Lawrence Berkeley National Laboratory
Recent Work

Title

Copper-Oxygen Intercalation and Related Phase Transformations in YBaCuO

Permalink

https://escholarship.org/uc/item/58c7n816

Authors

Fendorf, M.
Burmester, C.P.
Wille, L.T.
et al.

Publication Date

1990-07-01

eScholarship.org Powered by the California Digital Library
University of California

LBL-29680
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Applied Physics Letters

Copper-Oxygen Intercalation and Related Phase Transformations in YBaCuO

M. Fendorf, C.P. Burmester, L.T. Wille, and R. Gronsky

July 1990

| LOAN COPY |
|Circulates |
|for 2 weeks| Bldg. 50 Library.
Copy 2
LBL-29680

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

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-29680

COPPER-OXYGEN INTERCALATION AND RELATED PHASE TRANSFORMATIONS IN YBaCuO

M. Fendorf*, C.P. Burmester*, L.T. Wille** and R. Gronsky*

*National Center for Electron Microscopy
Lawrence Berkeley Laboratory, University of California
Berkeley, CA. 94720

**Florida Atlantic University
Science & Engineering Bldg.
Boca Raton, FL. 33431

Submitted to Applied Physics Letters

This work was supported a University of Houston subcontract under DARPA Grant No. MDA972-88-J-1002 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

COPPER-OXYGEN INTERCALATION AND RELATED PHASE TRANSFORMATIONS IN YBaCuO

M. Fendorf, C.P. Burmester, L.T. Wille†, and R. Gronsky

Department of Materials Science and Mineral Engineering, University of California at Berkeley, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory,1 Cyclotron Road, Berkeley, CA 94720, U.S.A.
†Department of Physics, Florida Atlantic University, Boca Raton, FL 33431, U.S.A.

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 Monte Carlo computer simulations. Micrographs reveal dislocations and stacking faults associated with the diffusion of copper and oxygen as the stoichiometric parameter x varies locally during a phase transformation, and these defects are accurately reproduced by the calculations in "snapshots" of the simulated structures. In addition, the simulations show the occurrence of the well-known $YBa_2Cu_3O_7$, $YBa_2Cu_4O_8$, and $Y_2Ba_4Cu_7O_{15}$ phases and predict the formation of $Y_2Ba_4Cu_9O_{17}$ and $YBa_2Cu_5O_9$ structures at higher oxygen partial pressures. Based on experimental images and Monte Carlo results, an atomic mechanism involving the intercalation and removal of extra CuO planes by partial dislocation climb is proposed for changes in the layered YBaCuO crystal structure.

The nature of phase changes related to CuO plane (Cu-O chain layer) occupation in YBaCuO is of great practical interest due to recent reports[1] correlating mixed phase microstructures with enhanced superconducting properties. Phase changes of this type, where only the number of CuO layers in a unit cell changes, lead to a family of related crystal structures with stoichiometries $Y_2Ba_4Cu_{6+x}O_{14+x}$. An experimentally obtainable example of the general structure change in this system occurs when 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 (see Figure 1). X-ray diffraction, electron diffraction, and high-resolution TEM reveal a variety of structural accommodation defects.[2] The most common defects observed in mixed-phase YBaCuO are extrinsic stacking faults with displacement vector **R** = 1/6[031],[3] along with bounding partial dislocations. These defects are found to be characteristic of the 1-2-4 to 2-4-7 transformation. A fault of this type appears at ① in Figure 1, with lateral extent of 50Å in the (001) plane. However, the associated strain field (revealed by deviations from axial orientation in the micrograph) is much larger, extending over approximately 80Å in the [001] direction and 100Å in the (001) plane. One of the partial dislocations is indicated by the hollow arrow in Figure 1, and a dislocation dipole with its characteristically restricted strain field can be seen at ②. Under sufficiently large strain, the CuO planes further respond by forming "steps", as at ③.

A static lattice, three-dimensional Monte Carlo calculation is used in this study 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 is based on an intercalation scheme[4] 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. 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. 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. 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. Rigid lattice configurations from this simulation are subsequently relaxed so that the output reflects elastic contributions contained in the interaction parameters. The derivation of this model will be discussed in greater detail in a forthcoming publication.

As the chemical potential of CuO in the simulation lattice is varied at constant temperature, broad concentration plateaus develop (Figure 2). Simulation "snapshots" in the phase plateau regions at moderate values of chemical potential reveal that the atomic arrangements correlate with the well known 1-2-3 (x = 0), 2-4-7 (x = 1), and 1-2-4 (x = 2) equilibrium structures.[5,8] This calculated variation of CuO concentration with chemical potential agrees remarkably well in form with the experimental results recently announced by Karpinski *et al.*[9] At higher chemical potentials new concentration plateaus are predicted, corresponding to 2-4-9 (x = 3) and 1-2-5 (x = 4) structures. Note that the distinction between phases is the number of CuO planes per unit cell. Using the present designation

for the system $Y_2Ba_4Cu_{6+x}O_{14+x}$, the number of CuO planes per Ba-Y-Ba sequence is [x+2]/2. When the direction of chemical potential change is reversed, the transformation between phases displays a small hysteresis in copper oxide chemical potential. By making a rough fit of the simulation results with available experimental thermodynamic data[11] obtained at 950°C, it is expected that the 2-4-9 phase transformation would occur only at very high oxygen pressures (roughly 500-1000 bar), giving some insight as to why these higher CuO-content phases are neither readily formed nor commonly observed.

In simulation snapshots of the 1-2-4 to 1-2-3 transformation, the predominant experimentally observed defect structures are accurately reproduced (cf. Figures 3 and 1). The present study suggests that the equilibrium structures in the x = 2 to 0 regime of the system will contain only single and double CuO planes. However, recent electron microscopy results[10] 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 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.

It follows from the proposed intercalation model that the propagation mechanism for these phase transformations is partial dislocation climb. By this mechanism the occupation of CuO planes changes as the transformation progresses, but the necessary rearrangement of the overall crystal structure is minimal. The partial dislocation climb mechanism is also supported by configurational data generated in the intercalation simulation. The strain compensation required to nucleate such transformations is readily provided at grain boundaries, which also provide high diffusivity paths for copper. Thus it is expected that these planar defects readily act as heterogeneous nucleation sites, and high resolution TEM images previously published in studies of other topics[12,13] indeed clearly show the intercalation of extra CuO planes originating from grain boundaries.

Coherence lengths[14] (calculated using the anisotropic Landau-Ginsberg theory[15-17]) for the superconducting $YBa_2Cu_3O_7$ phase correspond closely to the dimensions of the most common stacking faults accompanying 1-2-4 decomposition, suggesting these faults should have a significant effect upon superconducting properties. Recent experimental evidence[1] of a dramatic increase in intragrain critical current density for 1-2-3 phase material containing a fine dispersion of the double CuO layer structure indicates that such defects act as flux pinning centers. Because this microstructure is associated with the 1-2-4/1-2-3 phase transformation, a greater understanding of the entire family of copper-oxygen dependent transformations in YBaCuO (ultimately leading to precise control of the CuO plane configuration) may allow the large-scale fabrication of superconducting material more suitable for applications than any now available.

Grateful acknowledgement is given to C.W. Chu (TCSUH, Houston) and D.E. Morris (LBL, Berkeley) for providing the material used in this study. Technical assistance from E. Kvam and P. Narwankar is 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 Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. One of us (L. T. W.) is supported by DARPA Grant No. MDA 972-88-J-1006. Large scale numerical simulation was performed with funds provided by Cray Research, Inc.

REFERENCES

1. S. Jin, T.H. Tiefel, S. Nakahara, J.E. Graebner, H.M. O'Brien, R.A. Fastnacht, and G.W. Kammlot , Appl. Phys. Lett. **56**, 1287 (1990).
2. M. Fendorf, E. Kvam, and R. Gronsky, in: High Temperature Superconductors: Fundamental Properties and Novel Materials Processing, edited by J. Narayan, C.W. Chu, L.F. Schneemeyer, and D.K. Christen (Materials Research Society Symposium Proceedings,Vol. 169, December 1989, in press).
3. H.W. Zandbergen, R. Gronsky, and G. Thomas, Phys. Stat. Sol. A **105**, 207 (1988).
4. G. Kirczenow, Phys. Rev. Lett. **55**, 2810 (1985).
5. K. Char, R.W. Barton, A.F. Marshall, A. Kapitulnik, and S.S. Laderman, Physica C **152**, 475 (1988).
6. J. Karpinski, E. Kaldis, E. Jilek, S. Rusiecki, and B. Bucher, Nature **336**, 660 (1988).
7. D.E. Morris, J.H. Nickel, J.Y.T. Wei, N.G. Asmar, J.S. Scott, U.M. Scheven, C.T. Hultgren, A.G. Markelz, J.E. Post, P.J. Heaney, D.R. Veblen, and R.M. Hazen, Phys. Rev. B **39**, 7347 (1989).
8. H.W. Zandbergen, R. Gronsky, K. Wang, and G. Thomas, Nature **331**, 596 (1988).
9. J. Karpinski, S. Rusiecki, E. Jilek, and E. Kaldis, in: High T_c Superconductor Materials; edited by H.U. Habermeier and E. Kaldis (European Materials Research Society Symposium Proceedings, June 1990, in press).
10. R. Ramesh, S. Jin, and P. Marsh (personal communication).
11. D.E. Morris, N.G. Asmar, J.Y. Wei, J.H. Nickel, R.L. Sid, J.S. Scott, and J.E. Post, Phys. Rev. B **40**, 11406 (1989).

12. H. W. Zandbergen, R. Gronsky, and G. van Tendeloo, J. Supercond. **3**, 337 (1989).

13. S.K. Streiffer, B.M. Lairson, C.B. Eom, and J.C. Bravman, in: High-Resolution Electron Microscopy of Defects in Materials, edited by R. Sinclair, U. Dahmen, and D.J. Smith (Materials Research Society Symposium Proceedings, Vol. 183, April 1990, in press).

14. J.C. Phillips, Physics of High-T_c Superconductors, (Academic Press, San Diego, 1989), 268-269, 305-307.

15. D. St. James, E.J. Thomas, and G. Sarma, Type II Superconductivity (Pergamon, Oxford, 1969), 10, 22-31.

16. M. Tinkham, Introduction to Superconductivity (McGraw-Hill, 1975), 9-10, 105-114.

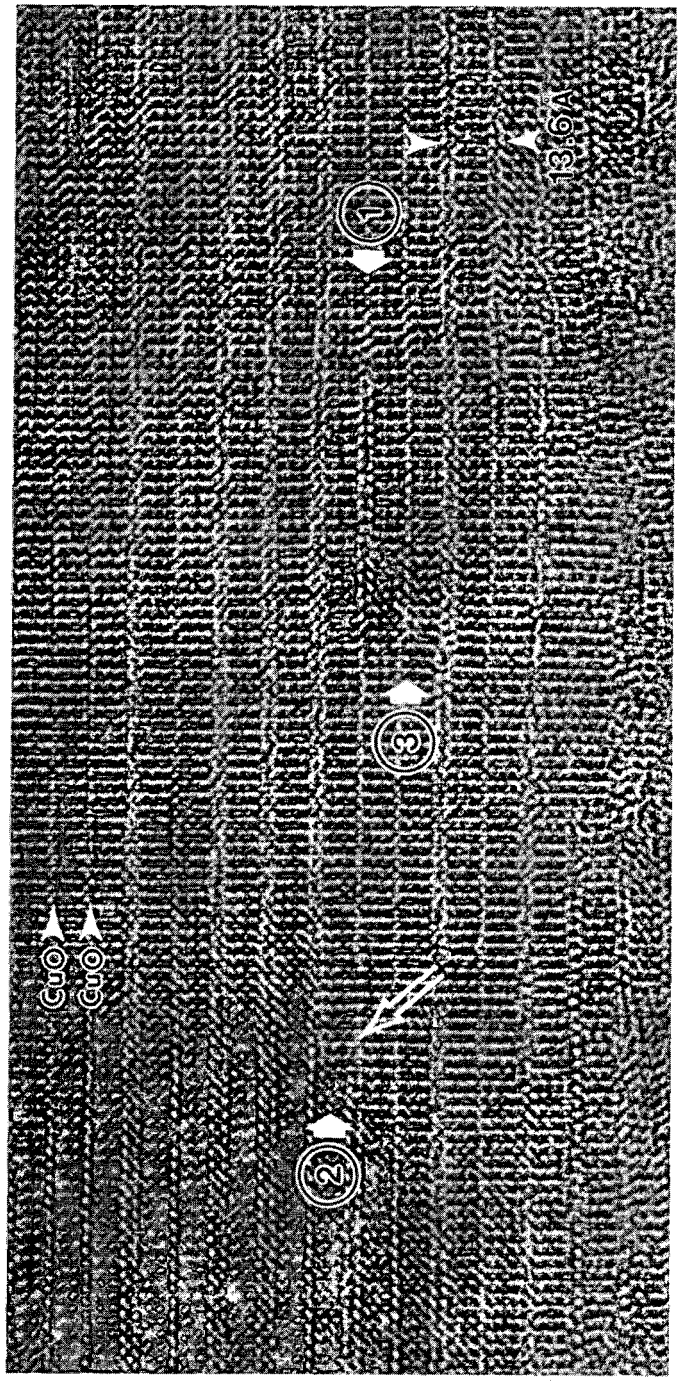
17. P. de Trey, S. Gygax, and J.P. Jan, J. Low Temp. Phys. **11**, 421 (1973).

FIGURE CAPTIONS:

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

Figure 2: Stoichiometric parameter (x) versus copper-oxide chemical potential (μ, linearly related to the logarithm of oxygen partial pressure) generated by Monte Carlo calculation for a temperature of $1.0\,|V_1|/k_B$. Concentration plateaus represent regions of constant crystal structure and correspond to proposed equilibrium phases in the $Y_2Ba_4Cu_{6+x}O_{14+x}$ system.

Figure 3: (a) Simulation-generated snapshot of mixed phase structure obtained during the 2-4-7 to 1-2-3 transformation for a copper oxide chemical potential (μ) of -3.4. Note the presence of the small planar defect corresponding to that delineated by ① in Figure 1. (b) Snapshot obtained during the 2-4-7 to 1-2-3 transformation for $\mu = -3.4$. Note the presence of complimentary, nearly strain-free dislocations corresponding to those delineated by ② in Figure 1. (c) Snapshot obtained during the 1-2-5 to 2-4-9 transformation for $\mu = 5.0$. This structure illustrates mixed 2-4-9 and 1-2-5 phases obtained at higher chemical potentials. In each snapshot, filled circles represent atoms in the CuO planes, filled dots atoms in the CuO_2 planes, small open circles yttrium atoms, and large open circles barium atoms. All configurations were obtained at a simulation temperature of $1.0\,|V_1|/k_B$.



XBB 9010-8368

Figure 1.

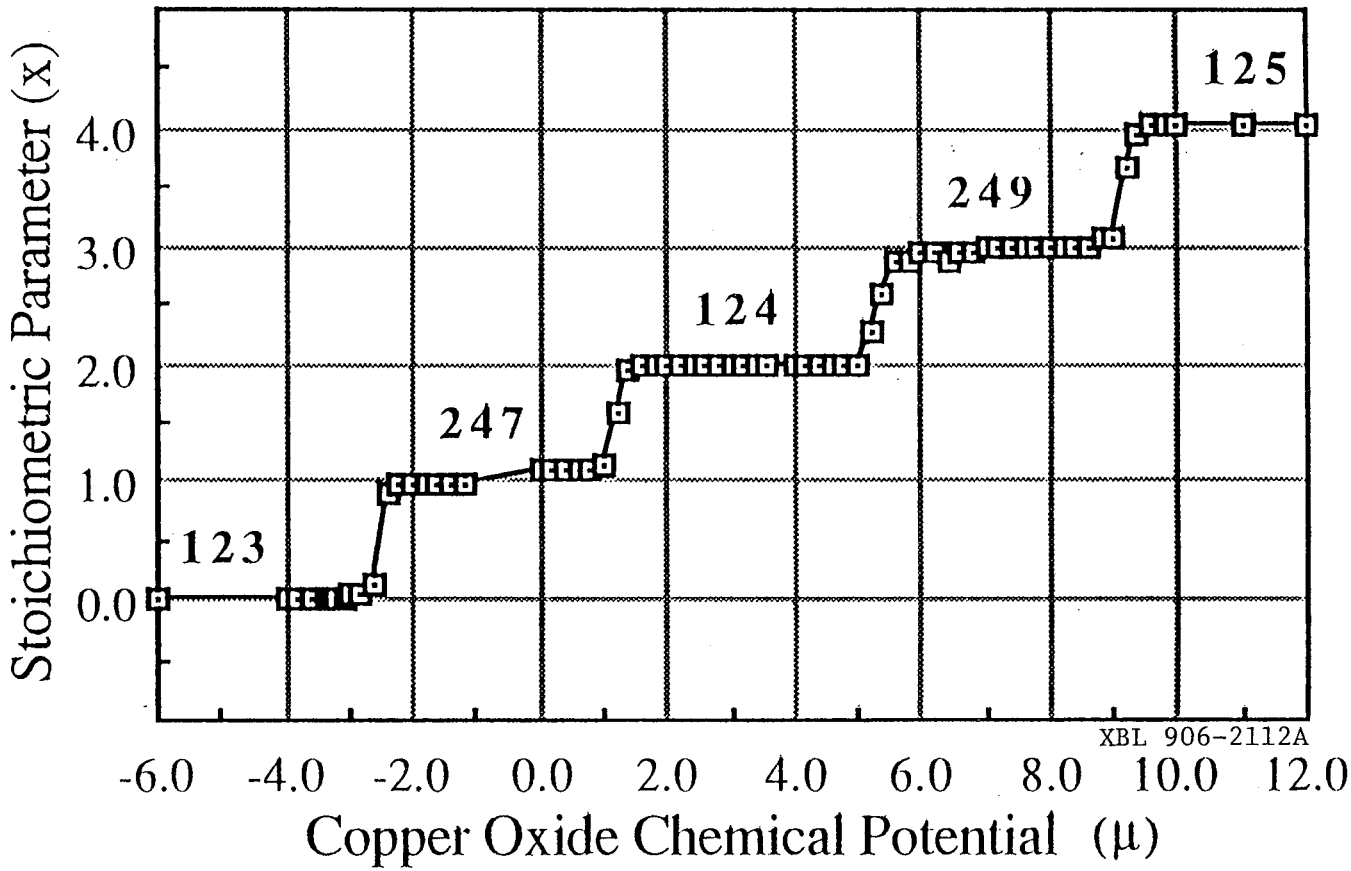
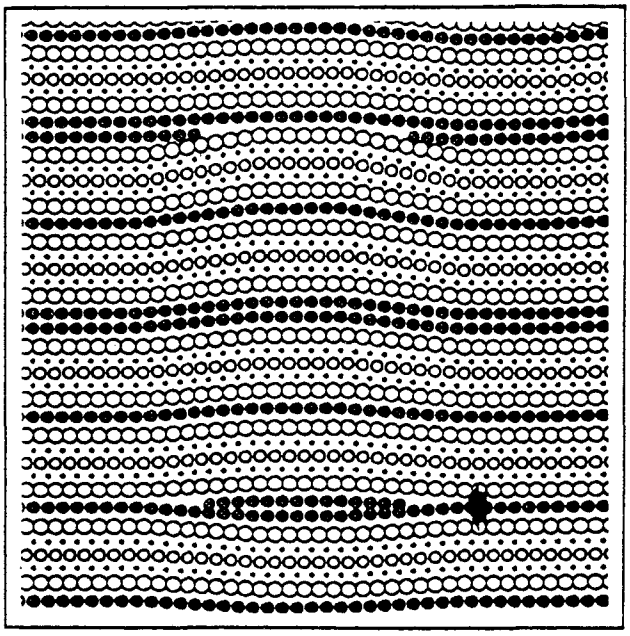
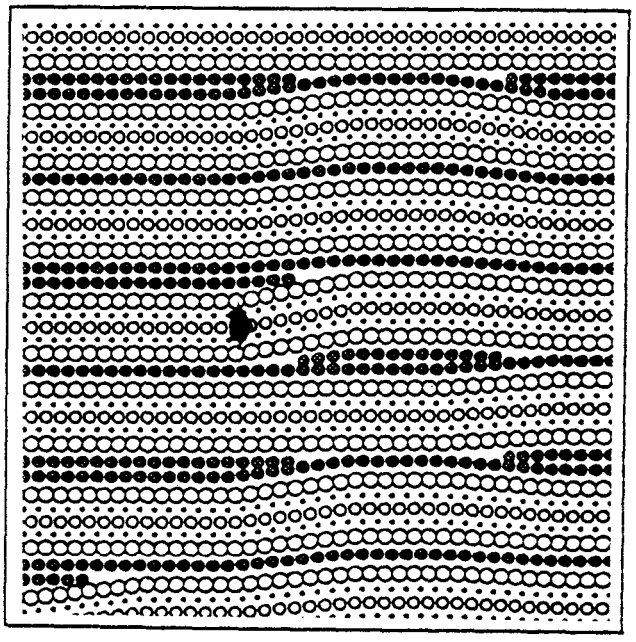

Stoichiometric Parameter (x)
4.0
3.0
2.0
1.0
0.0
123
247
124
249
125
XBL 906-2112A
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Copper Oxide Chemical Potential (μ)

Figure 2.



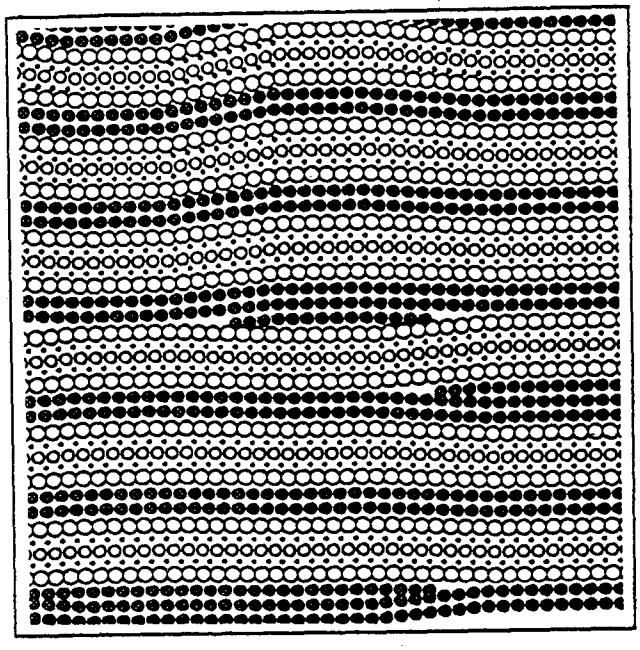
XBL 906-2217

Figure 3a.



XBL 906-2218

Figure 3b.



XBL 906-2219

Figure 3c.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720