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Structural Changes with Oxygen Content and Ordering of Defects in the High-T_c Oxide $YBa_2Cu_3O_{6+x}$

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From the study of the composition evolution of the atomic positions in the high-T_c superconducting system $YBa_2Cu_3O_{6+x}$, we suggest that for intermediate values of x the oxygen atom vacancies interact quite strongly so as to produce regions of separated Cu^{III} and Cu^{I} atoms. This result is both in accord with recent experimental work and consideration of stable geometries for the various oxidation states of copper.

Since the discovery of superconductivity with a T_c as high as 90 K in the Y–Ba–Cu–O system (*1*), considerable experimental effort has been expended to characterize this family of oxides. X-ray and neutron diffraction studies (*2–20*) are playing a key role in the determination of the structural characteristics of the superconducting phase. It is important to note, however, that these studies give only the average structure of the materials. The basic structure, now well-established for the oxide $YBa_2Cu_3O_{6+x}$, is simply derived from the perovskite arrangement as shown in Fig. 1. For $x = 1$ the site labeled O(5) is empty and the structure consists of $Cu^{II}(2)O_2$ sheets linked by rather long Cu(2)–O(1) linkages to $Cu^{III}(1)O_3$ chains. The sheets thus contain roughly square-pyramidal Cu^{II} atoms while the chains contain CU^{III} atoms in approximately square planar coordination, leading overall to an orthorhombic structure (*Pmmm*). For $x = 0$, all of the atoms labeled as O(4,5) are missing, the square planes have been replaced by linear O–Cu^{I}–O dumbbells, and the structure now is tetragonal (*P4/mmm*). Several structural determinations of phases with intermediate values of x have been carried out. We have recently reported (*3*) a single crystal neutron diffraction study of a material with $x = 0.26$. Detailed structural data are only available for $x < 0.32$ and $x > 0.68$, although diffraction studies show that single phases

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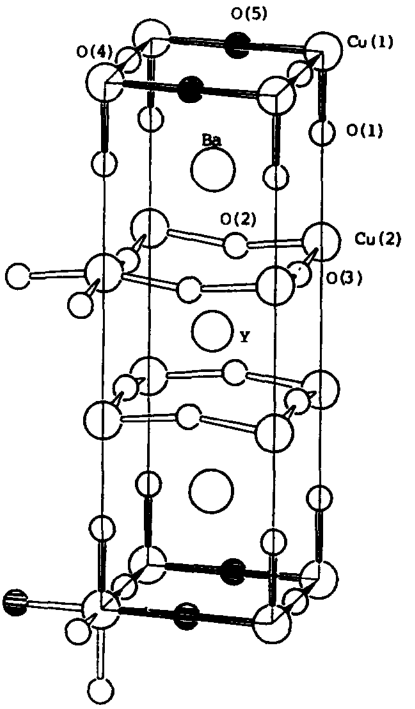

FIG. 1. Crystal structure of the high-T_c superconducting system $YBa_2Cu_3O_{6+x}$. For $x = 1$ the sites labeled O(5) are completely empty, and for $x = 0$ the sites labeled O(4) and O(5) are completely empty.

can be produced in the intermediate stoichiometry either by heating oxygen-rich samples (*16–19*) or by quenching samples from high temperature (*20*). One study on a sample with $x = 0.8$ (*14*) showed a temperature evolution of the occupation of sites O(4) and O(5), the population of the O(5) sites increasing with increasing temperature. Structural studies have also been performed at low temperatures and close to the superconducting transition temperature (*8, 13, 14*). From diffraction studies at room temperature and below, occupation of the site labeled O(5) appears to be the rule when $x < 1$. Tetragonal and orthorhombic structures are observed depending respectively on whether these two sites are occupied equally or not. Recent structural determinations (*16, 20*) have shown that the transition between the two occurs close to $x = 0.5$. These diffraction studies of course provide only an average occupancy of the O(4) and O(5) sites; an important additional question is whether there is local order in the crystal. As we have pointed out before (*21*), the vacancy ordering patterns are crucial in controlling the electronic structure at the Fermi level. We study this aspect of the structures of these fascinating systems in this letter.

Figure 2 shows how the geometric parameters which describe the atomic positions in $YBa_2Cu_3O_{6+x}$ vary with x. These plots show the change in distance (along the

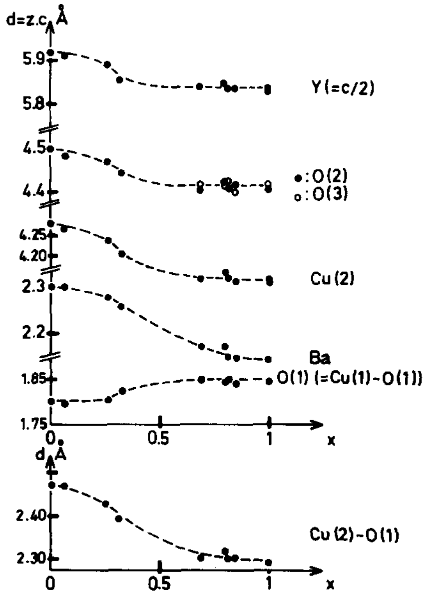

FIG. 2. Composition dependence of the distance of various atoms from the plane formed by the Cu(1) atoms in the crystal structure of the high-T_c superconducting system $YBa_2Cu_3O_{6+x}$. The values for O(1) are thus identical to the variation in the Cu(1)–O(1) distance. For comparison, the variation in the Cu(2)–O(1) distance is shown at the very bottom of the picture on the same scale. In all cases the errors in the measurements are equal to, or smaller than, the size of the solid dots used to indicate them. The structures used are as follows: $x = 0$, Ref. (*2*); $x = 0.06$, Ref. (*15*); $x = 0.26$, Ref. (*3*); $x = 0.32$, Ref. (*4*); $x = 0.69$, Ref. (*4*); $x = 0.80$, Ref. (*5*); $x = 0.81$, Ref. (*6*); $x = 0.85$, Ref. (*7*); $x = 1$, Refs. (*5, 8*).

c axis) of the various atoms in the structure from the plane formed by the Cu(1) atoms. The structures used in this plot are based on room-temperature determinations since it is clear that temperature plays an important role in determining both site occupancy and geometry. Included too are only structural determinations of systems with a full complement of metal atoms; the defects are thus associated solely with the oxygen atoms in the sites O(4) and O(5). One explanation for the structural changes with x is the following: The geometry changes can be visualized as being driven by the change in oxidation state of one-third of the copper atoms (associated with the coordination number change of chains to dumbbells) and the movement of the electropositive barium atoms in response to the presence of oxygen vacancies. In cuprite (Cu_2O) each copper atom is linearly two-coordinate (*22*) with a Cu–O distance of 1.849 Å. However, here each oxygen atom is four-coordinated by copper. In $YBa_2Cu_3O_6$ the oxygen atoms are just over one-coordinate and a considerable shortening of the Cu(1)–O(1) distance is to be expected compared to that in cuprite. As the Cu(1)–O(1) distance shortens the Cu(2)–O(1) distance must lengthen to maintain the bond valence sum at oxygen. It lengthens quite substantially. Triggered by the lengthening of this Cu(2)–O(1) bond the square pyramids at Cu(2) are flatter at $x = 0$ than at $x = 1$. This is evident from Fig. 2 where the change in the position of Cu(2) is larger than that of its associated oxygen atoms O(2,3) (*23*).[1] The change in position of the barium atoms is largest of all. We note that these atoms move away from the plane formed by the atoms O(4) and O(5) which are lost on moving from $x = 1$ to $x = 0$, an observation understandable in terms of simple electrostatics.

It is the shapes of these curves, however, which are particularly interesting. Notice that the dependence of the structural parameters on x is not the linear one, expected on the basis of Végard's law. In fact there seem to be two relatively flat regions for x close to 1, and for x close to 0, connected by a curve with a much steeper slope around $x \simeq 0.5$. Such behavior is typical of a system near a phase instability, where the parametric dependence on composition is determined by attractive like-with-like interactions. In the present case this interaction drives the orthorhombic–tetragonal transformation which corresponds to an order–disorder transition of oxygen positions on the O(4) and O(5) sublattices. A similar S-shape dependence of the lattice parameter c is observed when the transition is achieved upon heating (*16, 18*). These features result from a cooperative phenomenon associated with the oxygen positions. Thus, the defects are not likely to be distributed randomly for $x < 1$, but are organized so as to produce regions of Cu^{III} atoms separated from regions of Cu^{I} atoms. From such a simple picture the steeper slope at low x (larger fraction of Cu^{I}) compared to that at high x (larger fraction of Cu^{III}) implies that the clustering energy for Cu^{III} is stronger than that for Cu^{I}. It is particularly interesting to note that we may use plots such as those of Fig. 2 to extract more information concerning the *microscopic* structure than we can from an individual structural determination.

Such a conclusion is in accord with recent electron diffraction studies (*24–25*) which show that the oxygen vacancies are locally ordered. It is also in accord with the known stable geometries for the various oxidation states of copper. If the vacancies are randomly distributed, then for high x, the two copper atoms associated with the defect will now lie in a T-shaped environment. As we have shown earlier (*21*) their electronic configuration will be d^{10}, a geom-

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[1] Similar changes in bond length with bond angle are found for the trigonal bipyramid to tetragonal pyramid interconversion.

etry not found for this electron count (*26*).[2] If on the other hand the defects order such that a pair of vacancies is found around a single copper atom, then the linear two-coordination of the resulting d^{10} species is quite acceptable. We suggest that the actual ordering of the defects will be that which minimizes the number of copper atoms in T-shaped environments. This will locally preserve the chain-like features of the structure in the Cu(1) layers even in the tetragonal phase.

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[2] The only molecular example of such a structure is for a low-spin d^8 Rh^{I} species.