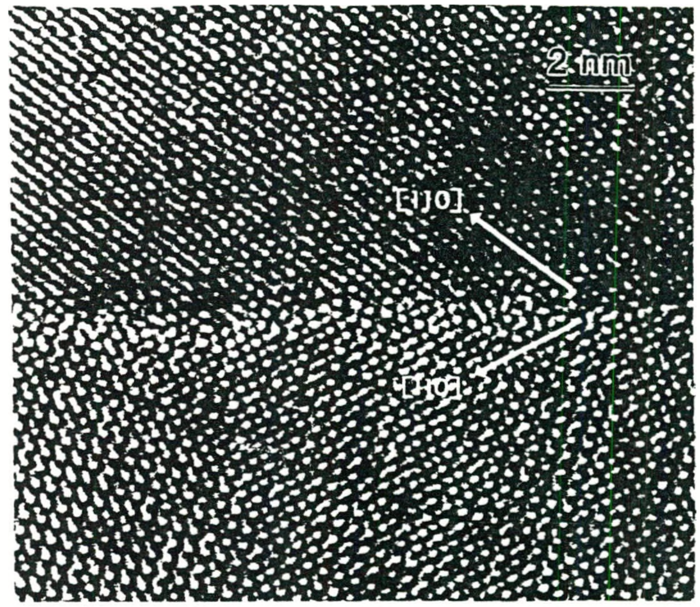
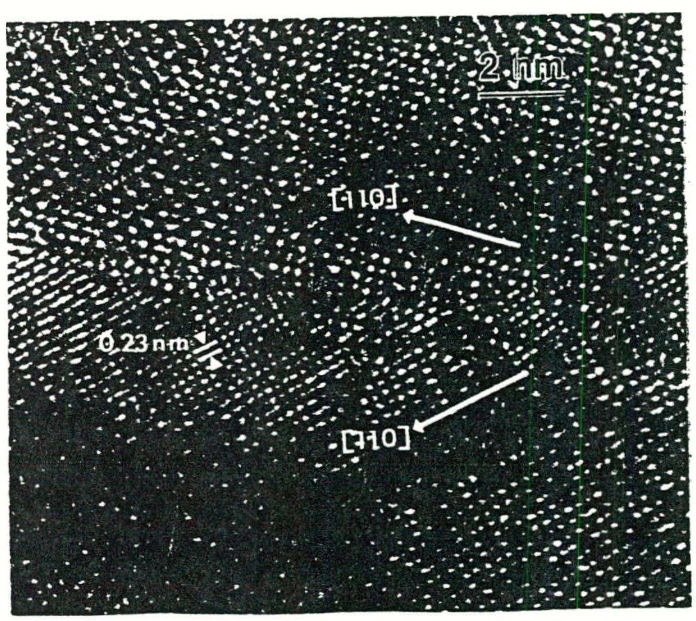


Figure 5. $J_{ct}(H)$ for 28° [001] tilt boundary (sample C28). 50 hrs/420° oxygenation changed the complete JJ behavior into a partial FP behavior.



a)



b)

Figure 6. HRTEM structure image for a) 26° [001] tilt boundary (sample C26) with JJ characteristic, and b) 43° [001] tilt boundary (sample C43) with resistive characteristic.

HRTEM examination of the C26 JJ boundary revealed that the 123 structure is maintained right up to the grain boundary. It is clear from these micrographs that the properties of individual $YBa_2Cu_3O_{7-\delta}$ boundaries can be determined at the atomic scale.[7,8]

7. DISCUSSION

In this overview of our recent studies of the critical current density and the microstructure of $YBa_2Cu_3O_{7-\delta}$ bicrystals, we have observed (i) that the properties of individual boundaries cannot be predicted on the basis of the misorientation angle alone; (ii) that there is, however, a general tendency for there to be a change from FP to JJ to R behavior as the misorientation of [001] boundaries increases; (iii) that the properties of some boundaries are sensitive to oxygenation conditions; and (iv) that it is possible to do HRTEM on the same bicrystals that have been electromagnetically characterized. These results all support the view that the local structure and composition of individual grain boundaries are variable and that the superconducting properties are sensitive to these variations. The behavior of the C28 is one example of this view. This bicrystal is particularly interesting in that the 28° rotation (near $\Sigma 17$) was the most frequent one found by Smith et al.[3] when they examined flux-grown bicrystals. Our supposition[2] was that such low energy misorientations of the two crystals might have favorable superconducting properties. This seems at least partially borne out by the results of Fig. 5.

The general similarity of the normal state properties of the JJ bicrystals to the epitaxially grown thin film HAGB bicrystals of Dimos et al.[1] can be seen by comparing their $\rho_n d$ properties. As Table 1 shows these vary from 0.75 to 26 $\Omega\mu m^2$, clustering in the range less than 10 $\Omega\mu m^2$. This is to be compared with values ranging from 0.02 to 7.65 $\Omega\mu m^2$ for the thin film bicrystals[1], values essentially similar to the present. So far as the superconducting properties are concerned, the thin film J_c (0, 4.2K) values ranged from about 1×10^4 to 5×10^5 A/cm^2. At 77K these values should be about 10 times less; these are about two orders of magnitude greater than the values measured on the present JJ bicrystals. However, the typical size of the grain boundaries in the present crystals is much larger than for the thin films. Our bicrystals are typically 50-100 μm (c-dimension) x 200-600 μm (a/b dimension) and should thus be considered as long Josephson Junctions. Current cannot therefore occupy the whole cross-section, since it will only flow to a penetration depth λ_J of order 1 μm. Thus for a typical junction only a thin perimeter λ_J (~ 1 μm thick) carries the supercurrent and J_{ct} normalized to this perimeter will be of order 10^2 tunes higher, this raising J_{ct} to the range 10^4-10^5 A/cm^2 observed for the thin film bicrystals. In summary, therefore, we conclude that the measured magnitude of J_{ct} cannot easily be used as a guide to the character of the grain boundary. A broader characterization, including a knowledge of the geometric form of the sample, is necessary to explain the values of J_{ct} observed on specific samples.

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