DEFECTS AND SUPERCONDUCTIVITY IN THE COPPER OXIDES

It is not enough to know what the ideal structures are, because superconducting properties depend very much on structural defects—and on the arrangement of defects.

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Few superconducting materials have presented us with the structural elegance and complexity displayed by the recently discovered high-T_c copper oxides. The structures of these materials, consisting of metal–oxygen layers stacked in a variety of sequences, with the metal atoms often in unusual coordinations, are interesting in their own right. More importantly, our present understanding of the properties of the oxide superconductors depends heavily on a knowledge of their structures.

We have learned, however, that knowing the average, or ideal, structure is not sufficient. We must also understand what defects are present, and whether they are ordered, before we can correlate the structural and superconducting properties and use structural information as a probe of the underlying physics.

The common structural feature of all of the copper oxide superconductors is the presence of one or more CuO_2 planes. Each copper atom in such a plane is strongly bonded, in a nearly square planar arrangement, to four oxygen atoms at a distance of approximately 1.90 Å (see figure 1).[1] The first copper oxide high-T_c superconductor discovered, $La_{2-x}Ba_xCuO_4$, contains single CuO_2 planes separated by corrugated La_2O_2 layers. As additional copper oxide superconductors were discovered, variations of this layered structure, always based on two-dimensional CuO_2 planes, were observed.

The crucial CuO_2 planes can occur singly or in groups. Within a group, individual CuO_2 planes are separated by metal atoms—yttrium or calcium, for example. These groups are intercalated by a variable number of LaO, BaO, CuO, TlO, BiO or PbO layers. Figure 1 shows the layered structure of the 90-K superconductor $YBa_2Cu_3O_7$. This structure contains two CuO_2 planes separated by yttrium atoms. The intercalating layers separating these double CuO_2 planes contain copper, barium and oxygen atoms. Given the possibility of varying the number of planes in a group, the metal atom separating the planes in a group, and the chemistry, thickness and structure of the intercalating layers, it is not surprising that a large number of superconducting copper oxides have now been discovered. These compounds and their structures are discussed in recent reviews.[1,2] In this article I will not attempt a review of the various structures of the oxide superconductors. Instead I will discuss the important ways that structural information has contributed to our understanding of the physics and chemistry of these new superconductors.

Charge-transfer models

A natural model that arises from the common structural features of the copper oxide superconductors is that the superconductivity occurs predominantly in the CuO_2 planes, while the other (intercalated) layers provide, in some fashion, carriers or the coupling mechanism necessary for superconductivity. Based on this hypothesis, it is instructive to view the layered copper oxide superconducting compounds as consisting of conduction layers (the CuO_2 layers) and charge reservoir layers (the intercalated layers), as shown in figure 1. Such models have come to be known as charge-transfer models.[3] The number of carriers in the conduction layer is controlled by the overall chemistry of the system and by the amount of charge transferred between the conduction layer and the charge reservoir layer. The amount of charge transferred depends on the structure, the available oxidation states of the atoms and the competition between charge transfer and oxidation or reduction of metal atoms in the charge reservoir layer.

$YBa_2Cu_3O_{6+x}$ ($0 \leqslant x \leqslant 1$) is perhaps the simplest and most extensively studied compound to which the charge-transfer model applies. One novel feature of this compound is that the copper atoms play two different roles. Two copper atoms per unit cell are in the conduction layer. It is the number of carriers in this region, measured approximately by the oxidation state of these copper atoms, that appears to control superconductivity. A third copper atom is located in the charge reservoir layer. The unusual coordination of oxygen atoms around this copper atom, forming a one-dimensional Cu–O–Cu–O–... chain-like structure along the b direction, has given rise to the term "Cu–O chains" to identify this part of the structure.

In $YB_2Cu_3O_{6+x}$ the oxygen content can vary over a large range—from six to seven oxygen atoms per unit cell.

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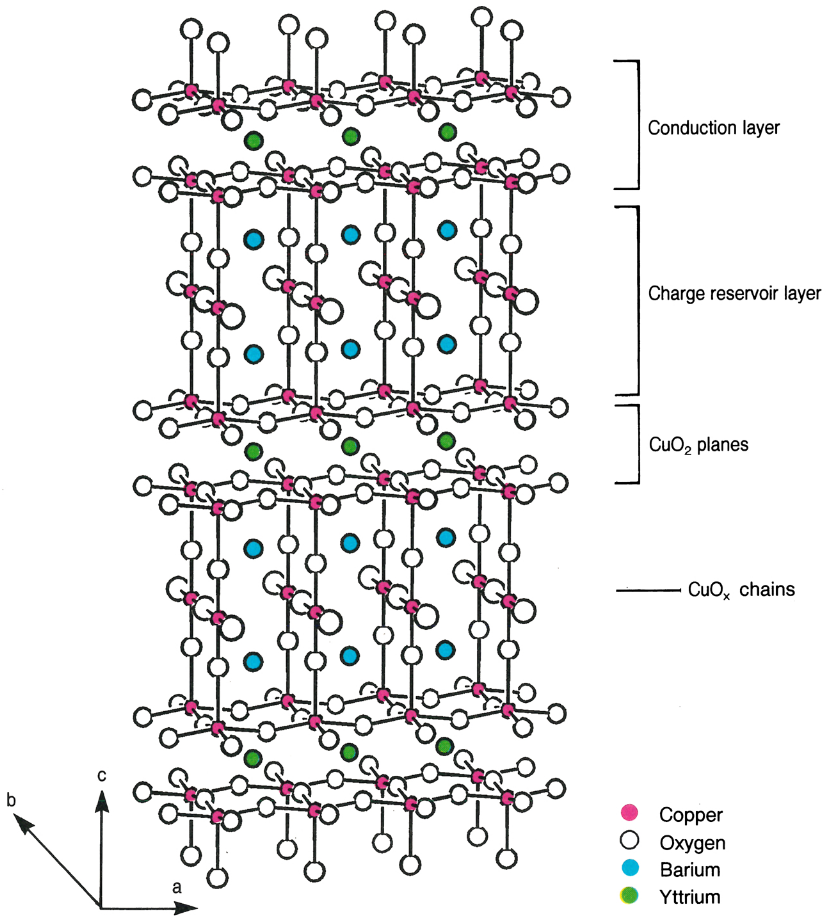


High-temperature superconductor $YBa_2Cu_3O_{6+x}$ has a structure in which alternating conduction layers alternate with charge reservoir layers. The conduction layers consist of two CuO_2 planes separated by yttrium atoms. The charge reservoir layers consist of CuO_x chains along the b direction and barium and oxygen atoms. The oxygen content near the copper atoms in the Cu–O chains is variable: x ranges from 0 to 1. **Figure 1**

The oxygen sites associated with this variation are the "chain" oxygen atoms in the charge reservoir layer. When there are seven oxygen atoms per unit cell, the oxygen atoms are fully ordered structurally to form the Cu–O chains shown in figure 1. As these sites are depleted, the degree of ordering is also reduced, with a finite number of oxygen atoms moving to sites (not shown in figure 1) halfway between the chain copper atoms along the a axis.[4] Eventually, when the remaining oxygen atoms become equally (and randomly) distributed between these two sites, the structure transforms from orthorhombic to tetragonal.

The dominant effect of this variation in oxygen content is to change the oxidation state of the chain copper atom. In general, its oxidation state depends on both the number of neighboring oxygen atoms and the coordination geometry. A minor effect of varying the oxygen content is to transfer charge between the charge reservoir layer and conduction layer. Hole carriers are created in the conduction layer when electrons are transferred to the charge reservoir layer. This redistribution of charge can be measured as a change in the oxidation state of the copper atoms in the conduction planes. A rather precise measure of changes in the oxidation state of the plane copper atom can be obtained from structural data by using the measured Cu–O bond lengths around this copper atom to calculate a bond valence sum.[5] Such a calculation yields the correlation between the transition temperature T_c and the effective charge on the plane copper atom shown in figure 2. This striking correlation attests to the validity and usefulness of the charge-transfer model for understanding the layered oxide superconductors.[3]

Similar charge-transfer ideas can be invoked to explain the relationship between structure and superconducting properties in the other layered copper oxide superconductors. In each case, the CuO_2 plane or group of planes can be viewed as a conduction layer and the intercalating metal–oxygen layers can be thought of as a charge reservoir layer. Modifying the chemistry of the charge reservoir layer changes the number of carriers in the conduction layer by a charge-transfer process. This modification of the chemistry of the charge reservoir layer is usually achieved by the creation of structural defects.

Defects as a doping mechanism

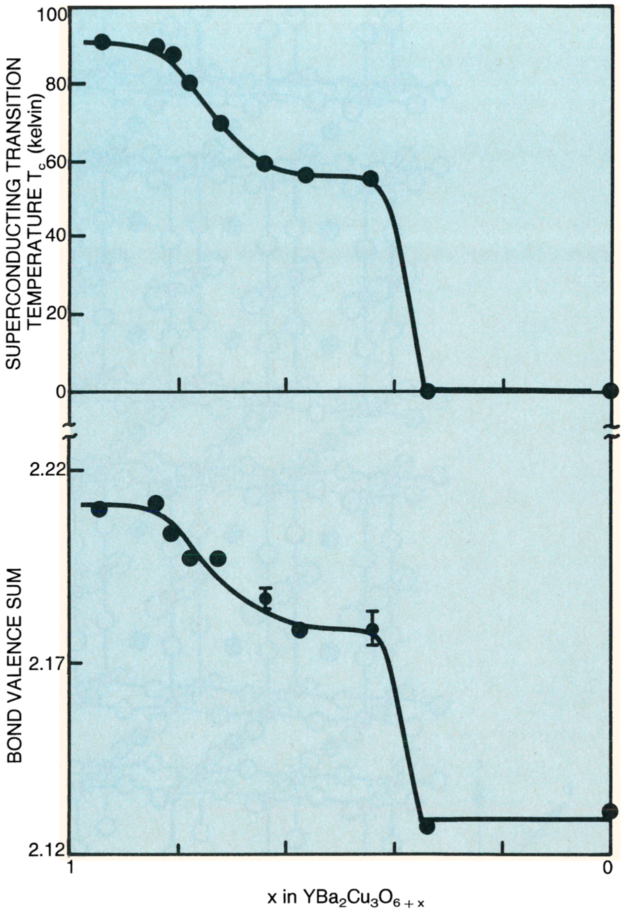
In $YBa_2Cu_3O_{6+x}$, the defects are oxygen atoms that can occupy, in a random or ordered way, available lattice sites in the chain region of the structure. The range of defect concentrations in this compound is unusually large, allowing the properties to be varied from insulating to superconducting. Though not all of the copper oxide superconductors show such a large defect concentration range, most of them can be understood in terms of a doping mechanism that depends on defects in the charge reservoir layer.[6]

There is a simple geometrical explanation for the creation of defects in the charge reservoir layer. In most of these structures, the natural dimensions of the CuO_2 conduction planes and the metal–oxygen planes making up the charge reservoir layer are not matched. The CuO_2 planes control the unit cell dimensions, and the intercalating metal–oxygen planes are "stretched" to match them.[1,5] The atoms in the intercalating planes respond to this stretching by relaxing their positions to form acceptable bond lengths. The excess space thus created can accommodate, and in fact favors the formation of, interstitial defects (interstitial oxygen atoms, for example) or substitutional defects on the metal sites.

Perhaps the simplest example of such behavior occurs in $La_2CuO_{4+\delta}$, where interstitial oxygen defects that form in the La_2O_2 layer are the doping mechanism responsible for the creation of carriers in the CuO_2 conduction plane. Figure 3 shows the defected structure[7] ($\delta \geqslant 0.08$) of $La_2CuO_{4+\delta}$. Superconducting behavior with a transition temperature T_c near 35 K is achieved in La_2CuO_4 when it is doped either with strontium on the lanthanum site to form $La_{1.85}Sr_{0.15}CuO_4$ or with interstitial oxygen to form $La_2CuO_{4.08}$. Assuming that the oxidation states of strontium, lanthanum and the interstitial oxygen are 2+, 3+ and 2−, respectively, the net change in the number of free electrons in the system is nominally the same for either doping mechanism. The simplicity with which the charge-transfer model applies to this system is evidenced by the fact that the same T_c is achieved in both compounds for doping levels that are electronically equivalent.

From a structural point of view, perhaps the most complex examples of doping and charge transfer occur in the layered copper oxide superconductors that incorporate bismuth and thallium in the charge reservoir layer. These compounds have the general formulas $Bi_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ and $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ (where m and n are integers) and are typically identified by the shorthand notation Bi(or Tl)$m2(n-1)n$—for example, Bi-2212, Tl-2223 and so on.[1] The defects proposed to occur in the charge reservoir layer include metal-site vacancies, metal antisite defects, oxygen vacancies and interstitial oxygen.[6] With so many possibilities, it is not surprising that structural studies have not been entirely definitive in sorting out how these defects control the carrier concentration in the CuO_2 conduction planes. Moreover, it has been proposed that as a result of competition between the oxidation or reduction of thallium atoms in the charge reservoir layer and charge transfer to or from the copper atoms in the conduction layer, the thallium-based compounds may be "self-doping," with no additional defects being required to achieve superconductivity.[8]

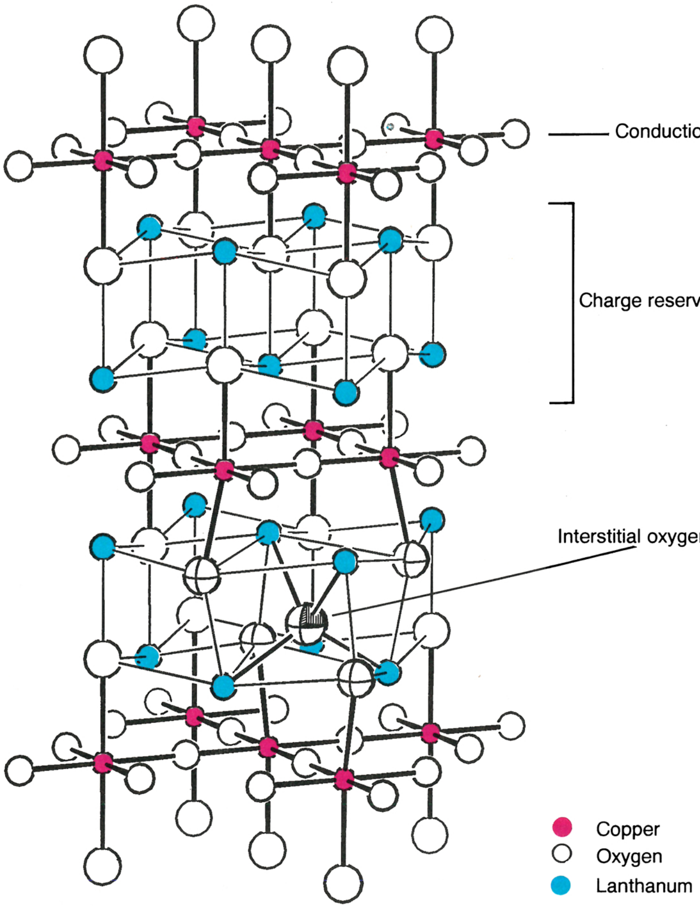
For the bismuth-based compounds, the situation is complicated by the fact that the mismatch between the dimensions of the CuO_2 and intercalating layers is so large that the structures display an incommensurate modulation. In such a structure, the atom positions no longer exhibit only the ideal translational symmetry of the basic unit cell. Rather, the atoms are displaced from their ideal positions with a periodicity that is not commensurate with the underlying unit cell. In the bismuth-based copper oxide superconductors, the modulation involves both atom displacements and substitutions (that is, the substitution of one type of metal atom onto the site normally occupied by another) and affects the CuO_2 planes as well as the intercalating layers.[9] Detailed x-ray diffraction studies of the modulated structure of Bi-2212 have been done that take advantage of the ability to adjust the bismuth scattering power by tuning the x-ray energy through the bismuth absorption edge. Their results lead to the conclusion that the defects in this system include bismuth-atom substitution on the strontium and calcium sites, strontium-atom substitution on the calcium site, vacancies on the strontium site and interstitial oxygen atoms at the end of a modulation period.[10] In spite of this complexity, the calculated average oxidation state for the copper atoms in the conduction layer is 2.21, in good agreement with the optimum values for superconductivity observed in the other copper oxide superconductors. Thus even in the complex bismuth- and thallium-based systems, charge-



Evidence for charge-transfer model. Top: Superconducting transition temperature T_c versus oxygen content for $YBa_2Cu_3O_{6+x}$. Bottom: Bond valence sum around the copper atom in the conduction layer versus oxygen content. The similar behavior seen in the two plots confirms that T_c is proportional to the oxidation state of the copper atoms in the conduction layer. (Adapted from ref. 3.) **Figure 2**

transfer models work well if all of the structural defects are understood.

In a few compounds, competition between charge transfer and the oxidation or reduction of metal ions in the charge reservoir layers can complicate the relationship among defect chemistry, charge transfer and superconductivity. Compounds from the family $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ (see figure 4) offer a particularly instructive example.[11] The conduction layer consists of two CuO_2 planes separated by yttrium (or calcium) atoms, as in the structure of $YBa_2Cu_3O_{6+x}$. The charge reservoir layer includes two SrO layers, two PbO layers and a CuO_δ layer in which the oxygen content can be varied over the wide range $0<\delta<2$. By analogy with $YBa_2Cu_3O_{6+x}$, one might expect that increasing the oxygen content in the charge reservoir layer would increase T_c. Just the opposite occurs. In superconducting compositions, which exhibit the highest T_c when $\delta=0$, the copper cations in the charge reservoir layer have an oxidation state near 1+, while those in the conduction layer have the required oxidation state above 2+. Remarkably, the average copper oxida-



Defected structure of $La_2CuO_{4+\delta}$. The defect oxygen ion occupies an interstitial site coordinated to four lanthanum atoms in the charge reservoir layer. Four near-neighbor oxygen atoms are pushed approximately 0.5 Å off their normal sites to accommodate the defect. **Figure 3**

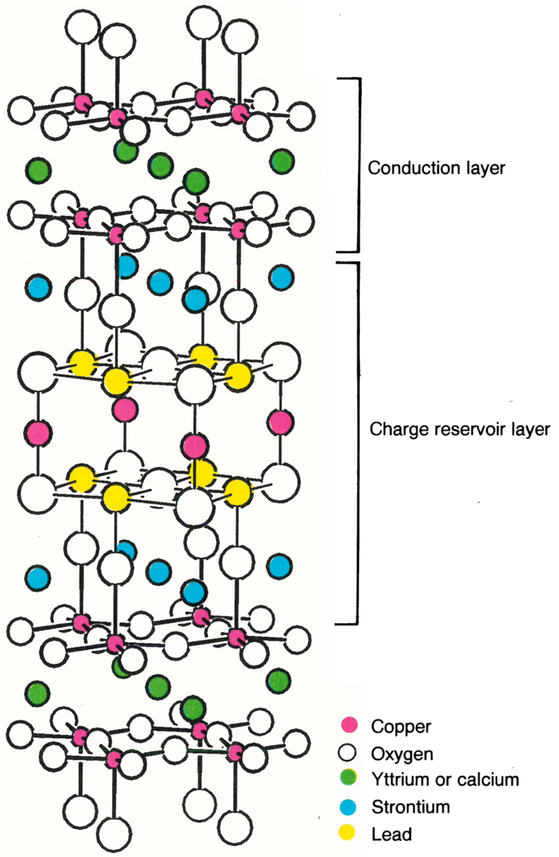
tion state for the compound is less than $2+$. The incorporation of excess oxygen oxidizes the Cu^{1+} ions to Cu^{2+} and some of the nearby Pb^{2+} ions to Pb^{4+}. As a result, an ordering between Pb^{2+} and Pb^{4+} is established, and this ordering hinders charge transfer and the creation of carriers in the conduction layer. The average oxidation state of copper cations in the conduction layer decreases, and superconductivity is destroyed. Measurement of Cu–O bond lengths for the copper atoms in the conduction layer confirms that charge-transfer models are still applicable to this compound, but the complex oxidation–reduction chemistry in the intercalating layers complicates the interpretation.

Defects that destroy superconductivity

Defects can also destroy superconductivity in copper oxide compounds that would otherwise be superconducting. Perhaps the most heavily studied[12] are defects involving chemical substitution at the various sites in the structure (for example, praseodymium on the yttrium site, or iron, cobalt, nickel and so on on the copper sites in $YBa_2Cu_3O_{6+x}$. Such deliberately created defects have been useful as probes of the properties of the copper oxide superconductors. However, in this brief review, I wish to concentrate on intrinsic defects (that is, during normal synthesis) that can destroy superconductivity, because understanding such defects can guide our search for new superconducting compounds.

The most important examples are those where defects form in the conduction layer. The first such case to be observed[13] involved the formation of oxygen vacancies in the CuO_2 conduction layer of $La_{2-x}Sr_xCuO_4$. In this compound the transition temperature T_c increases with increasing strontium concentration x to a maximum of 35 K when x is 0.15. For samples processed in 1 atm of oxygen, oxygen vacancies form in the CuO_2 layer when more strontium is incorporated (that is, as x is increased beyond 0.15). As a result, superconductivity is destroyed. It is not clear, however, whether the loss of superconductivity results from the cancellation of the strontium doping by the oxygen vacancies or from the disruption of the conduction layer by the vacancy defects.

The recent discovery of superconductivity at 60 K in $La_{2-x}Sr_xCaCu_2O_6$ has also called attention to the importance of defects that destroy superconductivity.[14] This family of compounds, based on the $La_2SrCu_2O_6$ structure shown in figure 5, had been discovered over two years earlier, but no superconductivity had been observed for any compositions in spite of the fact that the oxidation state of the copper ions in the CuO_2 conduction planes could be adjusted to the ideal value (that is, $+2.2$ to $+2.3$ as is seen to optimize superconductivity in other copper oxide compounds) by appropriate chemical substitution. The important feature of the superconducting composition $La_{2-x}Sr_xCaCu_2O_6$ is that the metal site between the two CuO_2 planes in the conduction layer (that is, the site equivalent to yttrium in the $YBa_2Cu_3O_{6+x}$ structure) is occupied exclusively by calcium atoms. In the nonsuperconducting compositions, this site is occupied by large lanthanum or strontium cations, allowing extra oxygen atoms (identified as the defect oxygen site in figure 5) to occupy sites adjacent to the lanthanum or strontium atoms and between the copper atoms in the CuO_2 planes.[15] These excess-oxygen defects apparently destroy superconductivity by disrupting the two-dimensional nature of the conduction layer.



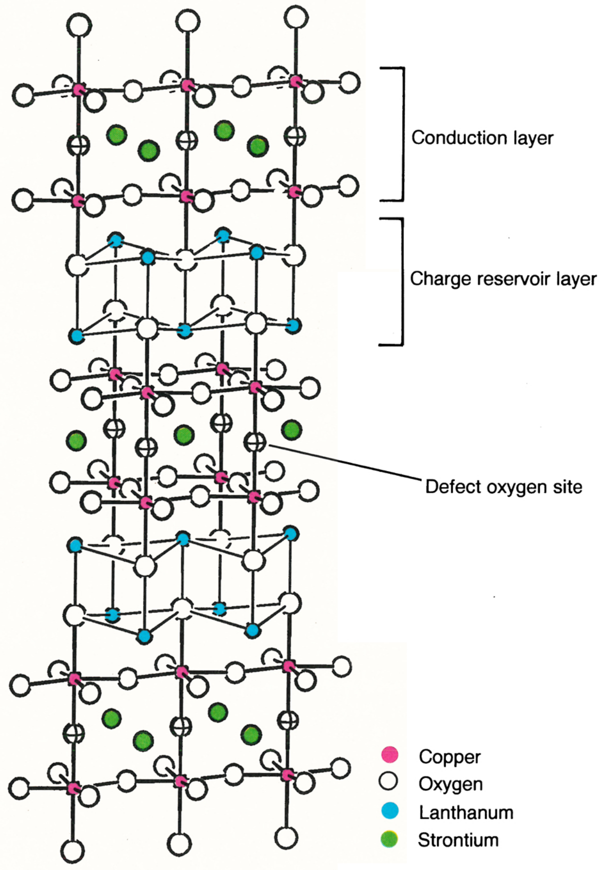
$Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ structure, shown for $\delta = 0$. Extra oxygen atoms ($0 < \delta \leqslant 2$) can be incorporated around the copper atoms in the charge reservoir layer. **Figure 4**

Defect ordering and superconductivity

It is increasingly clear that the ordering of defects can have a dramatic effect on superconducting behavior. $YBa_2Cu_3O_{6+x}$ has been the model system for studying such effects because it displays a wide range of defect concentrations (as x ranges from 0 to 1) and defect ordering configurations. I have already described the two structures that characterize the extremes of the defect concentration range. At the maximum oxygen concentration for which the compound is stable ($x = 1$), only half of the available sites in the charge reservoir layer are occupied by oxygen atoms. These oxygen atoms are perfectly ordered between chain copper atoms along the b axis to form one-dimensional Cu–O–Cu–O–. . . chains, resulting in an orthorhombic structure (figure 1). At the minimum oxygen concentration ($x = 0$), no Cu–O–Cu–O . . . chains exist and the structure is tetragonal. Conceptually, it is straightforward to visualize that one of these configurations can evolve smoothly into the other as the oxygen concentration varies from $x = 1$ to $x = 0$ and the degree of order (that is, the number of oxygen atoms in the chains minus the number between the chains) varies smoothly to zero. Such behavior indeed occurs at high temperatures, resulting in a continuous phase transition from orthorhombic to tetragonal symmetry.[5]

At lower temperatures, however, the behavior is more complex, because interactions between the oxygen atoms on the chain and interchain sites lead to various ordered structures. Figure 6 shows a calculated phase diagram[16] for $YBa_2Cu_3O_{6+x}$. The OI and T phases are the basic orthorhombic and tetragonal structures already discussed. The OII phase is an ordered orthorhombic structure characterized (at the ideal $x = 0.5$ composition) by alternating full and empty Cu–O–Cu–O–. . . chains, giving rise to a supercell doubled along the a axis. The calculations that yield this phase diagram also predict a number of additional ordered phases (not shown in figure 6) corresponding to more complex ordering patterns. The OII phase and many of the more complex ordered phases have been observed in diffraction experiments on oxygen-deficient samples at room temperature.[17] However, sluggish kinetics, resulting in the formation of the various ordered phases only over short length scales, has prevented a full experimental verification of the calculated phase diagram.

In spite of these experimental difficulties it is clear that defect ordering of this kind has a direct effect on superconductivity. In particular, the so-called 60-K plateau—T_c remains essentially constant at 60 K while oxygen content varies (see figure 2)—is associated with the formation of the OII ordered phase. Perhaps the simplest

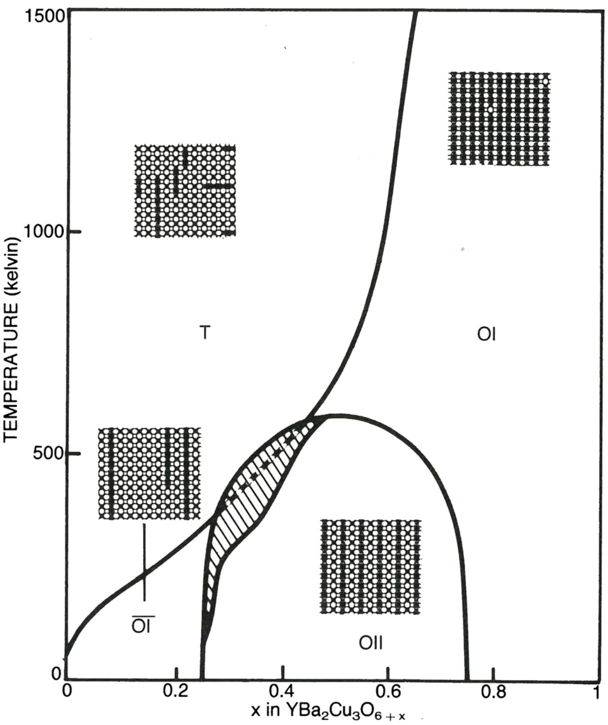


$La_2SrCu_2O_{6+\delta}$ structure. When oxygen atoms partially occupy the defect site near the strontium site in the conduction layer, superconductivity is destroyed. A superconducting composition has been made[14] by placing calcium atoms on the strontium site and a mixture of lanthanum and strontium atoms on the lanthanum site to form $La_{2-x}Sr_xCaCu_2O_6$. The smaller ionic radius of the calcium ion prevents the incorporation of oxygen atoms at the defect site. **Figure 5**

experimental confirmation of this conclusion is the observation that oxygen-deficient $YBa_2Cu_3O_{6+x}$ samples quenched from high temperature exhibit no 60-K plateau behavior, while those prepared by low-temperature methods (that is, methods that sample and preserve the features of the OII region of the phase diagram) exhibit a well-defined plateau.[18] It is believed that the transition temperature T_c remains constant in the 60-K plateau region as oxygen content varies because of the way defect ordering influences the competition between the oxidation or reduction of the chain copper atoms and the charge transfer between the chains and CuO_2 planes: T_c is nominally constant because the amount of charge transfer is constant.

The superconducting properties are strongly affected even when defect ordering occurs on a short length scale. This point has been made graphically clear by recent experiments in which the superconducting and structural properties of oxygen-deficient $YBa_2Cu_3O_{6+x}$ are monitored while the oxygen atoms diffuse toward an ordered configuration at room temperature.[19] Clearly, the diffusion lengths involved are short—on the order of 10 Å in 24 hours; thus, structural ordering can occur only on a short length scale, perhaps over a few unit cells. Nevertheless, the effects on the superconducting transition temperature are dramatic. Figure 7 shows the superconducting transition temperatures T_c for a sample of composition $YBa_2Cu_3O_{6.45}$ measured after successive annealings at room temperature.[20] A single crystal of $YBa_2Cu_3O_{6.45}$ was first equilibrated at 500 °C in the appropriate oxygen partial pressure to establish the desired oxygen concentration. The sample was then rapidly quenched to liquid nitrogen temperature, essentially freezing in the configuration of oxygen atoms that existed at 500 °C. The first measurement of T_c was made immediately after quenching. The sample is then repeatedly warmed to room temperature, annealed there for a specified amount of time and then cooled for measurement of the new T_c. Structural measurements confirm that the systematic increase in T_c resulted from the ordering of oxygen atoms on a short length scale as these atoms diffused to achieve a configuration more consistent with the equilibrium phase diagram at room temperature.[19] These observations lead us to the question of exactly how defect ordering influences superconducting behavior. It is clear that additional carriers appear in the conduction layer as the short-range ordering occurs. Cu–O bond lengths for the copper atoms in the conduction layer show the contraction expected for the observed increase in T_c based on charge-transfer models.[19] One straightforward explanation is that short-range ordering minimizes the number of unfavorably coordinated copper atoms in the charge reservoir layer. In simple chemical terms, this leads to charge transfer because the oxidation state of the chain copper atoms is a function of coordination geometry as well as coordination number.[21] If the oxidation state of the chain copper atoms changes, that of the plane copper atoms must respond. More sophisticated calculations of the electronic band structure lead to the same conclusion—that the formation of Cu–O–Cu–O–... chain fragments or ordered configurations in the charge reservoir layer enhances the carrier concentration in the conduction layer.[22]

We are presented with a challenging problem, however, in that the superconducting behavior is influenced by ordered domains that are too small to probe and characterize experimentally. One approach to this problem has been to obtain the relevant structural information from Monte Carlo computer simulations rather than experiments. In this way, Henning Poulsen and his colleagues at Risø National Laboratory in Roskilde, Denmark, were able to predict the T_c of $YBa_2Cu_3O_{6+x}$ as a function of oxygen content.[23] Their model assumes that the amount of charge transfer from domains of the OI phase leads to a T_c of 93 K, while that from domains of the OII phase leads to a T_c of 58 K. A single T_c for the sample is calculated by taking a simple average based on the number of oxygen atoms incorporated in each of the two kinds of domains. It is intriguing, and may be physically significant, that in this model only ordered orthorhombic domains contribute to superconductivity.

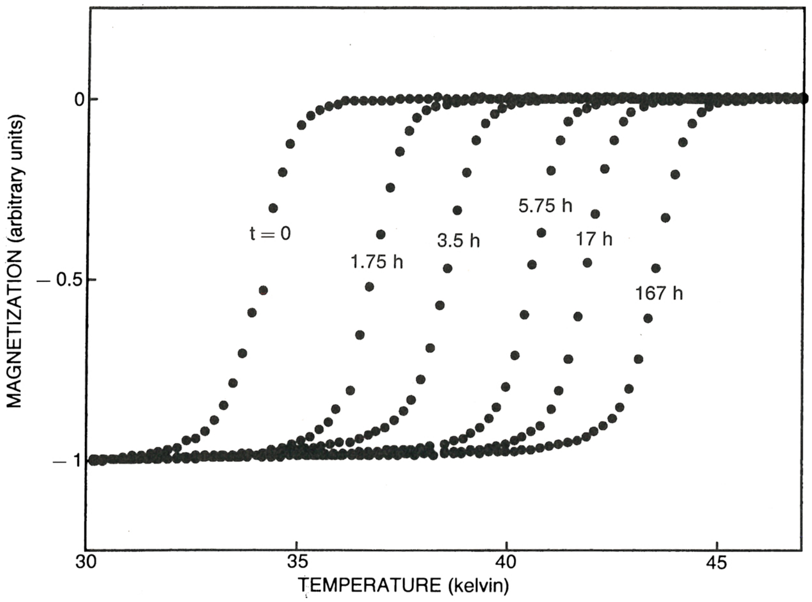


Calculated phase diagram of $YBa_2Cu_3O_{6+x}$. Phases OI and T are the normal orthorhombic and tetragonal phases. OII is an ordered orthorhombic phase in which full and empty Cu–O–Cu–O–... chains alternate, giving rise to a supercell doubled along the crystallographic *a* axis. For each phase, a schematic structure diagram (insets), obtained from Monte Carlo simulation, illustrates the pattern of oxygen site occupancy in the basal plane. Filled circles denote oxygen atoms, and open circles denote vacant oxygen sites. Thus, Cu–O–Cu–O–... chains or chain fragments appear as lines of filled circles. (Adapted from Ref. 16.) **Figure 6**

In spite of its success, however, such a model does not address important questions concerning the underlying physics. Most importantly, we still do not know whether an appropriate carrier concentration, controlled by charge transfer, is the only requirement for superconductivity in $YBa_2Cu_3O_{6+x}$ or whether an appropriate ordered structure, at least on a local length scale, also is required.

Future work

Although the average, or ideal, structures have been determined for all of the known copper oxide superconductors, it is clear that we cannot use the structural information to fully understand their superconducting properties until our knowledge of the structure is ex-



Diamagnetic shielding data for a single crystal of $YBa_2Cu_3O_{6.45}$, showing the effect of room temperature annealing on the superconducting transition temperature. The first measurement was made immediately after quenching into liquid nitrogen from 500 °C; subsequent data were taken after annealing at room temperature for times up to 167 hours. The systematic increase in T_c from 34 K to 43 K results from the ordering of oxygen atoms on the available sites to form Cu–O–Cu–O– . . . chain fragments. (Adapted from ref. 20.) **Figure 7**

tended to the local scale. We must investigate the defects that can form and their various ordered configurations. At present, structures are known at this level of detail for only a few of the copper oxides. Our structural investigations are hampered by the fact that defect ordering on a length scale too short to probe by most experimental techniques can substantially alter superconducting behavior. Clearly, much work remains to be done.

However, for those systems that have been studied in detail, a consistent picture emerges. If defects form in the charge reservoir layer, they can function as a doping mechanism that creates carriers and gives rise to superconducting behavior in a material that may normally be insulating. Defect ordering can enhance or suppress this charge transfer. Conversely, defects associated with the CuO_2 planes in the critical conduction layer can destroy superconductivity. These important concepts are already serving as a guide in the optimization of new superconducting compounds. Questions concerning direct relationships between structure and superconductivity—for example, the possibility of structure itself playing a role in the superconducting mechanism—remain to be answered.

References

1. I. K. Schuller, J. D. Jorgensen, Mater. Res. Soc. Bull., January 1989, p. 27.
2. R. M. Hazen, in *Physical Properties of High Temperature Superconductors II*, D. M. Ginsberg, ed., World Scientific, Singapore (1990), p. 121.
3. R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck Jr, L. W. Rupp Jr, Physica C **165**, 419 (1990).
4. I. D. Brown, J. Solid State Chem. **82**, 122 (1989).
5. J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).
6. J. D. Jorgensen, D. G. Hinks, Neutron News **1**(2), 24 (1990). J. D. Jorgensen, P. Lightfoot, S. Pei, Supercond. Sci. Technol. **4**, S11 (1991).
7. J. D. Jorgensen, B. Dabrowski, S. Pei, D. G. Hinks, L. Soderholm, B. Morosin, J. E. Schirber, E. L. Venturini, D. S. Ginley, Phys. Rev. B **38**, 11337 (1988). J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards, D. G. Hinks, Phys. Rev. B **40**, 2187 (1989).
8. J. B. Goodenough, A. Manthiram, J. Solid State Chem. **88**, 115 (1990).
9. V. Petricek, Y. Gao, P. Lee, P. Coppens, Phys. Rev. B **42**, 387 (1990). X. Kan, PhD thesis, University of Houston, October 1990.
10. P. Coppens, P. Lee, Y. Gao, H.-S. Sheu, J. Phys. Chem. Solids (1991), in press.
11. M. Marezio, A. Santoro, J. J. Capponi, E. A. Hewat, R. J. Cava, F. Beech, Physica C **169**, 401 (1990).
12. See, for example, the references cited in: J. T. Markert, Y. Dalichaouch, M. B. Maple, in *Physical Properties of High Temperature Conductors I*, D. M. Ginzberg, ed., World Scientific, Singapore (1989), chapter 6; J. M. Tarascon, B. G. Bagley, in *Chemistry of High T_c Materials*, T. Vanderah, ed., Noyes Publications, Park Ridge, New Jersey, (1991), chapter 8 (in press); J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).
13. D. G. Hinks, B. Dabrowski, K. Zhang, C. U. Segre, J. D. Jorgensen, L. Soderholm, M. A. Beno, Mater. Res. Soc. Proc. **99**, 9 (1988).
14. R. J. Cava, B. Batlogg, R. B. van Dover, J. J. Krajewski, J. V. Waszczak, R. M. Flemming, W. F. Peck Jr, L. W. Rupp Jr, P. Marsh, A. C. W. P. James, L. F. Schneemeyer, Nature **345**, 602 (1990).
15. P. Lightfoot, S. Pei, J. D. Jorgensen, X.-X. Tang, A. Manthiram, J. B. Goodenough, Physica C **169**, 464 (1990).
16. D. de Fontaine, G. Ceder, M. Asta, Nature **343**, 544 (1990); J. Less-Common Metals **164–165**, 108 (1990).
17. R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gur, R. A. Huggins, Nature **340**, 619 (1989).
18. C. Namjung, J. T. S. Irvine, A. R. West, Physica C **168**, 346 (1990).
19. J. D. Jorgensen, S. Pei, P. Lightfoot, A. P. Paulikas, B. W. Veal, Physica C **167**, 571 (1990).
20. B. W. Veal, A. P. Paulikas, H. You, H. Shi, Y. Fang, J. W. Downey, Phys. Rev. B **42**, 6305 (1990).
21. L. K. Burdett, G. V. Kulkarni, K. Levin, Inorg. Chem. **26**, 3650 (1987). C. J. Hou, A. Manthiram, L. Radenberg, J. B. Goodenough, J. Mater. Res. **5**, 9 (1990).
22. E. Orti, P. Lambin, J.-L. Bredas, J.-P. Vigneron, E. G. Derouane, A. A. Lucas, J.-M. Andre, Solid State Commun. **64**, 313 (1987). J. Zaanen, A. T. Paxton, O. Jepsen, O. K. Andersen, Phys. Rev. Lett. **60**, 2685 (1988). P. Lambin, in *Oxygen Disorder Effects in High-*T_c *Superconductors*, J. L. Moran-Lopez, I. K. Schuller, eds., Plenum, New York (1990), p. 101.
23. H. F. Poulsen, N. H. Andersen, J. V. Andersen, H. Bohr, O. G. Mouritsen, Nature **349**, 594 (1991). ■