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Formation of Coherent Twins in YBa$_2$Cu$_3$O$_{7-\delta}$ Superconductors*

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Abstract

A nucleation-and-growth mechanism for the twin formation in YBa$_2$Cu$_3$O$_{7-x}$ superconductors based on the oxygen uptake rate curve and published transmission electron microscopic observations is proposed together with an oxygen-depleted twin boundary model. The difficulty of reaching stoichiometric YBa$_2$Cu$_3$O$_7$ is explained.
1. Introduction

The 1-2-3 structure of the YBa$_2$Cu$_3$O$_x$ system, $6 \leq x \leq 7$, has a unique property—the so called "oxygen sponge," i.e., when cooling from the sintering temperature, $T_s$, usually around 950°C, oxygen content increases monotonically (Fig. 1a) and when heating up, oxygen content decreases. The oxygen disorder-order induced phase transition from the semiconducting tetragonal structure to the superconducting orthorhombic structure is accompanied by the formation of coherent twins at temperature $T_p$ and oxygen content $(O_x)_p$. Below $T_p$, the structure is orthorhombic with oxygen content $O_x > (O_x)_p$ when cooled slowly in an oxygen-rich ambient from the sintering temperature, $T_s$. Above $T_p$, the structure is tetragonal with $O_x < (O_x)_p$. The rate of oxygen uptake increases sharply at $T_p$ as shown in Fig. 1b which has the characteristic "A" shape of a second order phase transition. Below 650°C it drops back to about the same rate as just before $T_p$, and with further cooling decreases gradually until by about 300°C no further oxygen uptake occurs. Both $T_p$ and $(O_x)_p$ are a function of the oxygen partial pressure, in the ambient under equilibrium conditions, e.g., for $P_{O_2} = 1$ atm (in 100% pure oxygen ambient), $T_p = 700^\circ$C, for $P_{O_2} = 0.2$ atm (in air or 20% $O_2$-80% Ar ambient), $T_p = 670^\circ$C, and for $P_{O_2} = 0.02$ atm (in vacuum or 2% $O_2$-98% Ar), $T_p = 620^\circ$C, and $(O_x)_p$ in this partial pressure range is about 6.5 - 6.6; when $P_{O_2}$ decreases both $T_p$ and $(O_x)_p$ decrease.

Based on this information and in-situ transmission electron microscope (TEM) observations, a model describing the mechanism of formation of coherent twins is presented which can help to explain some of the observed experimental results. In the slow cooling step, which is essential for good quality high $T_c$ material, the cooling rate, $dT/dt$, is small and usually constant. The changing oxygen content $dO_x/dt$ can thus also be considered as $dO_x/dT$. Although the diffusivity of oxygen in the material also changes as temperature decreases, for slow cooling rates and in not too low a temperature range it can be assumed that equilibrium is approached at least in porous or thin specimens. As seen in Fig. 1b, $dO_x/dT = dO_x/dt$ is the order parameter for this phase transition.

2. Nucleation-and-Growth Mechanism

As revealed by in-situ neutron powder diffraction, at temperature just above $T_p$, i.e., the tetragonal structure, O(4) and O(5) sites are randomly occupied by equal amounts of oxygen with an average occu-
pancy of each site about 1/4. The O(1), O(2) and O(3) sites are all fully occupied. At $T_p$, the occupancy of the (0, 1/2, 0), O(4), b-chain sites, starts increasing at a faster rate than the decrease of occupancy on the (1/2, 0, 0), O(5), sites. This suggests that the increased uptake of oxygen from the ambient goes primarily to the b-chain sites and an oxygen ordering process is in progress. The overall oxygen content increases at a rate much larger than just above $T_p$ (Fig. 1b) indicating incorporation of oxygen from the ambient into the material is facilitated by the structural transformation. It is suggested here that this sudden increase of oxygen absorption rate is associated with a nucleation process, the formation of embryos of the orthorhombic phase.

Since the oxygen-ordered orthorhombic phase contains the linear chain structure on the basal plane, these embryos are assumed to consist of clusters of short parallel b-chains, i.e., Cu(1)-O(4)-Cu(1). They should first appear at the heterogeneous sites located at grain surfaces, i.e., grain boundaries and pore surfaces, since the internal stress due to the localized distortion associated with b-chain growth in the tetragonal matrix can be at least partially relaxed (Fig. 2). The formation of b-chain embryos at grain boundaries probably first develops by consuming oxygen in the O(4)-O(5) basal plane which would soon become depleted near the grain boundaries. Further growth of the orthorhombic ordered phase then would require a supply of oxygen from the ambient through the pore-grain boundary network (Fig. 2). Clusters of b-chains with b directions orthogonal to each other are equally probable because of the symmetry of the parent tetragonal structure. Furthermore, for stress compensation nucleation of an embryo with one b-chain direction tends to induce the nucleation of another with an orthogonal b-chain direction. Below $T_p$, the oxygen-ordered configuration on O(4)-O(5) basal plane has a lower free energy than that of the oxygen-disordered configuration.\(^6\) Once initiated at a grain surface the extension of b-chains should be rapid. An elongated embryo with an oxygen-depleted zone around it is expected.

In powder-sintered materials, depending on the pressing process and the sizes and kinds of powders, there are many voids and open channels among grains. For high porosity material, the total internal pore surface area may be larger than the total area of the grain boundaries. This free surface area may play a significant role in determining the physical properties of such a material. Grain boundaries also permit faster diffusion than that possible through a grain because of the looser structure. Significant diffusion of oxygen within a grain along the c-axis direction is unlikely to happen at temperatures below $T_p$. Oxygen from
the environment and from pore surfaces is likely to be distributed to the grains deep inside the sample primarily through this pore-grain boundary network. To diffuse into the grain, oxygen probably has to find a basal plane edge. Hence, grain boundary diffusion would often be required for supplying oxygen from the ambient to parts of the grains.

As b-chain clusters at grain boundaries grow, embryos probably also develop homogeneously or heterogeneously inside the grain by local oxygen ordering. They are probably formed somewhat later than those at grain surfaces, since the internal stress developed by the b-chain ordering can not be partially relaxed as at grain surfaces and the incorporation of the limited available oxygen is competitive among embryos in the central region of the grain. The available oxygen would be quickly consumed by the formation of such nuclei. Oxygen-depleted zones would be formed around these nuclei setting up a concentration gradient between center and surface of the grains, causing more oxygen to diffuse into the grain. These b-chain clusters have locally the orthorhombic lattice structure with the lattice constants, a and b on the basal plane, smaller and greater respectively than a, of the parent tetragonal lattice. The tetragonal matrix surrounding the elongated nucleus experiences contraction at the ends of the b-chains and expansion at the sides parallel to the b-chains. When two clusters with orthogonal b-chain directions approach each other, the oxygen depleted zones and the strain fields overlap causing a reduction of the stress along one <110> direction and enhancement along the orthogonal <110> direction; impingement of the two domains along the latter <110> direction eventually results in formation of a coherent twin boundary. The equilibrium width of the twin boundary zone is assumed in this model to be determined by a balance between the coulomb repulsion force of oxygen ions at opposite sides of the boundary and the chemical potential favoring extension of the b-chains. A "twin nucleus" within the grain with a narrow oxygen-depleted zone remaining at the twin boundary is expected (Fig. 2, left lower corner).

Either <110> direction on the basal plane can lie parallel to a twin boundary, i.e., the twin nuclei have two equally probable twin boundary orientations perpendicular to one another. These nuclei have been observed by in-situ TEM as randomly distributed and inter-penetrated orthogonal sets, a tweed-like structure (Fig. 3) (7,8,9). Other combinations of b-chain nuclei, quartet, etc., are also possible, but with smaller probability than doublet. When two b-chain clusters with the same b-chain direction approach each other, coalescence takes place resulting in a larger b-chain cluster.
Since oxygen content \( (O_x) \) is about 6.5 at \( T_p \), only half of the available b-chain sites of the orthorhombic phase in the grain are occupied by oxygen, i.e., the total volume of the orthorhombic twin nuclei is only about half the total volume of the grain. This leaves a relatively open structure for oxygen diffusion. Further transformation requires oxygen diffusion into the grain, the driving force being the tendency for further extension of b-chains, resulting in the observed sudden rise in rate of oxygen uptake at \( T_p \) as shown in Fig. 1b.

The b-chain clusters nucleated at grain surfaces grow most rapidly by incorporating oxygen readily supplied from the ambient. When the transformation is complete at grain surfaces, the diffusion of oxygen into the grain becomes more restricted, i.e., oxygen-depleted twin boundary zones. This can explain the sharp decrease of the rate of oxygen uptake below \( T_p \) (see Fig. 1b). The growth front of the twinned orthorhombic structure nucleated at grain surfaces gradually extends deeper into the grain by adding new b-chains at the growth front with oxygen being supplied from ambient via the pore-grain boundary twin boundary network and by incorporating twin nuclei that have already formed inside the grain.

During the last stage of twin formation, coarsening takes place eliminating some of the twin boundaries, and thus decreasing total free energy. Small domains included within larger domains tend to disappear by localized oxygen diffusion within the boundary. As long as the temperature is still high enough to permit oxygen diffusion, this climbing process continues to coarsen the twin domains until the widths of the twins are several hundred Å. Rapid cooling severely inhibits this coarsening process; the resulting structure contains more numerous fine twins. When cooling rate is very rapid, e.g., quenching from temperature above \( T_p \), the tetragonal structure is partially preserved with oxygen content less than 6.5. There is insufficient time for oxygen absorption and thus insufficient oxygen to complete the growth of the b-chain orthorhombic structure. Quenching from temperature between \(-350^\circ C\) and \( T_p \) yields intermediate \( T_c \) with oxygen contents between 6.8 and 6.6. Sintered polycrystalline \( YBa_2Cu_3O_7-\delta \) is usually given a low temperature annealing step to enhance its superconducting properties. The annealing temperature is typically chosen below \( T_p \) but above \( 400^\circ C \) in an oxygen-rich environment to permit further coarsening, stress relaxation and oxygen uptake.
3. Model and Simulation of Oxygen-depleted Twin Boundaries

A model of twin boundaries in orthorhombic YBa$_2$Cu$_3$O$_x$ superconductors with various layers (j) of oxygen vacancies at twin boundaries\(^{10}\) (Fig. 4) avoids the high energy state of neighboring oxygens and preserves the coherency at twin boundaries. The oxygen-depleted twin boundary width can be expressed as $W_{ab}(j) = 2j ab/(a^2 + b^2)^{1/2}$. Taking the estimated average twin width\(^{11}\) $W_t = ab/(b - a)$ and assuming a perfect stoichiometric YBa$_2$Cu$_3$O$_7$ within the twin domains and YBa$_2$Cu$_3$O$_6$ at twin boundaries, then the average oxygen content, $x$, in YBa$_2$Cu$_3$O$_x$, which is experimentally measured, would be

$$x(j) = 6 + \frac{W_t - W_{ab}(j)}{W_t} = 7 - \frac{W_{ab}(j)}{W_t} = 7 - \frac{2j (b - a)}{\sqrt{a^2 + b^2}}.$$  

Applying $a = 3.822$ \(\text{Å}\), $b = 3.891$ \(\text{Å}\) from the work of Cava et al.,\(^{12}\) the calculated values of $x(j)$ match the experimentally measured oxygen content very well (Table 1) suggesting that in their samples, near perfect stoichiometric YBa$_2$Cu$_3$O$_7$ may form within the twin domains but various layers of oxygen vacancies exist at twin boundaries. The oxygen deficiency study\(^{16}\) seems to indicate that under normal pressure processing, i.e., 1 atm O$_2$ or air, the ultimate oxygen stoichiometry is about 6.93 or equivalent to the case $j = 3$. However, it should be noted that there are always some vacancies dispersing within the twin domains at random or in an ordered structure.\(^{23}\) For oxygen concentration smaller than 6.93, most of the excess oxygen vacancies would disperse in the twin domains. Thus the number of oxygen vacant layers at twin boundaries may be smaller than the calculated $j$ which assumes all vacancies are condensed at twin boundaries.

<table>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<td>$x_{exp}$</td>
<td>6.975(^{12})</td>
<td>6.94</td>
<td>6.92 ± 0.01(^{15})</td>
<td>(6.9)</td>
<td>6.87</td>
<td>6.85</td>
<td>6.82</td>
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<td>14</td>
<td>13,15,16</td>
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<td>18</td>
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<td>22</td>
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<tr>
<td>$T_\lambda(°K)$</td>
<td>90(^{12})</td>
<td>89</td>
<td>95(^{16})</td>
<td>87</td>
<td>90</td>
<td>91(^{19})</td>
<td>91</td>
<td>NA</td>
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Simulated high resolution electron microscope (HREM) images of twin boundaries with various j values, different defocussing conditions and different sample thicknesses are shown in Fig. 5a-c respectively. The simulated images of the twin boundaries without oxygen vacancies [(Fig. 5a) top] show no contrast across the twin boundaries regardless of the objective lens defocus and sample thickness. However, when various layers of oxygen at twin boundaries are taken away, contrast across twin boundaries appears. The width of the contrast band increases in proportion to j as shown in Fig. 5a. Contrast at the twin boundaries varies markedly with defocussing conditions as shown in Fig. 5b. Note that the apparent boundary widths also should vary slightly. Contrast at twin boundaries due to sample thickness variation, as shown in Fig. 5c, should also be very dramatic. It can vary from almost no contrast to strong contrast. Various band widths and contrast at twin boundaries in real HREM images are commonly observed agreeing with the model proposed here (Fig. 6). Also, twin boundaries exposed to a focussed beam for a short time, e.g., 1 minute, show a decrease in contrast. Oxygen atoms in twin domains close to the twin boundaries may gain energy through the electron bombardment and diffuse into the twin boundary vacant sites. Thus, the contrast at twin boundaries might be expected to smear out as illustrated by the simulated images in Fig. 5d.

A study by Chen et al. shows that ordered vacancies within the body of the twin domains accounts for only 3% of the total volume in a stoichiometric \( \text{YBa}_2\text{Cu}_3\text{O}_6.72 \) sample. This discrepancy can be explained by the oxygen-depleted twin boundary model assuming \( j = 3 \) providing further evidence, along with TEM images such as the one shown in Fig. 6 which shows contrast similar in width to the simulated images for \( j = 3 \).

The equilibrium width of the oxygen-depleted zone at a twin boundary should be determined by a balance of the Coulomb repulsion force and the chemical potential, the resulting optimized configuration should have at least one layer of oxygen vacancies condensed at the twin boundary (\( j = 1 \) case). For \( j \geq 2 \), increasingly diffuse oxygen-depleted layers would be expected, i.e., oxygen-vacancy segregation at these layers would probably be incomplete. For simplicity, however, this diffuse atmosphere of oxygen vacancies has been described as a number of layers of oxygen vacancies, j.
4. Conclusion

In conclusion, we have proposed a qualitative description for the formation of the twinned structure in YBa$_2$Cu$_3$O$_{7.5}$. This model assumes oxygen-depleted twin boundary zones which serve as the primary oxygen diffusion paths from grain surfaces toward the interior of the grains and thus control the growth rate of the twins and the orthorhombic structure in the grain centers. These twin boundaries are formed during the growth of the b-chain embryos which are nucleated heterogeneously at grain surfaces. The width of the oxygen-depleted twin boundary zones should be determined by a balance of the chemical potential energy at the ends of the b-chains at the edges of the twin domains and the coulomb repulsion energy between oxygen ions on opposite sides of the twin boundaries. The rapid increase of oxygen uptake at T$_p$ is attributed to the open structure of the grain during early stages of the tetragonal to orthorhombic transformation caused by the formation of embryos which quickly consume a large fraction of the oxygen in the grain at T$_p$. Completion of the transformation by growth of twinned domains occurs most rapidly at the grain surfaces by absorbing oxygen from the ambient and more slowly in grain interiors. Coarsening of the twin domains then occurs by elimination of small domains included within larger domains by localized transfer of oxygen atoms across the twin boundaries. Annealing is essential for this coarsening process, for residual stress relaxation and for the reduction of residual oxygen vacancies within the twin domains. The observed oxygen deficiency remaining after annealing in oxygen can be explained if it is assumed that the equilibrium structure of coherent twin boundaries contains one or more layers of oxygen vacancies as proposed in this model.

Acknowledgments

The authors would like to thank Dr. K. Hiraga for sending the high resolution transmission electron micrograph of a twin boundary.

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REFERENCES


FIGURE CAPTIONS

Fig. 1. (a) Total oxygen content, \( x \), in \( \text{YBa}_2\text{Cu}_3\text{O}_x \) increases monotonically when cooled slowly from the sintering temperature in 1 atm \( \text{O}_2 \) ambient. Note there is a kink at the structure transition temperature \( T_p \). Data deduced from Ref. 1. Scale of \( O_x \) is for (a) only. (b) The differentiation of the curve in (a) reveals a peak at \( T_p \) forming the characteristic "\( \lambda \)" curve of a second order phase transformation. Oxygen ordering on the basal plane is in progress starting at \( T_p \).

Fig. 2. Proposed nucleation of ordered oxygen clusters starts at grain surfaces, i.e., grain boundaries or pore surfaces, where the stress due to structural transformation can be partially relaxed. When two neighboring clusters with orthogonal b-chain directions meet, coherent twin boundaries with an oxygen-depleted zone are formed. Twin nuclei (insert at lower left corner) are formed later in the interior of the grain. They consume most of the available oxygen content in the grain at \( T_p \) forming a heavily interpenetrated tweed structure (Fig. 3a). An oxygen concentration gradient between the grain surface and the grain interior is set up. Further growth of the twin laths in the grain is limited by diffusion of oxygen into the grain center. The twin nuclei at the grain surfaces can grow faster with the oxygen supplied directly from ambient via the pore-grain boundary network and the oxygen-depleted twin boundaries. During the growth, twin laths in the grain interior are incorporated at the growth front.

Fig. 3. (a) Interpenetrated twin laths leave the untransformed matrix oxygen-depleted inside the grain. (b) A fully grown tweed structure would form a two-dimensional mutually-modulated regular pattern, possibly observed in some in-situ transmission electron microscopy observations during cooling from high temperature. The electron diffraction pattern of this structure may reveal an effective unit cell with \( \sqrt{2}a \times \sqrt{2}a \times -3a \). However, the structure contains both twin boundaries and high energy 90°-rotation boundaries, therefore it would be a metastable intermediate product.

Fig. 4. Oxygen vacant twin boundary models for (a) 1 vacant layer \( (j=1) \), (b) 3 vacant layers \( (j=2) \), and (c) 5 vacant layers \( (j=3) \). Note: The angle at twin boundaries and the length difference between the lattice constants (a) and (b) are exaggerated. For simplicity, only oxygen atoms (black dots) are shown.
Fig. 5. Simulated HREM [001] images of twin boundaries. Simulation parameters are chosen to correspond to the operating conditions in the JEOL 4000 FX electron microscope. Sample thickness is 100Å and objective lens defocus is –800Å unless specified otherwise. (a) Changes with respect to $j$ from $j = 0$ (no oxygen depleted layer, top) to $j = 3$ (bottom). (b) Variation with respect to objective lens defocus; –400Å (top) to –1600Å (bottom) in increments of –400Å, $j = 3$. (c) Variation with respect to sample thickness; 50Å (top) to 200Å (bottom) in increments of 50Å, $j = 3$. (d) Total oxygen atom number fixed, but abrupt concentration changes at twin boundaries are gradually relaxed ($j = 3$).

Fig. 6. High resolution electron micrograph of a twin boundary in YBa$_2$Cu$_3$O$_x$ material reveals significant contrast across the twin boundary. (Photo courtesy of Dr. K. Hiraga.)
Fig. 1
(a) Heavily inter-penetrated twin-nuclei laths

(b) Regular tweed structure

Fig. 3