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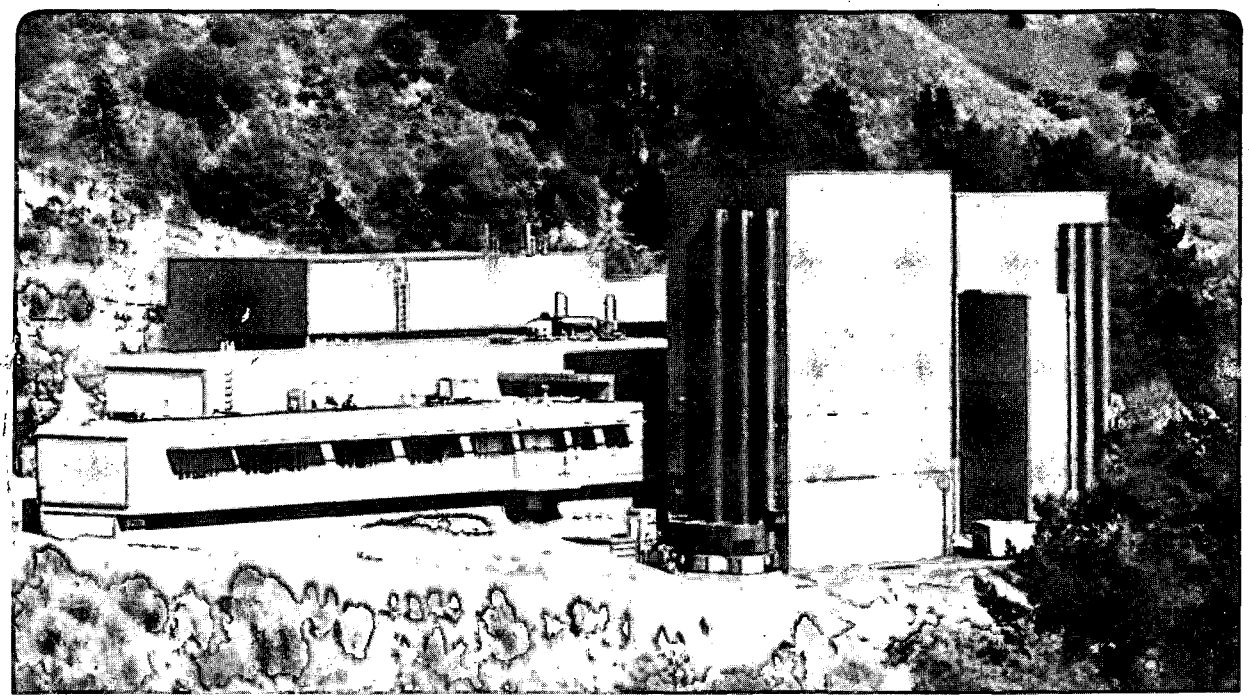
and R.A. Huggins

December 1989



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IN-SITU TRANSMISSION ELECTRON MICROSCOPY AND COMPUTER SIMULATION STUDY OF THE KINETICS OF OXYGEN LOSS IN $YBa_2Cu_3O_z$

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ABSTRACT

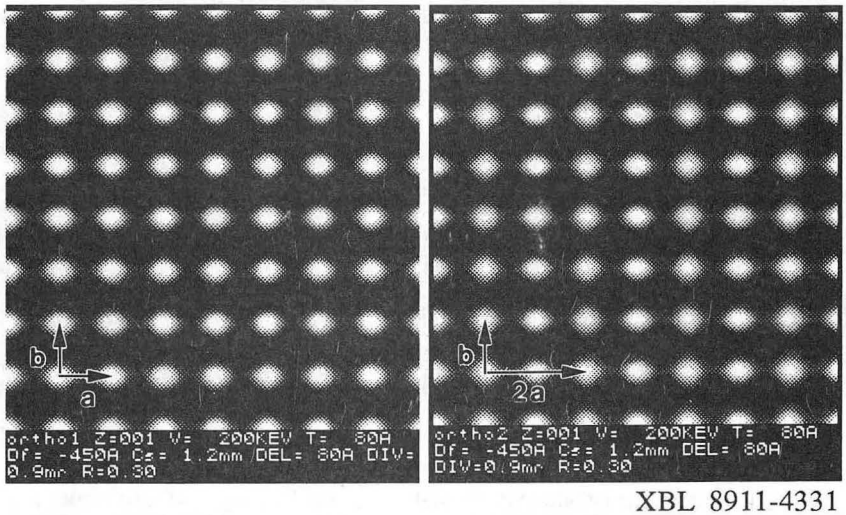
High resolution transmission electron microscopy during in-situ quenching of $YBa_2Cu_3O_z$ is used to study the kinetics of microdomain formation during oxygen loss in this system. Image simulations based on atomic models of oxygen-vacancy order in the basal plane of this material generated by Monte Carlo calculations are used to interpret high resolution micrographs of the structures obtained by quenching. The observed domain structures agree well with those obtained from the simualtions.

INTRODUCTION

Oxygen ordering in the basal plane plays a vital role in determining the superconducting properties of the $YBa_2Cu_3O_z$ system.[1] Upon cooling from the disordered, tetragonal phase, parallel O-Cu-O chains develop leading to the formation of the orthorhombic phase (Ortho I), a 90K superconductor, near z = 7. At lower oxygen content, a doubling of the orthorhombic unit cell leads to the formation of the orthorhombic Ortho II phase, a 60 K superconductor, near z = 6.5. Thus an understanding of thermodynamics of oxygen ordering is essential for the development and control of superconducting properties in this material.

EXPERIMENTAL

High resolution transmission electron microscopy is used to study the kinetics of oxygen loss associated with the low temperature Ortho I to Ortho II transformation. Image simulation using the NCEMSS program[2] reveals that small but distinct differences are detectable by HREM between the various oxygen ordered structures found in the basal plane of this material (Figure 1). Specimens of highly characterized oxygen content (±0.02 oxygens per formula unit) were prepared using a solid state ionic technique.[3] Transmission electron microscopy was performed using the JEOL 200CX microscope. The sintered material was prepared for microscopy by dry crushing into a fine powder and dispersing onto a lacy carbon grid immediately before observation to minimize specimen exposure to air and moisture.



XBL 8911-4331

Figure 1: High resolution simulated images of the Ortho I and Ortho II structures generated using the NCEMSS program. The Ortho II structure is distinguished from the Ortho I structure by a doubling of the distance in the a_o direction between the O-Cu-O chains.

Oxygen ordered domain formation is studied by beam heating homogeneous $YBa_2Cu_3O_z$ to destroy the existing order, and then "quenching" the specimen in the microscope. To avoid altering the state of order in the material while adjusting the microscope for imaging, the area of interest is first tilted into the [001] orientation while viewing under very low intensity in diffraction mode. It has been shown elsewhere that these materials can endure this degree of irradiation for long periods of time with no detectable change of the state of oxygen-vacancy order in the basal plane.[4] Once the area is tilted into the [001] orientation, astigmatism and focus are adjusted to obtain a high resolution image, and then an adjacent area, unexposed to beam irradiation during this initial procedure, is used for the in-situ quenching study. The initial state of oxygen-vacancy order in this area is ascertained by taking a through focus series of high resolution images. Diffraction mode pictures are taken both before and after this initial series of images to check that the initial state of oxygen order has not been affected by the high intensity beam used during imaging. After this series is obtained, the beam is used to heat the specimen until diffraction mode imaging reveals that the material has transformed to the high temperature, disordered tetragonal phase. The beam is then abruptly turned off, in this way effectively "quenching" the specimen to room temperature. After the material has cooled to room temperature, a second series of high resolution images and selected area diffraction patterns are taken of the heat treated area which is now seen to display the characteristic microdomain "tweed" contrast.[5]

DISCUSSION AND CONCLUSIONS

High resolution TEM images of the specimen before and after this heat treatment are compared allowing the study of domain formation (Figure 2). The diffraction patterns depicted in Figure 3, produced from 200Å diameter selected areas extracted from images before and after the heat treatment, show that the initially single domain structure has been re-ordered into intimately intermixed orthogonal microdomains. Basal plane oxygen ordered structures generated by Monte Carlo calculations (Figure 4), the details of which are reported elsewhere,[6] are used as input to the NCEMSS image simulation program to model the structures obtained by beam heating. Assuming out of plane correlation of the basal plane ordering, a three dimensional atomic model of the quenched structure is built up using the atomic positions of the tetragonal structure reported by Santoro, et. al.[7] as the symmetry of the quenched structure is nominally tetragonal.

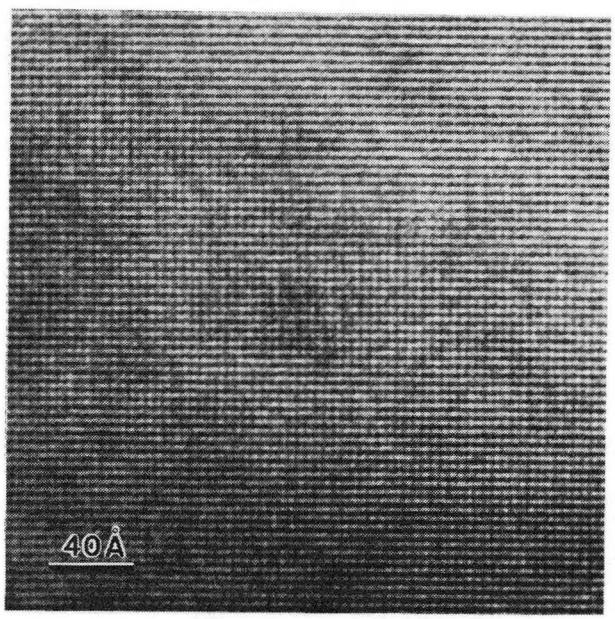


Figure 2a: High resolution [001] micrograph of $YBa_2Cu_3O_{6.5}$ obtained shortly before in-situ beam heating. Notice the uniform contrast similar to that represented in Figure 1. XBB 890-10391

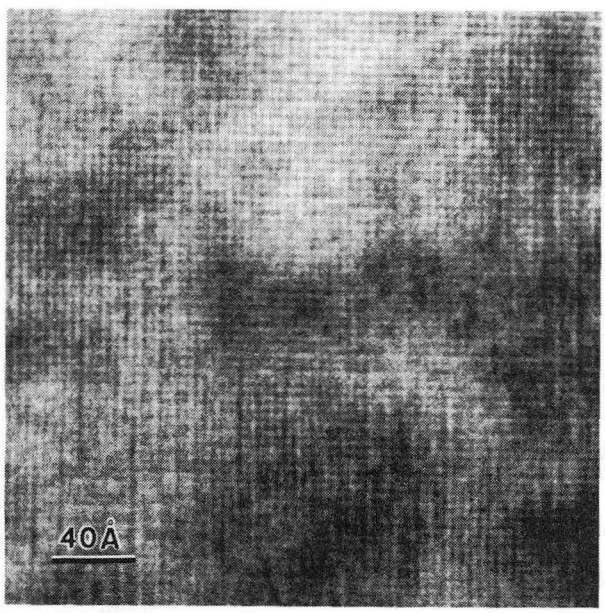


Figure 2b: High resolution [001] micrograph of $YBa_2Cu_3O_{(z<6.5)}$ obtained immediately after in-situ beam heating and subsequent quenching. Notice the development of a "tweed" contrast distribution reflecting the development of conflicting microdomains similar to that depicted in Figure 4. XBB 890-10390

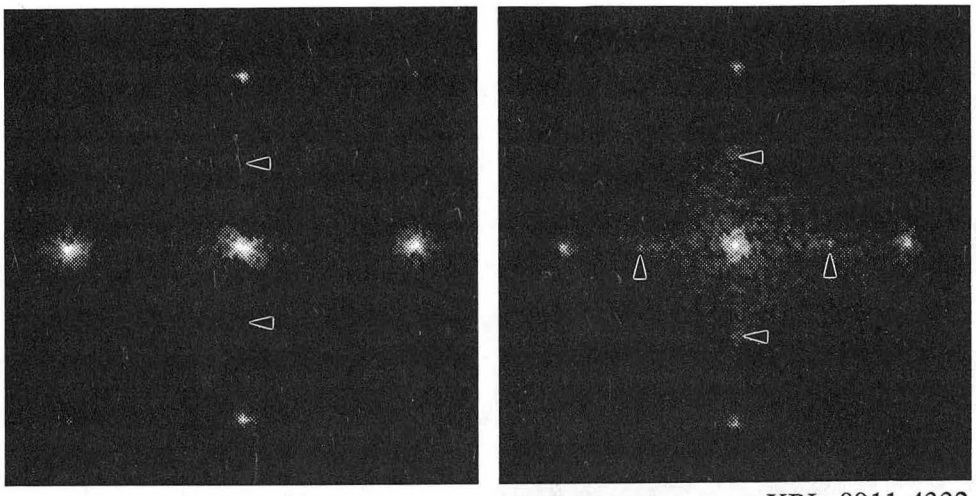


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Figure 3: [001] diffraction patterns of the areas depicted in Figures 6a and 6b. The diffraction pattern on the left displays superlattice reflections along only the [010] direction demonstrating the single domain nature of the image area (Figure 6a). The pattern on the right, obtained after beam heating, displays superlattice reflections along both the [100] and [010] directions indicating the formation of the orthogonal ordered microdomains observed in the corresponding image (Figure 6b).

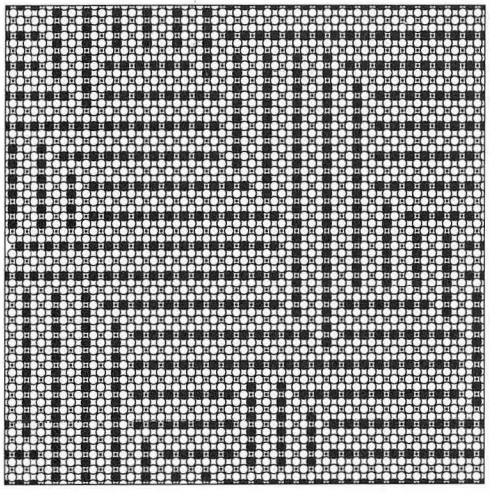

Figure 4: A quenched basal plane oxygen-vacancy ordered configuration generated by a Monte Carlo computer simulation. This structure exhibits the small conflicting Magneli-type microdomains typical of quenched $YBa_2Cu_3O_z$ specimens.[6] This structure was obtained by simulating a rapid quench from the disordered tetragonal phase to room temperature at constant chemical potential, as is done in the experiment (z = 6.50). Black dots represent copper atoms, filled circles oxygens, and open circles vacancies. XBL 8911-4333

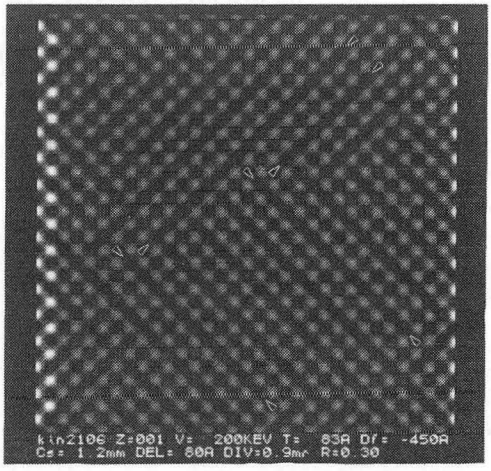

Figure 5: High resolution simulated image generated using the NCEMSS program and a three dimensional extrapolation of the basal plane configuration depicted in Figure 3 as input. The important feature to notice is the development of dark contrast fringes in the 'b' direction of each microdomain. These dark fringes give rise to the "tweed" microstructure seen in Figure 2b. The image is rotated 45 degrees with respect to Figure 4 and the higher intensity spots on the edge of the image are an artifact of the simulation. XBB 890-10392

To identify the thickness of the quenched area depicted in Figure 2b, a simulated imaged of the Ortho II structure was matched to the unquenched image and it was thus ascertained that the area was 80Å thick (Figure 6a). It is found that the contrast observed in the images of the quenched structures is consistent with that produced by conflicting Magneli-type microdomains whose formation and behavior was predicted and described previously.[6,8,9] The dark, continuous fringes observed in the quenched structure were identified in a simulated image of equal thickness to correspond with the orthorhombic 'b' direction of the microdomain. Thus, the many conflicting, orthogonal microdomains give rise to conflicting, orthogonal dark fringes producing the characteristic "tweed" contrast (Figure 6b). Using microdensitometer plots to measure the extent of these dark, parallel fringes, one can measure the extent of an individual microdomain. Work is in progress to identify the dependence of domain size, if any, on initial oxygen content.

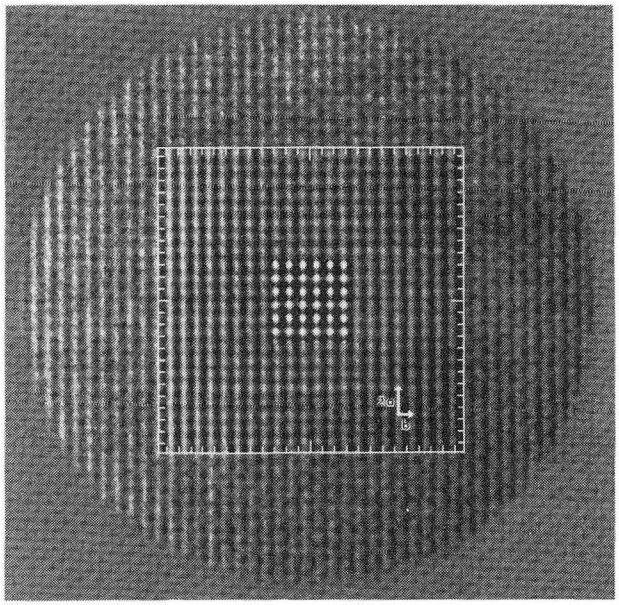

Figure 6a: Partially processed image of area extracted from a high resolution image obtained before beam heating (Figure 2a). The area inside the white frame has been processed to remove background noise. The innermost square is extracted from the simulated image of the Ortho II structure depicted in Figure 1. Notice the uniform fringe contrast reflecting a single Ortho II domain of the untreated structure. XBB 890-10394

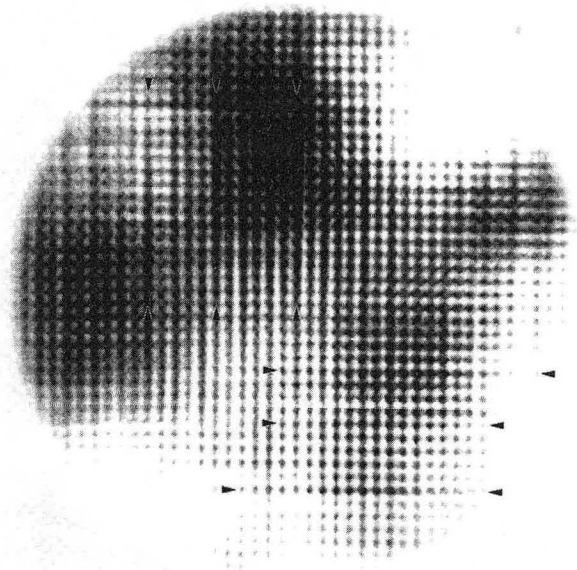

Figure 6b: Processed image of an area extracted from the high resolution image obtained after in-situ beam heating (Figure 2b). Notice the development of orthogonal dark fringes similar to those seen in the simulated image (Figure 5) reflecting the formation of conflicting microdomains in the quenched specimen.

XBB 890-10393

ACKNOWLEDGEMENTS

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REFERENCES

1. R. Beyers and T. M. Shaw, Solid State Phys. **42**, 135 (1989).

2. R. Kilaas, in *Proceedings of the 45th annual meeting of the Electron Microscopy Society of America*, edited by G. W. Bailey (San Francisco Press, Inc., San Francisco, 1987), p. 66.

3. B. T. Ahn, T. M. Gür, R. A. Huggins, R. Beyers, and E. M. Engler, in *Electro-Ceramics and Solid-State Ionics*, edited by H. L. Tuller and D. M. Smyth (the Electrochemical Society, Princeton, New Jersey, 1988), p. 112.

4. R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, Nature **340**, 619 (1989).

5. J. Reyes-Gasga, T. Krekels, G. van Tendeloo, J. van Landuyt, S. Amelinckx, W. H. M. Bruggink, and H. Verweij, Physica C **159**, 831 (1989).

6. C. P. Burmester and L. T. Wille, Phys. Rev. B. **40**, 8795 (1989).

7. A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, Mat. Res. Bull. **22**, 1007 (1987).

8. A. G. Khachaturyan and J. W. Morris, Jr, Phys. Rev. Lett. **61**, 215 (1988).

9. D. de Fontaine, M. E. Mann, and G. Ceder, Phys. Rev. Lett. **63**, 1300 (1989).

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