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Publication Date
2017-12-05

uc-404

LBL-27461

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Presented at the Materials Research Society Fall Symposium, Boston, MA, November 27–December 2, 1989, and to be published in the Proceedings

High Resolution Transmission Electron Microscopy Study of Defect Structures in Mixed-Phase YBaCuO

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December 1989

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY STUDY OF DEFECT STRUCTURES IN MIXED-PHASE YBaCuO

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ABSTRACT

Mixed-phase superconducting YBaCuO is characterized by means of high-resolution transmission electron microscopy. This technique reveals that such material contains numerous crystallographic defects of various types. Several of these are described in detail, and their origins discussed.

INTRODUCTION

It is now known that superconducting YBaCuO exists in at least three well characterized phases of differing copper content. [1,2] Due to the cation ratios (Y:Ba:Cu) these compounds are commonly referred to as the "1-2-3", "1-2-4", and "2-4-7" phases. When YBaCuO crystals are synthesized in practice, an intergrowth of more than one structure frequently occurs in order to accommodate local deviations from these ideal stoichiometries.

The superconducting materials examined in the present study were initially prepared as pure granular $YBa_2Cu_4O_{10}$ ("1-2-4"), and then "partially converted" to $YBa_2Cu_3O_7$ ("1-2-3") by annealing at constant temperature and oxygen pressure. X-ray diffraction studies indicate that the resulting material contains both the "1-2-3" and "1-2-4" phases, as intended.

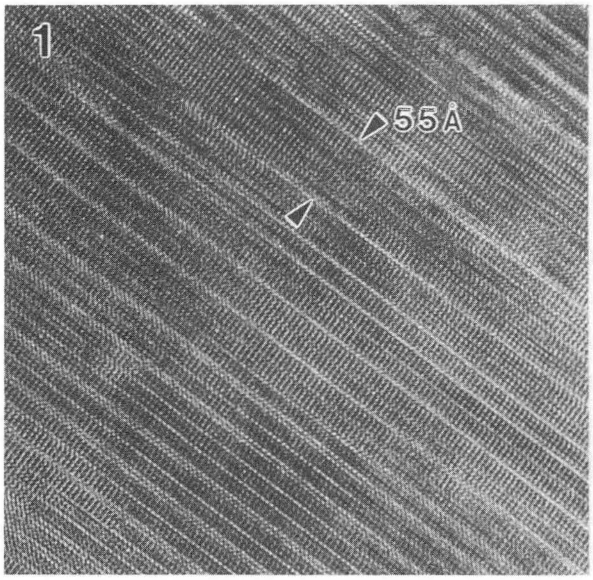
High-resolution Transmission Electron Microscopy (TEM) has been utilized to study partially converted YBaCuO. TEM specimens were prepared by crushing the material to a fine powder and by ion milling, as described in detail elsewhere. [3] The material was seen to be a mixture of the "1-2-3" and "1-2-4" phases, in agreement with the x-ray data. High-resolution TEM also showed that a variety of crystallographic defects are present in the partially converted samples, as expected when a mixture of phases with differing lattice parameters is present. The defects observed were volumetric, planar, and linear in nature.

RESULTS AND DISCUSSION

The volumetric defects found in partially converted YBaCuO were intergrowths which consisted of essentially random alternation in stacking of differing phases (i.e. polytypoid behavior), where "1-2-3" and "1-2-4" structures both appeared without any short-period sequential order. Regions containing such structural mixtures were generally inhomogeneously strained, as evidenced by the variations from axial orientations in high-resolution micrographs (see Figure 1).

Interestingly, no Cu or Cu-complex oxides were seen on a 5μm scale of observation, (c.f. grain size of about 1μm) meaning that if such phases exist, they must be coarsely distributed in comparison with the grain size. The presence of alternate Cu-containing phases has been variously reported for granular YBaCuO materials [4,5]. These may, in fact, have been present here, but unseen due to the working magnifications employed.

The most common planar defects observed in the mixed-phase YBaCuO were extrinsic stacking faults of the type **R** = 1/6[031], described by Zandbergen et al. [6] Such stacking faults are characteristic of the "1-2-3" / "1-2-4" transformation, and result from the fact that the "1-2-3" phase contains single CuO layers, while "1-2-4" contains double CuO layers. An isolated region of one of these defects may be seen in Figure 2; here the defect extent is limited to only 10nm, although most stacking faults were far larger. The volumetric defects above may similarly be considered highly extended arrays of multiple planar defects of this type.



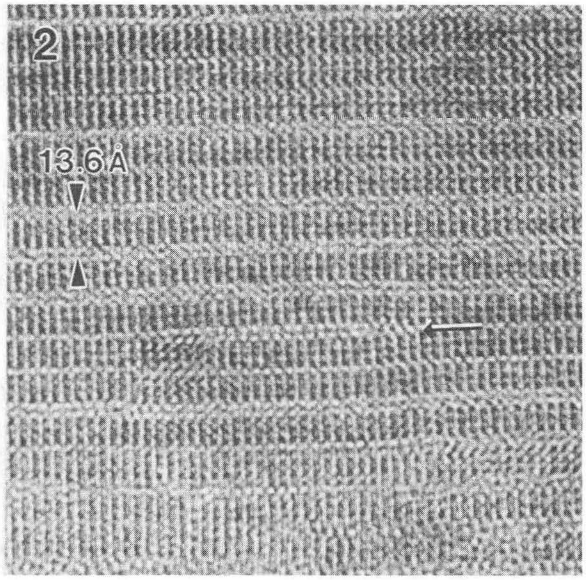


Fig. 1. Polytypoid behavior in YBaCuO, showing variations in stacking along [001].
Fig. 2. Extrinsic stacking fault (**R** = 1/6[031]) corresponding to extra CuO plane.

Two other planar defects of note were observed. The first was a low-angle 'special' grain boundary between the "1-2-4" and "1-2-3" phases, formed when larger domains of the two phases met (as seen in Fig 3). This boundary is characterized by [010] tilt, and was geometrically aligned to produce matching of (001) planes along the tilt axis, resulting in a high-symmetry boundary which nevertheless allowed the transformation interface to propagate. Continuity of atomic planes between phases can be verified by following the lattice planes visible in the image. The boundary can be modeled most straightforwardly by using very simple, purely geometrical arguments, as illustrated in Figure 4. In the present case, the misorientation angle is measured to be approximately 9°, the relevant lattice spacings are d_{123}=11.7Å and $d_{124}/2$=13.6Å, and the model thus predicts the grain boundary inclination angle to be 48°. Measurement from the image yields a value of about 50° for this angle, in good agreement with the expected value.

Although this special boundary should not be considered representative of the transformation in general, it does illustrate the similarity of the structures while emphasizing certain differences. Variations from axial alignment in the high resolution images showed that a substantial amount of residual strain is present in the "1-2-4" phase, while much less exists in the "1-2-3" region. This effect may have been from partial decomposition of the excess Cu-O layers in the "1-2-4" crystal. A regular faceted structure seems to have been developing along this grain boundary, suggesting that the simple 2-dimensional model presented above does not completely describe the interface. Unfortunately, only a small number facets were visible along the short length of grain boundary found (one of which is seen in Fig. 3), so more conclusive statements about the exact nature of this defect cannot yet be made.

The second additional planar defect of interest is a basal plane defect, and is also visible in Figure 3 (indicated by arrows). This defect is of particular interest because it has propagated across the "1-2-3"/"1-2-4" grain boundary and continued to grow into the "1-2-3" crystal, unlike most other defects which terminate at the boundary. The portion of the image where the defect passes through thick "1-2-4" material appears to be the same as images of other planar defects commonly observed in similar regions of "1-2-4" material. This indicates that the defect structure occurs with some frequency in "1-2-4" phase regions remaining in partially converted material. However, since in Figure 3 this defect continues into the very thin region of "1-2-3" phase as well, it can be seen to be associated with a shift of ~1/3[001]. The "1-2-3" region of the defect appears similar to a defect associated with presence of $Y_2Ba_2Cu_4O_x$ (2-2-4), recently reported by Ramesh, et al. [7] It is also possible that this defect is an extra Cu-O plane in the "1-2-4" structure (resulting in a "1-2-5" phase), since the transition from the "1-2-4" phase to the "1-2-3" phase results in "excess" copper content. Further studies are underway to characterize these types of defects as they occur in the "1-2-4" phase.

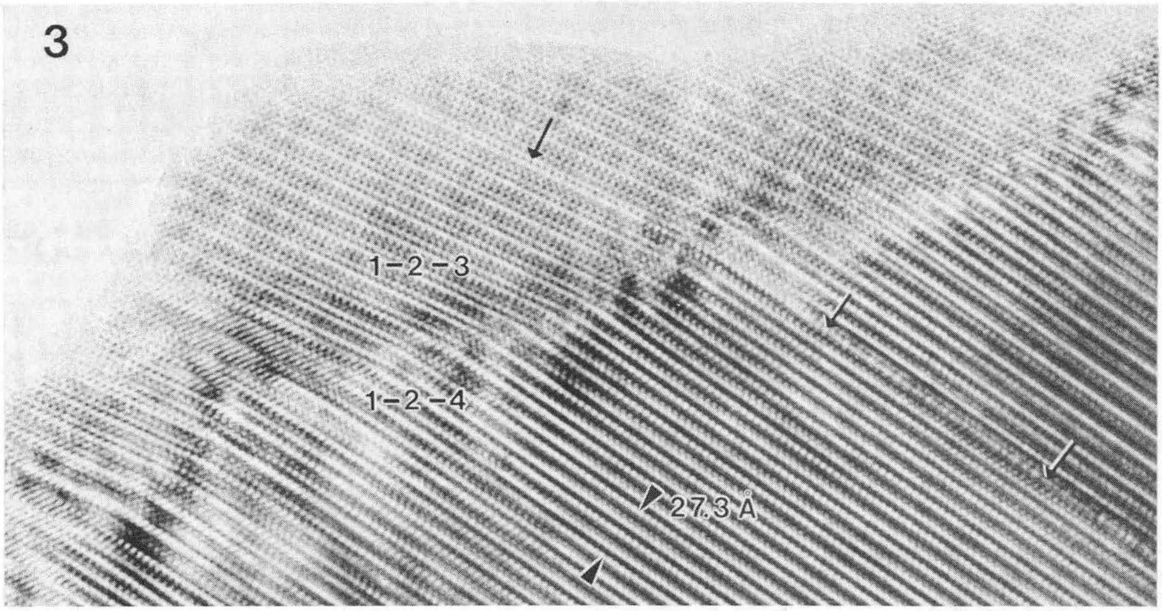
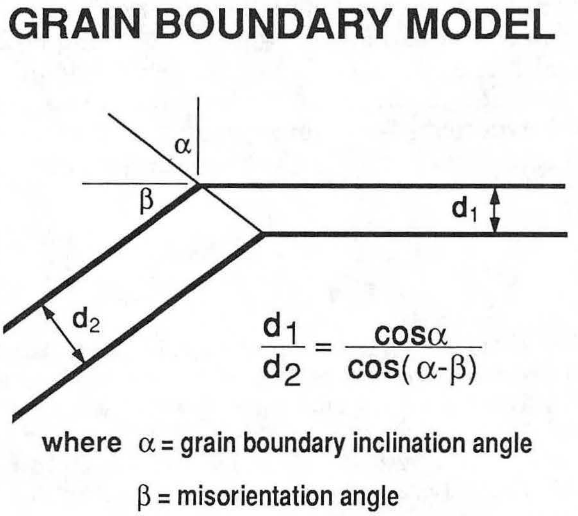


Fig. 3. Phase boundary between "1-2-3" and "1-2-4" structures.

Regions remaining as mostly "1-2-4" material also contained a large number of line defects, some of which could be identified as 1/6[031] partial dislocations associated with the type of stacking fault described above; one of these is shown in Figure 5. In one case, a region of very complex intergrowth, consisting of many partial dislocations and possibly other defects as well, was found . Image contrast suggests that the strain surrounding this region is quite high. The large number of partial dislocations observed indicates it is likely that the "1-2-3" / "1-2-4" phase transformation propagates by means of these defects.



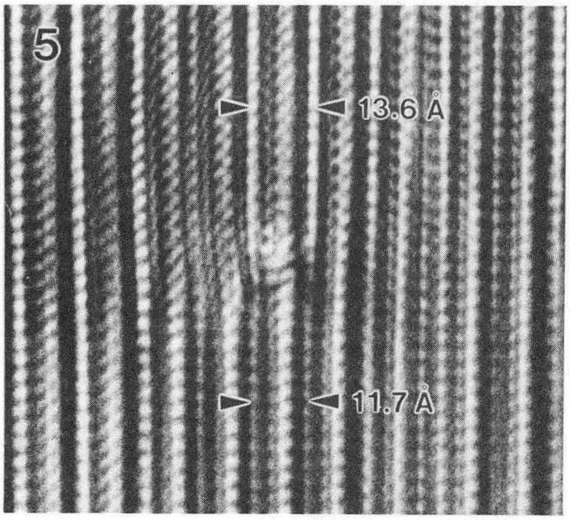


Fig. 4. Simple model of the "1-2-3"/"1-2-4" boundary, accommodating differing c-spacing.
Fig. 5. Isolated partial dislocation associated with the "1-2-4" to "1-2-3" transformation.

Another type of line defect observed was clearly of different character. One such defect appears in Figure 6a, and is notable because of the apparent absence of strain in the region immediately surrounding it. Although the nature of this defect is not yet positively identified, a plausible model involves meeting of "1-2-3" and "1-2-4" unit cells along a (010) plane, as shown very schematically in Figure 6b. This model predicts that Ba is replaced by Y along a particular (001) plane, thus requiring a second dislocation or anti-phase boundary in the vicinity in order to bring (001) planes back into registry again. Such a defect appeared to be present a distance of 40nm away from the original one.

We have used computer simulation of high-resolution images in order to verify the phases present in various regions of actual TEM images. In addition, comparison of simulated and experimental images revealed that the lattice planes which appear bright white in Figure 3 are the current-carrying CuO planes in the "1-2-3" and "1-2-4" crystal structures. These appear to be continuous across the grain boundary between the two phases, suggesting that this particular type of boundary may not greatly affect the superconducting properties of the material.

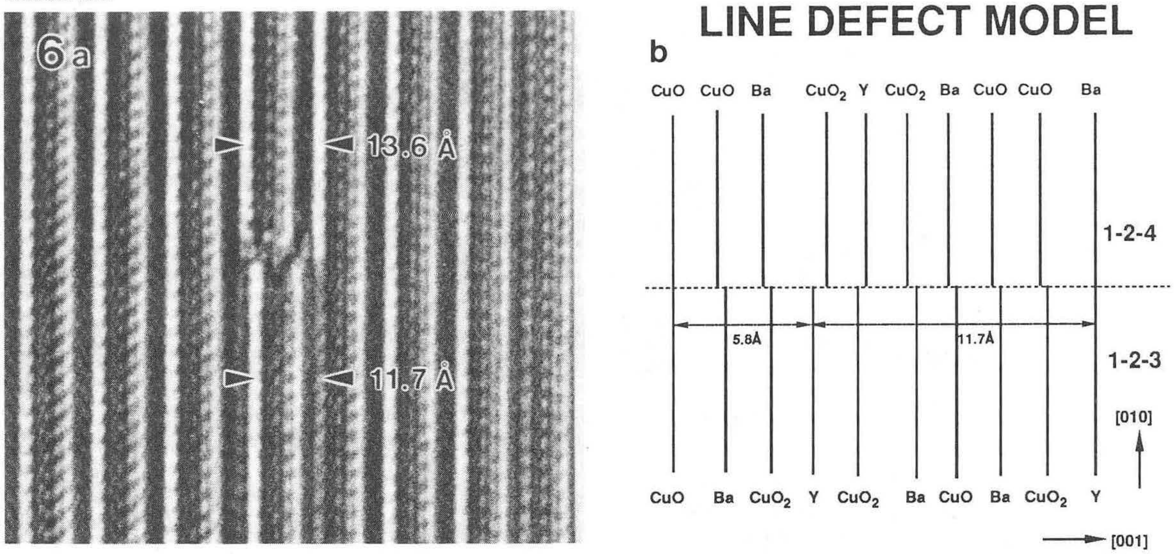


Fig. 6. (a) Second type of line defect. Note lack of distortion of lattice planes in the vicinity. (b) Possible model for this defect, involving meeting along a (010) plane.

SUMMARY AND CONCLUSIONS

A variety of defects of various types have been found in “partially converted” YBaCuO, and these are characteristic of the nature of the transformation from the "1-2-4" to the "1-2-3" structure. The defects observed in these mixed-phase specimens are likely to have significant effects on the superconducting properties of the material. In particular, the partial dislocations and related stacking faults described above are expected to contribute to limitations of critical current values, since current in these materials is carried in the Cu-O planes (i.e. perpendicular to the [001] axis).

ACKNOWLEDGEMENTS

Grateful acknowledgement is given to D. Morris and J. Nickel for providing x-ray diffraction data, and for supplying the materials used in this study. Technical assistance from M. Powers and helpful discussions with C.D.J. Hetherington are also greatly appreciated. Microscopy and image simulation were performed at the National Center for Electron Microscopy, Lawrence Berkeley Laboratory. This work is supported by a University of Houston subcontract under DARPA Grant No. MDA972-88-J-1002, and by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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