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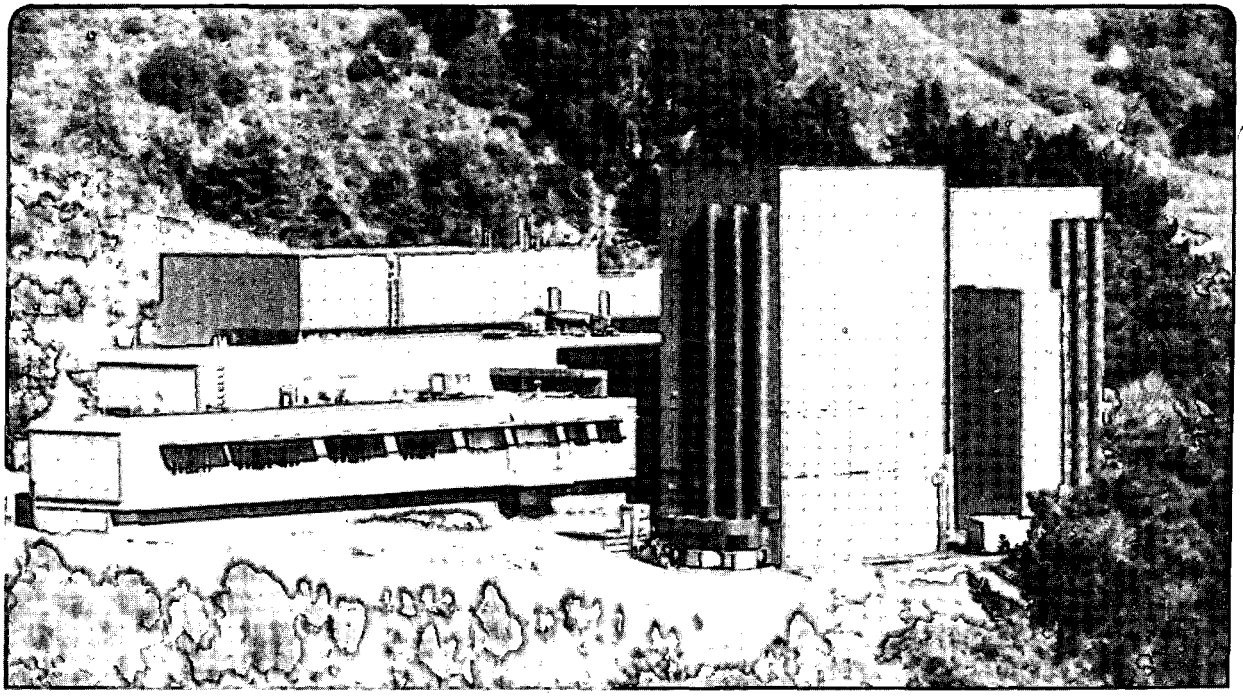

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THEORETICAL MODELING AND EXPERIMENTAL CHARACTERIZATION OF PLANAR DEFECTS IN $Y_2Ba_4Cu_{6+x}O_{14+x}$

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Crystallographic defects and phase transformations in the system $Y_2Ba_4Cu_{6+x}O_{14+x}$ ($0 \leq x \leq 4$) are investigated by high resolution transmission electron microscopy (TEM) and static lattice, three dimensional Monte Carlo computer simulations. High resolution images of partially transformed (x=2 to x=1) material reveal a prevalence of CuO planar defects (stacking faults) associated with the transformation and an absence of disturbance to the perovskite Ba-Y-Ba blocks. An atomic mechanism involving the intercalation and removal of extra CuO planes by partial dislocation climb, and requiring only a-b plane diffusion, is developed for the formation of such planar defects during changes in the layered YBaCuO crystal structure. Monte Carlo simulations based on the proposed transformation mechanism accurately reproduce the observed defects and known equilibrium structures.

1. INTRODUCTION

It has been widely documented that crystallographic defects can affect superconducting properties in various ways, and the high-temperature oxide superconductors are no exception to this generalization. Recent evidence[1-3] suggests that certain defects significantly enhance intragranular critical current (J_C) values in superconducting YBaCuO. One practical approach to producing such defects is by means of a phase transformation. Phase transformations where only the number of CuO layers in a unit cell changes lead to a family of related crystal structures[4-7] with stoichiometries $Y_2Ba_4Cu_{6+x}O_{14+x}$. When YBaCuO crystals are grown in practice, an intergrowth of more than one of these phases frequently occurs in order to accommodate local deviations from the ideal stoichiometries. Because of reports correlating the resulting faulted microstructures with improved superconducting properties, the nature of defects and mechanism of defect formation during phase changes related to CuO plane (Cu-O chain layer) occupation in YBaCuO is of great practical interest.

2. EXPERIMENTAL PROCEDURE

An experimentally obtainable example of the general structure change in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system occurs when the stoichiometric parameter x varies from 2 to 1 during the $YBa_2Cu_4O_8$ to $Y_2Ba_4Cu_7O_{15}$ (1-2-4 to 2-4-7) transformation. Partial transformation induced by short-term annealing of pure 1-2-4 material yields a mixed phase microstructure (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.[8] The NCEMSS software package[9] 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.

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. High-resolution TEM imaging of this material was then performed using a JEOL *JEM200CX* operating at 200kV and the Berkeley Atomic Resolution Microscope operating at 800kV.

3. EXPERIMENTAL RESULTS

The x-ray diffraction carried out on the as-sintered material displayed a single sharp peak corresponding to the c-spacing of the 1-2-4 structure, confirming that pure, single-phase, polycrystalline $YBa_2Cu_4O_8$ was produced. Electron diffraction patterns of such material display a single, well-defined periodicity in the c-direction, an additional indication that only one phase is present (as shown in Figure 1a). After subsequent annealing, the material yielded an electron diffraction pattern exhibiting marked streaking along [001], indicating that the resulting material is highly faulted (Figure 1b). In further analysis using high-resolution TEM imaging, a variety of crystallographic defects were found to exist in this material, as expected when a mixture of phases with differing lattice parameters is present. A number of these can be seen in Figure 2. Computer simulation of high-resolution images confirms that the planes which show bright white contrast in the figure 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.

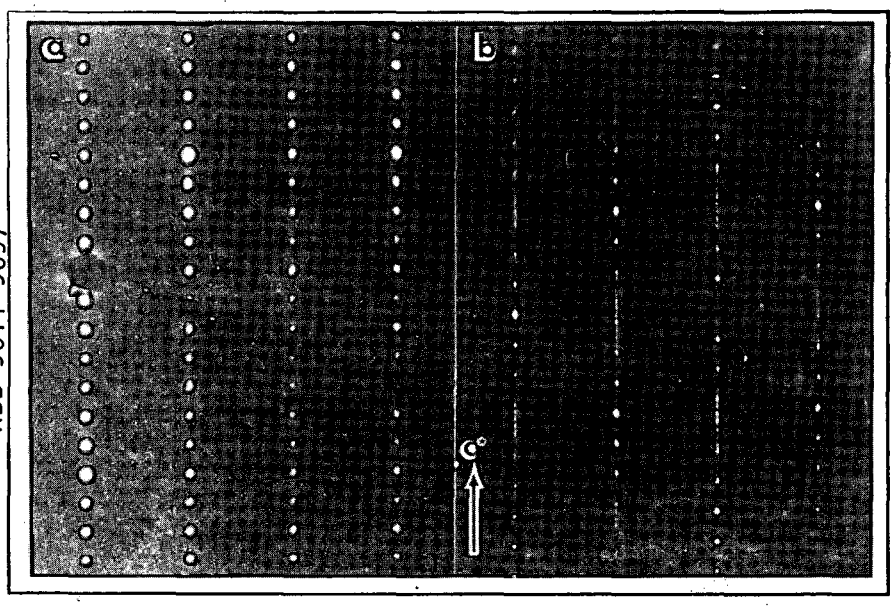

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Figure 1: (a) Diffraction pattern of phase 1-2-4 material. (b) Electron diffraction pattern of mixed phase YBaCuO material, showing streaking in [001] direction.

The most common planar defects observed are extrinsic stacking faults of the type R = 1/6[031].[10] Such stacking faults are characteristic of transformations between structures in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system, and occur at locations where the number of CuO layers per unit cell changes (e.g., from single to double). One fault of this type is indicated by ① in Figure 2. It can be seen that the dimensions of this fault are quite small, with lateral extent of 50Å in the (001) plane. However, the resulting strain field (revealed by deviations

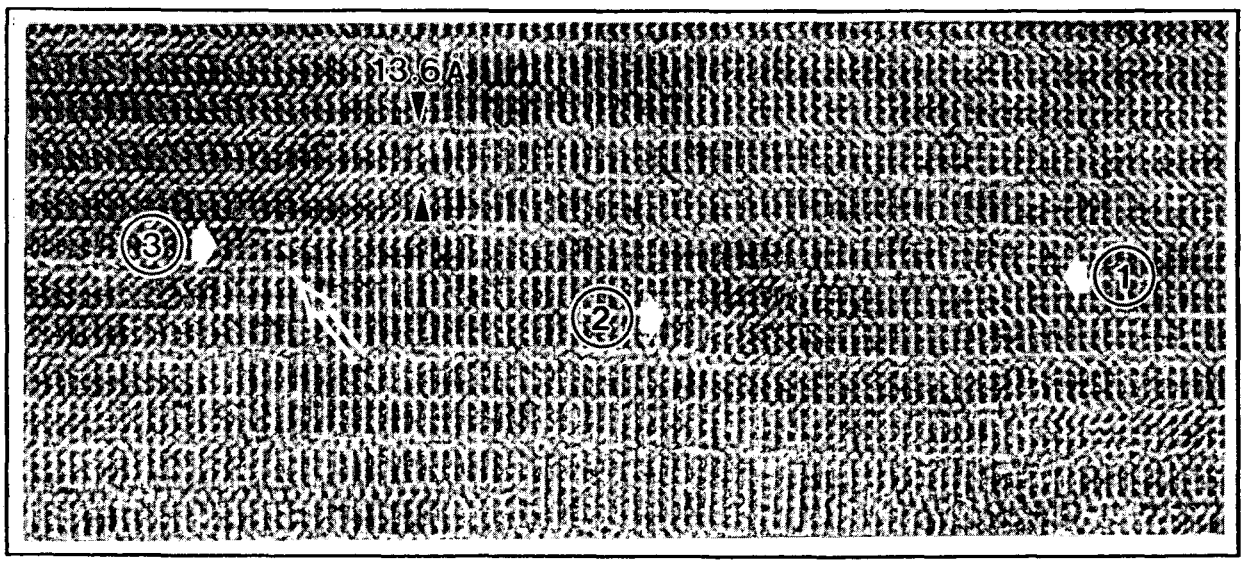

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Figure 2: High resolution TEM image of mixed phase YBaCuO.

from axial orientation in the micrograph) is much larger, extending over approximately 80Å in the [001] direction and 100Å perpendicular to this. One of the partial dislocations associated with this type of stacking fault is indicated by the hollow arrow in Figure 2. Two dislocations with opposite orientations, in close proximity to each other and separated in the [001] direction by a single Ba-Y-Ba stacking sequence, form a dislocation dipole with characteristically restricted strain field, seen for example at ②. Under sufficiently large strain, the CuO planes further respond by forming "steps", as at ③.

4. TRANSFORMATION MECHANISM

Previous work[11] has demonstrated that structural defects in the interior of the unit cell produce notable contrast in high-resolution TEM images. However, the defects observed in the present study were confined to the CuO basal planes (excluding the small displacements due to the stacking fault strain). The observation that the partially transformed 1-2-4 material contains a high density of extrinsic stacking faults, involving only the basal CuO plane, suggests that the transformation to phases of lower copper content proceeds via dislocation climb. Such a mechanism necessitates the diffusion of copper and oxygen to or from the dislocation site. The absence of any structural defects between basal planes of the partially transformed material, which would be expected in the event of c-axis diffusion, implies that the rearrangement of material is limited to the basal plane, making c-axis diffusion of copper and oxygen unlikely as part of the transformation mechanism. This suggestion is consistent with an investigation of available diffusion paths in the YBaCuO structures.

While atomic packing is not strictly dense in YBaCuO, the channels in the [001] direction of the unit cell are so small as to restrict severely the interstitial passage of the Cu^{2+} and O^{2-} ions. In particular, the BaO planes contain interstices no larger than 1.2Å in diameter, well below the ionic diameters for Cu^{2+} (1.44Å) and O^{2-} (2.64Å).[12] The same investigation reveals that the largest pores in the YBaCuO structure lie along the [010] direction and are sufficient to allow interstitial diffusion of copper in the a-b plane, but not of oxygen. However, oxygen diffusion in the basal plane of YBaCuO, widely studied for its role in the orthorhombic to tetragonal transformation in $YBa_2Cu_3O_{7-z}$, is known to occur.[13] The diffusion of oxygen must therefore occur by a slower substitutional mechanism in the basal plane, and this is expected to be the rate limiting step in the transformation. Thus transformations where x varies in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system proceed via partial dislocation climb accomplished by substitutional diffusion of oxygen in the basal plane accompanied by the cooperative basal plane diffusion of copper.

The partial dislocations associated with extrinsic stacking faults in the CuO planes are most easily nucleated at existing crystallographic defects such as grain boundaries and free surfaces where the necessary strain can be readily accommodated. These planar defects act as heterogeneous nucleation sites, and high resolution TEM images previously published in studies of other topics[14,15] indeed clearly show the intercalation of extra CuO planes originating from grain boundaries. Dislocations thus created climb in directions governed by a chemical gradient imposed by the transformation conditions. The oxygen partial pressure is likely to be the critical variable for the transformation potential since, as mentioned above, the diffusion of oxygen in this transformation is the rate limiting step.

5. COMPUTATIONAL INVESTIGATION

To characterize the proposed transformation mechanism, a static lattice, three-dimensional Monte Carlo calculation is used to simulate the evolution of the crystal structure as x varies from 0 to 4 in $Y_2Ba_4Cu_{6+x}O_{14+x}$. The calculation simulates dislocation climb utilizing an intercalation scheme[16] where copper oxide "particles" of a certain critical radius (ascertained by analysis of high resolution TEM micrographs) are allowed to move from simulated (100) grain boundaries into the lattice, parallel to existing CuO (001) planes. Once in the lattice, these particles diffuse in the canonical mode, simulating the substitutional motion of oxygen during this transformation. In the 1-2-3 structure, the configurational environment for particles entering above the existing single CuO plane is identical to that for particles entering below it. Planar regions corresponding to these two adjacent CuO layers are therefore included in the formulation of the Monte Carlo lattice, resulting in a set of three potential CuO planes for each Ba-Y-Ba stacking sequence (see Figure 3).

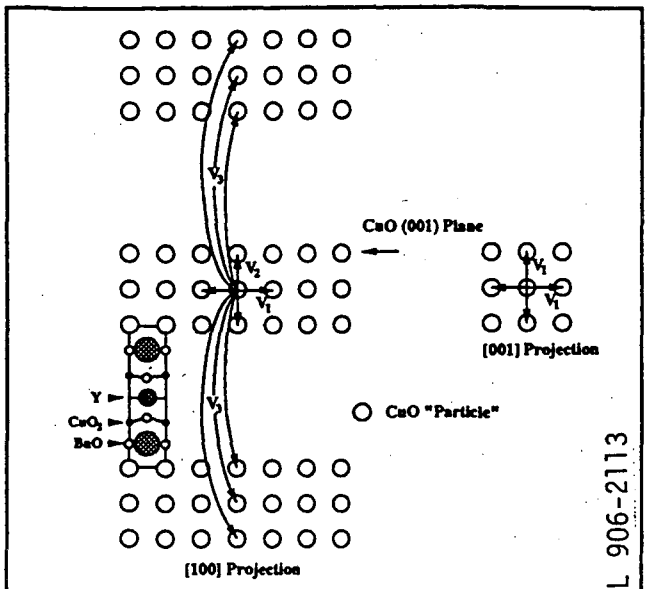

Figure 3: Illustration of Intercalation Pair Interactions

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 (Figure 3). 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, pair interactions for the 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. Note that 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.[17] Rigid lattice configurations from this simulation are subsequently relaxed so that the output reflects elastic contributions contained in the interaction parameters.

6. DISCUSSION

Monte Carlo simulations performed at different values of copper oxide chemical potential, plateaus of constant concentration develop, as discussed in previous work.[18] Simulation snapshots taken in the phase "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 calculated variation of CuO concentration with chemical potential agrees remarkably well in form with experimental results recently published by Karpinski *et al.*[19], in which concentration is plotted as a function of oxygen pressure during processing. This agreement equates the simulation CuO chemical potential with the experimental oxygen partial pressure to within a constant, supporting the assertion that oxygen diffuses substitutionally, since the relationship between experiment and simulation further implies that oxygen diffusion (and hence the oxygen chemical potential) is indeed the rate determining step of the transformation. It is also worth noting that copper as well as oxygen is necessary to drive the transformation to higher values of x. While oxygen in gaseous form can easily be introduced, the availability of copper is likely to limit transformations in this direction. This could explain why such transformations (e.g. 1-2-3 to 1-2-4) have not yet been achieved in bulk.

In simulation snapshots of the 1-2-4 to 2-4-7 transformation, the predominant experimentally observed defect structures are accurately reproduced (cf. Figures 4a and 1). The present study suggests that the equilibrium structures in the x = 0 to 2 regime of the system will contain only single and double CuO planes. However, recent electron microscopy results[20] have identified local occurrences of triple CuO plane configurations arising during this same transformation. This apparent anomaly can be explained purely in terms of intercalation kinetics. As the 1-2-4 to 1-2-3 transformation progresses, atoms within the CuO layers diffuse outward to grain boundaries due to the imposed chemical potential gradient (equivalent to the experimental procedure of annealing in an atmosphere where the 1-2-3 structure is stable). Monte Carlo simulations show that, during this diffusion process, localized regions of triple layer structures can and in fact do occur; this can be thought of as a "pile up" of the clustered CuO particles. The elastic distortion resulting from such a localized triple CuO layer will be minimized if such features are associated with adjacent single layer regions (1-2-3 structures) in the [001] direction. Thus, these defects will appear as localized, quasi-ordered sequences of 1-2-5 and 1-2-3 structures, alternating along the c-axis in a ratio

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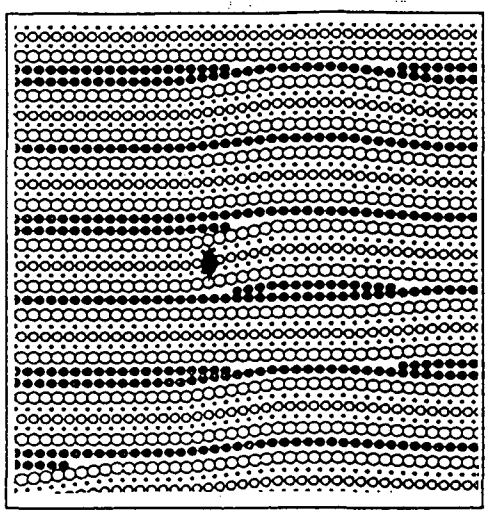

Figure 4a: Snapshot obtained during the 2-4-7 to 1-2-3 transformation at a chemical potential of -3.4 and a temperature of 1.0 $|V_1|/k_B$. Note the presence of complimentary, nearly strain-free dislocations corresponding to that delineated by ② in Figure 2.

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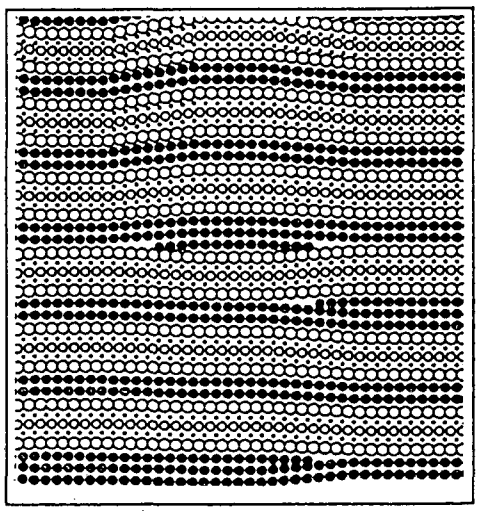

Figure 4b: Snapshot obtained during the 1-2-5 to 2-4-9 transformation at a chemical potential of 5.0 and a temperature of 1.0 $|V_1|/k_B$. This structure illustrates mixed 2-4-9 and 1-2-5 phases obtained at higher chemical potentials.

averaging to the overall composition at that point in the transformation. This description is attractive as it involves only in-plane diffusion and avoids invoking high energy c-axis diffusion across stable perovskite blocks, which, as previously noted, is an unlikely diffusion path in the YBaCuO layered structures.

Using the anisotropic Landau-Ginsberg theory[21-23], 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.[24] These dimensions correspond closely to those of the most common stacking faults observed as a result of the 1-2-4 to 2-4-7 transformation, and thus these defects are likely to serve as effective flux pinning centers. Increased flux pinning would explain the increased intragranular critical current values reported for YBaCuO with this type of faulted microstructure.

7. SUMMARY AND CONCLUSIONS

High resolution transmission electron microscopy investigation of mixed-phase YBaCuO reveals that extrinsic CuO basal plane stacking faults and their associated partial dislocations are the predominant defects produced during this transformation. The nature of these stacking faults suggests that the general transformation in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system propagates by means of partial dislocation climb driven by the substitutional diffusion of oxygen in the basal plane. This diffusion mechanism is demonstrated to be the most probable route for copper and oxygen transport in the YBaCuO structure. Grain boundaries and other pre-existing crystallographic defects provide sites at which the strain produced by this type of dislocation is readily accommodated, facilitating nucleation of the phase transformation.

Monte Carlo calculations which simulate the climb of partial dislocations by the intercalation of CuO planes accurately reproduce the defects observed experimentally. Furthermore, the computer investigation correctly describes the formation and evolution of the 1-2-3, 2-4-7, and 1-2-4 structures. The existence of crystal structures containing more than two adjacent CuO layers is predicted at higher oxygen partial pressures.

The defects observed in mixed-phase YBaCuO specimens are reported 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 values of these oxide superconductors. Because these defects are associated with phase transformations in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system, 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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