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Introduction.

In spite of a good deal of recent effort, the thermodynamic stability and kinetics of formation of ordered O-Cu-O chains in the basal plane of $YBa_2Cu_3O_{7-x}$ remain unclear. Because the chain disordering is associated with the orthorhombic-to-tetragonal phase transformation and the ensuing loss of superconductivity, a fundamental understanding of the nature of the oxygen-vacancy ordering has far-reaching implications for materials preparation and optimization (1,2).
It is now widely accepted that $YBa_2Cu_3O_{7-x}$ exists in at least three different phases: a non-superconducting tetragonal phase, Tetra, in which the oxygen atoms are distributed randomly over the basal plane sites, a superconducting ($T_c \approx 90$ K) orthorhombic phase, OrthoI, in which the oxygens form long O-Cu-O chains parallel to the b-axis, with oxygen deficiency $x \approx 0$, and a second superconducting ($T_c \approx 60$ K) cell-doubled orthorhombic phase, OrthoII, in which every second O-Cu-O chain has been removed ($x \approx 0.5$). Phase diagrams have been calculated in which this second phase is assumed to be stable (3) or metastable (4). In addition, small domains containing other unit-cell multiples have also been observed (5-8). Such structures have been proposed on theoretical grounds (9) and are generally called Magneli-phases. They are most likely metastable (9) or transients (10,11) although their stability cannot be ruled out conclusively.
In order to clarify some of these questions, we have undertaken a combined theoretical (first-principles) and experimental (HREM) study of the thermodynamic properties of the $YBa_2Cu_3O_{7-x}$ system.

Theoretical phase diagram and domains.

We have performed a large number of first-principles electronic band structure calculations for structures with different oxygen orderings and concentrations (12). The results clearly show the strong tendency of the system to form Cu-O chains, as well as indicating the stability (at zero temperature) of the double-cell phase. Because the total energy of the OrthoII $YBa_2Cu_3O_{6.5}$ structure is lower than the average for the $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ phases, the former will clearly not decompose into the latter two. Assuming that the statistical behavior of this system can be modelled in terms of a previously studied two-dimensional Ising-model with first- and anisotropic second-neighbor interactions (3), the set of total energies thus obtained can be used to extract interaction parameters for input into a calculation of the temperature-com-

position phase diagram (Fig. 1). In this phase diagram the concentration of oxygen in the basal plane, c_o, is related to the oxygen stoichiometric variable x by $c_o = (1-x)/2$. The underlying Ising model has a repulsive interaction ($V_1 > 0$) between nearest-neighbor oxygen sites, an attractive second-neighbor interaction ($V_2 < 0$) between sites with an intervening Cu-ion and a repulsive second-neighbor interaction ($V_3 < 0$) between sites without an intervening Cu-ion (3). The sign and relative magnitude of the calculated first-principles interactions are consistent with simple chemical bonding arguments.

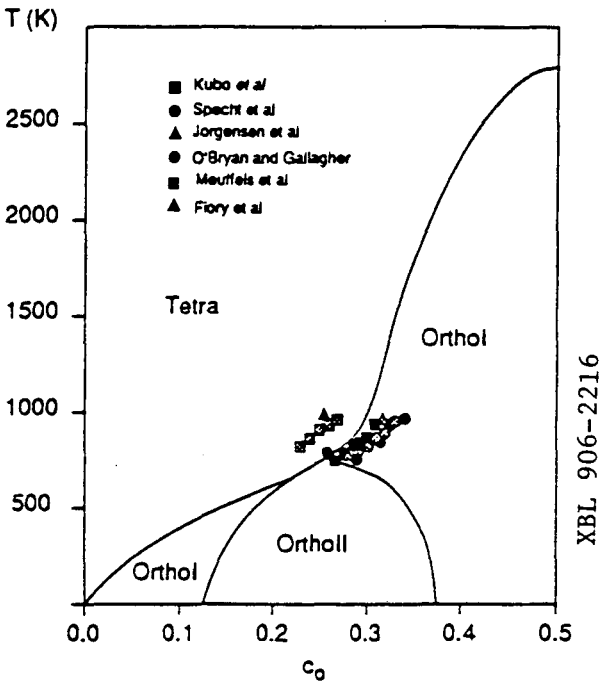

Fig. 1: First-principles phase diagram of $YBa_2Cu_3O_{7-x}$ ($c_o = (1-x)/2$). Experimental data points are from references (16-21).

Great care must be taken in deriving these values, since the total energies are of the order 10^3 Rydbergs, while the Ising parameters are only a few mRyd. It also needs to be emphasized that the interaction parameters were fitted to the set of total energies under the assumption of the validity of the two-dimensional anisotropic Ising model. Although the fit is certainly very good (as has been verified by back-substituting the interactions into an independent calculation) the presence of further-neighbor or even long-range interactions cannot be excluded. The phase diagram was obtained by means of Kikuchi's Cluster Variation Method using the Natural Iteration Method for the free energy minimization (13). A spurious first order transition between the OrthoII phase and the disordered Tetra and oxygen depleted Orthol' phases has been omitted, since all transitions in the assumed Ising model are now known to be second order (14,15). The Orthol' phase is the mirror image of the Orthol phase, with all occupied chains mapped into empty chains and vice versa. Its presence in the actual compound is not clear, since at such low concentrations oxygen atoms will also be removed from sites not in the basal plane and the two-dimensionality of the model breaks down. Certainly, the calculated phase diagram - obtained without any adjustable parameters - is in excellent agreement with experiment (16-21). No experimental data are available at high temperatures, since the compound tends to lose

oxygen as it is heated, while increasing the oxygen partial pressure only leads to a structural phase transformation to the $YBa_2Cu_4O_8$ structure (22). Very little is also known about the low-temperature phase boundaries because of kinetic effects.
While the equilibrium phase diagram is an important characteristic of a given material, perhaps equally important are its kinetic properties, in particular, insofar as they correspond to the actual thermal process used to produce this material. In this regard, it was very pleasing to find by Monte Carlo simulations (10,11) that the two-dimensional short-ranged Ising model supports the existence of long-lived transient mixed states that correspond very closely to the so-called Magneli-phases (9). That is, while those chain-ordered phases with n-fold unit cells ($n > 2$) are not stable within the assumed model, once they have formed, they exhibit an exceedingly slow evolution rate. At sufficiently low oxygen content or after slow annealing, chains are able to percolate throughout the sample (Fig. 2(a)), but a more common occurrence, especially at higher oxygen content or following a quench, is the creation of orthogonal domains in which the a and b axes are interchanged (Fig. 2(b)). Those domains bear a strong resemblance to the experimentally observed superstructures (5-8).

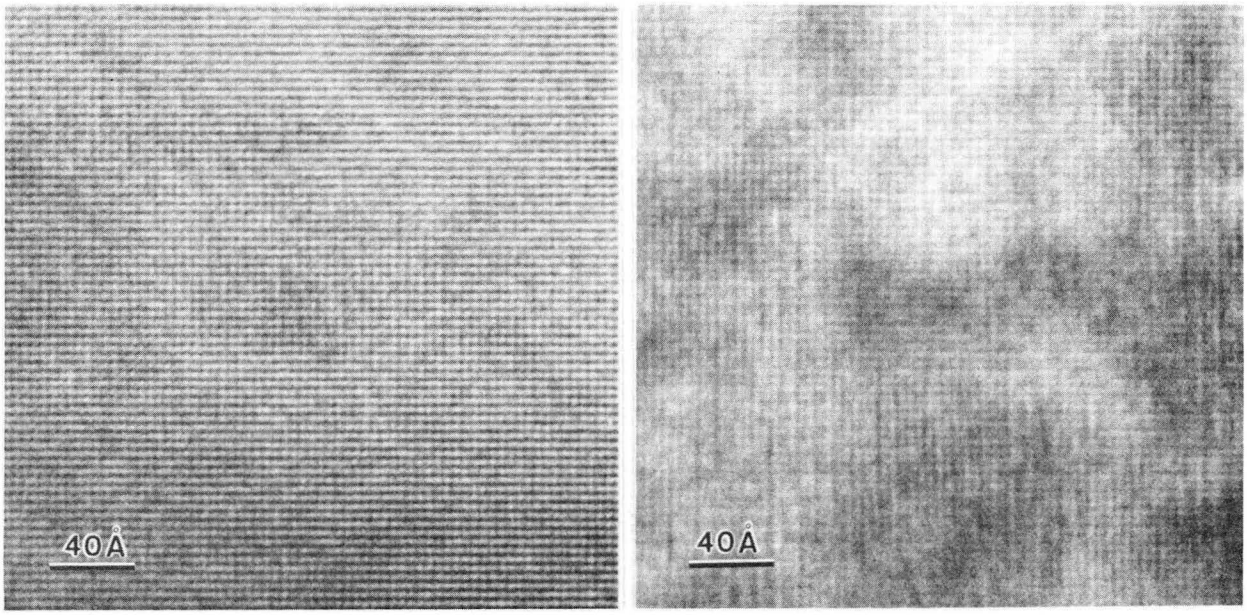

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Fig. 2: (a) Transient Magneli-structure obtained after annealing shows percolating chains; (b) Quenched configuration exhibits conflicting domains.

Experimental observations.

Using a solid-state ionic technique, a series of homogeneous $YBa_2Cu_3O_{7-x}$ ($0.0 \leq x \leq 1.0$) specimens with highly controlled oxygen content ($\pm$ 0.02 oxygens per formula unit) was produced (23). High resolution transmission electron microscopy was performed using a JEOL 200CX microscope operating at 200kV. The sintered material was dry crushed and dispersed onto a lacy carbon grid to prepare it for microscopy. A partially processed image of an area extracted from a high resolution micrograph for a specimen with $x \approx 0.5$ (corresponding to the OrthoII structure) is shown in Fig. 3(a). The area inside the larger square has been processed to eliminate noise, while that in the smaller square is obtained from a Monte Carlo snapshot similar to Fig. 2(a) using the NCEMSS image simulation program (24). The uniform fringe contrast reflects the presence of a single OrthoII domain, as is also confirmed by electron diffraction patterns which show superlattice reflections only along the [010] direction (25). Next, the existing order was destroyed by in-situ beam and stage heating until diffraction

imaging showed that the sample had transformed to the disordered, tetragonal phase. The beam was then turned off abruptly, thus 'quenching' the specimen to room temperature. After the material had reached thermal equilibrium, a new set of diffraction and high resolution images was obtained, which now exhibit the typical 'tweed' contrast (Fig. 3(b)). Orthogonal dark fringes are clearly visible, reflecting the formation of conflicting domains similar to those shown in Fig. 2(b). This is also confirmed by the [001] electron diffraction patterns, which now display superlattice reflections along both the [100] and [010] directions (25). The out-of-plane ([001] direction) correlation of basal plane ordering is also found to vary with oxygen content. In microdiffraction work performed earlier (7), [010] selected area diffraction patterns taken of material with oxygen concentration below x = 0.35 displayed spatially distinct superlattice reflections between the primary 000 and 100 beams indicating the presence of strong correlation between the basal plane ordering in the [001] direction. However, for specimens of higher oxygen content, these superlattice reflections lengthened into streaks running parallel to the c* direction indicating no [001]-correlation.

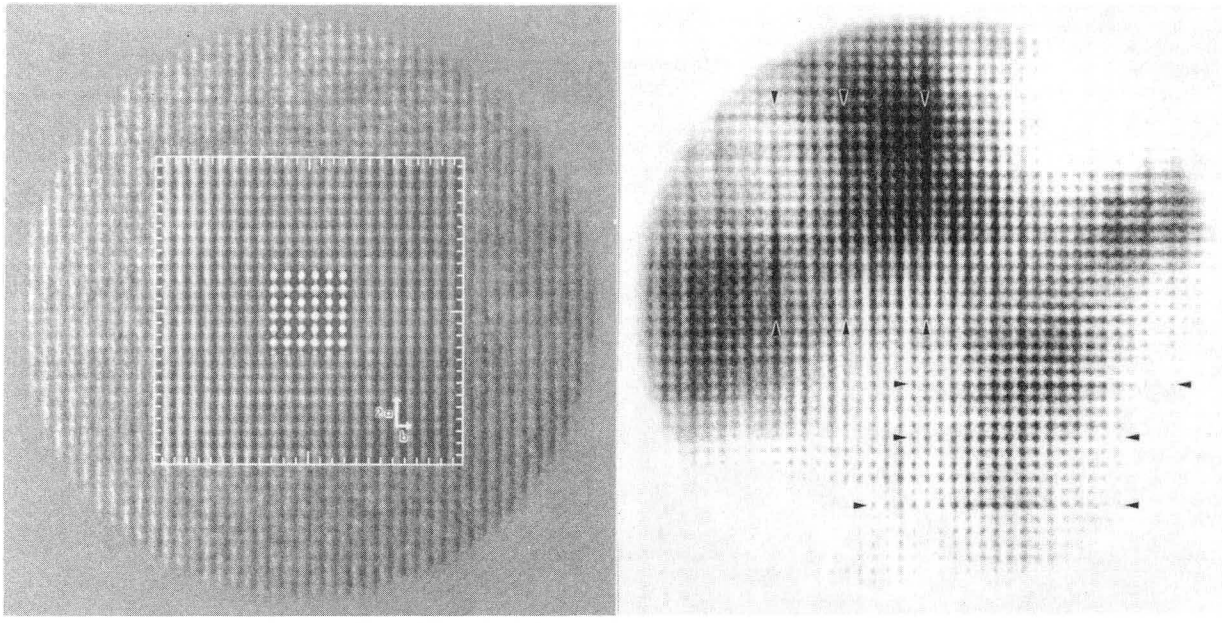

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Fig. 3: (a) Partially processed image extracted from a high resolution micrograph before beam heating. The area inside the large square has been processed to remove background noise, while that inside the smaller square is obtained from a Monte Carlo snapshot. (b) Processed image obtained after in-situ beam heating and subsequent quenching shows orthogonal dark fringes indicating the formation of conflicting microdomains.

Discussion.

Superconductivity in $YBa_2Cu_3O_{7-x}$ and the other high-T_c cuprate ceramics is associated primarily with the CuO_2 planes and the coherence length in the z-direction is very small. Nevertheless, it is by now well established that in $YBa_2Cu_3O_{7-x}$ the CuO_{1-x} basal plane studied here plays an equally important role. This plane has to possess a sufficiently high degree of order for superconductivity to occur at all, and in the ordered state, depending on the oxygen content, T_c seems to exhibit plateaus near 90 K ($x \approx 0.$) and 60 K ($x \approx 0.50$). It has been speculated that the plateaus are due to phase separation, although this is not expected to occur within the Ising model used here. It has also been suggested that an electronic mechanism is at work with the hole count

in the CuO_2 plane depending sensitively on the state of order in the CuO_{1-x} plane (26,27)

The present work shows both theoretically and experimentally that the oxygen ordering behavior in $YBa_2Cu_3O_{7-x}$ is unexpectedly rich. The first-principles calculations confirm unequivocally that the OrthoII double-cell phase near $x \approx 0.5$ is indeed a stable ground-state in this compound. This conclusion is independent of any Ising model to which the total energies are subsequently fitted. Within an anisotropic short-ranged Ising model (3), interaction parameters are obtained that are of the correct magnitude and sign and, moreover, lead to a phase diagram that is in excellent agreement with available experimental data. In addition, Magneli-type phases are obtained as long-lived frozen-in defects. However, it cannot be ruled out from the calculations performed here that those phases are actually stabilized due to the presence of long-range interactions. Such interactions would lead to a complete devil's staircase at zero temperature and narrow stability domains at low temperatures (28).

The presence of [001]-correlation of basal plane chain ordering suggests the existence of an attractive out-of-plane interaction for the above Ising model. Using Monte Carlo simulations expanded to include an arbitrary interaction between oxygen-vacancy sites in adjacent (001) planes, this phenomena is investigated. At higher oxygen concentration, the growth of [001]-correlated domains in quenched material is frustrated by the mutually orthogonal microdomains present. Previous basal plane simulations (10) revealed that the high concentration of oxygen slows the kinetics of domain growth thus "stabilizing" the as-quenched structure. Hence, the regrowth of domains with long range [001] order in the oxygen-rich material is not achievable in experimentally realizable annealing times. At lower oxygen concentration, the presence of sufficient stoichiometric vacancies alleviates this kinetic constraint and the resulting domain growth, governed by the additional out-of-plane interaction, is highly correlated. However, the competition between equally stable mutually orthogonal or antiphase domains limits this growth. Thus, the resulting structure of the oxygen-poor quenched material is ordered in the [001] direction but constrained by in-plane kinetics to consist of small domains. This type of structure is experimentally observed in the in-situ quenched $x \approx 0.5$ material (see Figures 2b and 3b). It is expected that further oxygen loss would allow the growth of larger [001]-correlated chain ordered domains. However, as this oxygen poor material readily transforms under electron irradiation into the tetragonal phase, the observation by electron microscopy of such structures in the quenched materials is unlikely.

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