RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 10 1 OCTOBER 1987

Domainlike defects observed in the high-temperature superconductor Y-Ba-Cu-O

C. S. Pande
Naval Research Laboratory, Washington D.C. 20550

A. K. Singh
Crystal Growth Associates, Lanham, Maryland 20706

L. Toth,* D. U. Gubser,* and S. Wolf
Naval Research Laboratory, Washington D.C. 20550

(Received 22 June 1987; revised manuscript received 27 July 1987)

Transmission-electron microscopy of the high-superconductivity-transition-temperature oxide $Y_1Ba_2Cu_3O_x$ reveals the presence of planar defects along [110] direction more-or-less uniformly spaced (spacing $\sim$300 Å) and dispersed throughout the specimens. These defects persisted on cooling down to the transition temperature (93 K), but disappeared on heating above 400 °C in *in situ* experiments inside the electron microscope. The possible role of these "domains" or interfaces in superconductivity is discussed.

The structure of the new (superconducting transition temperature above 90 K) superconductor $YBa_2Cu_3O_x$ has been found to be related to perovskites.[1] However, the value of x is not 9, as expected for a typical perovskite, but has a value in most cases of about 7, i.e., about one quarter of the oxygen atoms are missing. In addition, it appears that the high-temperature superconducting phase is not tetragonal but orthorhombic, the a axis being about 1.6% longer than the b axis. The orthorhombic structure may be a result of the way oxygen and vacancies occupy oxygen positions. In addition, several workers have reported planar defects in these materials, which have been variously identified as "twins,"[2] antiphase boundaries,[3] and/or extrinsic planar faults.[4] (Over 90% of the interfaces observed by us were twins.) The aim of this Rapid Communication is to report the results of a detailed transmission electron microscopy and electron diffraction study including *in situ* heating and cooling observations on thin foils of well-characterized high-T_c superconductors $Y_1Ba_2Cu_3O_x$ with a T_c of 93 K and T_c width of about 2 K. The bulk superconducting material was prepared by mixing and grinding appropriate portions of $BaCo_3$, CuO, and Y_2O_3 predried powders, then calcined for 6–12 h at 900–950 °C in air, with intermediate grindings, ground and cold pressed into pellets, sintered in flowing oxygen at 925 °C for 12 h, and finally cooled slowly in flowing oxygen at about 1 °C/min. This produced an almost single-phase compound with a well-defined orthorhombic distortion (as determined from x-ray measurements) of 1.6% from tetragonal. The composition of the superconducting phase is probably very close to $YBa_2Cu_3O_{6.5}$, i.e., oxygen deficient.

The electron microscope specimens were prepared either (a) by finely grinding the bulk specimen and floating the powder in water and scooping the thin flakes on electron microscope copper grids coated with carbon, or (b) by ion milling with grazing Ar ions at an accelerating voltage of 5 kV, till perforation. The planar defects as well as other lattice defects observed by electron microscopy on the specimens obtained by the two methods were indistinguishable from each other, indicating that the defects observed were not artifacts of our experimental procedure and that the defects are not due to radiation damage during ion milling. The transmission electron microscopy was done at an accelerating voltage of 200 kV using a JEOL 200CX transmission electron microscope.

Observing along the c axis [(001) orientation] all the grains invariably show the planar defects. Figure 1 is an electron micrograph and Fig. 2 a diffraction pattern from the same region. The direction of these faults is along [110]. The plates are twin related to each other and are shown edge on (i.e., twin boundary is parallel to electron beam). The electron diffraction pattern (Fig. 2) shows the splitting of spots along only one of the diagonals and the separation increases in higher-order reflections. This can be explained by twinning on a [110] plane in these orthorhombic crystals. Because of the slight difference in the a and b parameters and the twinning, the diffraction pattern will show the splitting of spots along one of the diagonal spots but not along the other diagonal. The direction of splitting will be perpendicular to the diagonal. This is exactly what we observe in the diffraction pattern. The angular value of the splitting, assuming a orthorhom-

FIG. 1. Transmission electromicrograph $YBa_2Cu_3O_x$ polycrystal. The parallel domains here are on the average $\sim$1000 Å apart, and aligned along [110] direction. The interfaces are seen edge on. The orthorhombic a and b axes are found to alternate along these interfaces.

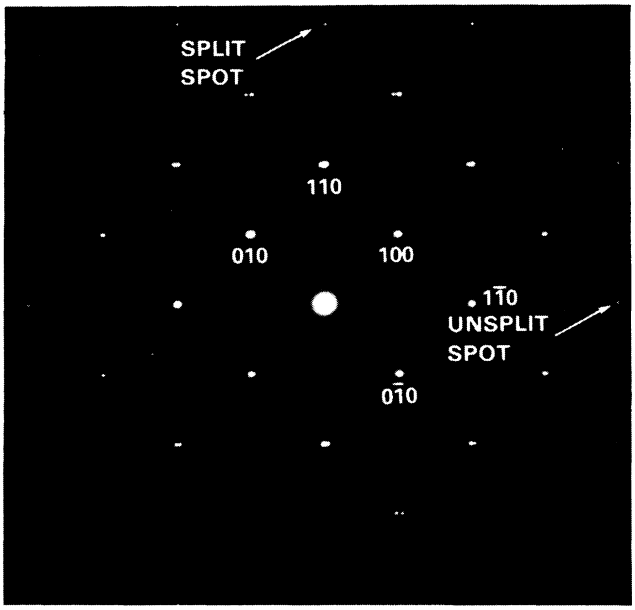

FIG. 2. Electron diffraction from the same region and orientation as in Fig. 1. Notice the splitting of spots along one direction.

bic structure and the fact that the splitting is due to twinning, can be derived to be

$$\theta = 4\tan^{-1}\left(\frac{a-b}{a+b}\right) \simeq 4\frac{(a-b)}{a+b}, \text{ if } a \simeq b \ ,$$

where the a and b values for the structure for the present compound were determined from x-ray measurement to be 3.886 and 3.822 Å, respectively, giving $\theta \simeq 0.03$ radian in excellent agreement with the experimental value measured (0.03) from Fig. 2. A schematic arrangement of the interface is shown in Fig. 3(a). The difference between the a and b axes is exaggerated. Figure 3(b) shows the arrangement of atoms and vacancies on the (100) plane across such a twin boundary. Across this boundary chains of oxygen and vacancies (along [110] direction) have a break, and in this sense the twin boundary can also be called an antiphase boundary (APB). In a strict sense, however, all these boundaries running along [1$\bar{1}$0] or [110] are twin boundaries with breaks in the ordering oxygen and also in the oxygen vacancies across these boundaries. Most of the grain boundaries have a second phase of width ~300 Å. A detailed characterization of the second phases on the grain boundaries and inclusions in the grains will be published elsewhere. After tilting as expected, these boundaries give the fringe contrast which is shown in Fig. 4. Figure 5 is another electron micrograph showing two orthogonal sets of domains, which are rarely observed. Electron diffraction can again be well explained on the basis of [110] twinning.

In situ heating and cooling experiments were done inside the electron microscope. First the specimen was cooled gradually to liquid-nitrogen temperature. No

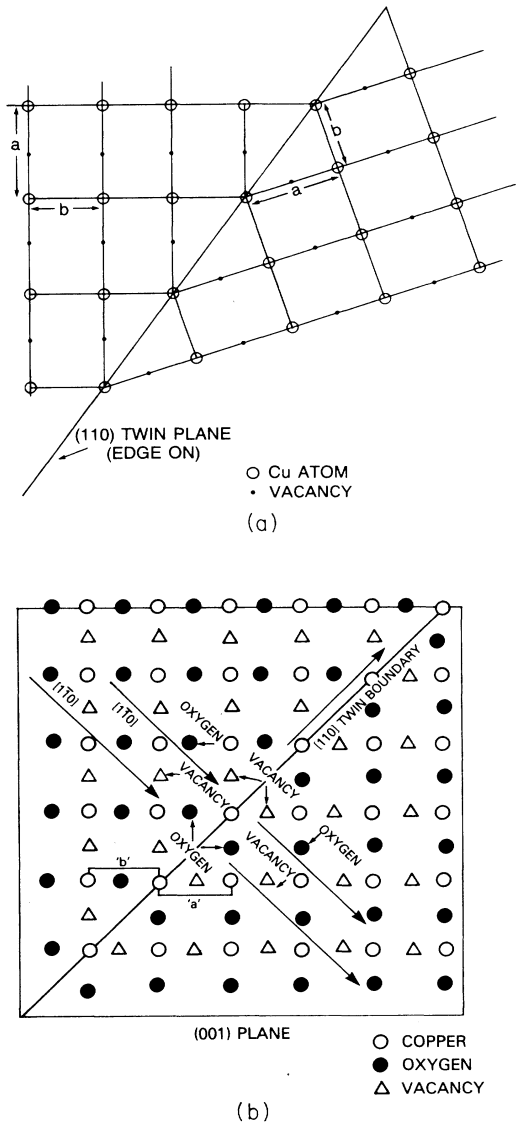

FIG. 3. (a) A schematic diagram of the interface. The difference between the a and b axes is exaggerated. (b) Another schematic diagram of the interface with $a=b$. Note the break in ordering of vacancies at the interface.

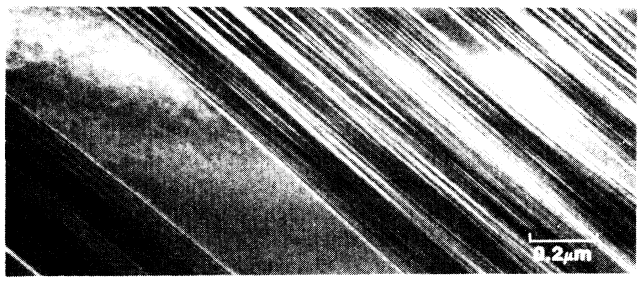

FIG. 4. Transmission electron micrograph of the interfaces showing fringe contrast.

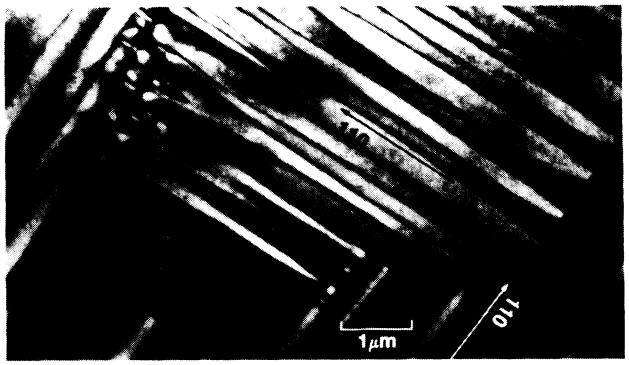

FIG. 5. Transmission electron micrograph showing two sets of interfaces at approximately right angles to each other.

change in shape or size or electron diffraction pattern was observed. It appears that cooling had no effect on these domains down to a temperature close to the transition temperature of the material. The specimen was then gradually warmed from liquid-nitrogen temperature up to a temperature of 150 °C. Again no visible changes were observed. All the observations were made at a magnification of around 50. The temperature was then suddenly raised to above 400 °C, when the twin interfaces became sharper and then quickly disappeared throughout the specimen. On cooling, many of the domains reappeared. The domains thus appear to be stable from about liquid-nitrogen temperature to up to about 400 °C.

Although it has not yet been determined from independent measurements that these oxide superconductors are ferroelectric, the planar interfaces observed by us bear strong resemblance to 90° ferroelectric domains. Planar interfaces in these superconducting compounds have been observed by several workers; however, this is probably the first time that they have been definitely characterized as twins by extensive transmission electron microscopy and electron diffraction. Chen *et al.*,[3] for example, identified these planar defects as APB's. Our results are in accord with their interpretation but we prefer not to call them APB's. Orthorhombic *a* and *b* axes were found to alternate across the boundary as pointed out by them. One interesting property of these interfaces is that they break the linear CuO chains and oxygen vacancy chain. Schuller *et al.*[5] have recently suggested that the main differences between the tetragonal and orthorhombic phase is that in the former, the long-range ordering of the oxygen vacancies in Cu-O planes is nonexistent, i.e., one-dimensional Cu-O chains are absent, whereas in the orthorhombic structure they are present. The ordering of oxygen and vacancies has recently been treated as an order-disorder problem by de Fontaine and Moss.[6] The other role of these interfaces could be in providing sites for a semiconductor-metal transition, assuming the interfaces to behave like a semiconductor.

Dislocations (observed rarely) were seen to be going right across the twin interfaces, indicating low misorientation at the twin interface in agreement with our observations. On heating, the twins disappeared but the dislocations remained visible.

A simple model for the occurrence of the alternate twin interfaces can be postulated as follows. There is a volume change during the tetragonal to orthorhombic transformation which occurs around 900 °C. This results in distortion. In order to minimize the distortion energy and accommodate volume change, alternate twins are created. Transformation takes place to alternate regions of volume F of the orientation of the product and (I-F) of its twin [see Fig. 3(a)], so that for some value of F vectors or lines in the original planes in tetragonal structures are on the average unchanged in length by the transformation, since any length changes will tend to cancel out over many alternating twin regions. Based on this simple idea, we predict that the spacing of the interfaces will be given roughly by (for $F=\frac{1}{2}$)

$$S=\frac{ab}{a-b}\simeq 250\ \text{Å}\ .$$

The actual spacing observed by us is variable, ranging from as low as 150 and as high as 4000 Å, but the average is found to be about 300 Å in rough agreement with the above estimate.

The authors are grateful to Dr. Roy Vandermeer for critical comments.

---

*On leave from the National Science Foundation.

[1]See, for example, L. E. Toth, E. F. Skelton, S. A. Wolf, S. B. Qadri, M. S. Osofsky, B. A. Bender, S. H. Lawrence, and D. U. Gubser (unpublished).

[2]R. Beyers, G. Lim, E. M. Engler, and R. J. Savoy, Appl. Phys. Lett. **50**, 760 (1987).

[3]C. H. Chen, D. J. Werder, S. H. Liou, J. R. Kwo, and M. Hong, Phys. Rev. B **35**, 8767 (1987).

[4]A. Ourmazd, J. C. H. Spence, M. O'Keeffe, R. J. Graham, D. W. Johnson, Jr., J. A. Rentschler, and W. W. Rhodes, in *Proceedings of the Meeting of the Materials Research Society, Anaheim, CA, 1987,* edited by D. U. Gubser and M. Schluter (Materials Research Society, Pittsburgh, PA, 1987); Nature (London) (to be published).

[5]I. K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Soderholm, J. P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. (to be published).

[6]D. de Fontaine and S. C. Moss (unpublished).

FIG. 1. Transmission electromicrograph $YBa_2Cu_3O_x$ polycrystal. The parallel domains here are on the average $\sim$1000 Å apart, and aligned along [110] direction. The interfaces are seen edge on. The orthorhombic *a* and *b* axes are found to alternate along these interfaces.

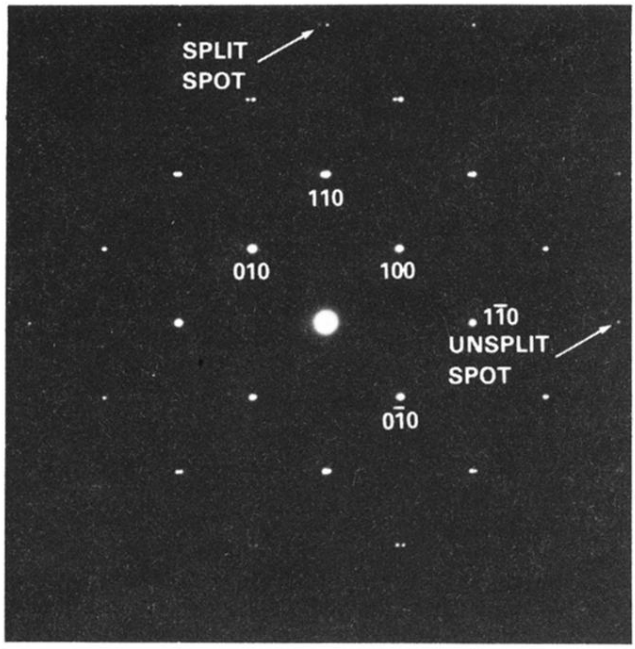

FIG. 2. Electron diffraction from the same region and orientation as in Fig. 1. Notice the splitting of spots along one direction.

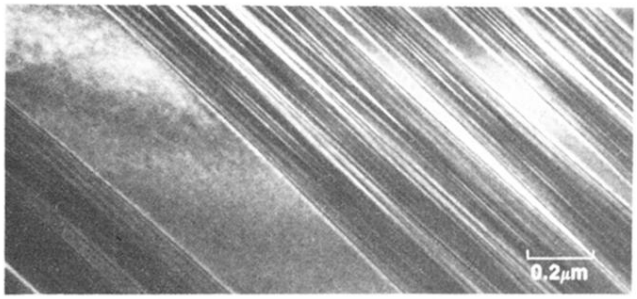

FIG. 4. Transmission electron micrograph of the interfaces showing fringe contrast.

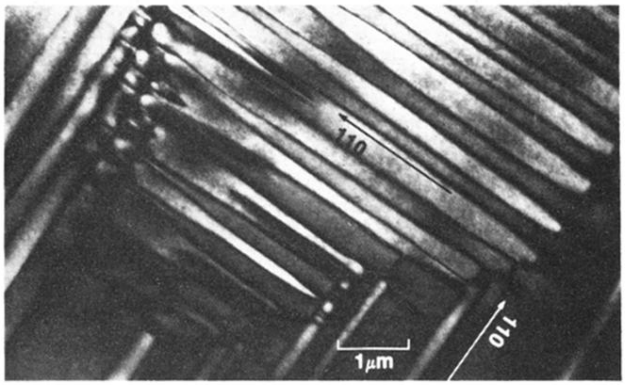

FIG. 5. Transmission electron micrograph showing two sets of interfaces at approximately right angles to each other.