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MONTE CARLO SIMULATION OF OXYGEN ORDERING IN $YBa_2Cu_3O_z$.

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Oxygen ordering in the basal plane of $YBa_2Cu_3O_z$ has been studied by Monte Carlo simulations of a two-dimensional anisotropic Ising model. The orthorhombic to tetragonal transition is found to be second order at high temperature in agreement with previous CVM calculations. At low temperatures, a cell-doubled orthorhombic phase appears near stoichometry z=6.5, intermediate between the single cell orthorhombic and tetragonal phases. At very low temperatures, long-lived transient O-Cu-O chain ordering is observed to lead to triple and fivefold unit cells. Where not obscured by transient ordering, the transition lines bordering the orthorhombic cell-doubled phase are found to be second order. The observed equilibrium and non-equilibrium structures correlate well with atomic resolution micrographs and diffraction data from the $YBa_2Cu_3O_z$ system.

A knowledge of the oxygen ordering behavior in $YBa_2Cu_3O_z$ is crucial to an understanding of the superconducting properties of this material. Upon cooling from the disordered, tetragonal state, parallel O-Cu-O chains are formed in the basal plane leading to the formation of the orthorhombic phase(OrthoI), a 90K superconductor, near z = 7. At lower oxygen content the spacing between the O-Cu-O chains doubles and gives rise to a second orthorhombic phase (OrthoII), a 60 K superconductor, near z = 6.5. In the absence of oxygen ordering the tetragonal material is non-superconducting. As reviewed recently[1], a large number of experimental results concerning this order-disorder transformation have been obtained, but theoretically the issue is still not completely resolved.

As was suggested in previous publications[2-4], the equilibrium properties of these transformations can be described by means of a two-dimensional Ising model with isotropic nearest and anisotropic next nearest neighbor effective interactions between oxygen sites in the Cu-O basal plane. In the proposed

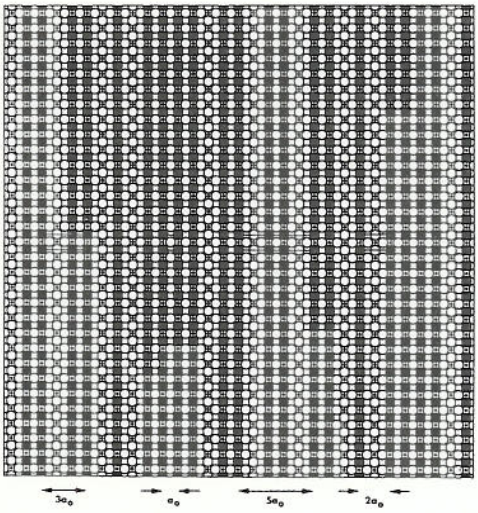

Figure 1: A typical single domain transient Magneli type structure formed by "quenching" from a disordered, high temperature ($T = 4.0V_1/k_B \cong 3000K$) to $T = 0.2V_1/k_B \cong 150K$. OrthoI ($a_o$), OrthoII ($2a_o$), and transient "unit cells" present ($3a_o$, $5a_o$) are indicated (z = 6.68). Shaded circles represent oxygens, open circles vacancies, and black dots Cu-ions.

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model, the V_1 interaction couples nearest neighbor oxygen sites, while the V_2 and V_3 interactions couple next nearest neighbor sites with or without an intermediate Cu atom[2]. Such a model permits the stability of the OrthoI and OrthoII phases as true ground-states[3]. Small domains with other partial states of order have been observed by transmission electron microscopy[5] and X-ray diffraction[7]. While these transient states have been described qualitatively[6], previous studies have not quantitatively addressed this transient ordering.

In previous work[4], the cluster variation method (CVM) was employed to estimate high-temperature phase boundaries in a temperature-oxygen concentration phase diagram. To clarify the low temperature behavior, a set of Monte Carlo calculations was initiated with the same parameters as used for the CVM phase diagram[4]: $V_1 > 0$, $V_2/V_1 = -1/2$, and $V_3/V_1 = +1/2$. These simulations were performed in the grand canonical ensemble using Metropolis dynamics, in which the system is allowed to evolve at constant chemical potential, equivalent to constant partial pressure of oxygen, as is done in experiment. The Monte Carlo results confirm the second order transition at high temperatures found in the CVM and give a transition temperature at $c_O = 1/2$ that is only 5 % lower than that calculated in the CVM. However, at low temperatures, a careful analysis shows the OrthoII phase region appearing between the OrthoI and tetragonal phases in a continuous, second order fashion, contrary to the CVM results.

In the course of these simulations, very slow kinetics leading to "transient" ordering is observed. For very low temperature simulations ($T < 0.35V_1/k_B \cong 260K$) performed with short annealing times, spurious specific heat maxima occurred at chemical potentials fields intermediate between the tetragonal to OrthoII and OrthoII to OrthoI second order transition lines. Examination of correlated lattice configurations revealed that the anomalies corresponded to the formation of states of somewhat irregularly spaced parallel O-Cu-O chains(see Fig. 1). These structures have been qualitatively decribed as "transient homologous structures" or "Magneli phases" elsewhere[6] but are put on a firm theoretical basis by the current findings. The generated structures were found to correlate exactly with structures imaged by high resolution transmission electron microscopy of low temperature annealed $YBa_2Cu_3O_z$[5] and were also consistent with reported electron diffraction evidence[7](see Fig. 2). For Monte Carlo calculations performed at temperatures corresponding to the observed partial ordering, the order of the transitions has to be estimated very carefully. It is felt that thermodynamic effects induced by the partial ordering act to obscure the true nature of the transitions in this very low temperature regime and this may well explain the disagreement between various experiments concerning the structure of the low temperature states.

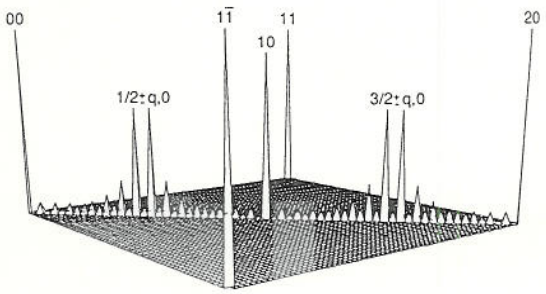

Figure 2: Fourier transform (amplitude squared) of typical transient structure showing characteristic split (1/2, 0) peaks and (1.0) streaks of intensity.

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