Electronic Stabilization of the Superconducting Composition of Cuprate Superconductors

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By making analogies between the behavior with interatomic separation of the electronic states of small molecules such as the alkali halides with those of the cuprate superconductors, a model is generated which allows insights into the nature of the electronic description of the latter. Interaction between the state where the holes are carried on the oxygen atoms and the state where they are located on the copper atoms leads to a stabilization of the lower energy state. At critical values of the doping level and copper–oxygen distance, such a stabilization leads to a state which is a local thermodynamic minimum with mixed electronic character. It is shown how fluctuations in this state may be important, how it is very sensitive indeed to chemical composition, and how it can rationalize the thermodynamic stability of the superconducting composition. © 1992 Academic Press, Inc.

Introduction

The electronic description of the high-temperature superconducting cuprates is a current theoretical challenge. An understanding of the structure and properties of these materials has, of course, the development of a workable model as a prerequisite. In terms of the chemistry and physics of this area, in addition to the obvious question of a superconducting mechanism, we need to be able to produce explanations at least for the following four observations.

(i) The compositional dependence of the critical superconducting temperature in a material such as $La_{2-x}Sr_xCuO_4$ shows an inverted parabolic shape (1) where T_c goes through a maximum at $x \sim 0.15$ for this particular compound. (We will ignore for present purposes the asymmetry of this peak found experimentally and the splitting found (2) in $La_{2-x}Ba_xCuO_4$.) Similar behavior is found for other systems.

(ii) In its undoped state La_2CuO_4 is an antiferromagnetic insulator, where the unpaired "copper $3d$ electron" is certainly localized on the metal or more strictly in an orbital with large Cu $3d$ character. On doping ($x > 0$) the material $La_{2-x}Sr_xCuO_4$ becomes a superconductor and eventually a normal metal. In the normal metallic state the valence electrons have to lie in some type of delocalized state. The superconducting region thus lies between normal metal and insulator, and thus between two very different electronic situations. The electronic description in the superconducting region is probably a hybrid of the two extrema. Certainly estimates (3) of W/U, the ratio of the bandwidth to the on-site electron–electron repulsion, are close to 1. How to describe

this effectively has been the aim of several recent studies, ranging from the traditional chemical picture (4) using INDO and ab initio calculations to computations employing simple Hubbard Hamiltonians (5).

(iii) There are some very interesting observations concerning the thermodynamic stability of these cuprates. Low-temperature superconductors are frequently systems which lie close to a geometrical instability. Superconductivity and charge-density waves often compete in these compounds, and the maximum critical superconducting transition temperature is frequently determined by how close the system can get to such an instability before a structural change occurs. The cuprate series seem to be rather different. Here the superconductors often appear to be generated as one of the components resulting from a 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. A phase separation occurs (6, 7) at around this temperature of the form $La_2CuO_{4+\delta} \rightarrow La_2CuO_4 + La_2CuO_{4.07}$, 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. 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. The phase separation is associated with the movement of oxygen atoms and results in crystalline regions of the solid where the oxygen concentration and thus the oxidation state of the planar copper atoms is higher. Interestingly, heating the $La_{2-x}Sr_xCuO_4$ compound at temperatures high enough to allow Sr mobility leads to phase separation of this material (8) and generation of $La_{1.85}Sr_{0.15}CuO_4$. A similar picture is found in the electron-doped régime. Superconductors are found for both $RE_{2-x}M(IV)_xCuO_4$ (9, 10) and $RE_2CuO_{4-x}F_x$ (11). Their geometrical structures appear to be very similar from diffraction results, and x is close to 0.17 in both cases. T_c is similar for the two systems and, importantly, they appear to be generated by a phase separation too. One interpretation of these results is that the superconducting properties are dominated by the oxidation state of the copper atoms in the planes, and that one of the roles of the reservoir material is to optimally dope these sheets. Associated with this is the idea that the optimal superconducting composition in many of these systems is the one which represents some local field of thermodynamic stability. Thus high-temperature superconductivity is associated with thermodynamically stable systems. The situation in the 1–2–3 compound and other more complex materials with thallium- and bismuth-containing interlayers is not as clearcut. In the latter, though, this is due largely to our much poorer understanding concerning the details of the structure.

Several workers have shown (12, 13) how such phase separation may occur in certain d-count regions from a three-band Hubbard model with judiciously chosen parameters. Here we are concerned with the generation of a more chemical picture with ties to existing bonding situations.

(iv) The superconducting state is extremely sensitive to changes in doping levels. The results for the 2–1–4 compound show a width at half maximum of the T_c versus x plot of 0.12 Sr atoms, but this is certainly set by the lack of mobility of the Sr atoms during the synthesis conditions. The width of the $La_{1.85}Sr_{0.15}CuO_4$ superconductor is considerably smaller. The superconducting properties of many other materials of this type are very sensitive indeed to tiny amounts of hydrogen or oxygen that can lead to a change in the copper oxidation state.

In this letter we show how such observations may be understood using a simple electronic picture.

Avoided Crossings between Electronic States

In the insulating state associated with un-doped La_2CuO_4, the electrons lie in an orbital which is largely copper $3d$, the wavefunction being localized in the Heitler–London sense on the metal atom. The electronic description of the heavily doped metallic state is dramatically different (4, 5). Here the wavefunction is delocalized, of course, but importantly the holes now lie in oxygen $2p$ orbitals. Thus there are two electronic changes which take place simul-taneously on doping. Since the level from which electrons are removed on doping re-mains metal–oxygen antibonding irrespec-tive of the localized or delocalized descrip-tion, there is a concurrent shortening of the Cu–O distance and hence an increase in the overlap between copper and oxygen or-bitals.

This change in orbital description on dop-ing leads us to make comparisons with an-other situation where there is a dramatic change in orbital character as the in-ternuclear separation is reduced. This is the well-known avoided crossing between ionic and covalent curves at distances larger than the equilibrium separation for the alkali ha-lide molecules, shown in Fig. 1. Such avoided crossings are commonplace in di-atomic species. Around the crossing point the wavefunction describing the adiabatic curves changes dramatically. For example, Hay, Kahn, and Shavitt have shown (14) for LiF how the dipole moments of the two states involved show violent changes on moving through the crossing region. Berry (15) examined how the wavefunction, writ-ten in general as $\psi = c_1\phi_1 + c_2\phi_2$, changed with distance by plotting dc_1/dr as a function of internuclear separation. He found peaked behavior for this function centered at r_{crit}, the internuclear separation appropriate for the crossing, with a width which increased and a height which decreased with the over-
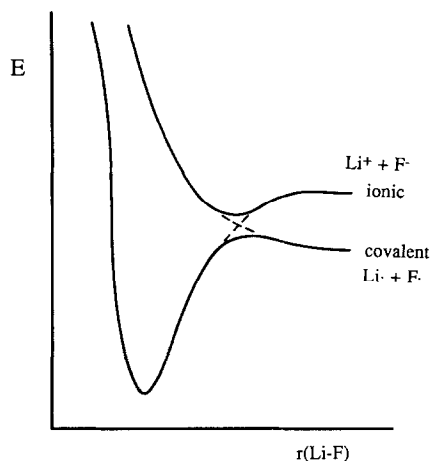

FIG. 1. The avoided crossing found for the "ionic" and "covalent" curves of alkali halide molecules as a function of internuclear separation.

lap between the two curves. We can envis-age a similar process in the high temperature superconducting cuprates.

Let us examine four different scenarios which could arise via such avoided crossing of the curves which we label for conve-nience as "oxygen" and "copper" curves. (We focus on the case of hole doping here.) They represent the evolution, as the Cu–O distance is shortened and the hole concen-tration increases, of the states where the electron holes are located on oxygen $2p$ and copper $3d$ orbitals. At long distances such states are localized, but at shorter distances delocalized. At long distances and with no doping the copper curve lies lowest in en-ergy; at shorter distances with hole doping the relative energies are reversed. They could well be quantitatively described by some GVB function using the Coul-son–Fischer approach. The coupling be-tween the two curves depends on their en-ergy separation and the overlap between the two states they represent. Addition of elec-trons to a state moves it closer to vacuum. Thus on doping, the oxygen state drops in energy and the (initially) lower energy cop-
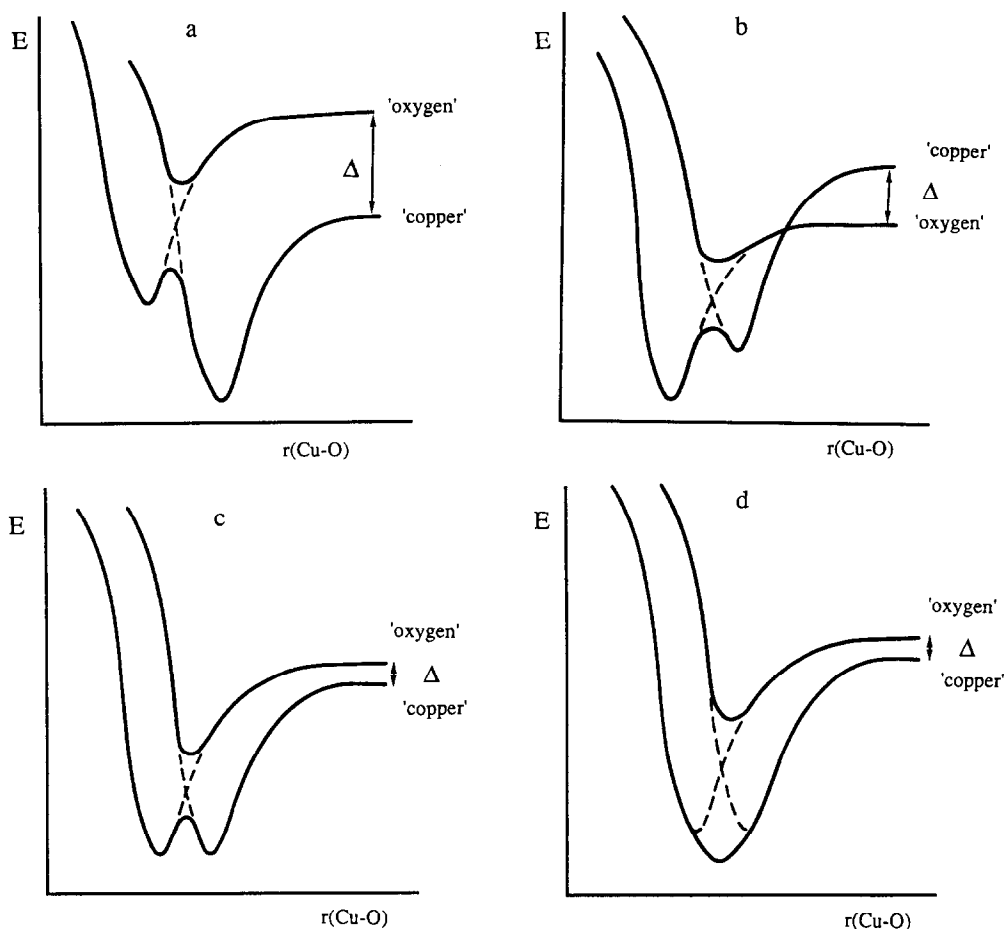
FIG. 2. Four possibilities for the intersection of "copper" and "oxygen" curves in the cuprates, by analogy with the behavior in Fig. 1: (a) the undoped case where the energy separation, Δ, at large $r(Cu-O)$ is large; (b) the heavily doped case where Δ is negative; (c) and (d) two intermediate cases, which differ in the magnitude of the interaction between the two curves. In (c) it is small but large enough in (d) to generate a single minimum.

per state rises in energy as a result. As a first approximation we can investigate the energetics of interaction by varying the energy separation of the two curves at large $r(Cu-O)$. This will become smaller as the doping level increases. Figure 2a shows the case of low doping where the avoided crossing takes place as a result of a short distance. It is not energetically significant, the system lying in a minimum set by the copper curve and with a localized electronic description.

Such a situation may be appropriate for the undoped La_2CuO_4 material. In Fig. 2b the other extreme is depicted. Here with heavy doping the energies of the two curves at large $r(Cu-O)$ are reversed. The avoided crossing is not significant here either. It takes place at a longer distance than the equilibrium internuclear separation. The electronic description is one of a delocalized, largely oxygen-located band. It would be appropriate for a heavily doped, metallic

$La_{2-x}Sr_xCuO_4$ system. One possible intermediate case is shown in Fig. 2c. Here the crossing point is important. It suggests that there are two states, either equal or close in energy. The state with the shorter internuclear separation is probably metallic and the state with the longer distance perhaps a semiconductor. (It is quite possible, however, if the crossing takes place at long internuclear separations, that both are localized states, or if the crossing occurs at much shorter distances, that both are metallic states.) Importantly, the electronic description of the states described by the two minima are quite different. One is copper and the other oxygen. An example of a closely related situation, where a change in pressure or temperature may switch the system from one minimum to another might be the classic "valence" changes found in rare earth compounds such as SmS (16).

Figure 2d shows a particularly interesting state of affairs. This is the one where the interaction between the two curves is so large that a single minimum results. The properties of such a magic state are unique and we claim that they are those of the high-temperature superconductor.

(i) The model provides a strong stabilization of that particular electron configuration which leads to the "degenerate" crossing of Fig. 2d. Such a stabilization is absent for other electron counts. Thus the theoretical model leads directly to the phase separation noted above for $La_2CuO_{4+\delta}$ and for $La_{2-x}Sr_x$ CuO_4. The "magic" electron count for the stable CuO_2 plane doping is 0.15. The role of the extra oxygen or Sr substitution is simply to dope the planes with holes and in this sense in these compounds the reservoir material is simply an innocent bystander.

(ii) Although the wavefunction at the bottom of the minimum of Fig. 2d is made up of equal contributions from the two starting states, small changes in the internuclear separation around this point will lead to large changes in the electronic description, just as in the alkali halide case described above. In fact the properties of the lower diabatic curve in Fig. 2d should be similar to those of the *upper* curve of Fig. 1 discussed in Ref. (17). Large changes in the charge distribution may occur as the result of fluctuations around the equilibrium position or some crystal motion which changes this particular coordinate. We suspect that virtually all phonon modes of the solid will in fact lead to changes in this coordinate. We mentioned above Berry's measure of the rate of change of the wavefunction on moving away from the crossing point. Another way of estimating the change is to plot Δc_1^2 for a given amplitude around the crossing point as a function of $r(Cu-O)$. We show this in Fig. 3 for three cases as a function of the dimensionless parameter η, the ratio of the relative slopes of the two interacting curves at the crossing point (assumed to be linear over this region) to the overlap integral between them. Note that just as in Berry's plot (15) the larger overlap integral (shorter distance) gives rise to a wider, flatter peak. We draw attention to the similarity of these plots to the T_c versus $r(Cu-O)$ plots of Whangbo and Torardi (1). Interestingly, they show some similar features: generally sharper plots as $T_c(max)$ and the corresponding value of $r(Cu-O)$ increase.

(iii) The generation of the single minimum with the properties described above is very sensitive indeed to the location of the two diabatic curves. Small changes in their positions lead to a single well which lacks this mixed character, and thus the magic state is lost. Thus small changes in the doping level or geometrical structure which change the location of the two intersecting curves can destroy it entirely. Such a result parallels the very sensitive behavior observed experimentally for T_c as a function of composition and structure. (As an example of the latter we note the cases of $TlMRECuO_5$ where superconductors are found (18) for $RE =$
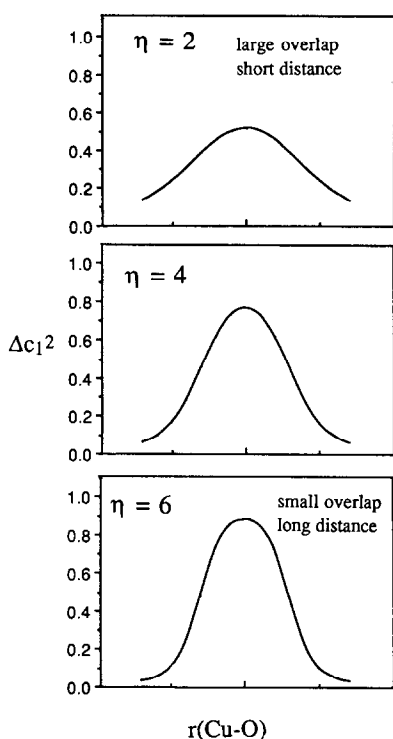
FIG. 3. Variation in Δc_i^2 for a given amplitude around the crossing point as a function of r(Cu–O). Three cases are shown for different values of the dimensionless parameter η, the ratio of the relative slopes of two linear interacting curves at the crossing point to the overlap integral between them.

La, Nd, and M = Sr, but not when M = Ba, even though the systems are isostructural. The difference in r(Cu–O) between the two is 0.05 Å.)

System Dependence

The discussion above suggests that it is the doping of the system which leads to the drastic changes in the details of the crossing of the copper and oxygen curves. Since the level generally described as "$x^2 - y^2$" is always Cu–O antibonding, correlations with Cu–O distance (such as the Whangbo–Torardi plots (*1*)) are in first order simply mimics of the dependence of properties on

doping level. However, we should realize that the copper/oxygen overlap integral decreases as the Cu–O distance increases. Thus if the crossing takes place at long distances or in a system where the Cu–O–Cu angle is much less than 180°, two cases where the Cu$x^2 - y^2$/O2$p\sigma$ hopping integral is reduced in magnitude, then the situation shown in Fig. 2d can be replaced by the one in Fig. 2c. Even if the doping level of the CuO$_2$ planes is correct, steric demands by the reservoir material can force an equilibrium distance at an r(Cu–O) longer than r_{crit}. In this case the electronic description becomes that of a doped semiconductor. This appears to be the case (*19*) in La$_{0.85}$Sr$_{1.15}$GaCuO$_5$.

At longer Cu–O distances, too, the nature of the states may change because now W/U is smaller than the critical value for generation of a metallic, or delocalized, state (*20*). Perhaps then the most apt description of the electronic state of affairs is a mixture of the doped Mott–Hubbard and doped charge-transfer insulator descriptions via the interaction between the copper and oxygen states. (A similar mixing of levels appears in the exitonic superconductor (*21*).) The latter change in nature as the ratio of W/U, set by the Cu–O distance and thus the doping level, changes. The criteria for generation of the case of the magic case of Fig. 2d are thus (a) a correct doping level so that the two states may interact to give a single minimum with its mixed electronic character, and (b) reasonable value of W/U such that the resulting states are delocalized in character. The first is a much more stringent requirement than the second. Both criteria have been recognized before via different routes (see Ref. (*22*), for example), but the present approach which focuses on the behavior of the states with distance allows new insight into the problem. Certainly a quantitative description of the electronic picture of this "unique thermodynamic state" (*23*) is not straightforward.

Acknowledgment

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