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Structural and Compositional Basis of High-Temperature Superconductivity: Properties of the Magic Electronic State

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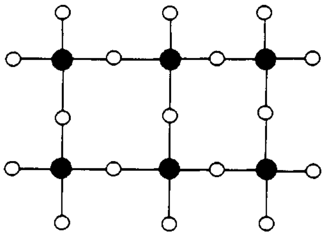
A new electronic model is developed along largely qualitative lines to account for some of the structural and compositional observations in the area of high-temperature superconducting cuprates. The model is based upon the avoided crossing with interatomic separation of two energetically close states, one containing electron holes on copper and the other electron holes on oxygen. If these two curves lie close together, both energetically and configurationally, then a new hybrid state is generated, described at the crossing point by an equal mixture of both. The generation of this state is very sensitive to copper oxidation level, and small atomic displacements around the energy minimum lead to large changes in the nature of the wave function and, hence, fluctuations in both spin and charge. It is suggested, without proof, that this electronic state-of-affairs corresponds to that of the high-temperature superconductor. The variation in the nature of the wave function with distance and, hence, the strength of these fluctuations show striking similarities with the system dependence of the superconducting transition temperature in the cuprate superconductors.

Introduction

There are several important questions which need to be answered for the high- temperature superconducting cuprates before the details of the superconducting state can really be addressed in these fascinating materials. They are associated with the nature of the electronic state which exists at the superconducting composition, how it may be reached by variation in chemical composition in the broadest sense, and how the details of the geometric structure and composition influence it. In this paper we take an electronic model, which we recently briefly presented,[1] and discuss its implications in terms of the structural and compositional basis for high-temperature superconductivity. Much of the discussion will necessarily be qualitative.

The volume of research that has been completed[2] in this area is enormous and so a brief review of some salient points will be important to direct attention toward some important general observations which we believe have a bearing on the problems at hand. There are now perhaps some fifty different superconductors of this type which are known, although counting all of the smaller variations in stoichiometry will lead to a larger figure.

(a) In all of these materials a common feature is the presence of the CuO$_2$ sheet shown in **1**. Typical Cu–O distances range from 1.88 to 1.94 Å in the hole-doped superconductors but longer in their electron-doped analogs and other cuprates. Very often the sheet is not completely flat, sometimes being folded or rumpled. Almost always there are one or two oxygen atoms coordinated above and below this plane but with considerably longer Cu–O distances (2.3–2.5 Å). Since the electronic configuration at copper in all of these compounds is close to d^9, this local structural distortion may be regarded as arising *via* a Jahn–Teller distortion of the regular octahedral arrangement. Between the sheets lie the rest of the structure, usually described as the "reservoir" (**2**).



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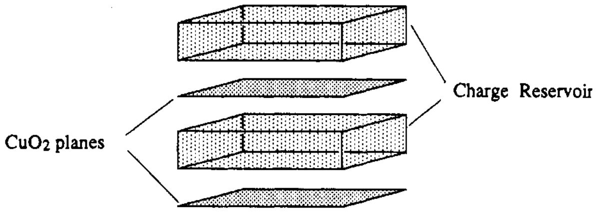

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Its exact electronic role varies from system to system, but its chemical composition and structure determines the amount of charge formally donated or removed from these CuO$_2$ sheets. There appears to be, in those cases where statements concerning copper oxidation state are possible, a critical doping level of the sheet for superconductivity. For example in the hole-doped system La$_{2-x}$Sr$_x$CuO$_4$ the maximum T_c is achieved (vide infra) for $x \sim 0.15$, and very similar copper oxidation state (Cu$^{\sim 2.15+}$) and T_c are found[3] in La$_{2-x}$Sr$_x$CuO$_{4.07}$. In the electron-doped systems both RE$_{2-x}$M$^{IV}_x$CuO$_4$[4,5] and RE$_2$CuO$_{4-x}$F$_x$[6] are known with similar T_c's, similar geometrical structures from diffraction results,

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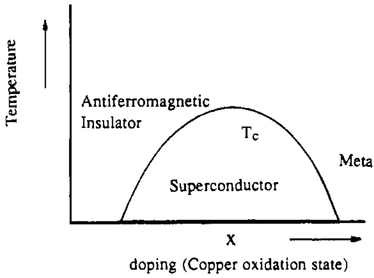
and, since x is close to 0.17 in both cases, similar copper oxidation states. (In most of the bismuth- and thallium-containing systems the stoichiometry is not known accurately and so neither is the copper oxidation state. In the 1-2-3 compound, $YBa_2Cu_3O_{7-\delta}$, the doping process arises via band overlap[7,8] and so similar quantitative comments may not be made from the chemical formula alone.)

(b) A striking feature of these superconductors is the degree to which changes in stoichiometry, invariably rather small, have on the superconducting transition temperature. The compositional dependence of the critical superconducting temperature in many of these materials has the inverted parabolic shape shown in **3**. In $La_{2-x}Sr_xCuO_4$ the maximum T_c lies at $x \sim 0.15$ (We will ignore for the present the asymmetry of this peak found experimentally[9] and the splitting found[10] in $La_{2-x}Ba_xCuO_4$.) Similar behavior is found for other systems but is often not as readily quantifiable. Thus the thallium 2212 compound shows striking variations in T_c with both oxygen[11] and thallium[12] stoichiometry. T_c may also be controlled by annealling[13] with hydrogen which leads to removal of oxygen. An inverted parabola is found for T_c vs x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$, to mention but one example.[14] In the sense that the Cu–O distance or the bond valence sum (BVS) at copper are measures of hole doping (vide infra), inverted parabolas are found for a series of superconducting families in the T_c vs BVS plots of Whangbo and Torardi.[15]



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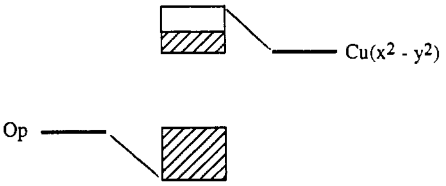
(c) The electronic implications of pictures such as that shown in **3** are far-reaching. The unpaired "copper 3d electron" is certainly localized in an orbital with large Cu 3d character in the undoped, antiferromagnetically insulating material La_2CuO_4. The doped material $La_{2-x}Sr_xCuO_4$ becomes a superconductor beyond $x \sim 0.05$ and eventually, at larger x, a normal metal. In the latter the valence electrons are described by a delocalized state. The superconducting region therefore lies between normal metal and insulator and, hence, between two very different electronic situations. Estimates[16] of the ratio of the on-site electron-electron repulsion to the bandwidth, U/W, are close to 1, an electronic regime which is usually difficult to describe, since correlation effects are very important here.

(d) There are some rather special observations concerning the thermodynamic stability of the cuprate superconductors. There is now quite a body of evidence which identifies the superconducting state with a region of thermodynamic stability on the phase diagram. This has been called[17] a "unique thermodynamic state". In contrast to the known low-temperature superconductors, the superconducting cuprates often appear to be generated as one of the components resulting from phase separation. An interesting example is the oxygen-rich material $La_2CuO_{4+\delta}$. At room temperature and below, $La_2CuO_{4+\delta}$ is not phase pure;[3] at around this temperature a phase separation occurs, $La_2CuO_{4+\delta} \rightarrow La_2CuO_4 + La_2CuO_{4.07}$, the proportions of the two phases being set by the value of δ. La_2CuO_4 itself is an insulator, but the $O_{4.07}$ material is a superconductor with a $T_c \sim 35$ K. As noted above, this system has a copper oxidation state ($Cu^{2.14+}$) and T_c very similar indeed to the optimum values for the $La_{2-x}Sr_xCuO_4$ series. In a related observation, heating the $La_{2-x}Sr_xCuO_4$ compound at temperatures high enough to allow Sr mobility leads to[18] generation of $La_{1.85}Sr_{0.15}CuO_4$, the stoichiometry with the maximum T_c. Phase separation is also found in the electron-doped regime for both $RE_{2-x}M^{IV}_xCuO_4$[4,5] and $RE_2CuO_{4-x}F_x$.[6] The situation for other more complex materials with thallium and bismuth containing interlayers is not as clear-cut. In the latter there are many phases, the systems are in general not well-characterized, and we have a much poorer understanding of the details of the structure.

Although there are many qualifications to the following summary, we may state the essential features of the problem briefly as follows. Superconductivity is associated with the CuO_2 planes. The superconducting state is generated by a particular oxidation state of the copper atoms in these planes, so that one of the roles of the reservoir material is to optimally dope these sheets. There is a thermodynamic stabilization of the CuO_2 planes at this particular composition.

Electronic Model



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There have been several theoretical studies which attempt to address the electronic description of these materials. LDA calculations,[7] in excellent agreement with the photoelectron spectra[19] of the 1-2-3 compound for example, point to the applicability of a traditional band model for the superconductor at least as far as these high energy excitations are concerned. **4** shows the general picture which comes from tight-binding theory too.[2c] The copper $x^2 - y^2$ and oxygen 2p orbitals are close in energy, are involved in strong interactions, and lead to the generation of "bonding" and "antibonding" bands. With the electron count appropriate for these systems, ~Cu(II) or d^9, the upper of the two bands is approximately half full. The Cu–O antibonding nature of this band is substantiated experimentally by the increase in Cu–O distance on electron doping and the decrease in Cu–O distance on hole doping.[20] These LDA calculations fail[21] however to reproduce the localized nature of

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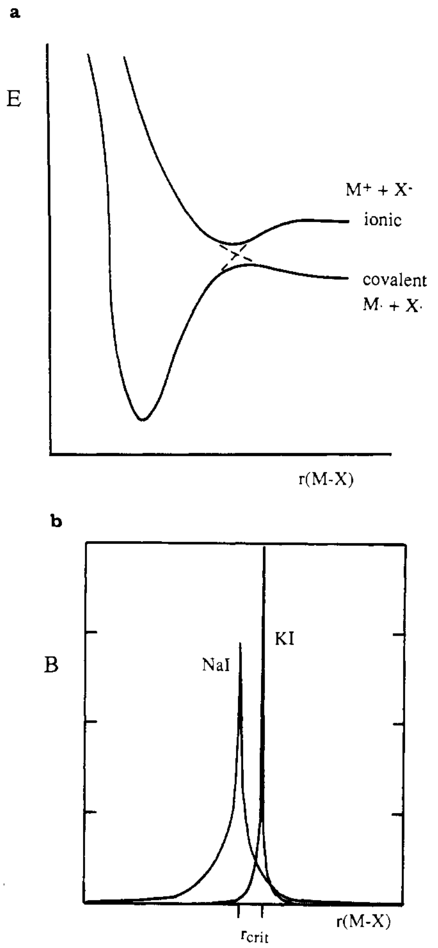
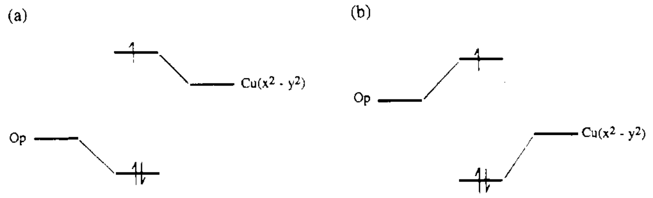


Figure 1. (a) Avoided crossing of covalent and ionic curves in the alkali halides as a function of internuclear separation. (b) Behavior of the Berry function, *B* (see text), for the two cases of NaI and KI. The wider function for NaI results from larger overlap between the two curves than for the KI case. (The *r*(M–X) scales are not coincident for the two cases.)

the bonding in the undoped 2-1-4 compound which is an insulator. Particularly interesting have been calculations using the Hubbard formalism[22] or INDO or *ab initio* molecular orbital methods[23] on small clusters, designed to mimic the infinite two-dimensional CuO_2 sheet. These show in a very clear way how the nature of the highest occupied levels change on doping for a fixed Cu–O distance. In the undoped state the electronic description is one where the unpaired copper electron is located in a localized orbital which is largely copper $x^2 - y^2$ in character. On doping however, the character of the state changes such that the holes now lie in a delocalized state which is largely oxygen in character. So, associated with the change from a localized to delocalized description (i.e., insulator to metal), there has been a significant change in the nature of the orbitals involved. This change in orbital character is relatively easy to understand from **5**. The higher energy level which results from the interaction of two nondegenerate orbitals is antibonding between the two and contains more orbital character from the less strongly bound starting level. Thus in **5a** the upper level is largely copper $x^2 - y^2$ and the lower level oxygen 2p. In **5b** the converse is true. Less easy to understand however, is how these "effective", or renormalized, starting energies vary with doping. However, certainly they will change, as evidenced by the numerical calculations of refs 22 and 23. With two energy levels and three electrons, two doublet states may be generated and are shown in **6**. The energetic ordering of the "oxygen" and "copper" one-electron levels which we have just described will determine the character of these two states. How they change in energy as the Cu–O distance is reduced is difficult to predict quantitatively, especially since in the solid state a band model is eventually a good electronic description. How the localized states at large internuclear separation evolve into delocalized states at shorter distances has been the object of many studies[24] and is still an area of considerable flux. Initially, however, we shall not concern ourselves with this question. We suggest, however, that each state will contain an energy minimum at some *r*(Cu–O) as shown in **7**. An important consequence of this picture is that since these two states have the same symmetry, there will be an avoided crossing between them.



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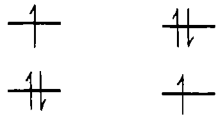

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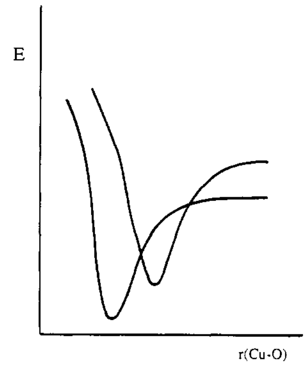

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It is profitable at this stage to recall the well-known avoided crossing between ionic and covalent curves for the alkali halide molecules.[25] These take place at distances larger than the equilibrium separation and the general picture is shown in Figure 1. Although such molecules have provided useful theoretical and experimental test-beds for avoided crossings,[26] the phenomenon is commonplace in chemistry. As the internuclear separation decreases in Figure 1, it is clear that at some point the electron effectively jumps from sodium to chlorine, Mulliken's "sudden electron transfer".[25] In the region close to the crossing point the wave function describing the adiabatic curves changes dramatically in accord with such an idea. From high-quality calculations Hay, Kahn, and Shavitt showed[27] how the dipole moments of the two states involved show dramatic changes on moving through the crossing region for LiF. Berry[26] showed that if the wave function is written as $\psi = c_1\phi_1 + c_2\phi_2$, where $\phi_{1,2}$ represent the

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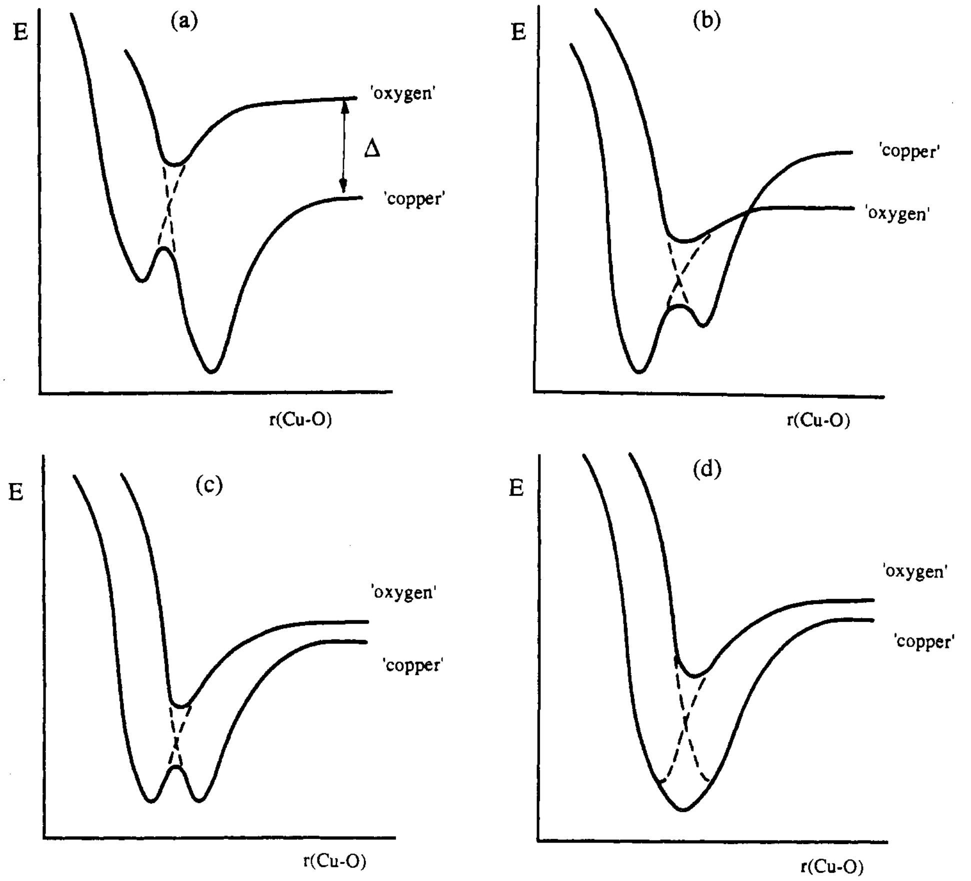

Figure 2. Four possibilities for the intersection of "copper" and "oxygen" curves in the cuprates, by analogy with the behavior in Figure 1. (a) Undoped case where the energy separation, Δ, at large r(Cu–O) is large. The electronic description is of a largely copper located, localized state. (b) Heavily doped case where Δ is negative. The electronic description is of a largely oxygen located, delocalized state. (c, d) Two intermediate cases, which differ in the magnitude of the interaction between the two curves. In (c) it is small, but it is large enough in (d) to generate a single minimum.

ionic and covalent wave functions, then a useful way of representing this sharp change in the nature of the state is to follow the parameter dc_1/dr as a function of internuclear separation. (In fact Berry used $B = \log((dc_1/dr)/c_2 + 1)$.) Peaked behavior for this function is found (Figure 1), centered at the internuclear separation appropriate for the crossing, r_{crit}. The width of the Berry function increases and its height decreases as the overlap between the ionic and covalent states increases. Of course the variation on the magnitude of the interaction between the two states varies with distance in the same way.

Superconducting Regime

The discussion of the last section sets up the problem which will be addressed here, namely how the behavior of the electronic states concerned is controlled by chemical composition and structure. It will be convenient to discuss four different cases[1] derived from the picture shown in 7. As noted above, the "copper" and "oxygen" curves (labels used to identify the location of the electron holes) will be shifted relative to each depending on the doping level. In the undoped material the "copper" state lies lower, in the heavily doped material the "oxygen" state lies lower, and in between the two are close in energy. Figure 2a shows the undoped case, appropriate for La_2CuO_4 itself. Because of the functional form of the two curves, the avoided crossing takes place at a short Cu–O distance. It is not an important event since the system lies in a minimum largely determined by the "copper" curve. Figure 2b shows the other extreme, the heavily doped case, where the energies of the two curves at large r(Cu–O) are reversed. The avoided crossing is not significant here since it takes place at a longer distance than the equilibrium internuclear separation. Appropriate for a heavily doped, metallic $La_{2-x}Sr_xCuO_4$ system, the electronic description is of a largely oxygen-located band.

The intermediate cases are particularly interesting since here the crossing of the two states is important. If the interaction between the two states, "copper" and "oxygen", is small, then, as shown in Figure 2c, there may be two states, either equal or close in energy. One is "copper", and the other, "oxygen". This state of affairs describes the series of interconfigurational fluctuation compounds[28,29] found for SmS and several rare earth compounds. Here a change in pressure or temperature may switch the system from one minimum to another. For SmS one of the states would be labeled as f^n and the other as the interconfigurational fluctuating state d^1f^{n-1}. The first is localized, and the second, metallic. The metallic state has the shorter Sm–S distance.

An especially interesting state of affairs is depicted in Figure 2d. Here the interaction between the two curves is large enough to generate a single minimum. We have described this as a "magic state" with a set of unique properties which we have suggested are those of the high-temperature superconductor. The major prediction of the model is that there is a single doping level for an isolated CuO_2 sheet which gives rise to the electronic requirements for the "degenerate" crossing of Figure 2d and that the resulting electronic stabilization of the system is absent for the other three cases. Such a prediction allows an explanation of the origin of the phase separation noted above[3,18] for $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$ and suggests that the "magic" d electron count for the CuO_2 plane is $\sim$8.85. The criteria for generation of such a state are just those identified some years ago,[30] namely copper and oxygen states which are close in energy and with a large interaction energy between the two. The present state of affairs differs from that discussed for SmS above in the important sense that there the interaction energy (between the d and f states) is

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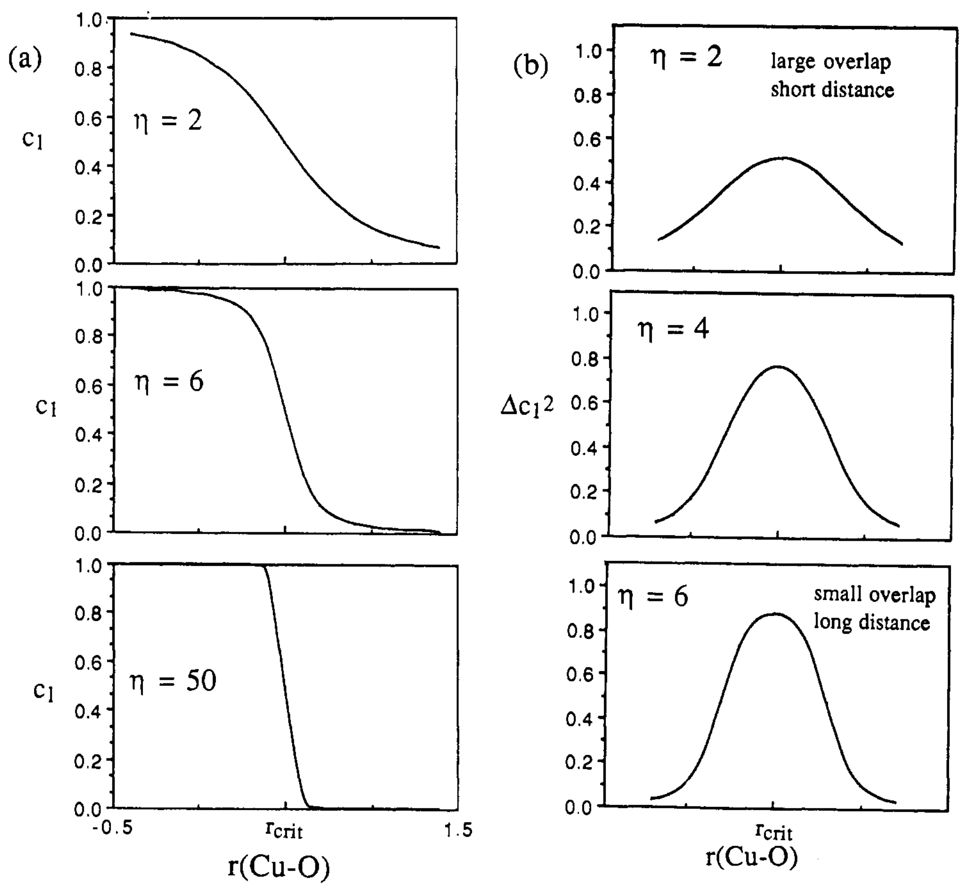

Figure 3. (a) Variation in the wave function (c_1) on moving through the crossing point (r_{crit}) of the two diabatic curves of Figure 2d as a function of the dimensionless parameter η. This is the ratio of the relative slopes of the two interacting curves at the crossing point to the interaction integral between them. (b) Variation in the parameter Δc_1^2. Notice that smaller η values, corresponding to larger interaction integrals, lead to the wider, flatter shapes for this function. The behavior of the Berry function (Figure 1) is similar.

smaller. The presence of this stabilization at the superconducting composition should show up in other ways, as a shortening of the Cu–O distance perhaps.

The electronic description of the magic state is very interesting. At the very bottom of the minimum of Figure 2d the wave function is composed of equal contributions from the two diabatic states. Following the discussion above for the alkali halides the wave function may be written as $\psi = c_1\phi_1 + c_2\phi_2$, where c_1 and c_2 are now the weights of the "copper" and "oxygen" states rather than the covalent and ionic states. Figure 3a shows how the wave function changes (variation in c_1) around the critical point. Figure 3b shows a plot of the change in the electronic description, Δc_1^2 for some arbitrary amplitude either side of the critical point. The behavior of Berry's function, dc_1/dr, as a function of internuclear separation is similar. The details of the change in wave function resulting from the interaction of any two states (assumed to be linear in the crossing region) is determined[31] by the dimensionless parameter η, the ratio of the relative slopes of the two interacting curves at the crossing point to the interaction integral between them. Notice that the larger interaction integral (presumably associated with a shorter distance) gives rise to a wider, flatter peak in Figure 3b. Vibrations centered around the magic point involve large movements of charge. Small displacements will take a state where the valence charge density is largely oxygen in character (e.g.) to one largely copper in character. We should therefore expect to see large infrared intensities for some of the vibrations of the system in this region. This has been observed[32] in the $YBa_2Cu_3O_{7-\delta}$ material for the 155-cm^{-1} phonon. Also the dramatic change in the nature of the electronic state on reaching the magic composition should be detectable by other means. In fact there are[33] extreme and hitherto unknown variations in the ratio of the SIMS emission intensities of Cu^+ and Cu^- ions on attaining a superconducting composition. Such changes have been suggested[34] to be indicative of the change in the nature of the chemical bonding in the solid.

It is now important to identify more clearly the electronic nature of the functions, $\phi_{1,2}$. Obviously in SmS one is delocalized but the other localized, leading to a pair of states, one insulating and the other metallic. Difficult to establish though is whether the diabatic states are localized or delocalized at the crossing point in Figure 2d for the cuprates. This comes back to the vexed question of whether the localised state evolves smoothly into the delocalized one on changing distance or doping level or whether the intermediate state is better described as a collection of small polarons. We can get some clues from the size of the Coulomb repulsion terms obtained from calculation. It is quite clear (see, for example ref 21) that the Coulomb U derived from a 3-band Hubbard model for these systems is considerably larger for copper 3d ($U_d \sim 10.5$ eV) than for oxygen 2p ($U_p \sim 4$ eV). These results suggest that the "oxygen" state is likely to be delocalized but the "copper" state not. Thus we need to go beyond the simple picture of **4**–**6** and include the correlation splitting of the "copper" band. In other words the interaction which takes place between the two states in Figure 2d is effectively between the delocalized oxygen band and the lower of the two Hubbard bands. This gives rise to the following sequence on doping: Figure 2a (undoped, localized, insulator) f Figure 2d (doped, hybrid state, superconductor) f Figure 2b (doped, delocalized, metallic). This hybrid state is thus a very interesting electronic entity. For the electron-

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doped systems we can envisage an exactly analogous process involving the upper Hubbard band. The discussion here of course is nothing short of reasoned speculation, but it does quite clearly identify some of the key, and as yet unanswered, questions concerning the electronic description of these materials.

What is the connection between this magic state and superconductivity? Until we have a model for the superconducting mechanism our comments can really only be speculations. However, it is important to point out that the nature of the electronic state at r_{crit} is very sensitive indeed to changes in interatomic separation as shown in Figure 3. Alternatively we could say that such a state will be involved in strong vibronic or electron–phonon coupling. In less traditional terms this electronic situation is probably ripe for an excitonic superconductor.[30,35] Just by considering the location of the electronic charge in the two states, one knows that large charge fluctuations can occur during small atomic displacements from Figure 3. The situation is, though, somewhat more complex. Electronic motion is generally assumed through the Born–Oppenheimer approximation to be faster than nuclear motion. However in the curve-crossing region the approximation may break down. Landau–Zener theory is well developed for the molecular case to handle this, but solid-state analogs have not been extensively pursued. Another question of importance concerns the nature of the two states that interact in Figure 2d. If one is localized and the other delocalized as suggested above, then there will be very strong spin fluctuations possible at r_{crit} too. Although these are important considerations they do not change the broad pictures of Figure 2. For our purposes here we note the similarity of the plots of Figure 3b to the inverted parabola of **3** and to the Whangbo–Torardi plots.[15] In our further discussions we will explicitly use the assumption that either the Berry function or the parameter Δc_1^2 measures the strength of these fluctuations and that they may be directly compared with the superconducting transition temperature.

Stability of the Magic State

The model described above provides a strong stabilization of that special electron configuration which leads to the generation of the magic state, such a stabilization being absent for other electron counts. At the lowest level of approximation then the role of the extra oxygen or Sr substitution in La_2CuO_4 is simply to dope the planes to the correct level for its generation. However, it is clear that ensuring the correct dopant level is not the sole requirement for observation of even metallic behavior in these systems. For example, the two systems[36] $La_{1-x}Sr_{1+x}ECuO_5$, where E = aluminum or gallium, both contain CuO_2 planes, folded in a slightly different way compared to those in $La_{2-x}Sr_xCuO_4$. When E = Al, the compound has a brownmillerite-like structure, can be made stoichiometric, and is an antiferromagnetic insulator with a half-filled band. For E = Ga, the brownmillerite structure itself is adopted, a stoichiometric material cannot be made as a single phase, but a compound with $x \sim 0.1$ can. Although the copper oxidation state is similar to that for superconducting $La_{2-x}Sr_xCuO_4$, the material is a semiconductor. In[37] $La_{2-x}Sr_xSnCuO_6$ semiconducting behavior is found at Sr doping levels which lead to superconductivity in La_2CuO_4. As a third example we note the case of $TlMRECuO_5$. Here superconductors are found[38] for RE = La, Nd and M = Sr but not when M = Ba. The systems are isostructural, but there is a small difference in r(Cu–O) between the two of 0.05 Å.

Obviously the equilibrium Cu–O distance is significantly affected by the doping level. As noted earlier the "$x^2 - y^2$" band is Cu–O antibonding, and thus metal oxidation leads to shortening of this distance. Hence the spectrum of behavior shown in Figure 2 does not take place within a rigid structural framework. In addition the reservoir material has structural demands of its own. We can envisage two types of behavior. The first is shown in Figure 4. Imagine a series of compounds which only differ in the size of the metal ions (M_k) which reside in the reservoir region with slightly different sizes. The doping level is such that the energetics look like that of Figure 2d, but only one of the possible choice of metal ions (M_i) has the correct size such that the system lies at r_{crit}. Energetically this shows up via the competing energetics of the "electronic" demands of the CuO_2 sheet (curve I) and the "size" demands of the reservoir (curve II). For $M = M_i$ the two plots of Figure 4a have identical minima, but for $M \neq M_i$ (Figure 4b) the two plots have different minima leading to an equilibrium geometry away from r_{crit}. This leads to rather different electronic descriptions as shown in Figure 4d as the metal ion size is varied. Figure 4e shows the experimental results[39] for the variation in T_c for the electron-doped materials as a function of the rare earth atom "size". The second type of behavior is much more drastic and will be found if the geometry demands of the reservoir are very different from those of the CuO_2 sheet. Even if the doping level is correct so that Figure 2d behavior is expected for the CuO_2 sheet, the internuclear separation may be forced completely away from r_{crit} by the size demands of the reservoir (Figure 4c). In this case the electronic description (Figure 4d) is uninteresting ($M = M_{big}$). We suggest that this state of affairs exists[36] in $La_{2-x}Sr_xSnCuO_6$, where the large SnO_4 layer stretches the CuO_2 sheets. (The system is a little more complex than this though.[37]) Figure 4e shows the observed dependence of T_c on the size of the rare earth for the electron-doped compounds. There are similar plots for other materials. A plot very similar to this one is found[38] for the pressure dependence of T_c for the $La_{2-x}Ca_{1+x}Cu_2O_6$ system. Here pressure is sufficient to tune T_c though a maximum value and back down again.

If the system is synthesized with a given stoichiometry away from the magic point under conditions where there has been no phase separation, then it is simple to follow the description of the electronic state by extending the picture of Figure 2. This is shown in Figure 5a–e. In case a the wave function is 100% "copper", in case b the mixed state which is produced has some "oxygen" character, in case c (the magic state of Figure 2d) the mixed state has equal weight from "copper" and "oxygen" states, in case d the resulting state is more heavily weighted toward "oxygen", and finally in case e the state is completely "oxygen" in character. The behavior of the parameter Δc_1^2 or the Berry function, dc_1/dr, as a function of internuclear separation (Figure 5f) looks very similar to that shown in Figure 4d.

Thus the generation of the single minimum potential with the interesting properties we have described is quite sensitive to the location of the two diabatic curves. Small changes in their position may lead to an electronic description which lacks this mixed character and thus loss of the magic state. Therefore small changes in the doping level or the geometrical structure, which change the location of the two intersecting curves, can destroy it entirely. We note similar sensitive behavior observed experimentally for T_c as a function of composition and structure. However the model does indicate that on doping, the localized "copper" state evolves smoothly into the delocalized metallic state through the magic state. This is in contrast to the behavior of Figure 2c, applicable for example to the transition from the localized f^n state to the fluctuating state $f^{n-1}d^1$ for SmS. Here the transition is predicted (and is observed) to be discontinuous under

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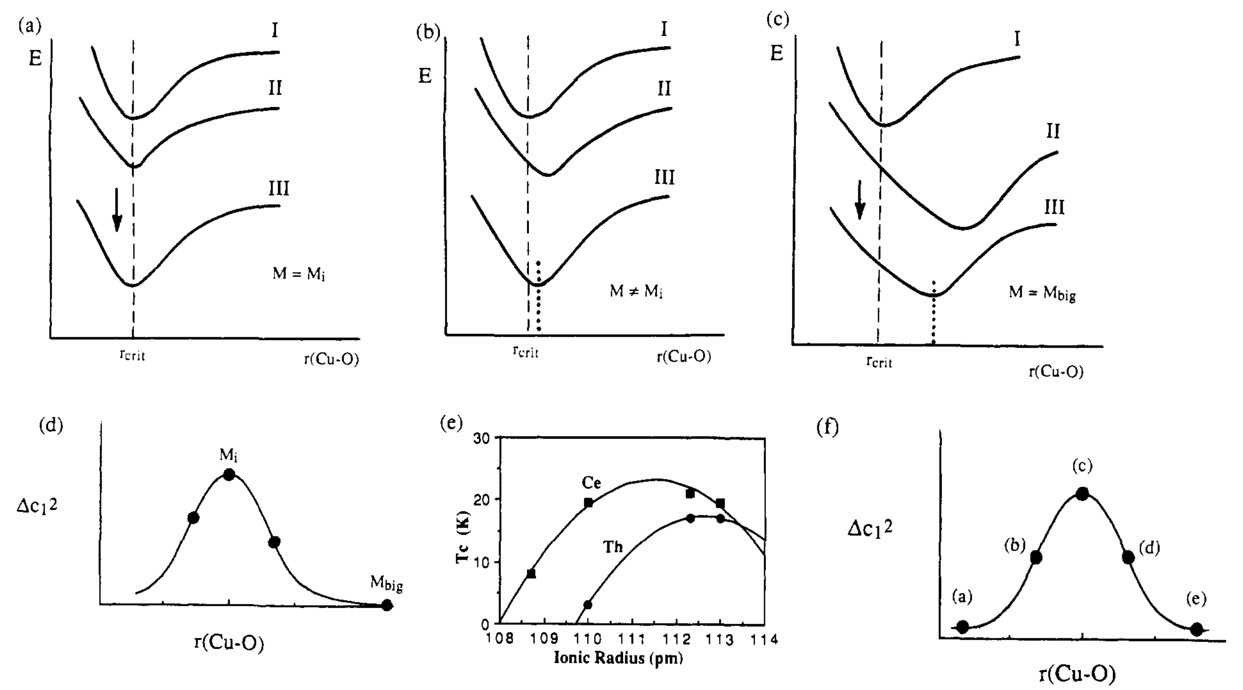

Figure 4. Interplay of the electronic demands of the CuO_2 sheet and the size demands of the reservoir material in setting the equilibrium Cu–O distance in optimally doped materials. In (a)–(c) are shown three cases where the energetic behavior of the CuO_2 sheet (curve I), identical to the lower energy curve of Figure 2d (with a minimum at the critical Cu–O distance, r_{crit}, where the avoided crossing occurs), and the behavior of the reservoir (curve II) combine to produce the resultant curve III. In (a) curves I and II have identical minima and so the equilibrium Cu–O distance lies exactly at r_{crit} labeled with a dashed line. In (b) the size match is not exact and thus the equilibrium distance (indicated by the dotted line) lies close to, but not exactly at, r_{crit}. In (c) the size match is very poor and the equilibrium distance lies far away from r_{crit}. (d) shows how the function Δc_1^2 which describes the fluctuations in the wave function is expected to behave for the three cases. The role of the reservoir is to move the Cu–O distance through the critical crossing region. (e) Observed[39] variation in T_c for the electron-doped superconductors $RE_{2-x}M_xCuO_4$ as a function of the crystal radius of the RE atom for the two series M = Th, Ce.

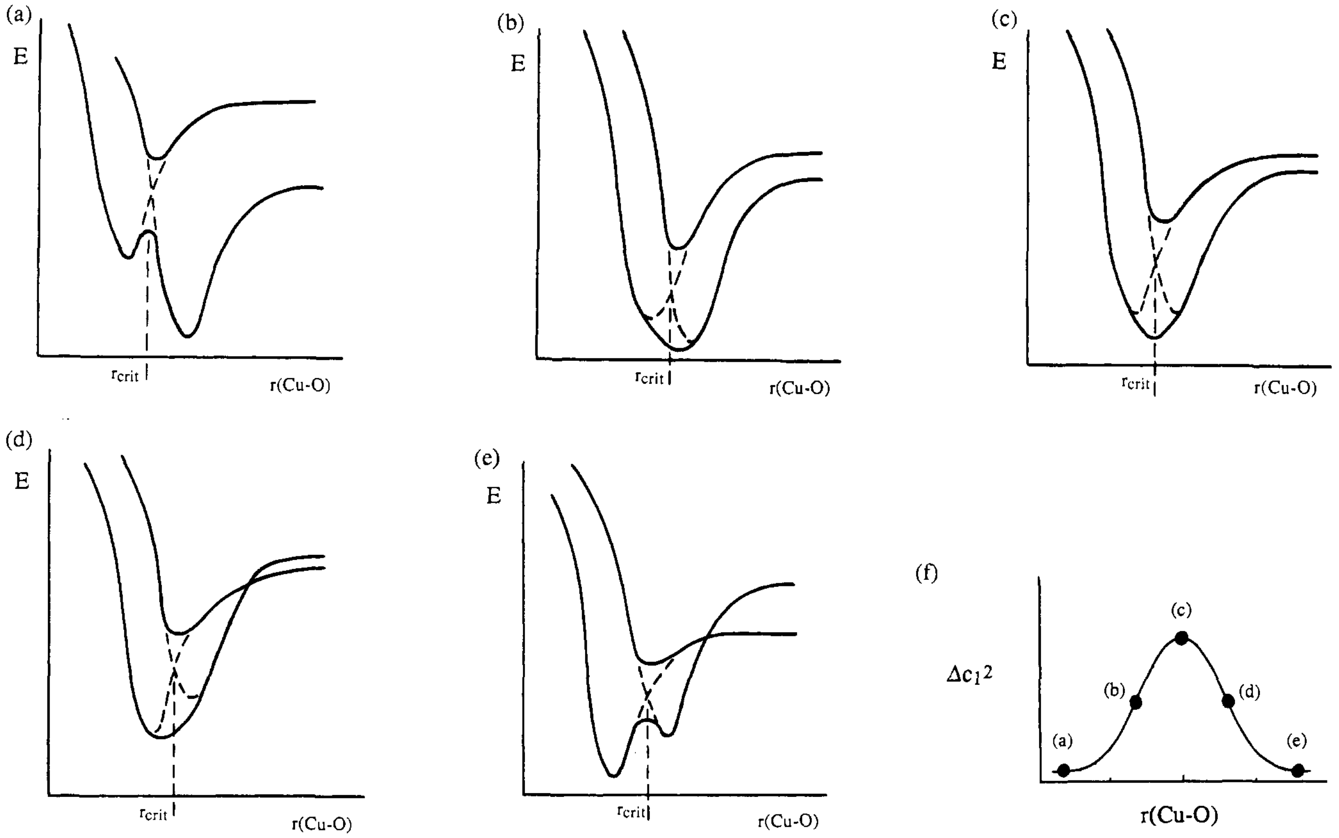

Figure 5. (a–e) Amplified views of the processes of Figure 2a,b,d. (c) is identical to Figure 2d, but (b) and (d) show small changes in doping level either side of this point. (f) shows how the function Δc_1^2 is expected to behave in the five cases. As the equilibrium distance moves away from the critical crossing point, so the wave function becomes increasingly composed of just one component.

pressure. A plot of lattice constant vs atomic number for the REX (X = chalcogen) systems shows[32] a discontinuity for Sm and Eu, the extent of the discontinuity being the difference in the equilibrium distance for the two states in Figure 2c.

$TlMRECuO_5$, mentioned above, and the 1-2-3 system,[41] $YBa_2Cu_3O_{7-\delta}$, are two examples where the doping of the CuO_2 sheets with holes takes place internally via the overlap[8,38] of copper and reservoir bands. It has been suggested[38] that the doping in the former species is controlled by the relative location of the two bands, set by the geometrical details of the structure. The larger Ba^{2+} ion is presumed to stretch the CuO_2 sheet, change the location of the x^2-y^2 band, and switch off the charge transfer. In $Tl(Sr_{1-x}Ba_x)LaCuO_5$ solid solutions[42] the lattice constants vary smoothly for $0 \leq x \leq 1$, but by $x = 0.3$ superconductivity is lost in accord with such an idea. Such a change with x is in accord with a combination of the pictures of Figures 4 and 5.

Somewhat smaller changes in T_c are found[43] in the 1-2-3 compound $REBa_2Cu_3O_7$ with variation in RE. There is a gradual drop in T_c as the size of the rare earth ion decreases. How the doping varies with δ in the 1-2-3 compound is quite complex[41] and has been the subject of much study. It depends too on the way the bands overlap and is clearly sensitive to the geometry and chemical identity of the chain region.[42] Here though there is a discontinuity in the T_c vs δ plot at $\delta \sim 0.6$ where T_c drops precipitiously to zero, and the system becomes a semiconductor for $\delta > \sim 0.6$. Such a point is associated with a structural change as well. The region with $\delta < \sim 0.6$ is associated with superconductivity and ordering of the interplanar oxygen atoms into chains where possible. The region with $\delta > \sim 0.6$ is not superconducting and the oxygen atoms in the interplanar region are disordered. We have argued elsewhere[44,45] that the ordering of these mobile oxygen atoms is vital for plane–chain electron transfer via band overlap. However, the presence of such chains in the structure sets up an orthorhombic strain in the structure and it is therefore not surprising that at some critical value of δ, corresponding to a critical chain concentration, there is a first-order transition to a tetragonal structure where the oxygen atoms are disordered among the two crystallographic sites $(0,{}^1/_2,0)$ and $({}^1/_2,0,0)$. Within the framework of the present discussion, the ordered, orthorhombic structure is stabilized by the mechanism of Figure 2d and is a superconductor, and the disordered, tetragonal structure is stabilized by loss of the orthorhombic strain but is a semiconductor. There are a series of experiments[46] in this system showing a gradual increase in T_c with time, as rapidly quenched samples are allowed to stand at room temperature. This is associated with ordering of the oxygen atoms into chains and is clearly driven by a stabilization of this arrangement.

System Specificity

Perhaps the most obvious question to ask at this stage is why high temperature superconductivity has only been found in the cuprates. We will rephrase this question and ask within the context of our discussion what are the criteria for generation of the magic state. Clearly the juxtaposition of metal and oxygen levels is important, as is a strong interaction between the "copper" and "oxygen" states, the factor that distinguishes the two cases of Figure 2c,d. These two requirements have been identified in earlier theoretical efforts.[30] Importantly too, the crossing point of the two states must take place close to the equilibrium bond length, an important new perspective and one absent in previous schemes. Thus solid NaCl (cf. Figure 1) will not be a candidate because of the unfavorable location of the crossing point. (Parenthetically we note that the properties of the lower adiabatic curve in Figure 2d should be similar to those of the *upper* curve of Figure 1 discussed in ref 47.) One of the important observations concerning these materials is that those with the highest T_c contain thallium or bismuth. Since the electronegativity of these atoms is much closer to that of the atoms of the CuO_2 sheet than in the 2-1-4 compound for example, the electronic separation between planes and reservoir used above is not as valid. In orbital terms, although the levels of the CuO_2 sheet are largely localized over the copper and oxygen atoms in the planes, in the 2-1-4 compound, they may contain significant Tl or Bi character in systems such as in $Tl_2Ba_2Ca_2Cu_3O_{10}$, for example. One of the results of this may be an effect analogous to the reduction in the magnitude of the atomic Racah parameters found for transition metal complexes and termed the nephelauxetic effect. In the solid we predict that such spatial delocalization of the electron density leads to a reduction in the effective Coulomb U parameter for the system and therefore a change in the functional form of the curves of Figure 2. It is difficult *a priori* to decide how the picture changes in detail, but if there is indeed a critical U/W for the crossing point, then this should occur at longer Cu–O distances where the band width W is correspondingly smaller too. Further progress will have to wait for more quantitative calculation.

The general thrust of this paper has then been to show that there is not only a new mechanism for providing electronic stability at special or "magic" electron counts,[48] but that the magic electronic state which is produced is a very unusual one. Although we have certainly not presented any theory which proves that this state is a superconductor, the properties of the $\Delta c_1{}^2$ parameter or of Berry's function, dc_1/dr, as a function of internuclear separation show striking similarities to the behavior of the critical superconducting transition temperature. Elsewhere[31] we show how an "isotope effect" may be generated using this approach. The approach is somewhat different from other mechanisms[49,50] for phase separation in these materials but gives a picture which is quite similar to Goodenough's unique thermodynamic state.[17]

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