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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF PARTIAL STATES OF OXYGEN ORDER IN $YBa_2Cu_3O_z$

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ABSTRACT

High resolution electron microscopy is used to investigate the effect of electron irradiation induced oxygen loss on the states of partial order in $YBa_2Cu_3O_z$. Contrast effects visible in the [001] zone image as a result of the degree of the out-of-plane correlation of these ordered states are investigated. Using statistical simulations to aid in the analysis of the HREM images, an interpretation based on a kinetically limited evolution of the variation of long range [001] ordering is proposed.

INTRODUCTION

Oxygen ordering in the basal plane of $YBa_2Cu_3O_z$ is vital to the superconducting properties of the system.[1] The high temperature, disordered tetragonal phase transforms upon cooling by an ordering reaction in which parallel O-Cu-O chains form leading to the development of the orthorhombic phase (Ortho I), a 90K superconductor. At lower oxygen content, a doubling of the unit cell a_o spacing leads to the formation of the cell-doubled Ortho II phase over which the critical temperature for superconductivity is known to vary from below 90K to 60K.[2] Disordering of these O-Cu-O chains at lower oxygen content leads to the formation of the semiconducting tetragonal phase (see Figure 1). Recently, a number of investigations have revealed the existence of states of partial order at intermediate oxygen concentrations.[2,3] These states of partial order lead to the development of extended orthorhombic unit cells which, for highly characterized values of oxygen content, are structurally well defined and persistent in nature. Basal plane ordering configurations and corresponding simulated HREM images of two such $4a_o$ variants are shown in Figure 2. Earlier microdiffraction work demonstrated that the out-of-plane correlation of the basal plane states of order varied with oxygen content.[2] For oxygen contents of $z \leq 6.65$, microdiffraction along the [010] zone axis produced patterns with well defined superlattice spots indicating correlation of the (001) oxygen ordering. However, for oxygen contents of $z > 6.65$, the superlattice reflections in the 001 pattern were shown to be streaks running parallel to the c* axis indicating that the basal plane ordering was not correlated in the [001] direction.

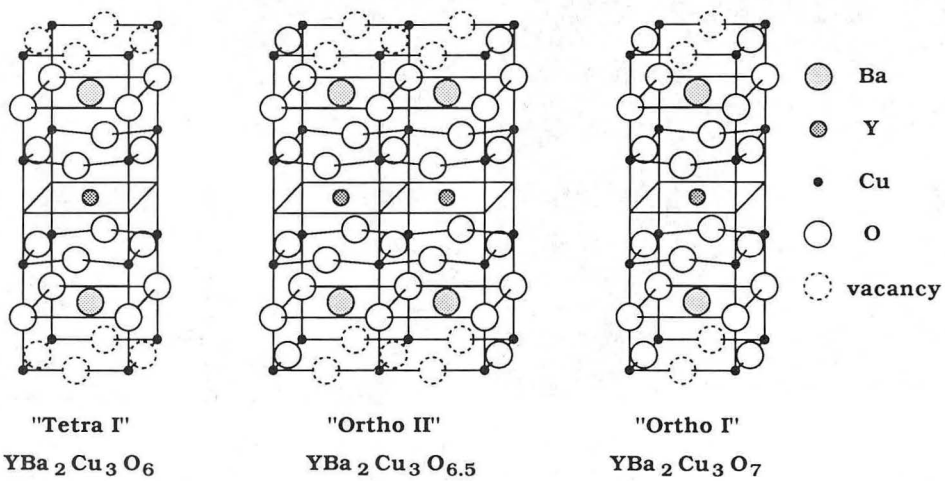


Figure 1: Structural unit cell models for the Tetragonal, Orthorhombic, and cell-doubled Orthorhombic $YBa_2Cu_3O_z$ phases. The Ortho II structure is distinguished from the Ortho I structure by a doubling of the distance in the a_o direction between the O-Cu-O chains.

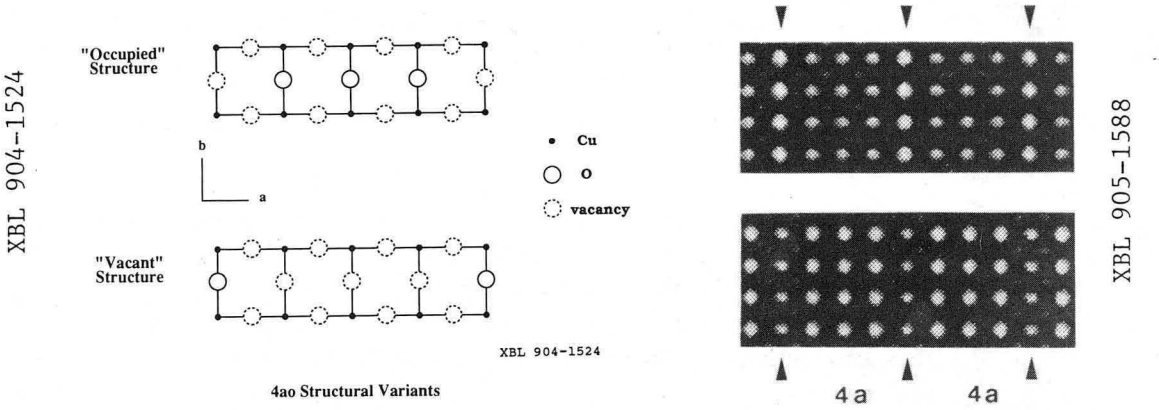
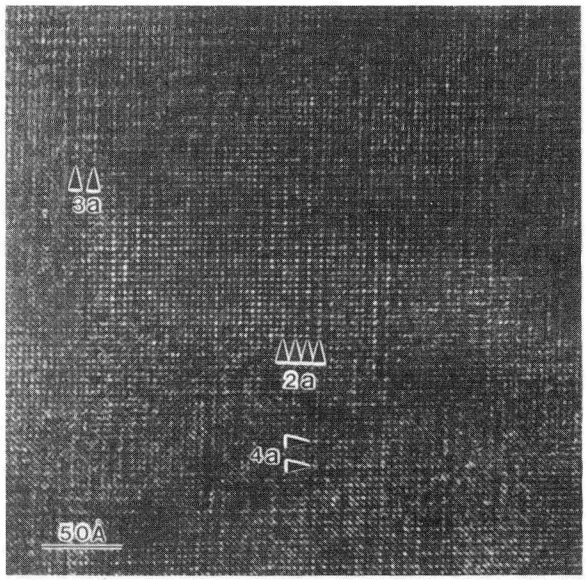


Figure 2: Basal plane ordering configurations for the occupied and vacant variants of the partially ordered $4a_o$ structures with their corresponding HREM simulated images calculated at Scherzer defocus for the JEOL 200CX using the NCEMSS program[4]. Borrowing a notation developed by de Fontaine et. al,[5] these structures can be compactly expressed as "<1110>" and "<1000>"; these symbols representing a periodic arrangement of three O-Cu-O chains (1's) and one vacancy-Cu-vacancy chain (0's) for the occupied $4a_o$ structure and the inverse for the vacant $4a_o$ structure, respectively.

Using high resolution electron microscopy and selected area diffraction, this phenomena is investigated further utilizing the specimens from this earlier diffraction study.

EXPERIMENTAL OBSERVATIONS

In an earlier study,[6] it was shown that when exposed to high intensity electron irradiation, an initially single domain orthorhombic $YBa_2Cu_3O_{6.5}$ specimen could be transformed into the disordered tetragonal phase by beam-induced heating, and, when quenched, lead to the formation of intimately intermixed, mutually orthogonal domains. This microstructure, which maintained long range correlation in the [001] direction, produced a characteristic "microtweed" contrast in the HREM image.[6] As was reported elsewhere, oxygen-vacancy motion can be induced in the electron microscope by using electrons of energy greater than 160kV.[7] In the current study, high resolution electron microscopy is used to study the contrast arising and the microstructures produced by imaging along the [001] direction during gentle in-situ oxygen loss produced by



XBB 904-3151

Figure 3a: High resolution [001] micrograph of beam heated $YBa_2Cu_3O_{6.71}$. Notice the presence of partial ordering of $2a_o$, $3a_o$, and $4a_o$ spacings. Image consists of overlapping domains of approximately 300Å in spatial extent giving rise to a macroscopic tetragonal symmetry.

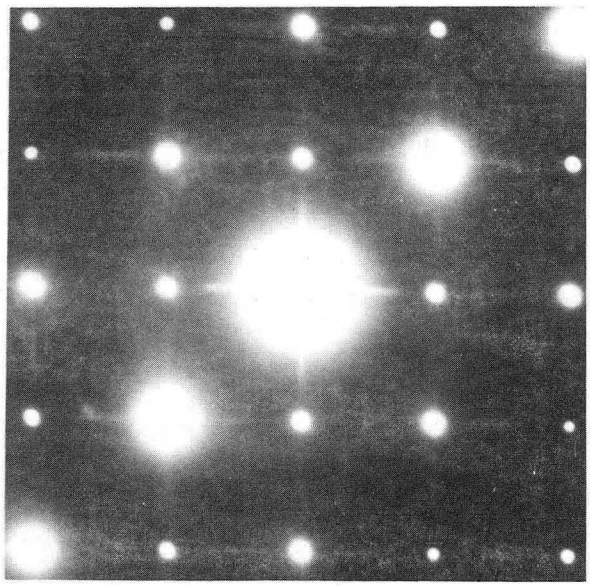


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Figure 3b: Selected area diffraction pattern corresponding to image in Figure 3b. Notice that the originally sharp superlattice reflections at <0.37 0 0> have been smeared out along the <1 0 0> directions reflecting the occurrence of oxygen loss and disordering of the chain spacings due to beam irradiation.

electron irradiation. Controlled oxygen loss is achieved by long exposure to 200kV electrons produced from a undersaturated LaB_6 filament. The low beam current reduces specimen heating and leads to slow oxygen loss allowing the investigation of the many kinetically achievable states of partial order at lower temperatures. As oxygen loss ensues, 001 selected area diffraction patterns of the irradiated area are taken to record the degree of oxygen loss and the state of oxygen order. Specimens of highly characterized initial oxygen content (±0.02 oxygens per formula unit) were prepared by a solid state ionic technique.[8] Transmission electron microscopy was performed under the imaging conditions described above using a JEOL 200CX microscope. The sintered material was prepared for microscopy by crushing and dispersing onto a lacy carbon grid immediately before observation to minimize specimen exposure to air and moisture. A specimen of initial oxygen content of z = 6.71 was used in the study of "low temperature" oxygen loss. Prior electron diffraction showed that all grains of the material had an ordering wave vector of $<0.37\pm0.02\ 0\ 0>$ and had no long range correlation of this ordering along the [001] direction.[2] It has been reported elsewhere that high intensity electron beam illumination will induce the orthorhombic to tetragonal transformation while producing characteristic $2a_0 \times 2a_0$ and $2a_0\sqrt{2} \times 2a_0\sqrt{2}$ deformation structures as a consequence of the intense irradiation. These structures were not observed during the low intensity imaging described here. Instead, diffraction patterns taken during this series revealed that gradual oxygen loss occurred in a way that avoided this high temperature route to the tetragonal transition and appeared to progress at relatively constant temperature allowing the investigation of microstructures of oxygen content ranging from z = 6.71 to below z = 6.50 before the low temperature transition occurred. At the onset of beam irradiation, partially interpenetrating and overlapping orthogonal ordered domains with unit cell spacings of $2a_0$, $3a_0$, and occasional $4a_0$ spacings were observed (Figure 3a). For the initial concentration of z = 6.71, it has been shown that the partially ordered states expected for this concentration would be primarily of the "$<(110)^2 10>$" chain ordering type.[5] It is felt that the electron beam exposure, although slight, has already caused oxygen loss, easily disordering this complex structure into the mixed spacings observed. This disordering is also indicated by the elongation of initially sharp superlattice reflections in the corresponding diffraction pattern (Figure 3b). Image simulation reveals that for partially and well correlated [001] oxygen ordering, the copper(1) sites along the copper(1)-oxygen(1) vacant chains image as bright dots elongated in the direction of the chain while the copper(1) sites in the copper(1)-oxygen(1) occupied sites image as symmetrical bright dots[6] (see also Figure 2). Thus the unit cell spacing in the a_0 direction can be determined directly by measuring the local spacing between the contrast enhanced copper(1)-vacancy(1) chains (see Figure 3a). Upon further oxygen loss, a new type of contrast emerges (see Figure 4a and 5b). Here, yttrium(1)-barium(1) columns image as bright dots which are further ordered into square coordinated clusters separated from each other by dark fringes. Image simulation of intimately intermixed but perfectly orthogonal $2a_0$ ("anti-correlated" in [001] direction) ordered states (see

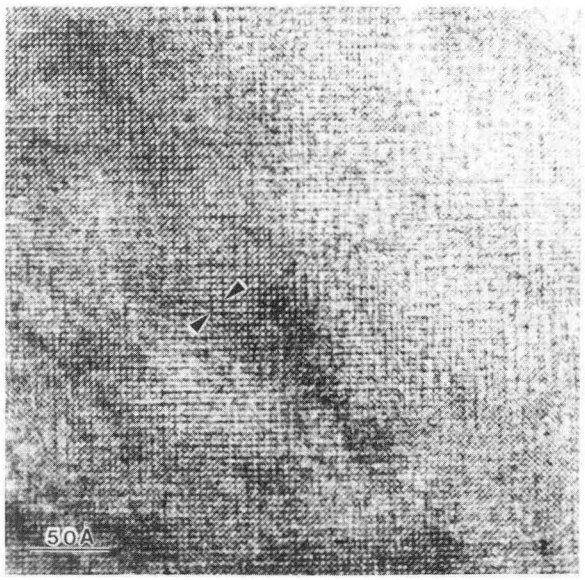

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Figure 4a: High resolution image after further oxygen loss. Note the development of the square coordinated contrast.

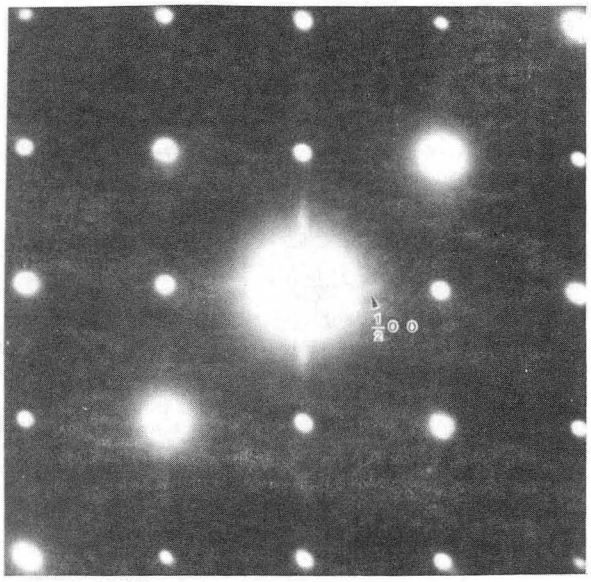

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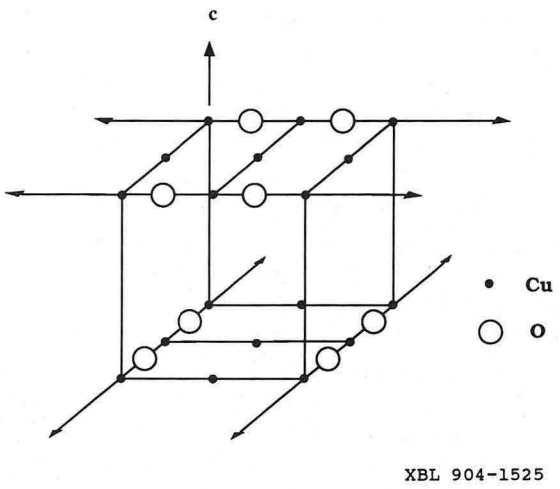
Figure 4b: Corresponding diffraction pattern. Note additional oxygen loss and the appearance of faint $<1/2\ 0\ 0>$ superlattice reflections.



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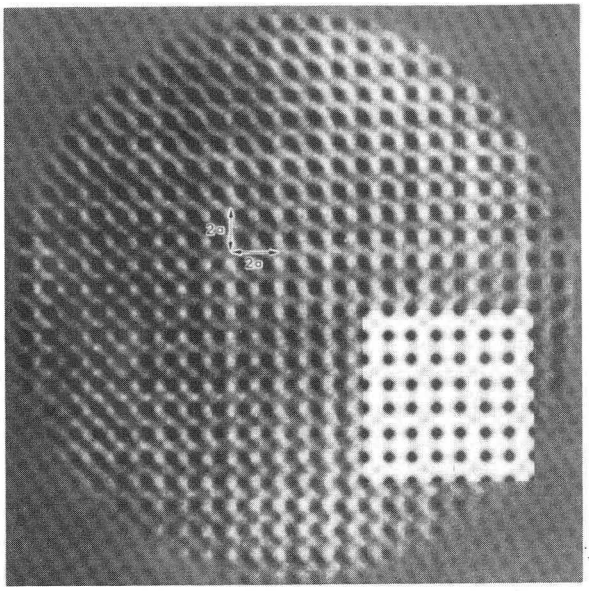
Uncorrelated Basal Plane O-Cu-O Ordering

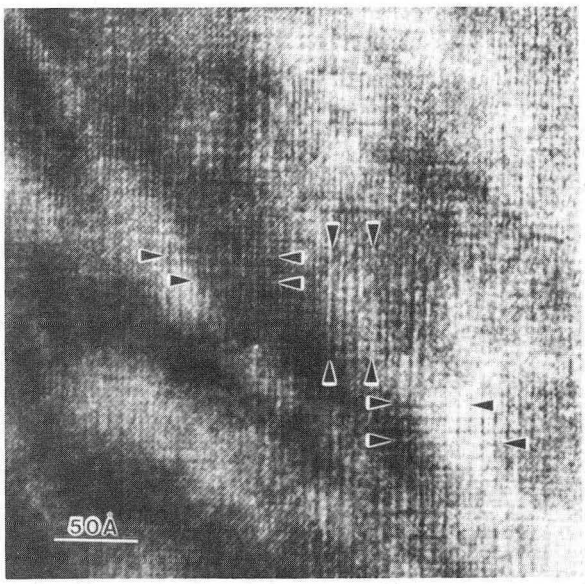
Figure 5a: Schematic model for perfectly anti-parallel states of oxygen ordering in the [001] direction of the "<10>" $2a_o$ type. Note that the out-of-plane ordering leads to a macroscopic tetragonal symmetry as is observed in the HREM images and SAD patterns.



XBL 905-1641

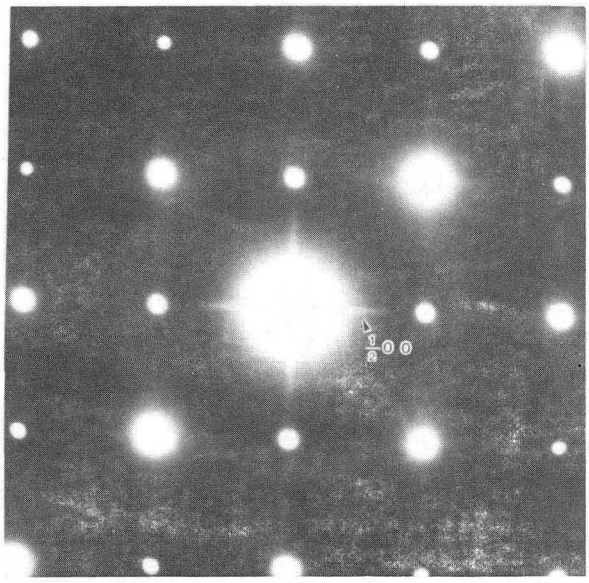
Figure 5b: Partially processed image of area extracted from Figure 4a. The image in the lower right corner is a simulated image of a completed structure having the out-of-plane correlation depicted by the model in Figure 5a.

Figure 5a) gives rise to an analogous form of contrast. A simulated and processed image are shown together in Figure 5b. As the out-of-plane correlation can be quite complex, it is difficult to obtain an exact match. However, the contrast developed by anti-parallel ordering in the [001] direction is sufficiently distinct from that produced by the correlated and the deformation structures to draw a quantitative distinction between these states. Further oxygen loss is heralded by the appearance of pronounced <1/2 0 0> superlattice reflections in the diffraction pattern (see Figure 6b) corresponding to the development of intermixed orthogonal cell-doubled orthorhombic ordering. Previous [010] microdiffraction of the z = 6.5 material displayed sharp <1/2 0 0> reflections indicating long range correlation along the [001] direction.[2] Image contrast consists of finely intermixed orthogonal $2a_o$ ordered domains producing a characteristic "microtweed" image



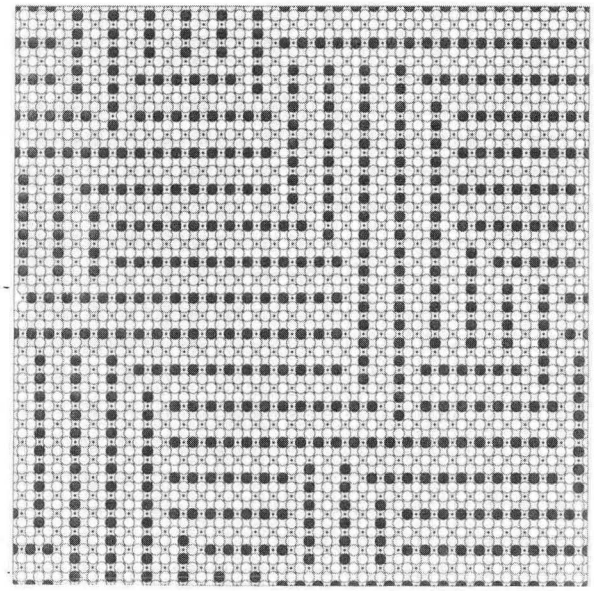
XBB 904-3155

Figure 6a: High resolution image displaying the "microtweed" contrast characteristic of the long range correlated finely intermixed Ortho II domains. Spatial extent of these domains is approximately 50Å.



XBB 904-3156

Figure 6b: Corresponding [001] diffraction pattern of area imaged in Figure 6a. Notice the development of defined <1/2 0 0> superlattice reflections indicating the development of the Ortho II structure and, hence, continued oxygen loss.



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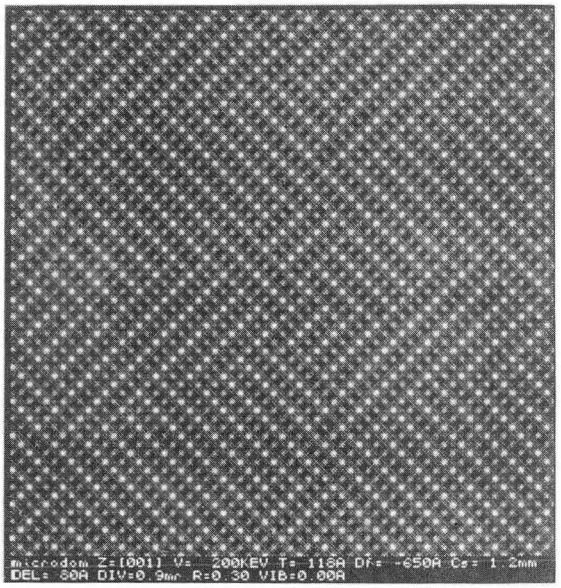

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Figure 7a: A quenched basal plane oxygen-vacancy ordered configuration generated by a Monte Carlo computer simulation. This structure exhibits the small conflicting microdomains typical of quenched $YBa_2Cu_3O_z$ specimens.[9] This structure was obtained 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.

Figure 7b: High resolution simulated image generated using the NCEMSS program and a three dimensional extrapolation of the basal plane configuration depicted in Figure 7a as input. The important feature to notice is the development of contrast fringes in the b direction of each microdomain. These dark fringes give rise to the "tweed" microstructure seen in Figure 6a. The image is rotated 45 degrees with respect to Figure 7a.

(Figure 6a). Image simulation of finely intermixed basal plane configurations of this type with perfect long range correlation produced by computer simulated quenching results in comparable image contrast (see Figures 7a and 7b).[6]

DISCUSSION

Static lattice Monte Carlo simulations based on an anisotropic Ising model[10], were used to investigate the effect of basal plane oxygen content on the kinetics of intermixed domain formation.[9] Results from this simulation aid in the interpretation of the states of [001]-correlation of basal plane partial ordering. From simulated image matching of the above variation of high resolution image contrast with in-situ oxygen loss, the following sequence of [001] basal plane ordering is found to occur: (1) Initially higher oxygen content material consists of partially correlated orthogonal domains ("diameter" ≈ 300Å) with uncorrelated overlapping boundaries, (2) further oxygen loss produces completely uncorrelated domains of approximately the same spatial extent, (3) oxygen loss leading to the development of the cell doubled ordering produces finely intermixed but highly [001]-correlated orthogonal domains of approximately 50Å in spatial extent. Monte Carlo simulation reveals that there are two sets of competing ordering interactions which effect the degree of [001]-correlation of basal plane ordering; the in-plane and out-of-plane interactions. For the in-plane interactions, the nearest and next-nearest neighbor interactions have been shown to be of primary concern in describing overall phase equilibria[11] (e.g. these are sufficient to stabilize the bulk tetragonal, orthorhombic, and cell-doubled $2a_o$ orthorhombic structures) although longer range interactions were demonstrated to be necessary to stabilize the periodicity of the lower temperature partially ordered cells.[5] Considering only these primary in-plane interactions, kinetic Monte Carlo simulations of the effect of oxygen content on the growth of partially ordered domains illustrate that at high oxygen content, the in-plane growth of homogeneously ordered domains is frustrated by the competition of equally stable mutually orthogonal or antiphase adjacent domains. However, at lower oxygen content, there are sufficient stoichiometric vacancies present to allow these quenched-in orthogonal domains to grow in experimentally realizable annealing times. The out-of-plane interaction leading to [001]-correlation of basal plane ordering would involve an interaction of yet unknown magnitude but of realizable

sign. The existence of out-of-plane correlation establishes its sign as attractive for this model. As this correlation interaction must compete with the kinetically frustrated in-plane ordering, at higher oxygen content the in-plane orthogonal frustration supersedes the out-of-plane correlation interaction. Thus higher oxygen content material consists of partially interpenetrating orthogonal microdomains with little [001]-correlation of (001) ordering, as observed by [010] microdiffraction and [001] image contrast. Oxygen loss allows the development of larger basal plane domains, but these are as yet still uncorrelated and produce the contrast observed in Figure 5b. Further oxygen loss now allows the growth of existing partially ordered domains which is biased by the [001] interaction to favor out-of-plane correlation of the basal plane structures. However, these domains are now additionally stabilized relative to each other by the effect of the out-of-plane interaction and thus are kinetically constrained to small spatial extent. This creates the highly correlated but finely intermixed orthogonal microdomains which produce the observed [001] high resolution "microtweed" contrast (see Figure 6b). It is expected that further oxygen loss would allow correlated domains to grow to larger size, but, under electron beam irradiation, this largely vacant orthorhombic structure readily transforms to the tetragonal structure making the observation of larger domains unlikely. It is felt that the correlation of the z = 7.00 orthorhombic structure is largely produced by elastic effects, neglected in this static lattice simulation, which would be expected to induce [001]-correlation at high oxygen content. As the ordering phenomena examined represent bulk transformations occurring homogeneously with time (and hence, with oxygen loss, verified by SAD evidence) in the irradiated area, it is appropriate to compare spatially separated regions within the same irradiated area, as is done here.

CONCLUSIONS

As a result of this imaging and diffraction analysis of [001] oriented $YBa_2Cu_3O_z$, it can be concluded that: (1) There is a variation in the degree of long range [001] correlation of the in-plane oxygen ordering with oxygen content. (2) This variation is the result of kinetics-limited, correlated, [001] domain growth. The second conclusion is supported by a computer simulation study of oxygen loss.

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