

Lawrence Berkeley National Laboratory

Recent Work

Title

States of Partial Order in $\text{YBa}_{2}\text{Cu}_{3}\text{O}_{z}$

Permalink

<https://escholarship.org/uc/item/11c7r9gx>

Authors

Fontaine, D. de

Mann, M.E.

Cecer, G.

Publication Date

1989-08-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Physical Review Letters

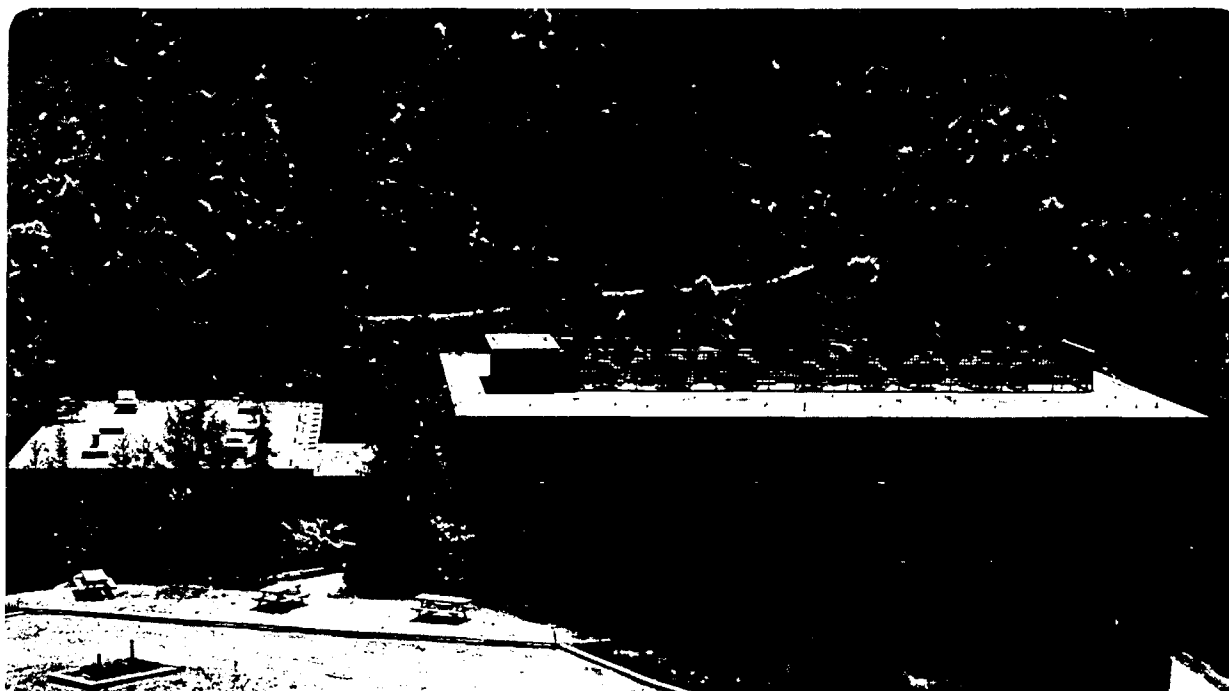
States of Partial Order in $\text{YBa}_2\text{Cu}_3\text{O}_z$

D. de Fontaine, M.E. Mann, and G. Ceder

August 1989

For Reference

Not to be taken from this room



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

Bldg. 50 Library.

COPY 1

LBL-27669

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.

STATES OF PARTIAL ORDER IN $\text{YBa}_2\text{Cu}_3\text{O}_z$

D. de Fontaine⁽¹⁾, M. E. Mann⁽²⁾ and G. Ceder⁽¹⁾

(1) Dept. of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, and

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, One Cyclotron Road, Berkeley, CA 94720

(2) Department of Physics, University of California, Berkeley, CA 94720

Monte Carlo simulation has been performed on a previously proposed model of Oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_z$: a two-dimensional Ising Model with isotropic first neighbor and anisotropic second neighbor effective pair interactions in the "chain plane". At low temperatures, states of partial order are observed in agreement with experimental findings. Such states of quasi one-dimensional order are a consequence of the asymmetric nature of the interactions.

PACS numbers: 74.70.Vy, 61.50.Ks, 64.60.Cn, 81.30.Hd

The nature of the tetragonal to orthorhombic transition in the $\text{YBa}_2\text{Cu}_3\text{O}_z$ (YBCO) compound is now fairly well understood (see, for example, the recent review by Beyers and Shaw¹ and references cited therein), but the low temperature (<500 C) behavior of the system remains puzzling. Various states of oxygen ordering have been reported²⁻⁸, and it is not clear which of these represent true equilibrium states. The purpose of this communication is to examine the conditions under which such ordered states may occur. The analysis is based on a previously proposed paradigm of ordering in YBCO: a two-dimensional Ising model of occupied and unoccupied oxygen sites with isotropic first and anisotropic second neighbor effective pair interactions.⁹⁻¹⁴ It will be shown, with the help of Monte Carlo simulation, that the anisotropic character of the model is essential: symmetric models^{15,16} cannot account for the observed states of order.

Oxygen ordering, responsible for the tetragonal to orthorhombic transition, takes place on the (001) mirror plane of the YBCO unit cell, the "chain" plane. The structure of this plane can be represented by three interpenetrating sublattices⁹: two (α and β) of oxygen sites, which may be occupied or vacant, and one of Cu (always occupied). To simplify the thermodynamical treatment, only three effective pair interaction (EPI) will be considered: the first neighbor interaction, which couples the two sublattices and is expected to be the dominant one, and two

second neighbor interactions: V_2 which is mediated by the Cu ions and V_3 which is not. Such ordering interactions are expected to converge rapidly with pair spacing¹⁷, hence this scheme should suffice to represent the main features of the system. It may be argued¹⁸ that V_1 should be positive (favoring unlike O-□ pairs) and V_2 negative (favoring like O-O and □-□ pairs), while Coulomb repulsion between parallel O-Cu-O chains suggests $V_3 > 0$.

The YBCO system is known to contain three distinct phases which differ by the oxygen arrangement on the mirror plane: the tetragonal phase (T) at stoichiometry $z=6$, which is non superconducting, the orthorhombic phase, Ortho I (or OI, for short), at stoichiometry $z=7$, which has a 90 K superconducting transition and a second orthorhombic phase, Ortho. II (or OII, for short), at stoichiometry $z=6.5$, which features cell doubling, has a 60 K transition, and for which ample experimental evidence is now available. In the framework of the present model all three structures have been proven to be ground states of the asymmetric Ising model¹⁰, and the conditions for stability of OII have been determined rigorously: the EPI's must obey the following inequalities $V_1 > 0$ and $V_2 < 0$ (precisely what is expected on physical grounds) and $0 < V_3 < 1/2 V_1$.

The Cluster Variation Method (CVM) was used to calculate two phase diagrams with EPI's within the specified range¹²⁻¹⁴. For comparison, a Monte Carlo calculation was performed with the following parameters: $V_1 > 0$, $V_2/V_1 = -0.5$, $V_3/V_1 = +0.50$. At high temperatures, agreement with previous CVM calculations¹² was quite satisfactory. At low temperature simulations, around $\tau \equiv k_B T/V_1 = 0.2$ ($k_B T$ has its usual "Boltzmann constant, absolute temperature" meaning), spurious specific heat maxima occurred in and around the OII phase field. The highest disordering temperature of OII is $\tau \approx 1.0$, or about $T \approx 700$ K. Examination of computer printouts revealed that these specific heat anomalies corresponded to states of somewhat irregularly spaced parallel O-Cu-O chains.

A typical such structure is shown in Fig. 1a where black dots denote Cu atoms, shaded circles are oxygen atoms and open circles are vacant sites. This structure was obtained by performing a Monte Carlo simulation on a 64×64 square network of oxygen sites at fixed chemical potential field (normalized by V_1) of $\mu = -4.7$. Oxygen coverage in the plane is $c_o = 0.2265$ or stoichiometry index $z = 6.453$. The system was "quenched" from a high temperature of $\tau = 5.0$ and the iteration was pursued to 1200 Monte Carlo steps per site. O-Cu-O chains are seen to be fully formed and are stacked in such a way as to form regions of OII (alternating full-empty-full chains on the α sublattice) separated by slabs of "Ortho. III" (OIII, full-empty-empty-full cell tripling structure). The corresponding intensity pattern, i.e. the amplitude-squared of the Fourier transform, or oxygen structure factor of Fig. 1a, is shown in Fig. 1b. Diffraction maxima are

located at $\langle 00 \rangle$, $\langle 20 \rangle$ and $\langle 11 \rangle$ which are the "Bragg peaks" in planar reciprocal space notation, and at $\langle 10 \rangle$ which are the OI "reflections". The $\langle \frac{1}{2} 0 \rangle$ reflections are split into satellite peaks at $\langle \frac{1}{2} \pm q, 0 \rangle$, with q not necessarily a simple fraction. At an earlier stage of the simulation (500 Monte Carlo steps/site), the chains were often faulted and both α and β oxygen sublattice occupancy domains were observed (see Fig. 2). Chain formation dynamics is discussed in more detail by Burmester and Wille.¹⁹

Another mode of "sample preparation" also was used in the simulations: first OI was produced at $\mu = -2.0$, then oxygen was extracted by imposing a chemical potential field of $\mu = -3.2$, this procedure being equivalent to reducing the partial pressure of Oxygen. After 8000 Monte Carlo steps/site, a structure consisting of mixed OII and OI slabs was obtained. The average planar oxygen concentration was $c_o = 0.297$, corresponding to stoichiometry $z = 6.594$. Once again the chains were fully formed but the OI and OII mixing was rather irregular, giving rise to a diffraction pattern consisting of a diffuse streak centered on $\langle \frac{1}{2} 0 \rangle$ along the a direction. It is easy to rationalize how such a structure could come about. Because of periodic boundary conditions, complete O-Cu-O chains are infinite and thus very robust. Eventually a chain is broken by action of the chemical potential field and it subsequently dissolves, thereby creating a slab of OII. The process is then repeated but in such a way that, at least for $c_o > 0.25$, no two empty chains form adjacent to one another. The reason for that is as follows: fully formed chains on a single sublattice interact only through the effective V_3 interaction which is repulsive ($V_3 > 0$), thus favoring unlike nearest neighbor parallel chains. Hence a mixed state of OI and OII domains results.

For $c_o < 0.25$ ($z < 6.5$), the situation is slightly different: the mixing is between OII and "anti-Ortho. I" domains. The anti-Ortho. I (\overline{OI}) phase can be regarded as the mirror image of OI in the sense that the roles of filled and empty chains on the occupied sublattice are interchanged. The \overline{OI} phase is distinct from the tetragonal (T) one: T consists of short-range ordered chains distributed on both α and β sublattices, whereas \overline{OI} has chains along a single sublattice only. Recent CVM calculations²⁰ indeed indicate that, at very low temperatures, T and OII phases are separated by an \overline{OI} phase region.

This quasi one-dimensional admixture of domains, OII + OI for $c_o > 0.25$, OII + \overline{OI} for $c_o < 0.25$, gives rise, locally, to structures resembling the Magneli phases described by Khachatryan and Morris (KM).¹⁶ However, such structures are actually inconsistent with the miscibility gap of the KM model as we will demonstrate. First, we should point out that an equivalence between the "method of concentration waves" used by KM to construct the reported phase diagrams^{15,16} and a

two dimensional Bragg-Williams model with first and second neighbor effective pair interactions can be rigorously demonstrated. A simple back-Fourier transform of the KM mean field internal energy, for their chosen star values of $V(0)$ and $V(k_1)$, immediately yields the required values (in our notation) of V_1 and $V_2 (=V_3)$, with ratio $V_2/V_1 = -0.4286\dots$. These values inserted into the Bragg-Williams model, as expected, reproduced exactly the KM phase diagram.

Next consider the "Magneli" structures proposed by KM: $[(O\Box)^j O]$ where O and \Box represent filled and empty chains on the α sublattice respectively, where the square brackets denote periodic repetition and where the parentheses indicate that the $O\Box$ element is to be repeated j times. Such structures are actually a subset of the well-known ground states of the one-dimensional Ising model and are stabilized by dominant *positive* (i.e. repulsive) first neighbor pair interaction J_1 along the Ising line^{22,23} which is the a direction in orthorhombic YBCO. But, as mentioned above, for fully formed chains, the only relevant interaction is the interchain repulsive interaction V_3 which is precisely J_1 . Hence, the presence of "Magneli" structures, stable or metastable, necessarily requires $J_1 \equiv V_3 > 0$. The KM phase diagram, however, is constructed with $V_2 = V_3 < 0$ so that this model is actually internally inconsistent, as was already noted earlier¹⁸. We checked by performing a Monte Carlo simulation employing the "symmetric" KM interaction parameters $V_2 = V_3 = -0.4286V_1$ and found, as expected, no Magneli-like ordered states, stable or otherwise. From the foregoing it is thus clear that *the presence of states of partial order necessarily implies that Ortho. II (OII) must be a stable phase in the system.*

At low temperature, the behavior of the proposed model with $V_2 > 0$ and $V_3 < 0$ is highly unusual: at $\tau \approx 0.2$, the interchain $O - O$ correlation length is expected to become greater than the dimension of the Monte Carlo periodic cell so that spurious results may occur as discussed for example by Selke²⁴ in the context of the two dimensional ANNNI model. The system essentially can be mapped onto a one-dimensional Ising model with nearest neighbor J_1 interaction for which only three ground states exist: the "ferromagnetic" (OI and \overline{OI}) and the "antiferromagnetic" (OII). Moreover, for $J_1 \equiv V_3 > 0$, any mixing of "ferro." and "antiferro." domains at fixed O -concentration yields the same energy so that complete degeneracy prevails.

The mixing of domains appears to be not completely random, however. Indeed, at intermediate temperatures when the full two-dimensional character of the system is recognized by the Monte Carlo simulation, OI , \overline{OI} or OII long range order (LRO) is observed at equilibrium. At low-temperature, the two-dimensional character of the model is not totally absent, especially during the early stages of chain formation (see Fig. 2) so that effective long-range (entropy driven) interchain repulsion may occur. Resulting structures and their Fourier transforms are clearly reminiscent of ordered structures and diffraction patterns observed from YBCO samples annealed

at low temperatures for long periods of time under reducing conditions with final oxygen stoichiometry of between about $z \approx 6.4$ and 6.75 ²⁵: split diffraction peaks and diffuse streaks are seen about the $[1/2,0]$ positions, but rather sharp peaks at positions $[1/3,0]$ and $[2/3,0]$ indicate, however, that actual longer-range repulsive interactions, beyond V_3 , may be present along the a direction.

The small apparent volume fraction of OII observed in electron micrographs⁶ can be explained¹⁸ by the limited correlation existing between mirror planes along the c direction: OII domains phase shifted from plane to plane will tend to project as OI, thereby causing appreciable underestimation of the "areal" fraction of OII on each plane. For $z = 6.5$ samples well equilibrated at low temperatures, c -axis correlations can be extensive, however, and OII can be observed even in neutron diffraction experiments²⁶.

To conclude, states of partial order in YBCO have been obtained by low-temperature Monte Carlo simulation in a two-dimensional Ising model with opposite-sign second neighbor interactions. Such ordered states cannot arise in a symmetric model and are thus incompatible with a miscibility gap phase diagram. Dimensionality plays an important role: states of partial order (SRO) arise because of the quasi one-dimensional character of the model at low temperature and equilibrium LRO is found at high and intermediate temperatures. OII is a true equilibrium state on individual mirror planes, but appears as three-dimensional SRO when c -axis correlation is limited.

The authors are indebted to Dr. L.T. Wille who wrote early versions of the Monte Carlo code used here, and to C.P. Burmester who performed initial simulations and pointed out an error in an earlier version of the manuscript. The authors also thank C.P. Burmester and C. Carter for programming assistance. A grant for supercomputer time from the U.C. Berkeley Central Computing Facility is gratefully acknowledged. One of the authors (G.C.) also thanks the Belgian American Educational Foundation for a Fellowship. The work was supported by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

¹R. Beyers and T. Shaw, in *Solid State Physics* Vol. 42, H. Ehrenrich and D. Turnbull, Eds., pp. 135-212, Academic Press, NY (1989).

²G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, *Solid State Commun.* **63**, 603 (1987).

³R. Beyers et al., *Mater. Res. Soc. Symp. Proc.* **99**, 77 (1987).

⁴C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenevas, J. L. Hodeau, and M. Marezio, *Phys. Rev. B* 36, 7118 (1987).

⁵Y. Kubo, T. Ichihashi, T. Manako, K. Baba, J. Tabuchi, and H. Igarashi, *Phys. Rev. B* 37, 7858 (1988).

⁶C. H. Chen, D. J. Werder, L. F. Schneemeyer, P. K. Gallagher, and J. V. Waszczak, *Phys. Rev. B* 38, 2888 (1988).

⁷D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, *Phys. Rev. B* 37, 2317 (1988).

⁸F. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, and J. V. Waszczak, *Phys. Rev. B* 37, 7920 (1988).

⁹D. de Fontaine, L. T. Wille, and S. C. Moss, *Phys. Rev. B* 36, 5709 (1987).

¹⁰L. T. Wille and D. de Fontaine, *Phys. Rev. B* 37, 2227 (1988).

¹¹A. Berera, L. T. Wille, and D. de Fontaine, *J. State Phys.* 50, 1245 (1988).

¹²L. T. Wille, A. Berera, and D. de Fontaine, *Phys. Rev. Lett.* 60, 1065 (1988).

¹³A. Berera, L. T. Wille, and D. de Fontaine, *Physica C* 153, 598, (1988).

¹⁴A. Berera and D. de Fontaine, *Phys. Rev. B*, 39, 6727 (1989).

¹⁵A. G. Khachatryan and J. W. Morris, Jr. *Phys. Rev. Lett.* 59, 2776 (1987).

¹⁶A. G. Khachatryan and J. W. Morris, Jr., *Phys. Rev. Lett.*, 61, 215 (1988).

¹⁷F. Ducastelle and F. Gautier, *J. Phys. F* 6, 2039 (1976).

¹⁸D. de Fontaine in *Proceeding of Fifth Meeting of Japanese Committee for Alloy Phase Diagrams*, June 1988.

¹⁹C. P. Burmester and L. T. Wille (to be published).

²⁰R. Kikuchi and J. S. Choi (preprint); G. Ceder, M. Asta, W. C. Carter, M. Sluiter, M. E. Mann, M. Kraitchman and D. de Fontaine (submitted).

²¹G. Ceder, unpublished research at U. C. Berkeley.

²²S. Katsura and A. Narita, *Prog. Th. Phys.* 50, 1750 (1973); M. Kaburagi and J. Kanamori, *Prog. Th. Phys.* 54, 30 (1975).

²³A. Finel, *Thèse de Doctorat d'Etat*, Université Pierre et Marie Curie, July 1987 (unpublished) and references cited therein.

²⁴W. Selke, *Z. Physik B - Condensed Matter* 43, 335 (1981).

²⁵R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. J. Gür, and R. A. Huggins, *Mat. Res. Soc. Symp. Proc.* 156 (1989), in press.

²⁶S. K. Sinha (private communication).

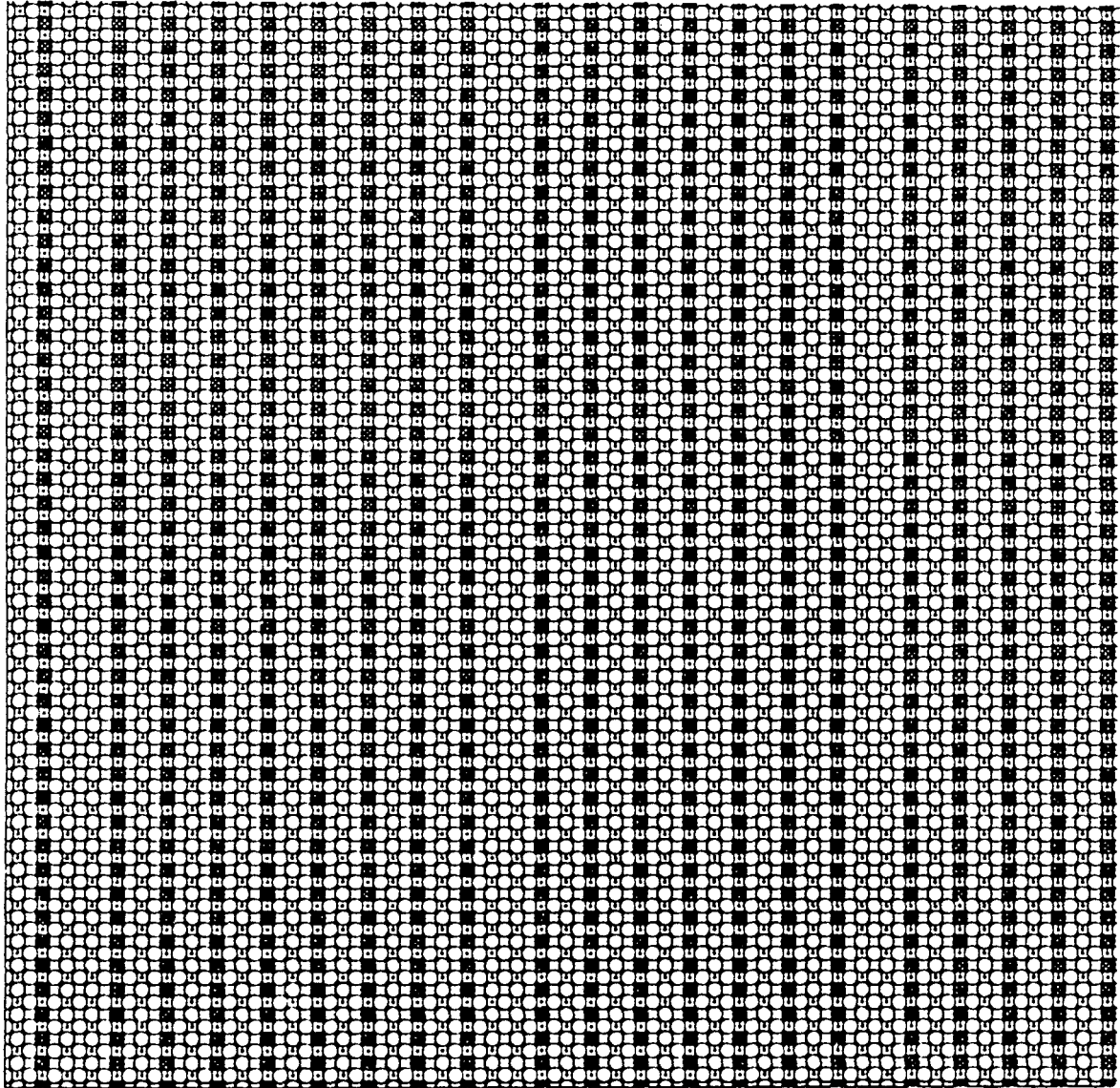
Figure Captions

Fig. 1a. Chain configuration for Monte Carlo system quenched from $\tau = 0.2$ at constant $\mu = -4.7$, after 1200 Monte Carlo steps/site. Closed circles denote oxygen ions, open circles are vacant sites, and small dots (perhaps not readily visible) indicate Cu ions. Concentration is $c_o = 0.2265$ or oxygen stoichiometry index $z = 6.453$. Structure is one of mixed OII and $\overline{\text{OI}}$ domains.

Fig. 1b. Fourier transform (amplitude squared) of configuration of Fig. 1a showing characteristic split $(1/2, 0)$ peaks and (1.0) streaks of intensity.

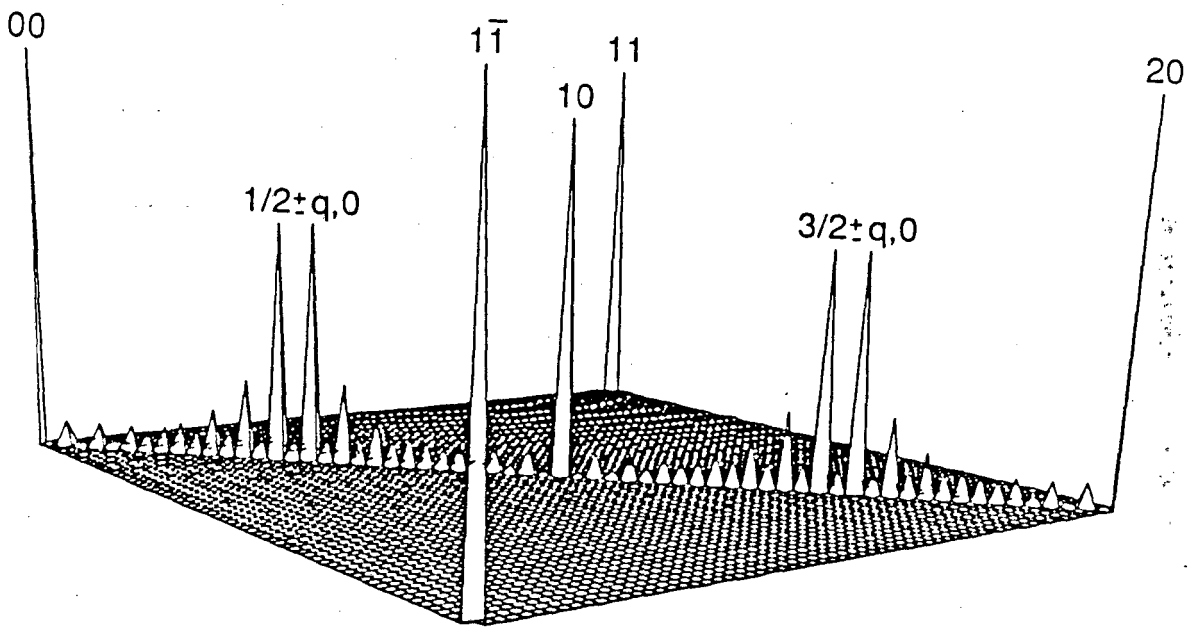
Fig. 2. Chain configuration for Monte Carlo system of Fig. 1a but at an early stage of iteration (500 Monte Carlo steps/site).

Fig. 3. Chain configuration for a Monte Carlo system initially in Ortho. I state, equilibrated at $\mu = -3.2$. Concentration is $c_o = 0.297$ or $z = 6.594$. Structure is one of mixed OI and OII domains.



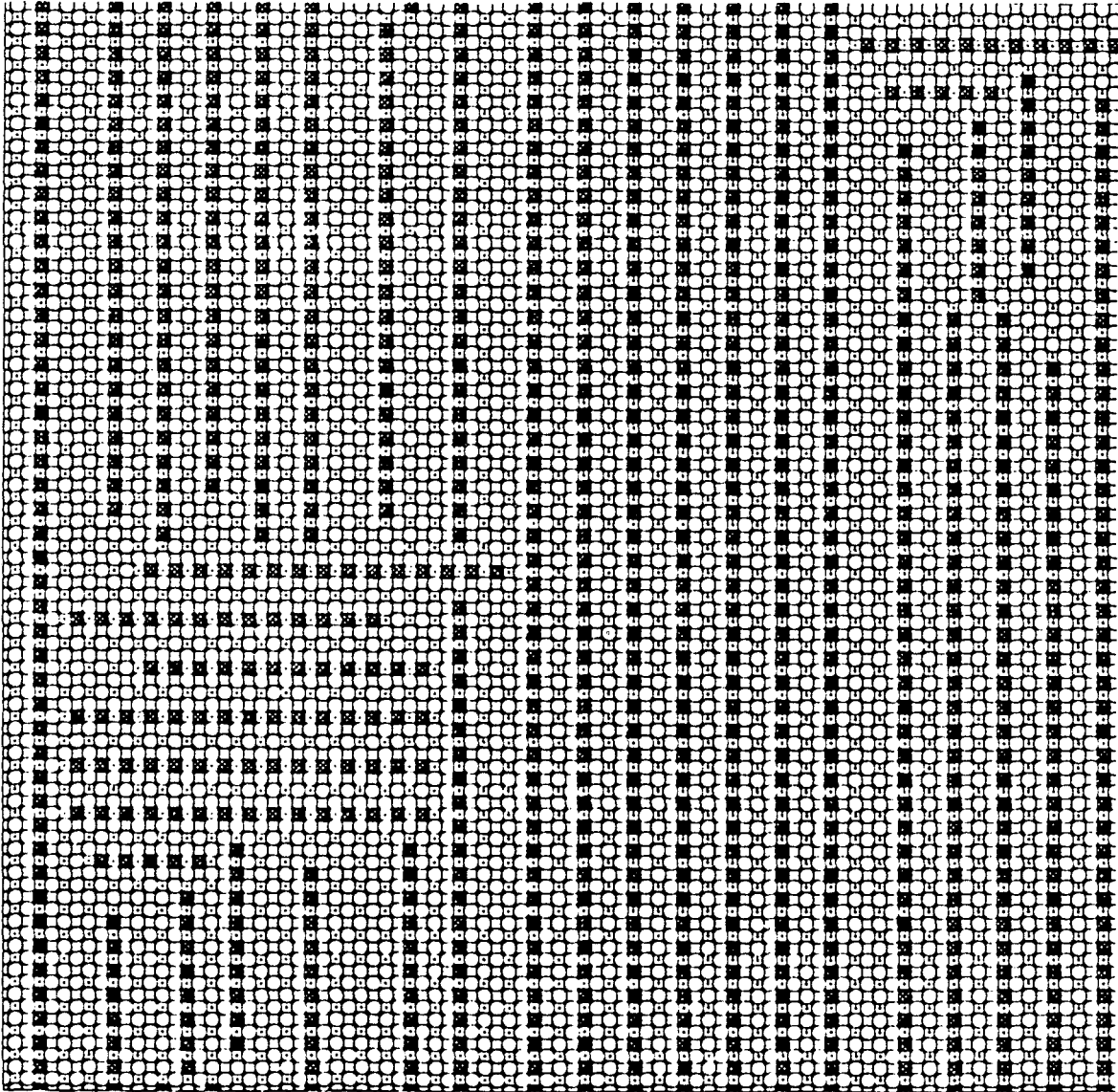
XBL 894-1387

Fig. 1a



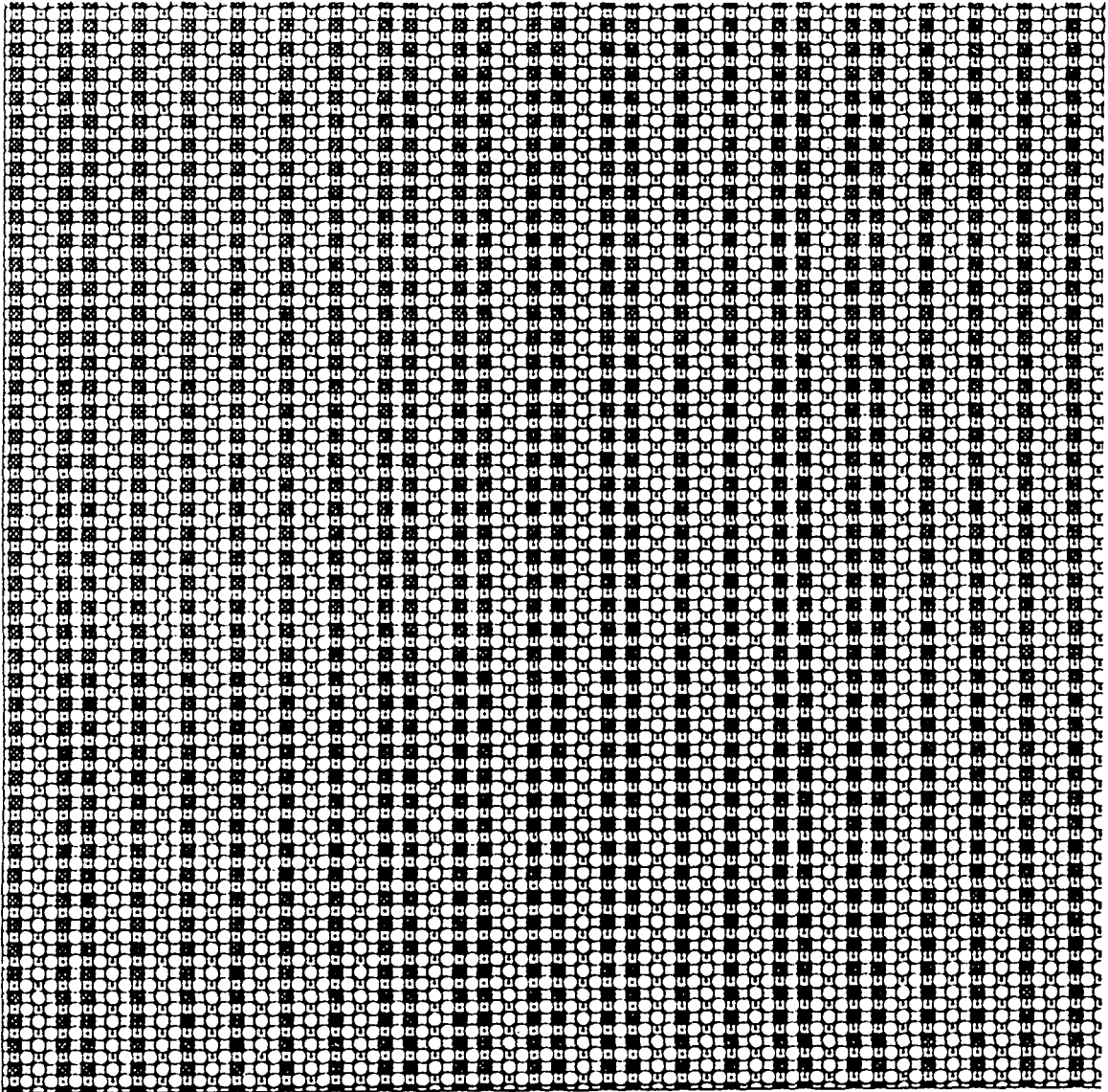
XBL 894-1388

Fig. 1b



XBL 894-1389

Fig. 2



XBL 894-1390

Fig. 3

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720