# Ordered-defect structure in epitaxial $YBa_2Cu_3O_{7-x}$ thin films

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An ordered defect structure in superconducting Y-Ba-Cu-O thin films has been characterized by both x-ray diffraction and transmission electron microscopy. The defect structure, which is observed growing epitaxially within the grains of normal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure, has the diffraction characteristics of a distinct phase whose volume fraction can be correlated with changes in film composition. The diffraction characteristics are consistent with an orthorhombic unit cell  $(a \cong b = 3.86 \text{ Å}, c = 27.19 \text{ Å})$  with space group *Ammm*. These are the characteristics to be expected from a structure in which extra copper-oxygen layers create fault planes, which are inserted at every unit cell in the parent YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure. The composition expected for the pure phase is Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>8</sub>O<sub>20-x</sub>. Preliminary transport measurements on films containing this extra phase are characterized by lower normal-state resistances and a lower Hall constant.

# **I. INTRODUCTION**

While the pseudoternary phase diagram for the high- $T_c$  superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> has been generally established, <sup>1,2</sup> finer details of the phase equilibria near this composition are still of great interest. Several researchers have recently reported observations of defect structures in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> phase and have attempted to correlate these with the presence of various superconducting transport properties.<sup>3-7</sup>

Transmission electron microscopy (TEM) studies by several researchers<sup>4,8,9</sup> have reported *c*-axis defects in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> phase which locally expand the *c*-axis spacing by 16%. Zandbergen,<sup>8</sup> using image calculations of high-resolution TEM images, modeled this expansion as the insertion of an extra CuO plane between barium layers in the normal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure. Narayan *et al.*,<sup>3</sup> as well as others,<sup>10,11</sup> reported an apparently new phase with lattice fringe spacing uniformly expanded by the same amount (*c* = 13.55 Å). This phase appeared in small volume fractions growing epitaxially on the parent YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> phase.<sup>3,11</sup>

Narayan *et al.*, <sup>3</sup> however, have not, to our knowledge, reported high-resolution images or a diffraction analysis of their new phase. All of the above observations have been carried out on bulk or "powdered" specimens. The appearance of structural defects in these studies has been attributed by some to a decomposition of the sample surface, <sup>8,12,13</sup> and by others to an artifact of the TEM sample preparation process (specifically ion milling). <sup>14-16</sup>

In this paper we present observations of an ordered defect structure in thin-film samples of  $YBa_2Cu_3O_{7-x}$ . An important aspect of our results is the correlation between TEM and x-ray diffraction patterns, clearly demonstrating the existence of such a structure independent of the TEM specimen preparation method. Further, we show that this structure can exist in large volume fractions of the films, its appearance correlated to variations in film composition instead of annealing or atmospheric condition. We show evidence that at high concentrations the ordered defects can form a distinct crystallographic phase with a unit-cell parameter of 27.2 Å. From preliminary transport measurements we associate the presence of this phase with lower normal-state resistivities and a lower Hall constant. Finally, our results show this phase to be consistent with an extension of the Zandbergen model, specifically, an ordered array of extra Cu-O planes.

### **II. EXPERIMENTAL METHODS**

The films reported on here were made by reactive magnetron sputtering and by electron-beam evaporation onto (100) SrTiO<sub>3</sub> substrates. Details of each of these techniques have been reported previously.<sup>17,18</sup> A distinctive characteristic of each of these deposition processes is the use of separate metal sources pointed at sample holders that contain long arrays of samples. In this manner a continuous set of film compositions is obtained in one run. It has therefore been possible to make good correlations of both sample properties and microstructures with composition. When expressed as a ratio of metal atoms, for example, the variations in copper concentration within a 6 mm by 6 mm sample were typically within 1 at.% absolute, while copper concentrations across two rows of 10 samples each were as much as 8%. A typical sample employed in this study had nominal metal ratios of Y<sub>18</sub>Ba<sub>29</sub>Cu<sub>53</sub>. Thicknesses were either 1800 or 4000 Å.

All of the samples as removed from deposition chambers were found to be highly disordered by x-ray diffraction. The samples then underwent similar annealing procedures, resulting in crystallization and oxidation of the Y-Ba-Cu-O superconducting phase(s). Given the similarities of the post-annealing process, we have not Procedures for characterizing epitaxial films in a fourcircle x-ray diffractometer have also been described previously.<sup>17</sup> The films are generally polycrystalline, though restricted to a limited number of orientations on the SrTiO<sub>3</sub> substrate. The c axis of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure is usually found in a mixture of 90° orientations, either normal to the substrate or parallel to one of the SrTiO<sub>3</sub> crystal axes in the plane of the film. In the symmetrical or Bragg-Brentano geometry only those peaks originating from  $a^*$  or  $c^*$  axes are detected. In order to detect peaks with mixed Miller indices it is necessary to rotate the sample about one of the axes in the film plane.

We often distinguish between films with either *a*- or *c*axis orientation, referring to that crystalline axis which appears predominantly in the normal direction. We have not yet made quantitative distinctions between *a*- or *b*-axis orientations;<sup>17</sup> in this paper "*a* axis" refers to either orientation. It is known that the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure is heavily twinned,<sup>4,12</sup> causing a large amount of coincidence between *a* and *b* axes.

Planar sections of both *a*- and *c*-axis oriented films were thinned for TEM studies by grinding, dimpling, and ion milling from the substrate side until perforation. The surface of the film was also ion milled slightly so as to examine the interior of the film. Ion milling was carried out in a liquid-N<sub>2</sub> cold stage and with low ion beam conditions (5 kV, 0.3 mA gun current) so as to minimize potential heating and ion bombardment damage to the specimen. TEM analysis was carried out on a Philips 400ST equipped with an EDAX 9100 energy-dispersive spectrometer. High-resolution images were obtained on a Philips 430ST.

# III. RESULTS A. Structural properties

Figure 1 is an x-ray diffraction pattern of a c-axis oriented sputtered film (sample A). Typical substrate and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> peaks are seen. Extra peaks, marked by asterisks are observed, all of which can be indexed according to a c-axis spacing of 13.6 Å (001) or 27.2 Å (001, l=2n). The larger unit cell is consistent with a superlattice structure seven times the length of the fundamental perovskite unit cell. The intensity of these extra peaks indicates a volume fraction of the new structure comparable to the total oriented volume of the normal  $YBa_2Cu_3O_{7-x}$ phase. Variations in the x-ray intensities and widths of these peaks have been observed to correlate to variations in sample composition, the intensities generally increasing in samples prepared with simultaneous excesses of yttrium and copper. Samples reported on here contained typically three excess atomic percent of each element.

A number of films made by both deposition techniques



FIG. 1. X-ray diffraction pattern of a "mixed-phase" sample (sample A). The strongest peaks are due to  $SrTiO_3$  (001) and (002), the others are due to 00*l* peaks of either the YBa<sub>2</sub>Cu<sub>3</sub>-O<sub>7-x</sub> structure or the new phase. Peaks from the new phase are marked by asterisks and correspond to multiples of a 13.6-Å spacing.

and with predominantly either *a*- or *c*-axis orientation were examined in TEM. The data shown here originated from one sputtered film (sample A) and one evaporated film (sample B). Each film was Cu and Y rich relative to the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> composition. *a*-axis grains in each film showed characteristic defect regions such as are typified in Fig. 2. This TEM micrograph shows *c*-axis fringes in two perpendicular YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> grains. The region of de-



FIG. 2. A-axis grains of  $YBa_2Cu_3O_{7-x}$  (sample B) at 90° to each other. Defect regions several hundred angstroms in width are observed along the (001) planes within the grains.

fects runs along the length of each grain, the individual faults lying parallel to (001) planes in  $YBa_2Cu_3O_{7-x}$ . The defect regions shown here are representative of those observed in many other samples as well as in at least one bulk specimen. They tend to occur within grains rather than at grain boundaries, parallel to (001) planes, and energy dispersive microanalysis indicates that they are somewhat Cu rich. Defect regions are generally unstable under the electron beam. Degradation or amorphization of the lattice tends to occur more quickly during observation of these regions than it does in the normal  $YBa_2Cu_3O_{7-x}$  material.

In addition to the defects shown in Fig. 2, a significant number of small, randomly oriented second-phase particles were observed in the TEM. Microanalysis of these particles revealed them to be Y rich, with a composition approximating that of the  $Y_2BaCuO_5$  phase.

A high-resolution image of a defect region from the same grain of sample B is shown in Fig. 3. The left side of this micrograph shows normal  $YBa_2Cu_3O_{7-x}$  material with characteristic 11.7-Å c-axis fringe spacing. The right side shows defects, appearing as local expansions of the unit cell. The expansion is approximately 16% of the c-lattice parameter. The defects occur at a density of one per unit cell. If one refers to the high-resolution image calculations reported by others 5,8,9,19,20 then one can assign the specific position of the local lattice expansion to an area between adjacent barium-oxygen layers. The defects in Fig. 3 are therefore similar to those observed by Zandbergen, Gronsky, and Thomas,<sup>8</sup> except that they are occurring at a much higher density. In observations over many different grains and in several different samples we have observed considerable variations in ordering: from structures with isolated defects, to structures with defects in every other or every third unit cell, to the densely



FIG. 3. A high-resolution image of the grain in Fig. 2 shows the normal  $YBa_2Cu_3O_{7-x}$  structure on the left and the defect region on the right. The strong white fringes at 11.7 Å of the normal structure are the Cu-O planes between the Ba-O planes. These regions are expanded in the defect region indicating insertion of extra planes. Occasional "good" interfaces (arrows) also are seen in this region.

packed and well-ordered structures shown in Fig. 3.

Microdiffraction patterns of similar well-ordered defect regions occurring within [100]- and [110]-oriented YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> grains are shown in Fig. 4. The first two patterns are from sample A, the third from sample B. Because defects occur epitaxially in narrow bands within grains of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> material, controlled tilting experiments on particular regions have not yet been possible. Each of the patterns shown in Fig. 4, however, shows marked deviations from the normal superlattice-sublattice symmetries observed in neighboring  $YBa_2Cu_3O_{7-x}$  material (cf. Refs. 13, 15, and 19). For example, normal  $YBa_2Cu_3O_{7-x}$ , [100] diffraction patterns are characterized by a square perovskite sublattice and a superlattice, occurring in the  $c^*$  rows, indicative of the tripled (11.7 Å) unit cell. The new phase, as represented in Fig. 4, is characterized by either a smearing or a complete absence of intensity in the vicinity of the first  $c^*$  subcell reflection [what would be (003) in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>]. The second  $c^*$ subcell reflection [formerly (006)] now appears as the seventh spot in the row. A similar sevenfold superlattice periodicity can be observed between sublattice spots labeled 017 and 01(-7) in Fig. 4(a). The *d* spacings between spots in  $c^*$  rows correspond to multiples of 13.6 Å, in agreement with the extra peaks observed in x-ray diffraction.

Systematic extinctions in the diffraction patterns of this new phase can also be observed by comparing the patterns obtained within defect regions to those in neighboring YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> material. When moving the beam between neighboring regions it is observed that the spacings between reciprocal-lattice rows remain the same, while the arrangement of spots within a row varies. Figures 4(a) and 4(c), for example, show reflections along the  $c^*$ axis which are offset by  $\frac{1}{2}$  in alternating rows. This suggests a true periodicity for the material of 27.2 instead of 13.6 Å. A consistent interpretation of the three patterns can be obtained by assigning them to the zone axes [100], [010], and [110], respectively. All special conditions for the reflections can then be described by the single formula k+1=2n. These conditions are characteristic of sidecentered unit cells. The diffraction spots in Fig. 4 have been indexed accordingly.

Summarizing our interpretations of Fig. 4, we find an orthorhombic unit cell with a single formula for special conditions k+1=2n. This symmetry is consistent with each of four space groups, A222, Amm2, Cmm2, and Ammm.

Using the systematic extinctions observed in Fig. 4 as a guide, we have been able to identify further x-ray peaks from the phase by tilting a sputtered sample (A', similar to that shown in Fig. 1) away from its symmetrical axis on the four-circle x-ray diffractometer. A listing of observed peak positions and approximate intensities is given in Table I for identification purposes. The peaks listed here were then used to refine the dimensions of the unit cell, giving  $a \cong b = 3.86 \pm 0.02$  Å and  $c = 27.19 \pm 0.07$  Å. The peaks observed in samples A and A' (Fig. 1) are relatively broad and asymmetrical, perhaps because the faults in defect regions are not completely ordered. This resulted in relatively large error bars from the cell refinement. Sub-



hkl	d <sub>expt</sub> (Å)	Intensity
002	13.22	s
004	6.66	5
006	4.52	w
008	3.41	w
104	3.35	vs
106	2.90	5
0010	2.74	S
108	2.56	vs
0012	2.28	vs
0016	1.69	<i>s</i>
1113	1.66	w
1115	1.52	vs

sequently, we have synthesized samples with significantly narrower peak widths, yielding the same *c*-axis lattice parameter to an accuracy of 0.03 Å. As another consequence of the observed peak broadening, and the fact that oriented grains in our thin films appear randomly aligned with respect to a 90° rotation about the *c* axis, we have been unable as yet to make accurate distinctions between *a*- and *b*-axis lattice parameters.

### **B.** Transport properties

Preliminary measurements of transport properties in these films have been obtained. A more in-depth study of superconducting and normal-state properties is still in progress. All of the films reported on here are 90-K superconductors, the superconductivity being most likely due to the presence of significant fractions of  $YBa_2Cu_3O_{7-x}$ . No resistive anomalies between 90 and 300 K have been observed. Films with significant volume fractions of the new phase are primarily distinguished by lower normal-state resistivities. The resistivity observed in one mixed-phase sample is  $100 \ \mu \Omega$  cm at 100 K. While this resistivity is not particularly low (subsequent films of  $YBa_2Cu_3O_7 - x$  at different thicknesses have been observed in the range of 80  $\mu\Omega$  cm) when compared to samples prepared at the 1:2:3 composition in the same runs  $(\rho = 300 \ \mu \Omega \text{ cm} \text{ at } 100 \text{ K})$ , resistivities in mixed-phase samples are lower. Additionally, one mixed-phase sample was observed to have an anomalously low Hall coefficient  $+7.4 \times 10^{-6}$  $\mu \Omega \text{ cm/G}$  compared to  $+2.0 \times 10^{-5}$  $\mu \Omega \text{ cm/G}$  for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. The lower Hall coefficient suggests the existence of higher carrier concentrations in mixed-phase samples (as high as  $10^{22}$  cm<sup>-3</sup>). Measurements are underway on recently prepared samples which contain higher volume fractions of the new phase.



FIG. 4. Microdiffraction patterns from defect regions appearing within (a and b) [100] and (c) [110] YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> grains. (a) and (b) are from two different grains of sample A, (c) is from sample B. The symmetry shown in each pattern is distinct and yet related by epitaxy to that of the neighboring YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> material. A consistent indexing of the spots can be obtained by assigning the zone axis of the patterns to [100], [010], and [110], respectively.

# **IV. DISCUSSION**

#### A. Structural model

Our real-space images and diffraction patterns demonstrate the existence of an ordered array of *c*-axis stacking faults. A structural model for a new phase based on these stacking faults will now be considered.

Considering first the diffraction data alone, one can try to fit the new unit-cell dimensions and symmetries to models in which either extra Y planes, extra Ba-O planes, or extra Cu-O planes have been inserted into the normal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> structure. In each case one might look for the presence of two counterbalancing fault planes per unit cell. With the addition of two extra planes then, of average thickness  $\frac{1}{6}C_{123}$ , one would expect a resultant *c*-axis dimension of

 $C_{\text{new}} = C_{123} \times 2 \times 1 \frac{1}{6}$ ,

yielding C = 27.255 Å. This agrees within experimental error to the c parameter refined from Table I. Differences from this value may be attributable to relaxed thicknesses in the two stacking faults.

Chemical precedents for the structure of stacking faults can be derived from model compounds such as  $La_2CuO_4$ (Ref. 21) or SrCuO<sub>2</sub>.<sup>22,23</sup> In the former compound, extra Ba or La atoms are accommodated in a perovskite structure by formation of a body-centered unit cell. SrCuO<sub>2</sub> appears to be more relevant to the present case, however, since it demonstrates that extra planes of copper atoms can lead to the formation of a side-centered unit cell, in agreement with our diffraction results.

Zandbergen et al.<sup>8</sup> proposed a model for isolated c-axis defects in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> based upon high-resolution TEM images. They showed that their images, similar to ours, can be modeled with the insertion of an extra Cu-O plane between adjacent Ba-O layers. Besides the appropriate expansion of the lattice by 16%, this also results in a lattice shift across the defect by  $\frac{1}{2}$  [010]. The insertion of one such plane in every unit cell would produce a side-centered 27.2-Å phase, consistent with our diffraction results. This model also accounts for the excess copper concentration observed in our defect regions. (Extra yttrium concentrations, present in our thin-film samples, have been observed as incoherent precipitates, probably the Y<sub>2</sub>BaCuO<sub>5</sub> phase.)

The space group for this new phase, based upon the Zandbergen defect model, would be Ammm. A schematic of the structure is shown in Fig. 5. The composition would be  $Y_2Ba_4Cu_8O_{20-x}$ . Since neither our real-space images nor our diffraction data are very sensitive toward oxygen concentrations, we are unable to comment at this time on the existence or nonexistence of Cu-O chains in either of the copper-oxygen layers. Some evidence for plane or chain structure might arise in the future from measured differences between a and b lattice parameters. We note that, in a study of the compound SrCuO<sub>2</sub> (Ref. 23) where two CuO planes were found to exist between SrO layers, a chain structure in the layers was reported. An interpretation of transport properties however, as presented below,



FIG. 5. Schematic structure of the new phase  $Y_2Ba_4Cu_8$ -O<sub>20-x</sub> with space group *Ammm*. For reasons of clarity, oxygen atoms have been omitted.

may argue against the existence of chains.

Based on the observation that Cu-O stacking faults exist as isolated entities as well as in ordered arrays, it is reasonable to conclude that a range of solid solutions exists between the limits of  $YBa_2Cu_3O_{7-x}$  and  $Y_2Ba_4-Cu_8O_{20-x}$ , at least in metastable equilibrium. While such a metastable equilibrium might be restricted to materials in thin-film form, it would be interesting to look for greater quantities of this phase in bulk materials.

# **B.** Transport properties

The question of oxygen stoichiometry and placement in  $Y_2Ba_4Cu_8O_{20-x}$ , which cannot yet be determined from our data, will certainly be important to the study of electronic transport properties. It might be expected that, if the ratio of extra oxygen atoms to extra copper atoms were greater than one to one, then the resulting material would be doped, i.e., it would have a greater concentration of holes. This might explain the observation of lower Hall constants in materials containing the second phase. Adding extra oxygens in this ratio to extra coppers, however, argues against the existence of Cu-O chains in the additional layers. Certainly we expect the chemical environment of the coppers to be different in this new material, where two  $CuO_x$  layers now exist side by side. The differences between  $Y_2Ba_4Cu_8O_{20-x}$  and  $YBa_2Cu_3O_{7-x}$ may allow for significant comparisons of transport properties in the  $CuO_x$  layers of different types.

# **V. CONCLUSIONS**

Based on images as well as diffraction patterns we conclude that ordered arrays of stacking faults can form a distinct phase in the Y-Ba-Cu-O system near the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> composition. In many regions the ordering of the faults is nearly complete, giving unique electron diffraction symmetries. X-ray diffraction indicates that the new phase exists in volume fractions comparable to that of its parent YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. Both composition and diffraction information support a model based on extra Cu-O planes, identified as Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>8</sub>O<sub>20-x</sub>. The existence of the new phase may be associated with unusual transport properties in the films such as low normal-state resistivities and higher carrier concentrations.

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FIG. 2. A-axis grains of  $YBa_2Cu_3O_{7-x}$  (sample B) at 90° to each other. Defect regions several hundred angstroms in width are observed along the (001) planes within the grains.



FIG. 3. A high-resolution image of the grain in Fig. 2 shows the normal  $YBa_2Cu_3O_{7-x}$  structure on the left and the defect region on the right. The strong white fringes at 11.7 Å of the normal structure are the Cu–O planes between the Ba–O planes. These regions are expanded in the defect region indicating insertion of extra planes. Occasional "good" interfaces (arrows) also are seen in this region.



FIG. 4. Microdiffraction patterns from defect regions appearing within (a and b) [100] and (c) [110]  $YBa_2Cu_3O_{7-x}$  grains. (a) and (b) are from two different grains of sample A, (c) is from sample B. The symmetry shown in each pattern is distinct and yet related by epitaxy to that of the neighboring  $YBa_2Cu_3O_{7-x}$  material. A consistent indexing of the spots can be obtained by assigning the zone axis of the patterns to [100], [010], and [110], respectively.



FIG. 5. Schematic structure of the new phase  $Y_2Ba_4Cu_8$ - $O_{20-x}$  with space group *Ammm*. For reasons of clarity, oxygen atoms have been omitted.