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EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF THE YBa$_2$Cu$_3$O$_7$/YBa$_2$Cu$_4$O$_8$ PHASE TRANSFORMATION

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EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF THE YBa$_2$Cu$_3$O$_7$/YBa$_2$Cu$_4$O$_8$ PHASE TRANSFORMATION

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The YBa$_2$Cu$_4$O$_8$ to YBa$_2$Cu$_3$O$_7$ transformation in mixed phase, superconducting YBaCuO is investigated by high resolution transmission electron microscopy and static lattice, three dimensional, Monte Carlo computer simulations. Micrographs reveal dislocations and stacking faults associated with the transformation that are accurately predicted by the calculations and seen in "snapshots" of the simulated structures. An atomic mechanism involving the intercalation of extra CuO planes by partial dislocation climb is proposed for the YBa$_2$Cu$_4$O$_8$/YBa$_2$Cu$_3$O$_7$ phase change.

1. INTRODUCTION

It is now known that superconducting YBaCuO exists in at least three well characterized phases of differing copper and oxygen content.[1-3] Due to their relative cation ratios (Y:Ba:Cu), these compounds are commonly designated as the "1-2-3", "1-2-4", and "2-4-7" phases. The first of these contains a single CuO layer in each unit cell, while the latter two occur when an additional copper oxide plane intercalates into every unit cell and every other unit cell, respectively. The additional CuO planes are found to be shifted by one half unit cell in the [010] direction.[4]

When YBaCuO crystals are grown in practice, an intergrowth of more than one phase frequently occurs in order to accommodate local deviations from the ideal stoichiometries. Recent reports in the literature indicate that certain defects related to the coexistence of two phases may actually enhance the superconducting properties of YBaCuO.[5] Therefore, the nature of the phase transformations between the various possible superconducting crystal structures, including associated defects, is of great practical interest.

2. EXPERIMENTAL PROCEDURE

The YBa$_2$Cu$_4$O$_8$ to YBa$_2$Cu$_3$O$_7$ (1-2-4 to 1-2-3) transformation is investigated here. Intermediate structures between these two phases are produced by annealing pure 1-2-4 starting material under conditions where the 2-4-7 phase is known to be stable (as described below). The resulting mixed-phase YBaCuO is characterized by means of high-resolution transmission electron microscopy (TEM).

Specimens for TEM were prepared by non-reactive ion milling at 4.0 to 4.5kV, and by crushing the material to a fine powder using procedures described in detail elsewhere.[6] The NCEMSS software package[7] developed at the National Center for Electron Microscopy was used for simulation of high-resolution TEM images.

Homogeneous, single-phase 1-2-4 material was fabricated by sintering a stoichiometric mixture of yttria, barium oxide, and copper oxide for 15 hours at 900°C in an oxygen pressure of 200 bar. This material was then re-ground, compacted, and annealed for an additional 15 hours under the same conditions. X-ray diffraction of the resulting material displayed a single sharp peak corresponding to the c-spacing of the pure 1-2-4 structure.

In order to produce regions of lower copper concentration, this 1-2-4 material was heated to 930°C at an oxygen pressure of slightly less than 1 bar. The specimen was then slowly cooled and held at 775°C until x-ray diffraction showed that approximately 10% of the material had been converted to the 1-2-3 phase. Subsequent TEM imaging was carried out using a JEOL *JEM200CX* operating at 200kV and the Berkeley Atomic Resolution Microscope operating at 800kV.

3. EXPERIMENTAL RESULTS

The x-ray diffraction study confirmed that the starting material was single-phase, polycrystalline $YBa_2Cu_4O_8$ (1-2-4). After annealing, high-resolution TEM imaging showed that the resulting material was multi-phase. A variety of crystallographic defects were found to exist, as expected when a mixture of phases with differing lattice parameters is present. Many of these can be seen in Figure 1. The defects observed were volumetric, planar, and linear in nature, and an overview is given in earlier work.[8] Computer simulation of high-resolution images confirms that the planes which show bright white contrast in Figure 1 are indeed the CuO planes, and that the Y and Ba positions appear as prominent black dots, while the CuO_2 planes produce very weak contrast.

The most common planar defects observed in the mixed-phase YBaCuO are the ones of interest in the present study. These are extrinsic stacking faults of the type $R = 1/6[031]$, and have been described previously by Zandbergen et al.[9] 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. One fault of this type is indicated by ① in Figure 1. It can be seen that
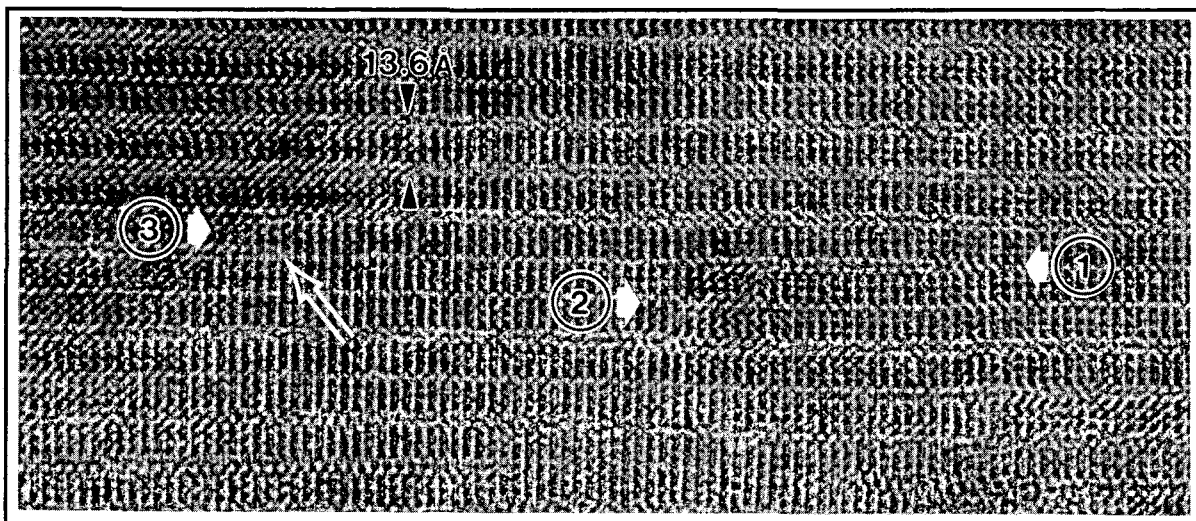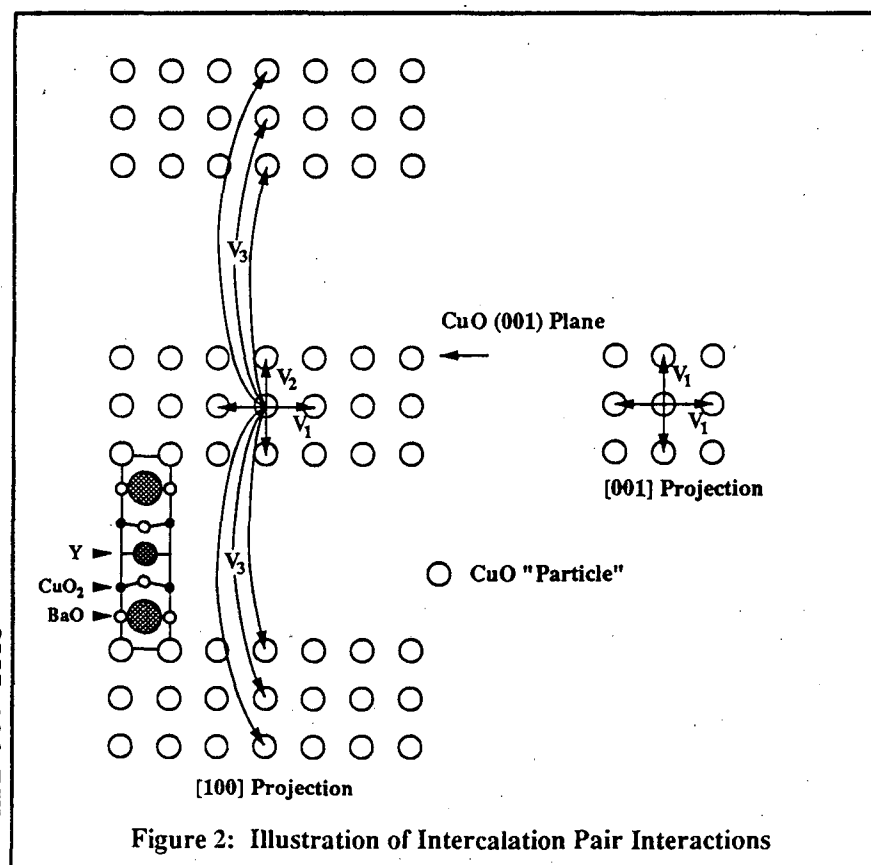

Figure 1: High resolution TEM image of mixed phase YBaCuO. Features indicated by ①, ②, and ③ correspond to the simulation generated defect structures depicted in Figure 5.

the lateral dimensions of this fault are quite small, extending only approximately 50Å in the (001) plane. However, the associated strain field (revealed by deviations from axial orientation in the micrograph) is much larger in spatial extent: approximately 80Å in the [001] direction and 100Å in the (001) plane. When the lattice strain from any source reaches a certain level, it is seen that the CuO planes may compensate by forming "steps", as at ② in Figure 1.

Line defects which could be identified as partial dislocations associated with the type of stacking fault just described were of course also prevalent in the mixed-phase material; one of these is indicated by the hollow arrow in Figure 1. It should be noted that when two of these dislocations, with opposite orientations, are in close proximity to each other and separated in the [001] direction by a single Ba-Y-Ba stacking sequence, a dislocation dipole is formed. Because of the complementary arrangement of the two dislocations in this case, the resulting strain field is quite small, as can be seen at ③ in Figure 1.

4. COMPUTER MODELING

A static lattice, three-dimensional Monte Carlo calculation was used to model the 1-2-3/1-2-4 transformation. The simulation is based on an intercalation scheme[10] where copper oxide "particles" of a certain critical radius are allowed to move into the lattice parallel to existing CuO (001) planes. The CuO particles move into the three-dimensional lattice from simulated grain boundaries consisting of (100) planes bounding the "grain" under consideration. Once in the lattice, these particles diffuse in the canonical mode, otherwise known as a site exchange transport mechanism. For a simulated 1-2-3 structure, the configurational environment for particles entering above the single existing CuO plane

Figure 2: Illustration of Intercalation Pair Interactions

is identical to that for particles entering below it. Thus, planar regions corresponding to these two adjacent planes are included in the formulation of the Monte Carlo lattice, creating a set of three potential CuO planes for each YBaCuO layer (see Figure 2).

It is found that three pair interactions are adequate to model the phase transformation: V_1, a basal plane nearest neighbor interaction, V_2, an out-of-plane nearest neighbor interaction, and V_3, an inter-(001) plane interaction. These interactions are illustrated for a single central CuO site in Figure 2 but apply identically to any site in the lattice of the simulation. Since the CuO planes enter the material as continuous sheets, forming the partial dislocations observed, the V_1 interaction is taken to be attractive to model this clustering behavior. Purely elastic effects establish the co-linear V_2 and V_3 interactions to be repulsive and to decrease in magnitude with distance. Unique values of V_2 and V_3 are obtained for this simulation by assuming an average over the small spatial variation of these parameters within a set of CuO planes. Making a canonical choice of the magnitudes of the interaction parameters based on the above considerations, the pair interactions for the current simulations were chosen such that $V_2/V_1 = -2.0$ and $V_3/V_1 = -1.0$ where $V_1 = -1.0$ is used as a temperature scaling factor. Rigid lattice configurations from this simulation are subsequently relaxed so that the output reflects elastic contributions contained in the interaction parameters.

5. DISCUSSION

As the copper oxide chemical potential (a linear function of the logarithm of oxygen partial pressure) for the CuO material in the simulation lattice is varied at constant temperature, broad concentration plateaus develop, as can be seen in Figure 3. Simulation snapshots taken in the phase
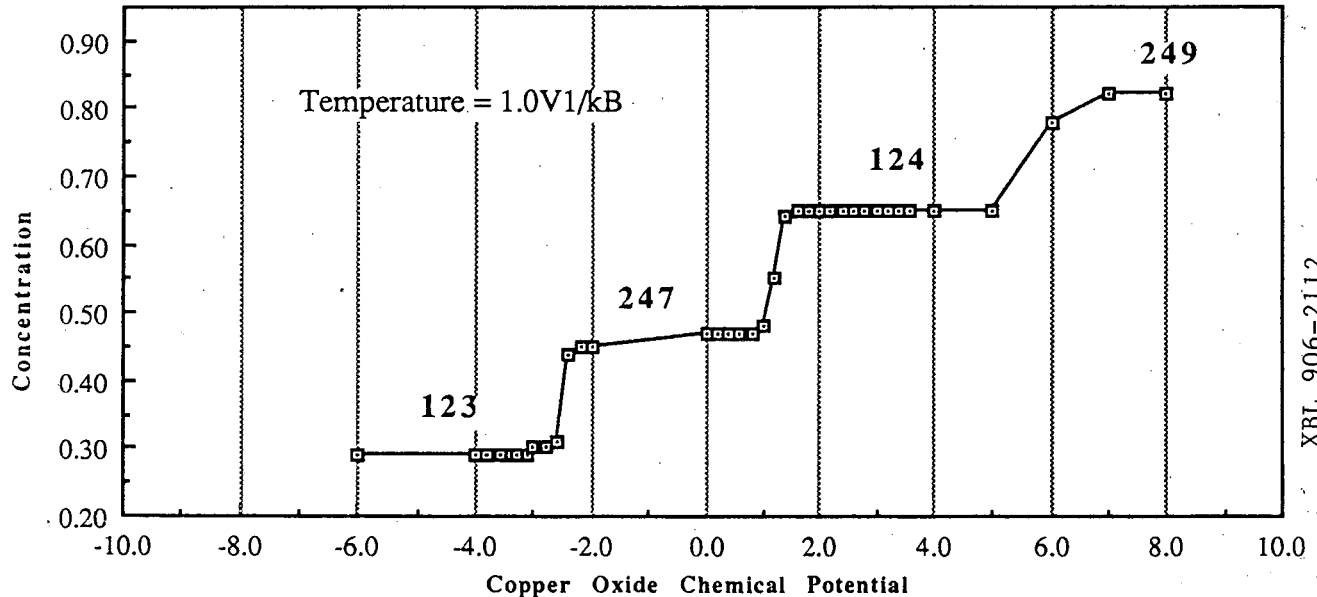

Figure 3: CuO Concentration vs. Chemical Potential

"plateau" regions for moderate chemical potential values reveal that the atomic arrangements correlate with the well known 1-2-3, 2-4-7, and 1-2-4 equilibrium structures. At higher chemical potentials new concentration plateaus appear. These are found to correspond to 2-4-9 and 1-2-5 structures, both of which contain some triple CuO layers. The corresponding five phases of YBaCuO are illustrated schematically in Figure 4. It is found that each transformation between these YBaCuO
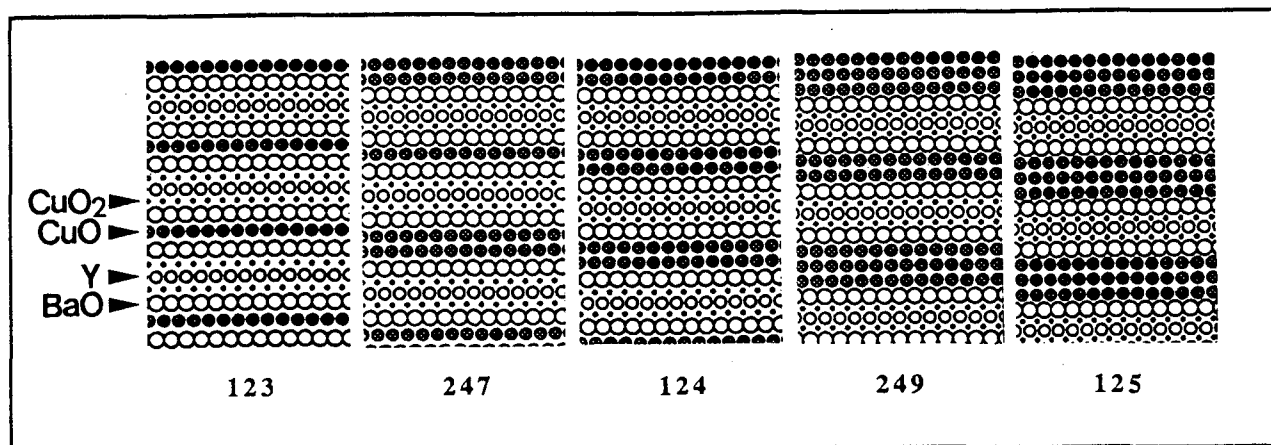
Figure 4: Calculated YBaCuO Equilibrium Phases.

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phases appears to display a small hysteresis in copper oxide chemical potential. The variation of CuO concentration with chemical potential is found to be in remarkable agreement with the experimental results of Karpinski et al.[11]

By examining snapshots obtained during the 1-2-4 to 1-2-3 transformation, it is seen that the predominant defect structures observed experimentally are accurately predicted (compare Figures 5 and 1). In addition, recent electron microscopy work[12] has suggested the existence of local regions of the previously unobserved triple CuO-layer configurations. By making a rough fit of the simulation results with available experimental thermodynamic results[13] obtained at 950°C, it is found that the 2-4-9 phase transformation would occur at very high oxygen pressures (roughly, 500-1000 bar), under conditions where sufficient copper is available. Thus it is understandable why these higher CuO content phases are neither readily formed nor commonly observed.

The way in which a single CuO layer meets a double layer is determined by the relative magnitudes of the interaction potentials V_1 and V_2. Since in the current model, $V_1 < V_2$, the lowest energy configuration will be one in which the single CuO plane of the 1-2-3 phase remains continuous into the 1-2-4 phase, with a second CuO plane appearing next to it in order to form the new phase. The alternate configuration (energetically favorable for $V_1 > V_2$), where the single CuO plane in the 1-2-3 phase terminates at the midpoint between the two CuO planes in the 1-2-4 phase, is therefore not expected. As can be seen in the image shown in Figure 1, the $R = 1/6[031]$ stacking faults described above correspond to the former arrangement, and confirm that this is the one which actually occurs in the mixed phase YBaCuO.

Using the anisotropic Landau-Ginsberg theory[14-16], the coherence length for the superconducting $YBa_2Cu_3O_7$ phase has been calculated to be 3.8Å perpendicular to and 35Å parallel to the (001) planes.[17] These dimensions correspond closely to those of the most common stacking fault defects observed as a result of the 1-2-4 to 1-2-3 transformation (see Figure 1), and this suggests that significant effects on superconducting properties can be expected. In fact, there is now experimental evidence[5] showing a dramatic increase in critical current density for 1-2-3 phase material containing a small residual amount of the 1-2-4 phase (i.e., "pieces" of extra CuO planes), indicating that these defects are acting as flux pinning centers. However, it is worth noting that the
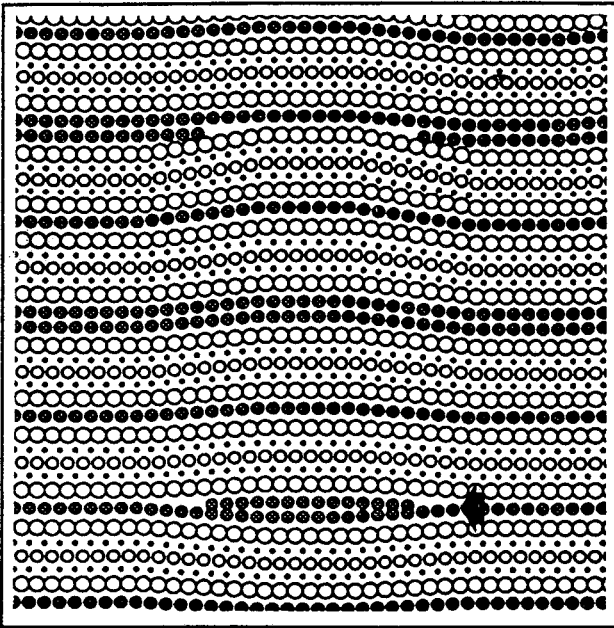
Figure 5a: Simulation-generated snapshot of mixed phase structure obtained during the 2-4-7 to 1-2-3 transformation for a chemical potential of -3.4 and a temperature of 1.0 $|V_1|/k_B$. Note the presence of the small planar defect corresponding to that delineated by ① in Figure 1.
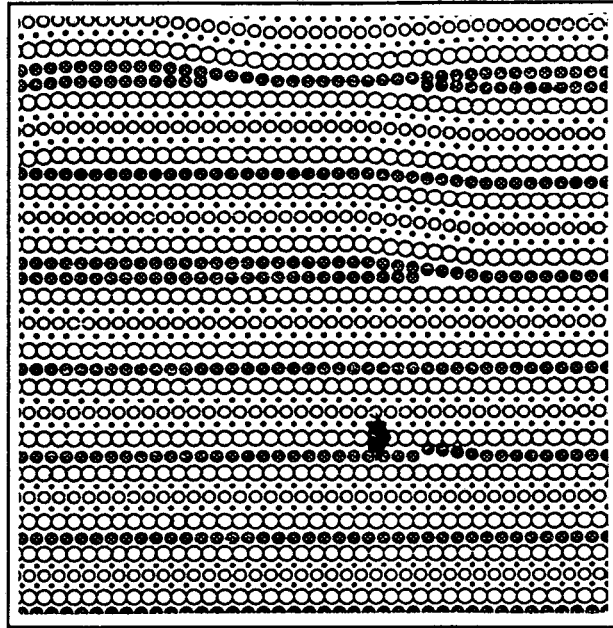
Figure 5b: Snapshot obtained during the 2-4-7 to 1-2-3 transformation at a chemical potential of -3.6 and a temperature of 1.0 $|V_1|/k_B$. Defects of the type indicated in this figure correspond well with those observed in HREM images (see ② in Figure 1). Such shifts are found to occur in response to a local strain field. The corresponding strain field for the above defect is located to the lower right of this snapshot (out of the field of view).
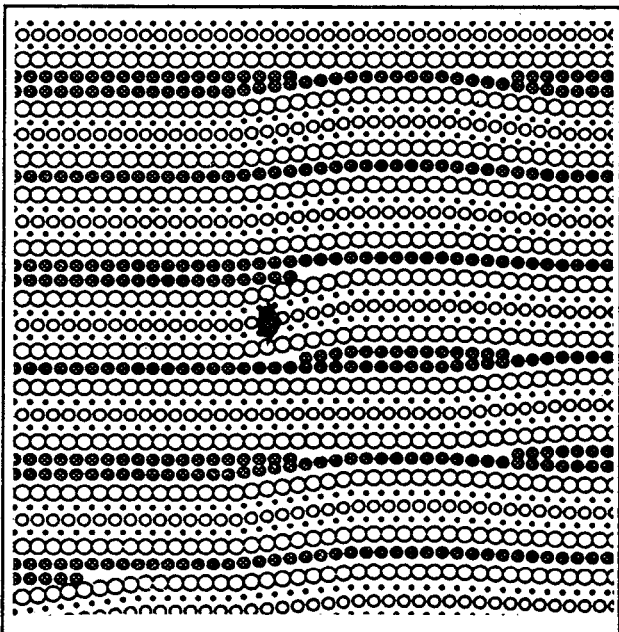
Figure 5c: Snapshot obtained during the 2-4-7 to 1-2-3 transformation at a chemical potential of -3.4 and a temperature of 1.0 $|V_1|/k_B$. Note the presence of complimentary, nearly strain-free dislocations corresponding to that delineated by ③ in Figure 1.
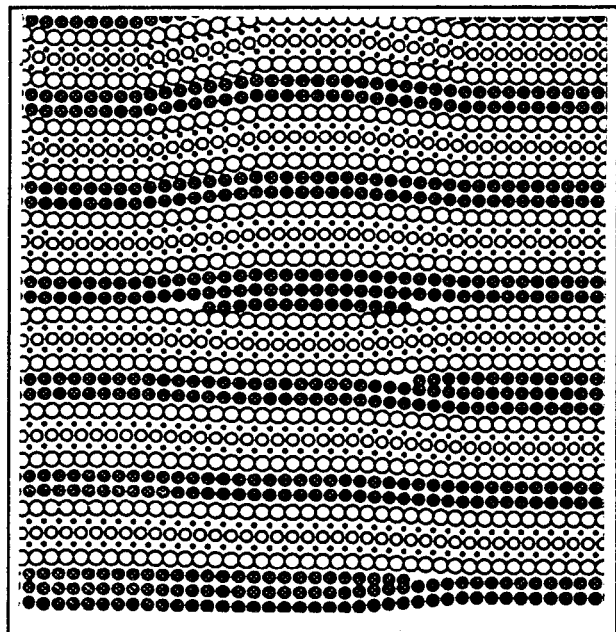
Figure 5d: Snapshot obtained during the 1-2-5 to 2-4-9 transformation at a chemical potential of 5.0 and a temperature of 1.0 $|V_1|/k_B$. This structure illustrates mixed 2-4-9 and 1-2-5 phases obtained at higher chemical potentials.

dimensions of the much larger strain field actually exceed the coherence length, particularly in the [001] direction.

The nature of the stacking faults described here suggests that the 1-2-3/1-2-4 transformation propagates in either direction by means of a partial dislocation climb mechanism. In this case, even though the occupation of CuO planes is changing as the transformation progresses, the necessary rearrangement of the overall crystal structure is minimal. The climb mechanism is also well confirmed by configurational data from the intercalation simulation. Grain boundaries and other pre-existing crystallographic defects provide sites at which the strain necessary to nucleate this type of transformation is readily accommodated. In addition, since diffusion of Cu in or out of the material is required during any transformation between different CuO-layer structures, it is expected that grain boundaries can play a role in initiating this transformation by providing a high diffusivity path. In fact, previous studies[18,19] include high resolution TEM images of YBaCuO which clearly show the intercalation of new CuO planes from grain boundaries.

6. SUMMARY AND CONCLUSIONS

A variety of crystallographic defects has been found in "partially converted" mixed phase YBaCuO. These are predominantly extrinsic stacking faults and their associated partial dislocations which accompany the transformation from the 1-2-4 to the 1-2-3 structure, and which are predicted by Monte Carlo calculations that model the intercalation of CuO planes. The simulations furthermore accurately describe the formation and evolution of an entire family of layered equilibrium and defect crystal structures in YBaCuO. Based upon these findings, an atomic mechanism for the transformation from the 1-2-4 phase to the 1-2-3 phase is proposed, which involves climb of partial dislocations associated with CuO planes.

The defects observed in 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 here exist over small enough spatial extent to serve as effective flux pinning centers to measurably increase the critical current (J_c) values of these oxide superconductors. Because these defects are associated with the 1-2-3/1-2-4 phase transformation, a greater understanding of the transformation (ultimately leading to precise control over it) may allow the fabrication of superconducting material more suitable for applications than any now available.

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