Epitaxy and disorientations in the ferroelastic superconductor $YBa_2Cu_3O_{7-x}$

V. K. Wadhawan
Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, Maharashtra, India
(Received 2 May 1988; revised manuscript received 7 July 1988)

Certain features of twinning reported recently in the literature for the Y-Ba-Cu-O superconductor are reinterpreted as being due to the presence of multiple disorientations in this ferroelastic material. The possibility of coherent and incoherent twin boundaries existing in the same crystal is pointed out. It is suggested that disorientations (and their local variations) could be providing an additional strain-relieving mechanism not incorporated so far in the spinodal-decomposition model of Khachaturyan *et al.*

I. INTRODUCTION

The superconductor $YBa_2Cu_3O_{7-x}$ has a propensity for occurring in a heavily twinned state.[1,2] The most commonly observed twin walls are (110) and $(1\bar{1}0)$. The number density of the twin walls can be extremely high, with a typical domain size of only 500–1000 Å. The effect of twinning on the superconducting properties of the material is certainly very important, although at present it is also a source of considerable controversy. Deutscher and Müller[3] have argued that twin walls can act as intragrain Josephson junctions, and the dense network of these junctions divides the grains into weakly coupled superconducting domains. Elimination of twin walls can be expected to lead to a higher critical current according to this viewpoint. According to an apparently opposite viewpoint, the twinning not only results in "twinning-plane superconductivity" (with a slightly higher T_c at the twin wall than in regions away from the wall), but may also be fundamental to the mechanism by which the superconducting transition occurs at a temperature as high as 95 K.[2,4,5] According to this school of thought, if the twinning planes are spaced sufficiently close, their mutual interaction results in a reduction of the proximity effect, and the result is a high value of T_c.[1,5,6] However, there are reports of superconductivity with high T_c in crystals of Y-Ba-Cu-O which are seemingly untwinned at room temperature.[7] High-T_c superconductivity has also been observed in Fe-doped Y-Ba-Cu-O, which has tetragonal symmetry and is presumably untwinned.[8]

Twinning constitutes an essential ingredient of the "percolating network" mechanism of superconductivity proposed by Garcia *et al.*[9] Horovitz, Barsch, and Krumhansl[4] have discussed evidence for collective twin-boundary oscillations in high-T_c oxide superconductors. The concentration-wave model of Khachaturyan and coworkers[10,11] is receiving increasing attention.[12,13] A consequence of this model, which stipulates ordering and decomposition in Y-Ba-Cu-O, is the occurrence of twins of the orthorhombic phase embedded in a disordered tetragonal matrix of lower oxygen concentration. Bhargava, Herko, and Osborne[14] exploited, somewhat unwittingly perhaps, the occurrence of this inhomogeneous, metastable, twinned state to achieve a higher T_c (159 K) by low-temperature cyclic annealing. Mueller *et al.*[2] have reported that such an annealing cycle below room temperature (between 85 and 230 K) results in the formation of additional twin walls with a spacing of only 250 Å. These authors also observed that excellent superconducting samples (which displayed a very high diamagnetic shielding effect) were invariably twinned in every grain; by contrast, poor samples with a significantly lower shielding effect had many grains with no twinning. Dinger *et al.*[7] also observed low Meissner expulsion (4–17%) in untwinned single crystals, even though 100% diamagnetic shielding was observed in the same crystals.

A detailed symmetry analysis of the twin walls expected in this superconductor has been carried out recently.[15] In the absence of substantial experimental results, this analysis was restricted to a "classical" treatment, where only the spontaneous strain[16] of domains or twins was considered, and their spontaneous rotation or disorientation[17–19] was ignored. In this follow-up paper consequences of some of these latter aspects such as disorientations and epitaxial growth are examined.

You *et al.*[12] have recently carried out a careful x-ray diffraction study of twinning in Y-Ba-Cu-O. They have interpreted their single-crystal data on two crystals in terms of the commonly observed (110) twins in one crystal, and the so-called "90° twins" in the other. Since they observe superconductivity even in the crystal which they believe contains only 90° twins, they conclude that (110) twins are not necessary for superconductivity in this material. While this conclusion may be correct (the controversy regarding the role of twinning notwithstanding), it is argued below that some of the data of You *et al.* suggest an alternative interpretation in terms of disorientations, and that thin regions with {110} twins may be present even in the 90° twin. Some other experimental studies and models are also discussed in the context of the present analysis.

II. ORIENTATION STATES, EPITAXIAL GROWTH, AND DISORIENTATIONS

Y-Ba-Cu-O is a ferroelastic material. Twin domains are readily introduced in it during grinding, etc.[7,20] Direct observation under the optical microscope of ferroelastic switching induced by a small uniaxial stress on sin-

gle crystals has also been carried out in our laboratory.[21] As discussed in an earlier paper,[15] the observed domain structure[3,20] can be explained by postulating that the prototype symmetry group for this ferroelastic is $Pm3m$. The room-temperature phase, as well as the superconducting phase, has orthorhombic point symmetry mmm. These phases therefore belong to the Aizu species $m3m$ $Fmmm$.[15] The crystal makes a high-temperature phase transition to tetragonal symmetry $4/mmm$. Heating leads to loss of oxygen, and eventually a phase reaction to a compound with a different chemical formula takes place.[22] The cubic prototype is therefore hypothetical, although there have been some reports of an additional phase transition at high temperatures.[23,24]

Almost all the discussion in the literature on twinning in this material has been in terms of the {110} twins derivable from the tetragonal-to-orthorhombic phase transition. In what follows, we shall focus attention on this (and related) type of twinning only. For this it is convenient to factorize the Aizu symbol $m3mFmmm$ as follows:[25]

$$m3mFmmm = m3mF4/mmm \cdot 4/mmmFmmm . \quad (1)$$

Further discussion will be restricted to $4/mmmFmmm$ only. Substantial experimental data are not available yet for considering in detail the consequences of the factor $m3mF4/mmm$ in Eq. (1).

The groups $4/mmm$ and mmm are of orders 16 and 8, respectively, so that two orientation states (say S_1 and S_2) can result from this symmetry reduction. S_1 can be mapped on to S_2 by any of the eight symmetry operations which are present in $4/mmm$, but absent in mmm. These are called F operations. A representative F operation is $m(110)$ or m_{xy}. Another such operation is 4_z, that is, a rotation of 90° around the z axis or the c axis. Thus, at the orientation-state level there is no difference between the two types of twinning observed by You *et al.*[12] The difference is relevant when one considers the "disorientations," a term used by Boulesteix.[18]

The F operations are not exact twinning operations because of the presence of a nonzero spontaneous strain. In the case of $m(110)$, for example, the total twinning operation comprises reflection across m_{xy} (in the coordinate system of the prototype) plus a small rotation or disorientation about the z axis. Shuvalov, Dudnik, and Wagin[19] refer to the latter as "spontaneous rotation," in the same spirit in which the strain arising in the absence of applied stress is described as spontaneous strain.

If one considers the mechanism by which the orientation states arise as transformation twins, the question of their epitaxial growth at the interface with the tetragonal phase becomes relevant. A high degree of strain compatibility and coherence can be achieved if the emerging orthorhombic phase adopts those orientations for which the area of contact of its unit cell with that of the tetragonal phase is conserved at the interface. To a first approximation, this requires that the diagonals of the basal planes of the unit cells of the two phases be superimposed at the interface.[18] This is shown schematically in Fig. 1.

The dotted lines in Fig. 1 show the tetragonal cell $ABCD$. The orientation state S_1 can adopt two suborientations $EBFD$ (S_1^+) and $ALCK$ (S_1^-) because the diagonal chosen for epitaxial matching with the tetragonal cell can be either BD or AC. (In the symbol S_1^+, the superscript "+" denotes an anticlockwise disorientation of the orientation state S_1.) Similarly, S_2 can nucleate and grow as S_2^+ and S_2^-. These four suborientation states are represented as line segments at the center of Fig. 1. The line segments are drawn parallel to the longer of the two sides of the corresponding rectangular unit cell. The angles made by these line segments with the x axis are straightforward to compute. For S_1^+, for example, this angle (θ) is given by

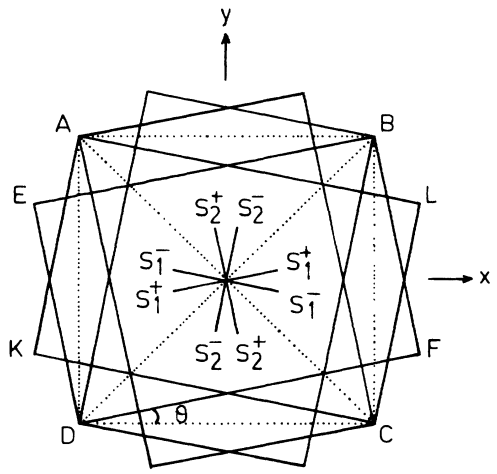

FIG. 1. Orientational and epitaxial relationship between the tetragonal phase (depicted in projection on the basal plane by the square $ABCD$) and the orthorhombic phase of Y-Ba-Cu-O. The figure is not drawn to scale; the orthorhombic distortion is highly exaggerated for clarity.

$$\tan(45° - \theta) = a/b . \quad (2)$$

For Y-Ba-Cu-O, $a = 3.82$ Å, $b = 3.88$ Å,[20] giving $\theta = 0.45°$.

The four suborientation states have the following orientations for Y-Ba-Cu-O [measured in terms of the angle made by the longer axis (b axis) with the x axis of the prototype]: 0.45° (S_1^+), 89.55° (S_2^-), 90.45° (S_2^+), and 179.55° (S_1^-). If no other local constraints are present, coherent walls will result between S_1^+ and S_2^-, and between S_2^+ and S_1^-. The relative angle of twins in each of these cases will be $(90° - 2\theta)$ or 89.10°. Also, if S_1^+ and S_2^+, or S_1^- and S_2^-, share an interface, the result will be the 90° twins observed by You *et al.*[12] The twin walls in this case are incoherent and strained. They may also be "semicoherent"[17] (coherent though strained regions punctuated by misfit dislocations).

The following *general rule* can be stated in terms of the notation used here: Coherent walls result only when those suborientation states are contiguous for which subscripts (1,2) and superscripts (+, −) are both different.

The twin states usually nucleate at defects (including surfaces). If two or more such states nucleate at different points on the surface of the grain and travel inwards, their mutual interaction can result in several possibilities. Very often the ferroelastic may respond to the buildup of stress

by switching to an alternative (and more favorable) twin state. This can happen repeatedly in a self-accommodating manner, giving rise to a network of twin walls. In the case of Y-Ba-Cu-O this network is particularly dense; the observed thickness of twins is typically only 500 Å. Since strain compatibility can result in an overall lowering of the free energy, it is reasonable to expect that those new twin walls will be favored which result in strain compatibility. Matching of diagonals, used above for describing the epitaxy of the suborientation states S_1^+, S_1^-, S_2^+, S_2^- with the tetragonal parent phase, can also be applied for calculating the orientations of the additional suborientation states which can match coherently with any of the existing four (orthorhombic) substates. Consider, for example, the state S_1^+ (rectangle *EBFD* in Fig. 1). We have already used the diagonal *BD* in obtaining matching with the tetragonal phase. Once S_1^+ has nucleated and grown, another suborientation state can also arise by matching coherently with the other diagonal, *EF*. The orientation of this new state can be easily shown to be $90° - 2\delta - \theta$ [mod (180°)], where δ is the larger of the two angles between the diagonals *BD* and *EF*. For Y-Ba-Cu-O, $\delta = 90.90°$, so that the orientation of the new state is 91.35°. Orientations of other new states can be obtained similarly. The process can be repeated a number of times by applying this criterion of strain-compatible matching on the diagonals of the newly obtained suborientation states.

The general result is that suborientation states can occur, in principle, at any of the orientations

$$[(1 \pm 2n)\theta] \text{ or } [(1 \pm 2n)\theta + 90°] \text{ [mod}(180°)],$$

where $n = 0,1,2,\ldots$ and $\theta = 0.45°$. The twin walls separating any two of these states will be coherent or incoherent depending on the pair of states involved. Further, the exact orientation of the twins can become modified in regions in which two or more twin walls tend to intersect. The effect of this can be particularly serious in a material such as Y-Ba-Cu-O in which a very dense network of twin walls occurs.

III. DISCUSSION

In this paper we have considered both heterophase and homophase interfaces to enumerate the possible disorientations in Y-Ba-Cu-O. We have seen that, in principle, an arbitrarily large number of twin orientations can arise. In practice, however, the number will be determined by sample history, inhomogeneities, etc. Fourfold splitting of Bragg reflections (corresponding to the four suborientation states depicted in Fig. 1) has been reported by three different groups.[26–28]

Y-Ba-Cu-O has a very short superconducting coherence length, and according to Deutscher and Müller,[3] the presence of closely spaced twin boundaries results in the occurrence of a "superconducting glass state," with superconducting loops forming *within* the grains of the ceramic. As a rule, domain walls in ferroelectrics and ferroelastics are much thinner than in ferromagnetics.[29] If we assume for the twin domains in Y-Ba-Cu-O a thickness of 1000 Å, and a domain-wall thickness of 50 Å,[13,30] only 5% of the material is structurally affected by the twinning, provided the twin walls do not intersect. Although no detailed experimental studies are available yet, it is unlikely that entire grains are filled with only one set of parallel, coherent twin walls. A more likely situation is as follows: When the transformation twins nucleate (presumably on the surface of the grain), they do so independently at different points on the surface, and the growing sets of twin walls ("accommodation twins") travel inwards. Since two mutually perpendicular orientation states S_1 and S_2 can nucleate and grow independently, the twin walls will tend to intersect in many regions of the grain. Not only is the long-range translational periodicity of the crystal violated in such regions, they also act as sources of strain fields, the effect of which is felt at distances far greater than the typical thickness of the twin walls. Strain fields also interact with stoichiometric variations. Overall, a fairly large fraction (considerably larger than 5%) of atoms in Y-Ba-Cu-O may not be in their "correct" crystallographic positions ("static disorder"), and one can expect a quasi-noncrystalline state even from a structural point of view. Strain fields and structural disorder also influence oxygen vacancy ordering. Evidence for structurally glassy behavior has been presented by some workers.[30,31]

In a given region of the grain (or single crystal) a repetition of parallel twin walls, with the states S_1^+ and S_2^- (or S_2^+ and S_1^-) occurring alternately, is favored because the walls can be coherent and strain compatible. However, it is important to note that both coherent and incoherent twin walls may coexist in a crystal.[17] An example of this is shown schematically in Fig. 2. It follows from our analysis that if S_1^+ and S_2^+ are contiguous, or if S_1^- and S_2^- are contiguous, they would be 90° twins (Fig. 1). Figure 2 is a possible example of a twinned crystal where most of the material comprises 90° twins (S_1^+ and

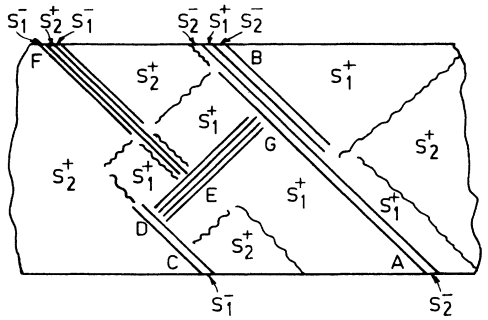

FIG. 2. Coexistence of coherent and incoherent walls in the same crystal of Y-Ba-Cu-O. Coherent walls are shown as straight lines, and incoherent walls as wavy lines. The rule for contiguity across coherent walls, arrived at in the text, is used for labeling the various twin states. For simplicity, only four suborientation states (S_1^+, S_2^+, S_1^-, S_2^-) are used in drawing this schematic diagram. *AB*, *CDEF*, and *CDGB* are the possible "channels" along which superconducting current can flow between the two flat faces of the crystal if the presence of coherent {110} twin walls indeed contributes to the enhancement of superconductivity in this material.

S_2^+), and yet a small amount of it, which sustains coherent {110}-type twin walls, is spread all over the specimen. This can happen even when the fraction of the specimen occupied by the coherent twins is far below the sensitivity of an x-ray diffraction experiment. Only a combined x-ray and optical study can reveal whether a so-called 90° twin[12] is completely free from {110}-type coherent twin walls.

You *et al.*[12] observed a discrete fine structure in the Bragg reflections, and attributed it to the occurrence of individual values of the lattice-parameter difference $(a-b)$ for each twin domain. While this possibility cannot be ruled out, especially in view of the concentration-wave model of Khachaturyan and Morris,[10] an alternative (or rather additional) explanation in terms of disorientations emerges from our analysis. We have shown that in the absence of any local strains, twin orientations can differ either by 90° or by multiples of 0.9°. If the parent phase is trapped in certain regions, twin orientations may also differ by 0.45°, or multiples thereof. (Experimental evidence[13] as well as theoretical reasons[10,32] exist for the presence of a trapped tetragonal phase.) When local strains are present (for example, due to the crisscrossing of twin walls, or due to stoichiometric variations), angles other than 0.45° (or its multiples) can occur locally. A number of reports have indeed appeared about such "misorientations."[33–35] That these can lead to the occurrence of a quasidiscrete fine structure of the Bragg reflections appears plausible. In any case, You *et al.* introduced a mosaic spread of 0.5° to obtain a good fit between the observed and calculated diffraction patterns of the twinned crystal. The way to settle this question will be to investigate the effect of a small uniaxial stress on the fine structure of the diffraction peaks. If the fine structure changes significantly and instantly under such a stress (signifying ferroelastic switching),[29] the interpretation offered here can be considered more likely. Further information can also be derived from γ-ray diffractometry, which is ideally suited for this problem. Since γ-ray diffractometry is essentially a forward-scattering experiment, small variations in d spacings have a negligible effect on the Bragg peak positions.[36] Consequently, any multiple peaks in the γ-ray rocking curve of a Bragg reflection can be attributed almost entirely to the occurrence of the disorientations discussed here.

Hewat *et al.*[35] observed a disorientation angle of 1.6° between two twins. This is nominally twice the basic disorientation angle of 0.9° deduced by us from Fig. 1, and is probably a manifestation of *multiple* disorientations anticipated in this paper.

An attempt has been made recently to obtain an empirical relationship between the spacing of twin walls observed in a particular region of the crystal and the orthorhombicity parameter $(b-a)/a$ for that region.[13,30] Such an attempt has not been very successful. Perhaps better results can be obtained if disorientations (and their local variations) are incorporated as an additional strain-relieving mechanism, over and above the contribution from oxygen-vacancy ordering. However, extensive experimental data are not available yet for a satisfactory analysis of this problem.

Although high-T_c superconductivity can occur in untwinned Y-Ba-Cu-O, the untwinned state is clearly unstable.[4,9–11,13] The fact is that real Y-Ba-Cu-O is almost always heavily twinned. Any realistic theory of its physical properties must not ignore this basic feature. Admittedly, the overall situation is quite complex, what with the presence of stoichiometric variations, oxygen ordering, impurity phases, quasi-noncrystalline regions, disorientations, and strain fields caused by crisscrossing twin walls and other factors.

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