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Bonding and electronic structure in high-T_c superconducting oxides: A case for the importance of the cations

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It is suggested that the chemical bonding in the high-T_c superconducting oxides is strongly influenced by the large fields induced by the very ionic cations (e.g., barium) and that the presence of such cations is a necessary requirement for superconductivity. The electronic effect of this field is thus to modify the interaction between the oxygen and copper atoms in the cuprate anion of the superconductor. The experimental evidence for these ideas come from a comparison of core- and valence-level photoemission spectra of the superconducting oxides with those of typical transition-metal oxides on the one hand and the very ionic oxides (e.g., BaO) on the other.

INTRODUCTION

In the numerous discussions concerning the composition, structure, and bonding in the new high-T_c superconducting oxides (see, for example, the symposium proceedings, Refs. 1–3) the obvious importance of the omnipresent Cu, and in particular the significance of the two-dimensional sheets of Cu and O, have dominated attention. This emphasis has led many authors to refer collectively to these systems, by way of a simple classification, as "copper oxides." It is also apparent that numerous experimental and theoretical studies have been devoted to investigating the apparent direct relationship of the high-T_c superconductors to the various simple copper oxides.

Contrary to the above supposition, it is our opinion,[4] based on a comparison of the x-ray photoelectron spectra of the various compounds involved, that there is little electronic-structure justification for a description of the superconducting materials in terms of conventional copper oxides. Rather, a key factor in the compounds that are superconducting is the (necessary) presence of very ionic cations (e.g., Ba), which apparently induce extremely large ionic fields. This, plus low-lying core levels adjacent to the O($2p$) valence band, modify the bonding between the Cu and O atoms in the Cu-O counterions (anions), which should thus be described as unique, very ionic, cuprates rather than copper oxide structures. In these cuprate anions the O($2p$) band extends down to E_F, whereas in the copper oxides there is a several eV gap between the top of the O($2p$) band and E_F. The rationale for these statements is the nature of the oxygen derived features in the x-ray photoelectron spectrum of the superconducting oxides, and a comparison to those of copper oxides (and other transition-metal oxides) on the one hand, and to those of the very ionic oxides (e.g., BaO) on the other. In making these comparisons between photoelectron spectra it is essential to be sure that the inherently surface sensitive spectrum of the superconducting material is, in fact, that of the intrinsic material and not of contaminant phases such as $BaCO_3$, $Ba(OH)_2$, etc., which are ubiquitously present at the surface of these materials unless they are prepared and maintained under very exacting, UHV, conditions. One of the authors, with coworkers,[5,6] has gone to some lengths to establish the veracity of the photoemission spectra of $Y_1Ba_2Cu_3O_7$, and to demonstrate that the vast majority of papers published on the photoelectron spectra of this material to date represent predominantly, and in some cases even entirely, contaminant phases thereby adding nothing (except confusion) to the subject of the electronic structure or the superconductivity mechanism. This fact has also been recognized by other authors,[7–9] whose own results on the x-ray photoemission spectroscopy (XPS) of $YBa_2Cu_3O_7$ confirm the salient features of the photoelectron spectra referred to here and reported in more detail elsewhere.[6]

In the following sections we will discuss these salient features for the superconducting oxides and the comparable ones for the transition-metal oxides and very ionic oxides and then attempt to relate these features to appropriate descriptions of the bonding effects involved.

"SIMPLE" COPPER OXIDES

The XPS spectra of the common copper oxides, Cu_2O and CuO, have been well established for more than 15 years, and it is well known that Cu^{II} species are easily distinguishable from Cu^{I} species by the chemical shift and presence of a shake-up satellite in the Cu($2p_{3/2}$) and Cu($2p_{1/2}$) spectra for the Cu^{II} species.[10–13] It is also common knowledge that to differentiate Cu^{O} from Cu^{I} requires the additional use of the Cu Auger spectra, where a chemical shift exists between the two species, which does not exist in the Cu($2p_{3/2}$) XPS spectra. Perhaps not so well known, but certainly extensively discussed by several authors including both of the present authors,[10–13] is the fact that though there is the abovementioned large difference in Cu(2*p*) spectra for Cu_2O and CuO, the binding energy (BE) of the O(1*s*) level is essentially fixed at around 530.1±0.4 eV and does not vary significantly (by more than a few tenths of an eV), even following alloy formation with other metals.[13–15] In fact, a BE of 530.0±0.5 eV brackets the range of *many* oxides, particularly those of almost all the transition metals.[16,17] Values for some of these oxides are included in Table I. Oxides with O(1*s*) values in this range have been characterized as "normal' ionic oxides (NIO) by one of the present authors.[18] It is critical to the arguments developed later also to note that these types of oxide systems also have valence-level O(2*p*) bands that are characteristic of the group. These valence bands have been studied in detail by such authors as Wertheim and Hufner,[19] for copper oxides and phenomenologically described by Goodenough.[20] In this regard, the Cu_2O and CuO Cu(3*d*) valence bands were found to be fairly narrow with distinct peaks at around 3 eV above E_F (Fig. 1). The O(2*p*) bands are weaker and broader, being centered at 7 eV and spreading down to an onset point at approximately 3–4 eV (Fig. 1) with little distinction between Cu_2O and CuO, as is the case for the O(1*s*) levels as described above. Many other transition-metal and other oxides have very similar O(2*p*) behavior.[20] According to Wertheim and Hufner,[19] this relatively distinct separation of the metal *d* and oxygen *p* bands is typical of most transition-metal oxides. This is also an important feature of our subsequent arguments.

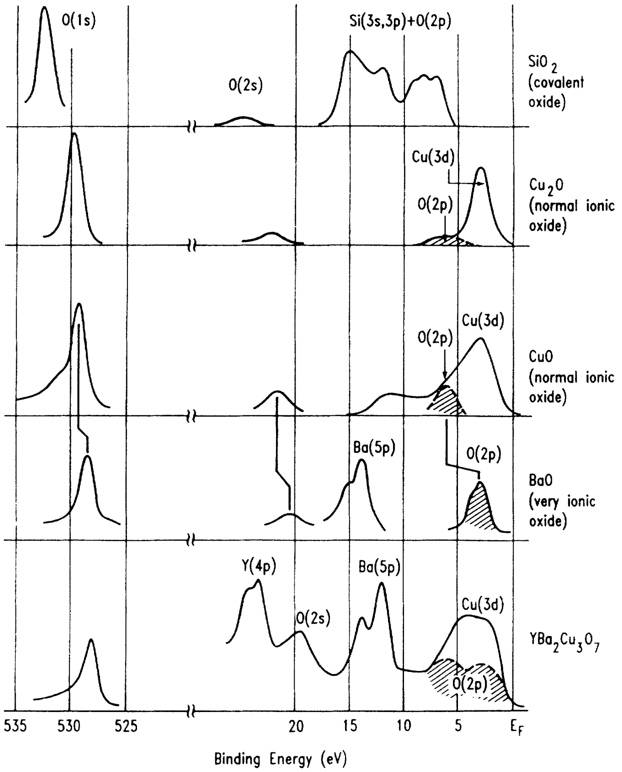

FIG. 1. Schematic representation of the O(1*s*) core and the valence band and near valence-band XPS spectra of some representative oxides in the covalent (e.g., SiO_2 or Al_2O_3), normal ionic, where the BE falls in the range 530±0.5 eV, (e.g., Cu oxides), and very ionic (e.g., BaO) classes. For more details on these spectra, see Refs. 18, 19, and 20. The equivalent spectra for a *good* single crystal of $Y_1Ba_2Cu_3O_7$ (Ref. 6) is also shown for comparison to the Cu oxides and the BaO spectra. Note the trend of *decreasing* O(1*s*), O(2*s*), and O(2*p*) BE's as one moves from covalent to normal ionic to very ionic classes.

SUPERCONDUCTING COPPER CONTAINING OXIDES

When prepared as a *cleaned, undamaged,* surface, the best example of which is an *in situ* cleaved, *good quality* single crystal (good quality means high-T_c value, narrow transition width, and high Meissner signal), $YBa_2Cu_3O_7$ samples exhibit, at room temperature, the following features distinctive of the true superconductivity phase

TABLE I. O(1*s*) XPS binding energies in eV for selected oxides. Highest (common) valent oxide; BE values are ±0.2 eV. Binding energies of insulators fixed by several methods, including C(1*s*)=284.6 eV for adventitious carbon, Ref. 18. Cs value is from Ref. 31. Au is from Ref. 39. Deltas (Δ) are the approximate separation of lowest-lying cation core peak from centroid of O(2*p*) dominated valence band: 11–13 eV Δ; 8–10 eV $\Delta\Delta$; 5–8 eV $\Delta\Delta\Delta$. (d) designates the *d* state; (*p*) designates the *p* state. Bold indicates VIO oxides.

IA	IIA	IIIA	IIIB	IVB	VIIIB	IB	IIB
Na ~529.7	**Mg** ~530.9	Al ~531.5	Sc	Ti 529.7	Ni 530.0	Cu ~529.5	Zn 530.3 $(\Delta\Delta d)$
K	Ca ~529.8	Ga 530.5 (Δd)	**Y** 529.3 (Δp)	Zr 529.9	Pd 530.1	**Ag** 528.3 $(\Delta\Delta\Delta d)$	**Cd** 528.6 $(\Delta\Delta\Delta d)$
Rb ~529.0 $(\Delta\Delta p)$	**Sr** ~529.0 (Δp)	In 530.1 (Δd)	**La** 528.8 $(\Delta\Delta p)$	**Ce** 529.1 (Δp)	Pt 530.0	Au 530.0? $(\Delta\Delta\Delta\Delta d)$	Hg ? $(\Delta\Delta\Delta\Delta d)$
Cs ~528.5 $(\Delta\Delta\Delta p)$	**Ba** ~528.5 $(\Delta\Delta\Delta p)$	Tl ? $(\Delta\Delta\Delta d)$					

material above T_c. The Ba, $(3d_{5/2})$, $(4d_{5/2})$, and $(5p_{3/2})$ levels produce *single-featured, sharp peaks,* at BE's much lower (by 2–3 eV) than the equivalent Ba features for contaminant phases such as $BaCO_3$ or for the oxygen deficient, nonsuperconducting version of this material, $YBa_2Cu_3O_{\leq 6.5}$.[5,6] The Y$(3d)$ and $(4d)$ features are also single featured and characteristic of Y^{3+} with BE's very similar to those for Y_2O_3. The Cu$(2p_{3/2})$ spectrum is dominated by a Cu^{II} line shape, which is only slightly different from that of Cu^{II} in CuO.[6,10] When the features described above are obtained free of any peaks due to contaminants, the O$(1s)$ level has a dominating feature located at ~528 eV (Fig. 1). Thus, for the intrinsic superconducting material the O$(1s)$ BE exhibits a unique, very low BE in no way indicative of a copper oxide. In fact, the O$(1s)$ BE is very close to that in BaO, Fig. 1. The same conclusions can also be drawn concerning the less-studied O$(2s)$ level (Fig. 1).

Other studies have revealed several interesting additional facts related to the above results. First it should be noted that though the majority of literature reports represent contamination (see papers in Refs. 1–3), there are independent literature confirmations[7–9] of the BE patterns described above for the $Y_1Ba_2Cu_3O_x$ materials, though they usually show some additional features in the Ba core and O$(1s)$ regions, which were recognized by the authors as surface contamination. The conventional La_2CuO_4 system also has the same low BE for O$(1s)$.[8,21] Finally, there have been a number of literature reports on the layered Bi superconductivity materials, for which clean surfaces are apparently much easier to obtain, which also show an O$(1s)$ at a similar low BE position.[22]

GENERAL ARGUMENTS ON OXIDE BONDING

In order to understand the reasons for the results discussed above, it is useful to consider the general nature of oxides and how the different classes relate to one another. One of us (T.L.B.) has tried to systematize, using XPS, the bonding patterns exhibited by a variety of metallic oxides.[18,23,24] From this work we provide, in Table I, a selection of O$(1s)$ BE's for these oxides. A detailed discussion of all the factors affecting O$(1s)$ BE's, including photoemission final-state effects, is given elsewhere.[18,23] As noted above, many of the metallic oxides usually classified as ionic, including the Cu oxides, exhibit an O$(1s)$ BE in the range 530.0±0.5 eV, whereas more *covalent* oxides, such as Al_2O_3 or SiO_2 have considerably higher O$(1s)$ BE's (see Fig. 1). Based on the modification of the Phillips–Van Vechten method[25] of estimating ionicities used by Levine,[26] we estimate that the oxides in the group with O$(1s)$ BE's of 530.0±0.5 eV have ionicities ranging between 76 and 89%. It is this class we refer to as normal ionic oxides (NIO).[18,23,24] The valence bands of group A oxides, which fall within this NIO class (e.g., Na_2O and CaO but not Al_2O_3), are thus almost entirely dominated by electron density from the O$(2p)$ orbitals, the only contributions from the metal valence orbitals being from the small residual covalency (11–24%). Within this group it has been found that this oxygen-dominated valence band shifts slightly closer to the pseudo-Fermi edge as the oxygen become more and more negative [i.e., as the percentage ionicity and the corresponding percentage O$(2p)$ contribution to the valence band increases]. Thus, as we move to the *left* and *down* in the Periodic Table for NIO oxides formed from group A metals, the progressive small increase in ionicity generally causes the leading edge of the valence band to move increasingly to lower binding energies.[18,23]

This "movement" of the O$(2p)$ edge towards E_F with increasing ionicity is stopped if large density metal d bands are placed in the gap between the O$(2p)$ band and E_F, e.g., for the group-*B* transition-metal oxides.[19,20] Thus, as was described earlier for the Cu oxides, we end up with O$(2p)$ bands centered near 7 eV and reasonably separate metal $3d$ bands between this value and E_F.[20] Based on our previous ionicity argument, it also seems reasonable to refer to most transition-metal oxides as NIO.[18,23,24]

For those oxides formed by metals from the bottom of group A, and also for some oxides at the bottom of group B, the O$(1s)$ values [and also the O$(2p)$ band centers] move substantially *lower* than the NIO norm (see, for example, Table I, Rb,Cs,Sr,Ba,La,Ce). Based on our arguments to date,[18] we would expect these to be the most ionic oxides of all, and indeed they are, producing a group we classify as very ionic oxides (VIO) with ionicities clustered around 94%. The increase in ionicity of this group compared to the NIO group is only, about 7–9%, however, which is less than the spread of ionicities in the NIO group. We would therefore have expected only *slight* additional decreases in O$(1s)$ BE and O$(2p)$ band centers for this VIO group compared to the NIO group. Instead a relatively *large* decrease is observed. For example, BaO (a typical VIO) produces an O$(1s)$ of ~528.5 eV and a corresponding downfield shift in its O$(2p)$ valence band to a band maximum near 3 eV and a leading edge near 1.5 eV. These are larger changes for a few percent ionicity increase than that observed, for instance, in going from GeO_2 to CaO, where the ionicity increase is 25–30%.[18,23,24]

Before discussing the possible significance of these shifts in the superconductors, it will be useful to consider why the shifts are so large, i.e., what effects there are in the VIO group, in addition to the relatively small increase in ionicity, which might affect the O$(1s)$ and O$(2p)$ BE's.

Possible contributions include the largely ignored final-state effects in the photoionization process. It is also certain that the growth in size of the cation and structural changes should play a role. These effects are not specific to the VIO group, however, so they should only contribute to the general trend and are unlikely to explain the large sudden effect on O$(1s)$ and O$(2p)$ BE's. One other effect stands out, which has not yet been considered. All of the oxides in the VIO class have a relatively intense cation core-level state close to the valence band, and the gap between these two states decreases as the principle quantum number of the cation increases. Thus, in the case of BaO, the Ba$5p$ level is only about 8 eV from the centroid of the O$(2p)$-dominated valence band. The *proximity* and *symmetry* of the cation level and the O(2p) band ensures their quantum-mechanical interaction. Based on simple molecular-orbital perturbation arguments, we expect the interactions to increase in proportion to the square of the cross-sectional intensity of the core state and inversely with the separation between it and the valence band. The result of this interaction will be to push the two states further apart, the state with the weaker density, the valence band, moving most. It is estimated for BaO that the effect is about 1 eV, i.e., the O(2p) band is pushed closer to E_F by 1 eV by the presence of the Ba5p level. All other oxygen dominated states, i.e., the O(2s) and O(1s) levels, of course, also move down by similar amounts in response to the O(2p) valence level changes. Thus, it would seem that this cation core-level–anion O(2p) band interaction may be a principal reason for the downshifted BE's for oxygen-related levels in the VIO group, *including the superconducting oxides.*[18,23,24] Examination of Table I also shows two elements, Ag and Cd, which one would not have expected to be highly ionic and yet have lower than normal O(1s) values. Again we ascribe this to the effect of the interactions of the low-lying Ag and Cd(4d) levels [cf., the Ba(5p) levels] with the O(2p) band.

CONNECTION BETWEEN THE GENERAL OXIDE ARGUMENTS AND THE SUPERCONDUCTORS

The critical features that we believe connect the arguments above to the nature of the bonding in the high-T_c oxides can be presented in a series of statements as follows.

(1) It is, by now, well established that the controlling feature for many of the properties of the superconductivity oxides, including the superconductivity itself, manifests itself in the nature of the O(2p) band (e.g., that band crosses E_F and the superconductivity is transported by holes in the oxygen band at E_F).[1-3]

(2) We believe that a *critical electronic behavior* of the oxide anions in these systems is primarily controlled by the presence of VIO cations, such as Ba^{2+} (or Sr^{2+}).

(3) In all cases there must be present, as a prerequisite to the possibility of superconductivity, a substantial percentage of the total cation contribution in this VIO form, i.e., there must be present a significant number of cations from near the bottom of the periodic table, e.g., Ba, which have near-valence core states capable of interaction with the O(2p) band.

(4) The superconducting oxides are, in effect, constructed into *complex oxides* in which the *normal* ionic cation (e.g., Cu) becomes part of a complex anion, (e.g., $Cu_3O_7{}^{-7}$) balanced by a *very* ionic action (e.g., Ba^{2+}). Though the bonding between the complex anion and the VIO cation is very ionic (i.e., essentially full charge is donated to the complex anion) the internal bonding between Cu and O in the complex anion is rather covalent, i.e., as discussed in detail elsewhere,[27] the introduction of a VIO oxide (e.g., BaO) into the lattice of an NIO oxide (e.g., CuO) will tend to enhance the covalency of the metal-oxygen bonds in the latter. The net result of these effects suggests the ability of an oxide ion to "polarize."[27]

(5) Though one can substitute one type of VIO cation for another and maintain superconductivity capability, e.g., Sr^{2+} for Ba^{2+}, our argument that there is a special effect of these ions on the O(2p) BE implies that, for instance, swapping Mg^{2+} or even Ca^{2+} for all Ba^{2+} will damage the possibility of superconductivity since neither Mg^{2+} or Ca^{2+} are VIO cations.

(6) It is important to reiterate at this point that the principle thrust of our paper is to note that the bonding between the Cu and O in these superconductors is very substantially altered by the imposed effect of the very large ionic field of the VIO cation, such that there is *no* resemblance, electronically, to copper oxides. The proof of this is, in our opinion, contained in the observation that the O(1s) and O(2s) BE's in XPS of the superconductors are close to those of BaO and far from those of the copper oxides (Fig. 1), or other normal ionic oxides.[28,29] It is a prerequisite for superconductivity in these systems for this VIO interaction to be present.

MECHANISTIC SUGGESTIONS

There is nothing in the above list of statements that directly relates to the *mechanism* of the superconductivity process. In fact, we should emphasize that we have not examined the XPS of these systems below T_c, although others have been successful in observing small changes at E_F, on passing through T_c, which can be interpreted within the framework of the BCS theory for superconductivity.[30] Despite our lack of data under superconducting conditions, the obvious interdependence of our VIO concept and the existence of superconductivity in these complex oxides seems to suggest a possible scenario, which we present here.

In the case of the copper oxides it has been demonstrated phenomenologically by Goodenough[20] and confirmed experimentally by Wertheim and Hufner[19] that the valence band consists of two components, designated as the Cu(3d) and O(2p) bands, which, though in close proximity, are relatively distinct. The O(2p) band lies at higher BE than the Cu(3d) and is centered at about 7 eV for both Cu^{II} and Cu^{I} oxides. BaO and the other VIO oxides, on the other hand, are typified by oxygen states pushed to low BE, e.g., the O(2p) band for BaO is centered around 3 eV.[18] The O(2p) band in the high T_c superconductivity oxide systems is thus also pushed by the dominant VIO interaction (i.e., extreme ionicity, plus the cation near-valence core states) several eV closer to E_F than is the case for the copper oxides. As a result of this, the O(2p) band in $YBa_2Cu_3O_7$ (and related superconducting systems) is pushed directly under the Cu(3d) band.[32] This should create the ingredients needed for an extensive ligand field-type interaction between the two bands. It would be expected that this interaction should affect the lower-density O(2p) band much more than the Cu(3d). We postulate that, owing to this interaction, the part of the O(2p) band (predominantly ionic in nature) originally *below* Cu(3d) is shifted to lower binding energy by the additional 1 eV necessary to couple to the Fermi edge, while the part originally *above* Cu(3d) is shifted up enhancing the covalent aspect of this part of the band (see Fig. 1). Thus, one has the O($2p$) character at E_F necessary for the production of holes,[33] plus the possibility of resonance covalency in the Cu-O planes, which may correspond to the resonant valence bond models of Pauling,[34] and of Anderson *et al.*[35]

Another way of expressing the arguments above is to relate them to the formal band models that have been used for oxides,[36,37] and recently for superconducting oxides.[38] In order to try to explain the electronic behavior of oxides, Hubbard[36] introduced the *one-band* (metal d) Hamiltonian, with the inclusion of dd' correlation. Recently Sawatsky and his colleagues[37] have borrowed an idea of Anderson and provided an extension to the Hubbard model to include *two-band* (metal d and oxygen $2p$) effects. As a result, (dp) mixing terms were introduced, such as hopping or hybridization (t_{ij}) and mixed Coulomb repulsion (U_{pd}) integrals. Shen *et al.*[38] have extended those arguments to the high-T_c superconductors. They have, however, largely just expanded upon the same model that confirms that CuO is an insulator. Our model, on the other hand, would result in a novel *three band,* Hubbard-Hamiltonian in which (for $Y_1Ba_2Cu_3O_7$) Ba($5p$) states are coupled with the O($2p$) band and, through this combination, with the Cu($3d$). Thus, much more involved t and U terms occur, and the initial O($2p$) band is more like that of BaO than CuO. Perturbation solutions with this three-state Hamiltonian shift cause part of the O($2p$) band to make contact with the Fermi edge resulting in the equally unusual metallic behavior above T_c.

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in the O(1s) XPS is, however, not relevant to any of the arguments in this paper, since we are concerned with the effect of Ba^{2+} on the dominant O(1s) feature in the spectrum, and therefore on *all* the O atoms.

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