MECHANISM OF TWIN FORMATION DURING THE TETRAGONAL TO ORTHORHOMBIC TRANSFORMATION IN $YBa_2Cu_3O_{7-x}$

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The formation of twins in the $YBa_2Cu_3O_{7-x}$ system has been studied theoretically on the basis of transmission electron microscopy observations. The shape of the tips of the twinned domains is determined from two elastic strains, one associated with the twin boundary and the other with the lattice distortion at the tip region. The tangent of the angle at the tip which was calculated from the model agrees with experimental observations sufficiently well. The growth mechanism of the twinned domains is analyzed with an energy minimization approach. The similarities of transformation characteristics in this system to those of other systems are briefly discussed.

INTRODUCTION

Many aspects of $YBa_2Cu_3O_{7-x}$ and related oxides which exhibit superconductivity above 90 K are under study. From such studies, some of the phase transformation characteristics of the $YBa_2Cu_3O_{7-x}$ phase have been well established. These are: (i) the superconducting form of the $YBa_2Cu_3O_{7-x}$ has an orthorhombic (O) structure with a space group *Pmmm* with a bulk *b* lattice parameter slightly larger than *a* and $c \cong 3a$ [1]; (ii) the orthorhombic phase is an ordered lattice of the tetragonal (T) phase in which oxygen atoms and vacancies preferentially order along [010] and [100] directions, respectively [2]; (iii) the T→O transformation is second-order in character and takes place around 1000 K during cooling or heating [2-3]; (iv) as the T→O transformation involves a shape change, strains are developed in the a-b plane ($\sim 1\%$) [4] which are accommodated by the formation of transformation twins [5-10]; and (v) the formation of twins results in the development of a non-homogeneous structure with local variations in oxygen ordering and stresses in both single and polycrystalline samples [11] and, hence, causes variations in superconducting properties [11], notably in T_c and possibly in J_c [12-13].

In conjunction with the above studies, the crystal structure of the materials has been characterized with bulk (e.g., x-ray diffraction and neutron diffraction) [1, 4, 14] techniques and the ordered oxygen domains by high spatial resolution transmission electron microscopy [15-16]. However, a detailed analysis of the microstructural features and their correlation with the phase transformation characteristics in the $YBa_2Cu_3O_{7-x}$ phase is still lacking. More notably, the formation of twins, their morphology and structure, and their influence on the T→O phase transformation are not fully understood [5,10,17-19]. The present work [20] was undertaken to address some of these questions in relation to similar transformations [21-23] observed in other systems [20-22]. In the present paper, specifically, we analyze the shape of the tip of twins in terms of their formation.

OBSERVATIONS AND THEORETICAL UNDERSTANDING OF THE MICROSTRUCTURE AT THE TIP OF TWINS

Twins form on the {110} family of planes, and two variants, (110) and ($\bar{1}10$), can form in a single grain. On numerous occasions, the configuration shown in Figure 1(a) has been recorded. This configuration corresponds to a situation where both the variants A and B have different nucleation sources. Therefore, the arrangement in Figure 1(a) suggests that variant A has grown first in the direction of the arrow (or in the equivalent opposite direction) and that variant B has ceased growing as it approached the boundary C. Therefore, the twin domain C is common to both variants. In such a condition, the growing tips of the twins in variant B relax and assume an equilibrium configuration. In general, the twin boundary spacing λ varies across a single grain [9, 11]. The variation in λ is attributed to the local variations in $\Delta a/a$, where $\Delta a = b - a$, and *b* and *a* are lattice parameters in the orthorhombic phase [11]. Some critical observations about the tip region shown in Figure 1(b) are as follows. All twin boundaries taper at the tip and converge at a point inside the twin region C. Measurements indicate that the ratio of the length of the tapered region to twin boundary spacing λ is 6.5 ± 0.5, which corresponds to a tip angle of

Mat. Res. Soc. Symp. Proc. Vol. 169. ©1990 Materials Research Society

9.0° ± 0.5°. Since it is expected that microstructural features play an important role in determining superconducting properties, elucidation of the mechanism of twin formation, as shown in the configuration in Figure 1(b), is necessary in order to understand the transformation and to control the microstructure. In this paper, we analyze the lattice structure at the tip region of the twin and derive the energy equation which describes the shape of the tip.

We analyze the shape of the curves near the tip C of the twin boundary in Figure 1(a) and obtain information about the twin boundary energy, elastic energy near the tip, and also about the nucleation and growth mechanism of twin boundaries [20]. We derive the equilibrium shape of the curve by minimizing the energy near the tip region. The rest of the analysis is explained in detail in Ref. 20.

We assume the curve in Figure 2(a) is symmetric and write one side as $y(x)$ as in Figure 2(b). The tip of curve C in Figure 2(a) is at $x = 0$. The y function is 0 at $x = 0$ and goes to y_0 as x goes to infinity. The value y_0 is $d/2$, i.e., a half of the stable twin region spacing written as $d = ab/\sqrt{2\Delta a}$ in Ref. 9. The lattice structure at the tip is shown in Figure 3.

The shape $y(x)$ is determined by the condition that the energy (attributed to the shape of the twin tip) is at a minimum with respect to the variations of $y(x)$. The energy consists of two contributions, as written below. The first, $f(y)$, is a function of y. As the width of the center II region in Figure 2(a) becomes narrower than the stable width, tetragonality increases and thus the local elastic energy increases. This energy increase is written as $f(y)$ and is defined for the range $0 \le y \le y_0$. It is at a maximum at $y = 0$ and decreases to zero at $y = y_0$. The second contribution to the energy comes from the large elastic strain along the twin boundary when the Λ-Λ′ length or the B-B′ length is short. It is reasonable to use the square gradient shape $\kappa(dy/dx)^2$ as was used by Cahn [24].

$$F[y(x)] = \int_0^\infty \left\{ f[y(x)] + \kappa \left(\frac{dy}{dx}\right)^2 \right\} dx \ . \tag{1}$$

The integral F is a function of $y(x)$. The stable form of $y(x)$ can be obtained for a minimum of F, with certain boundary requirements for $y(x)$: The minimization leads to:

$$\kappa\left[\left(\frac{dy}{dx}\right)^2 - \left(\frac{dy}{dx}\right)_0^2\right] = f[y(x)] - f[y(0)] \ . \tag{2}$$

where $f[y(0)] \equiv \varepsilon$. Then, the θ in Figure 2(b) satisfies

$$\tan\theta = \left(\frac{dy}{dx}\right)_0 = \sqrt{\frac{\varepsilon}{\kappa}} \ . \tag{3}$$

Eq. (3) can be used to derive the functional form $f[y(x)]$ based on experimental observation dy/dx. As an example, when we approximate the observed tip shape as linear, $dy/dx = a$, then $f[y(x)] = \varepsilon = constant$ for $y < y_0$. Here,

$$\varepsilon = \frac{1}{2} w_\varepsilon \mu \left(\frac{\Delta a}{a}\right)^2 \quad \text{and} \quad \kappa = 2 w_\kappa E \left(\frac{\Delta a}{a}\right)^2 \ , \tag{4}$$

where μ and E are elastic moduli; $w_\varepsilon = a_o$ (lattice parameter) and $w_\kappa = y_o$.

An intuitive interpretation of the formation of the boundary shape discussed above is that there is competition between the two terms in the Eq. (1) integrand. When we approximate the shape of the tip region in Figure 2(b) by a straight line, for example, which cuts the $y = y_0$ line at $x = \ell$, then the two terms in Eq. (1) contribute the integrals $\varepsilon\ell$ and $\kappa y_0^2/\ell$:

$$F = \varepsilon\ell + \kappa \frac{y_0^2}{\ell} \ . \tag{5}$$

The first term increases linearly with ℓ, the second term decreases inversely, and the competition results in a minimum

$$F = 2y_0\sqrt{\kappa\varepsilon} \qquad \text{at} \quad \frac{y_0}{\ell} = \sqrt{\frac{\varepsilon}{\kappa}} \ . \tag{6}$$

The first integrand in Eq. (1) is significant only in the bulk phase and vanishes near the twin boundary. The second integrand represents the lattice mismatch at the boundary (the elastic field is analogous to that of dislocation) [25]. Thus, it is estimated that:

$$w_\kappa E \left(\frac{a}{2x_1}\right)^2 = \kappa \left(\frac{y_0}{x_1}\right)^2 \quad \text{then as previously} \quad \tan\theta = \sqrt{\frac{\varepsilon}{\kappa}} = \sqrt{\frac{1}{4}\frac{w_\varepsilon}{w_\kappa}\frac{\mu}{E}} \ . \tag{7}$$

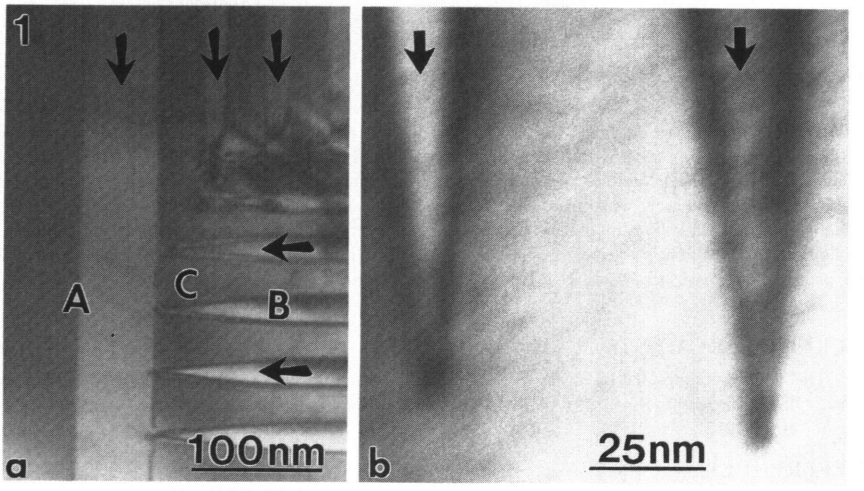
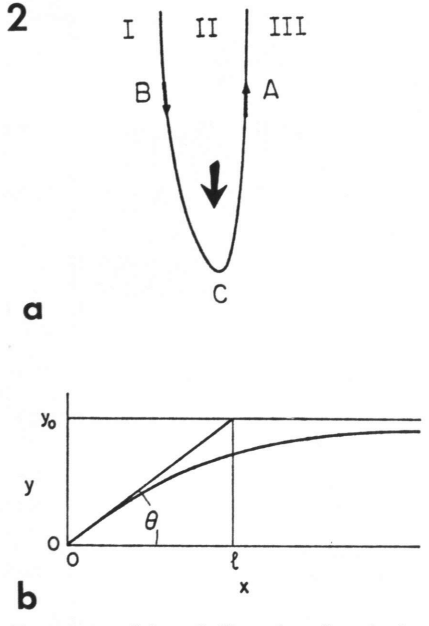


Figure 1 (a) A bright field (BF) transmission electron micrograph (TEM) shows the microstructure of $YBa_2Cu_3O_{7-x}$. Note two variants, (110) and ($1\bar{1}0$), of twins indicated by A and B, respectively. (b) BF TEM image reveals the microscopic details of the twin tips. Arrows indicate the direction of growth of twins.



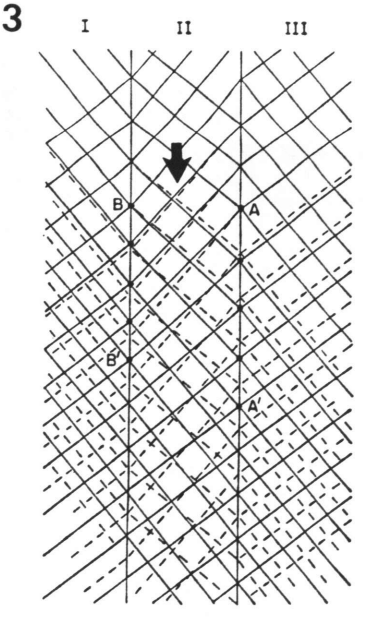


Figure 2(a) Schematic illustration of a twin tip. Arrows indicate the direction of the strain field.
Figure 2(b) The plot of y versus x.
Figure 3 Schematic illustration of lattice variation near the tip region of a twin.

Substituting the values for w_K and w_E, and setting $\mu \cong E$, and $\Delta a / a = 0.0168$, then $\tan 0 = 1/9$. This compares with the observed value of 1/13, and the agreement substantiates the approach taken here.

CONCLUDING REMARKS

Twins can also form in many other technologically important systems, such as in Fe-C (face centered cubic to body centered tetragonal) [23], $BaTiO_3$ (cubic to tetragonal) [22], ZrO_2 (tetragonal to monoclinic) [21], where the transformation is fundamentally martensitic (shear type). Twins, therefore, form to accommodate the shape change and are major defect structures within the lattice. They are important from a technological point of view, as twins are directly (or indirectly) related to the physical properties of these materials. From a scientific point of view, understanding their formation characteristics, boundary structures, and ultrastructures will help to elucidate the mechanisms of the martensitic transformation in these systems. By controlling the twin structures, it will be possible to control the development of microstructures to a high degree.

ACKNOWLEDGMENTS

This work was supported by the Defense Advanced Research Projects Agency (DARPA) and the Air Force Office of Scientific Research (AFOSR) through a contract with Boeing Electronic Aerospace Co., Grant No. HB 2121.

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