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Alexander H. King, *State University of New York at Stony Brook*
Abha Singh, *State University of New York at Stony Brook*

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A geometrical rationalization of the special properties of the 14° [001] grain boundary in $YBa_2Cu_3O_{7-\delta}$

A. H. King and Abha Singh
Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275

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14° [001] tilt grain boundaries in $YBa_2Cu_3O_{7-\delta}$ have been found to exhibit anomalously good superconducting critical currents, associated with magnetic flux pinning, although no special interfacial structure has heretofore been associated with this misorientation. We present an analysis of the geometry of the grain boundary in question and show that it can correspond to a special interface, within the definition of constrained lattice coincidence, which may lead to new understanding of the superconducting behavior of grain boundaries. Our analysis shows that the tetragonal-to-orthorhombic phase transformation may have important effects upon grain boundary structure and properties, indicating new approaches to producing high-current superconductors.

INTRODUCTION

The low critical currents of polycrystalline yttrium barium copper oxide are a major barrier to the successful technological application of this high-T_c superconducting material, and they are associated with weak-link behavior of large-angle grain boundaries. Dimos *et al.*[1] showed that there is a rapid decline of grain boundary critical current with misorientation and that for rotations about [001] all boundaries with misorientation Θ greater than about 8° have effectively the same, very low current carrying capacity. In the large-angle regime, there are a few reported observations of special properties associated with misorientations corresponding to coincidence-site lattices (CSLs). Smith *et al.*[2] found a high incidence of coincidence-related boundaries between melt-grown single crystal tablets, implying that these boundaries embody low energies. Babcock and Larbelestier[3] observed grain boundary dislocation networks in large-angle $YBa_2Cu_3O_{7-\delta}$ grain boundaries and related them, in some cases, to CSL structures. In all of their analyses, they utilized CSLs derived directly from the widely studied cubic crystal systems, effectively treating the $YBa_2Cu_3O_{7-\delta}$ unit cell as a vertical stack of three nearly cubic units. Chan *et al.*[4] found that grain boundaries with 90°/[001] misorientations do not have deleterious effects upon critical current in thin-film $YBa_2Cu_3O_{7-\delta}$ in zero-field conditions and described the boundaries as $\Sigma1$ coincidence-related interfaces. Investigations of bulk bicrystals in high-field conditions were performed by Babcock *et al.*,[5] who found a number of interfaces that lacked weak-link behavior. Among these were bicrystals with misorientations of 3°, 14°, 22°, and 38° at about [001] and one of 90° at about [010]. These were described as $\Sigma1$ (small angle), $\Sigma41$, $\Sigma13$, $\Sigma5$, and $\Sigma3$, respectively. The 3° boundary is consistent with the observations by Dimos *et al.*,[1] but other findings indicate that there are large-angle boundaries that can potentially sustain large currents, and that they are related to lattice coincidence. The results are problematical in one respect; while the 14° case is close enough to the misorientation for $\Sigma41$ (12.68°) to be considered coincidence-related, using the usual criteria such as that of Brandon,[6] it is also close enough to be classified as $\Sigma25$ (16.25°). Before the improved properties of this boundary can be ascribed to coincidence, it is necessary to establish to which coincidence system it belongs. The problem is further complicated since the use of CSLs derived from the cubic system ignores the orthorhombic structure of $YBa_2CU_3O_{7-\delta}$ in which the *a* and *b* axes are not of equal length. Dislocation arrays are required in the grain boundary to accommodate this distortion in addition to any deviation in misorientation from the ideal value.[7]

Although special boundary properties are often found to persist over some angular range about the exact coincidence misorientation, the properties of the 14° boundary are not unequivocally related either to $\Sigma41$ or $\Sigma25$. We have, therefore, chosen to study the possible coincidence relationships of the 14° misorientation in $YBa_2Cu_3O_{7-\delta}$.

In this article we discuss the geometry of the 14° [001] boundary in $YBa_2Cu_3O_{7-\delta}$ and show that its structure may correspond to a new low-Σ (high-coincidence) coincidence-site lattice when analyzed correctly. Our finding supports the notion that lattice coincidence or short-wavelength periodic structures in the grain boundary may be associated with improved grain boundary critical currents. This provides some cause for cautious optimism that polycrystalline $YBa_2Cu_3O_{7-\delta}$ can be fabricated, through some form of "grain boundary engineering,"[8] with improved critical current. Other implications are introduced concerning the range of CSLs that must be considered in studying $YBa_2Cu_3O_{7-\delta}$, as are problems related to the tetragonal-to-orthorhombic phase transformation.

COINCIDENCE GEOMETRY

For the study of lattice coincidence arising from rotations about [001], it is sufficient to consider only the basal plane of the crystal lattice containing the *a* and *b* crystal axes. Coincidence along the *c* axis always exists for [001] rotations. Because *a* and *b* are so similar in length for

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TABLE I. Coincidence-site lattices for $YBa_2Cu_3O_{7-\delta}$ for rotations about the [001] axis with $\Sigma \leqslant 50$, and $0.950 \leqslant a/b \leqslant 1.001$.

a/b	Σ	θ (deg)	a/b	Σ	θ (deg)
0.951	20	87.134	0.972	35	88.363
0.951	32	38.625	0.972	43	54.451
0.953	21	87.271	0.973	37	88.451
0.953	27	50.977	0.973	47	51.901
0.956	22	87.395	0.975	24	54.315
0.956	38	35.335	0.975	39	88.531
0.957	14	55.150	0.976	22	68.676
0.957	23	87.508	0.976	26	52.020
0.957	34	19.750	0.976	38	32.637
0.957	37	38.392	0.976	41	88.602
0.957	38	65.099	0.976	43	72.403
0.957	47	29.268	0.976	47	60.701
0.957	49	69.700	0.977	43	88.667
0.959	24	87.612	0.977	47	66.156
0.961	16	51.318	0.978	45	88.727
0.961	25	87.708	0.979	29	54.112
0.961	40	18.195	0.979	47	88.781
0.961	43	35.516	0.979	49	28.652
0.962	26	87.796	0.980	25	78.463
0.962	30	60.000	0.980	31	52.200
0.962	42	38.213	0.980	35	44.415
0.964	27	87.877	0.980	49	88.831
0.964	33	54.847	0.982	30	66.422
0.965	28	87.953	0.982	34	53.968
0.965	48	35.659	0.983	36	52.330
0.966	29	88.024	1.000	5	36.870
0.966	31	69.216	1.000	5	53.130
0.966	37	51.565	1.000	13	22.620
0.966	41	44.983	1.000	13	67.380
0.966	47	38.072	1.000	17	28.072
0.968	16	75.522	1.000	17	61.928
0.968	17	65.684	1.000	25	16.260
0.968	19	54.623	1.000	25	73.740
0.968	23	42.343	1.000	29	43.603
0.968	31	88.151	1.000	29	46.397
0.968	32	28.955	1.000	37	18.925
0.968	47	81.435	1.000	37	71.075
0.970	21	51.753	1.000	41	12.680
0.970	33	88.263	1.000	41	77.320
0.970	36	27.266			

$YBa_2Cu_3O_{7-\delta}$, the basal plane is usually considered only as a square lattice. Under these conditions, CSLs are found at the [001] misorientations that are familiar from studies of grain boundaries in cubic metals. These are included in Table I, for comparison with our new results that will be described later. One result of the use of a square lattice is that all rotations of angle θ greater than 45° are equivalent to rotations of 90°-θ. When the lattice is considered to be rectangular, however, rotations up to $\theta = 90°$ may be unique. All previous considerations of the [001] boundaries in $YBa_2Cu_3O_{7-\delta}$ have been made under the assumption of a square lattice in the basal plane.

The formation of three-dimensional CSLs is possible for these particular grain boundaries when the ratio a^2:b^2 is rational, and the use of rational values close to those of the real crystal leads to the formation of constrained coincidence-site lattices (CCSLs) described, for example, by Chen and King.[9] For the present case we find CCSLs corresponding, among others, to a^2:b^2 values of 1:1 (constraining to the square lattice in the basal plane), 16:19; 8:9; 16:17, and 15:16, all of which are close to the true axial ratio of the crystal, which is δ dependent, but varies between 0.982 and 1.000.[10] We have used methods described elsewhere[11] to find the CCSLs associated with these axial ratios for rotations about [001]. The results for $\Sigma \leqslant 50$ are given in Table I. It can be seen that there are several new coincidence systems, compared to the more familiar ones given for the axial ratio of unity, but none with $\Sigma < 25$ is found for a misorientation close to 14°.

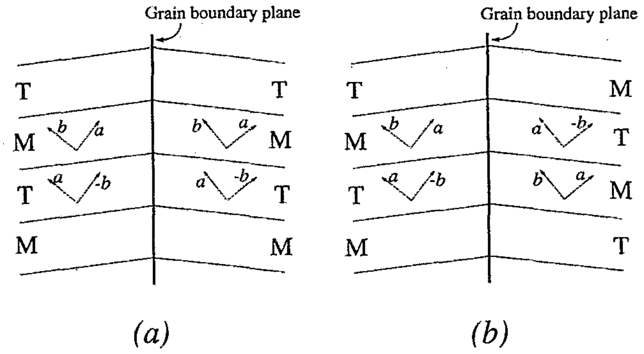

FIG. 1. The effects of correlated twinning on grain boundary misorientation. The labels *M* and *T* refer to matrix and twin orientations of the crystals abutting the grain boundary, respectively, and the crystallographic axes are represented schematically. (a) Normal twin correlation, for which the M–M and T–T interfaces are formed, giving 14° misorientations. In (b) we show the case of anticorrelation of the twins, giving M–T and T–M interfaces with misorientations of 75° and 105°, respectively; these are symmetrically equivalent to each other and both give the $\Sigma 16$ structure.

At this point it is necessary to consider an additional effect associated with the rectangular shape of the basal plane lattice in $YBa_2Cu_3O_{7-\delta}$. The material twins on the (110) and $(1\bar{1}0)$ planes, corresponding (approximately) to the interchange of the *a* and *b* axes.[12] This can also be described as a lattice rotation of between 89° and 90° (depending on the exact axial ratio) about [001]. Twinning can therefore result in a new misorientation of 89°-θ, as illustrated in Fig. 1. What has previously been described as a 14° grain boundary should, therefore, also be considered as possibly representing a 75° boundary if twin correlation (or, perhaps more precisely, anticorrelation) is found at the boundary plane, as might be expected in this case.[13] For a misorientation of 75.522°, we find a CCSL with $\Sigma = 16$, corresponding to a short periodicity of structure in the boundary plane. The coincidence-site lattice is illustrated in Fig. 2. It is important to note that the high-coincidence boundary structure corresponding to this case is found only through the constrained coincidence-site lattice theory, and the use of a square-latticed-crystal approximation is demonstrated to be inadequate.

The unit cell of the $\Sigma 16$ CCSL is more than usually equiaxed, all of its edges having nearly equal lengths. This results in the boundary exhibiting relatively small changes of structural periodicity with changes of boundary plane. It is not clear whether this has any important effect on the

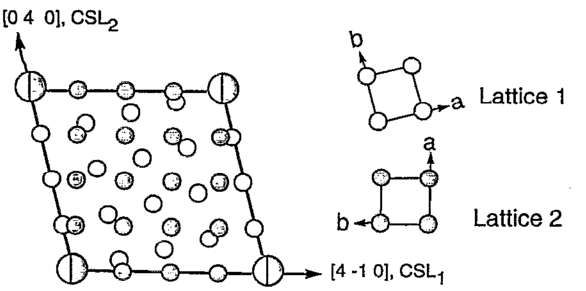

FIG. 2. The unit cell of the $\Sigma16$ coincidence-site lattice formed at a rotation of 75.522° and an axial ratio $a/b=0.968$.

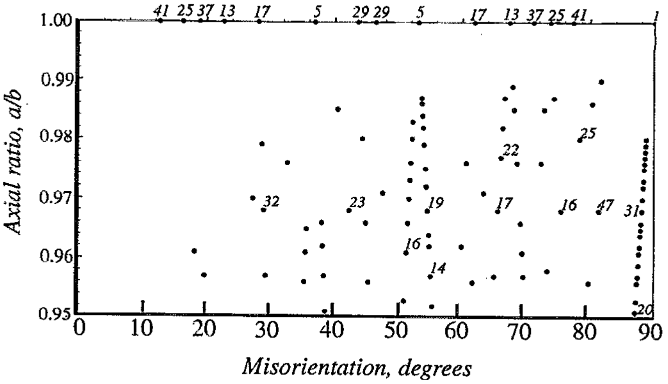

FIG. 3. Misorientations and axial ratios giving CSLs with $\Sigma<50$ for rotations about [001]. Each dot represents a CSL and the Σ values are marked for some of them.

variation of boundary energy or superconductivity with changes of boundary plane inclination, but we speculate that any anisotropy will be minimal for this misorientation.

DISCUSSION

The special properties of the so-called 14° boundary can now be associated with the short period structure corresponding to the 75.52° misorientation, and we postulate that the high critical current observed for this boundary originates in some way from this short period boundary structure, rather than from $\Sigma25$ or $\Sigma41$, both of which have longer structural periods and greater anisotropy. It is further likely that twin correlation at this boundary will favor the formation of 75.52° boundaries over 14° boundaries if the boundary periodicity also gives rise to low boundary energy. The only CCSLs with $\Sigma\leqslant100$ that can be identified for a near-14° boundary have $\Sigma=77$ ($\theta=13.087°$; $a/b=0.918$), $\Sigma=73$ ($\theta=13.443°$; $a/b=0.943$), $\Sigma=69$ ($\theta=13.829°$; $a/b=0.970$), $\Sigma=65$ ($\theta=14.250°$; $a/b=1.000$), $\Sigma=61$ ($\theta=14.712°$; $a/b=0.968$), and $\Sigma=89$ ($\theta=14.919°$; $a/b=0.917$). Since these all have very large Σ values, we speculate that there is a significant energy difference between matrix–matrix or twin–twin boundaries (i.e., 14°) and matrix–twin or twin–matrix boundaries (i.e., 75°) and that the latter are favored. High resolution electron microscopy of complete boundaries will be required in order to substantiate this hypothesis and establish whether supercurrents can be carried locally, where there are appropriately correlated twins; but the identification of a high-coincidence boundary associated with a high critical current is essential. Other CCSLs given in Table I should also be considered as candidates for boundaries with improved current carrying capacity on the basis of the present findings.

The possible correlation between boundary periodicity and the J_c found in this analysis confirms some of the earlier findings[5] and may be important in identifying the physical origin of the weak link behavior of less periodic boundaries. It may help to identify ways of overcoming the problem in order to create polycrystalline materials with higher current carrying capacity.

Unfortunately, grain boundaries in solid $YBa_2Cu_3O_{7-\delta}$ are formed at high temperature, in the tetragonal phase, so any preferential misorientations will be determined by the lattice geometry of that phase, with its square-shaped basal plane. This has been demonstrated by Smith *et al.*,[2] who observed a high incidence of misorientations in flux-grown $YBa_2Cu_3O_{7-\delta}$, corresponding to several of the CSLs listed in Table I for the axial ratio of unity. Upon cooling, the material transforms into the orthorhombic structure, with the exact a/b ratio determined by the oxygen content, and the boundary periodicity may be modified or completely destroyed during this phase transformation. Figure 3 gives the locations of all of the CCSLs with $\Sigma<50$ for rotations about [001], as a function of misorientation and a/b ratio. The effect of the tetragonal-to-orthorhombic phase transformation is to move the point representing any boundary vertically downward from the horizontal line representing $a/b=$unity. What is a special boundary at the processing temperature (and therefore reasonably easy to generate) is represented by a dot on the $a/b=$unity line. After the phase transformation, however, such interfaces seem, in general, not to correspond to special (or periodic) structures. Conversely, the 75° boundary is not particularly special once the material is tetragonal rather than orthorhombic, the closest CSL being $\Sigma25$. It is, therefore, not likely that it can be induced to form with sufficient frequency to improve bulk J_c values via high-temperature processing. It is possible, however, that other misorientations may be sufficiently close to coincidence to be "special" both above and below the orthorhombic-to-tetragonal transformation temperature. Otherwise, routes to higher J_c polycrystalline materials must be found through processing methods at temperatures at or below the tetragonal-to-orthorhombic phase transformation, for which boundary parameters may readjust to reflect the orthorhombic geometry.

SUMMARY

Special current carrying properties seem to be associated with structurally short-period grain boundaries when correctly identified. This does not yet, however, point to any simple means of optimizing the boundary behavior of any bulk or thin-film polycrystalline $YBa_2Cu_3O_{7-\delta}$ product.

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