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Origin of the Ba core-level binding-energy difference between tetragonal and orthorhombic $YBa_2Cu_3O_{7-\delta}$

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Sintered bulk samples of the orthorhombic, superconducting, phase of $YBa_2Cu_3O_{7-\delta}$ exhibit a $\simeq 1.5$ eV Ba core-level decrease compared to the tetragonal, nonsuperconducting phase. This is also observed for thin-film material in the two phases. Using *ab initio* cluster calculations, we show that shifts of this magnitude are explainable by isotropic contraction of the Ba—O bond length in the 0.01- to 0.02-Å range, values compatible with the known lattice-parameter changes between the phases. Finally, even *in situ* cleaved good-quality single crystals of the orthorhombic phase show a chemically shifted Ba component for some regions of the surface, which may be due to Ba—O bond-length contractions at the surface-vacuum interface.

In the myriad of x-ray-photoemission-spectroscopy (XPS) studies of $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) superconductors the interpretation of the Ba core-level ($5p,4d,3d$) binding energies (BE's) has generated controversy.$^{1-8}$ Two components are generally observed, separated by up to $\simeq 2$ eV. There have been many explanations invoked,$^{1-8}$ but it is now quite clear$^{8-11}$ that the bulk orthorhombic superconducting phase ($\delta \simeq 0.1$) is represented by the *lower* component ($5p$, $4d$, and $3d$ BE's at $\simeq 12.0$ eV, 87.0 eV, and 777.6 eV, respectively$^{8-12}$) and that the nonsuperconducting, tetragonal phase ($\delta > 0.5$) has the higher values. Thus a mixture of the two phases within the surface region probed will give two-component spectra. In addition, there are several contaminating compounds [BaO, $Ba(OH)_2$, $BaCO_3$, and $BaCuO_2$] that, if present at the surface, will also give high-lying Ba BE's.^{2} These contaminants usually are present for samples not cleaved *in situ*, and they can even be present sometimes under the latter circumstances.

Establishing that the superconducting phase is represented *solely* by the *lower* Ba core level$^{8-12}$ allows us to refute arguments that (i) the higher BE represents this phase,^{7} (ii) both components represent this phase^{1,3,5} through final-state splitting or nonequivalent Ba site effects, or (iii) the high-BE component is a surface core-level shift of the orthorhombic phase.^{6} It remains important, however, to understand the electronic origin of the BE difference between Ba in the orthorhombic and the tetragonal phases. There are several possibilities: (i) a significant change in the Ba-O covalency, (ii) the electrostatic plus Pauli repulsion changes induced by changing the oxygen-ion content around the Ba^{2+} ion, (iii) similar changes caused by changing the Ba—O bond lengths, and (iv) a strong difference in core-hole final-state screening induced by a metallic versus a nonmetallic host. Of course, it is possible that all the above possibilities contribute, and, indeed, Ba—O bond length changes in Y-Ba-Cu-O go together with changes in oxygen stoichiometry, making a meaningful experimental separation between (ii) and (iii) difficult. In this paper we address the bond length effects by means of comparing results from *ab initio* structure electronic cluster calculations with XPS data from cleaved bulk material, thin films, and cleaved single crystals. We show that simple isotropic contractions in Ba—O bond length, in the 0.01–0.02-Å range, can account for the lower Ba BE in the orthorhombic phase.

Data were obtained in two different instruments in different laboratories. *In situ* cleaved single-crystal data^8 and also *ex situ* prepared thin-film data^2 were obtained using a Surface Science Laboratories XPS spectrometer with a monochromated Al $K\alpha$ source and a 300×450-μm^2 spot size. The BE's were referenced to Au $4f_{7/2}$ at 84.0 eV. For the single-crystal results the vacuum was $\leq 1\times10^{-9}$ torr, no carbonate contamination was observed, and the spectra were stable over long periods, except for the slow build up of hydrocarbon. The spectra reported in Figs. 1(a) and 2(a), and in Figs. 1(b) and 2(b) represent the extremes observed in the Ba $3d_{5/2}$ and Ba $5p_{3/2,1/2}$ regions, respectively, between different locations on the same surface immediately after cleavage. Curves (a) are closer to representing "pure" orthorhombic Y-Ba-Cu-O, being essentially single featured. Curves (b) show a strong component of the high-BE Ba feature.

Spectra of tetragonal and orthorhombic sintered bulk samples of Y-Ba-Cu-O,^{12} were obtained using a Physical Electronic model 5300 spectrometer with a monochromatic Al $K\alpha$ source. The BE scale was referenced to the Ag Fermi edge. Instrument pressures were better than 5×10^{-10} torr. The bulk samples, which were prepared following a procedure that eliminates carbonates,[12] were fractured *in situ*. The Ba spectra of the orthorhombic phase with $\delta = 0.1$, are shown in Figs. 1(c) and 2(c). The spectra of the tetragonal phase, with $\delta = 0.5$, are shown in Figs. 1(d) and 2(d). The phase of each sample was determined by x-ray diffraction. These data confirm unambiguously that the higher-BE line in the Ba $3d_{5/2}$ spectra represents the tetragonal phase and that the lower-BE line represents the orthorhombic phase. The same is true for the Ba $5p$ levels (Fig. 2), and the other Ba core lines (not shown). These results are in agreement with the data reported in an earlier paper,[2] where it was shown that sputter-deposited thin films of Y-Ba-Cu-O, which were oxygen deficient and not superconducting, i.e., in the tetragonal phase, exhibited only the *high*-BE Ba features, as shown in Figs. 1(f) and 2(f). Annealing these films in oxygen, to produce the superconducting orthorhombic phase, induced the presence of the *low*-BE Ba component, Figs. 1(e) and 2(e). Also in this case the identification of the major structural phases was done by x-ray diffraction.

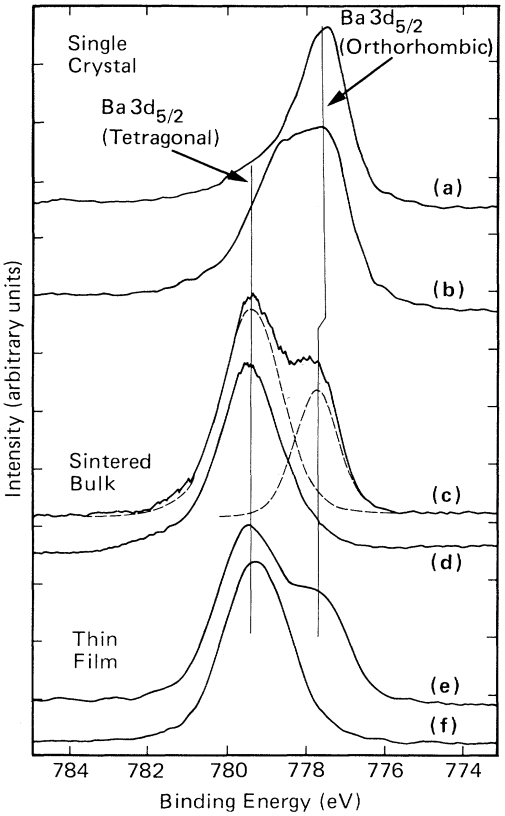

FIG. 1. Ba $3d_{5/2}$ XPS spectra for various Y-Ba-Cu-O samples: (a) and (b) represent the extremes observed from different regions of the *in situ* cleaved surface of a good-quality (high-T_c, sharp-transition) single crystal (Ref. 8). (c) and (d) are from *in situ* cleaved sintered bulk samples of the orthorhombic phase [curve (c) $\delta = 0.1$] and tetragonal phase [curve (d) $\delta = 0.5$] (Ref. 12). (e) and (f) are from thin-film samples prepared *ex situ* by sputter deposition [tetragonal, curve (f)] followed by oxygen annealing [orthorhombic, curve (e)] (Ref. 2).

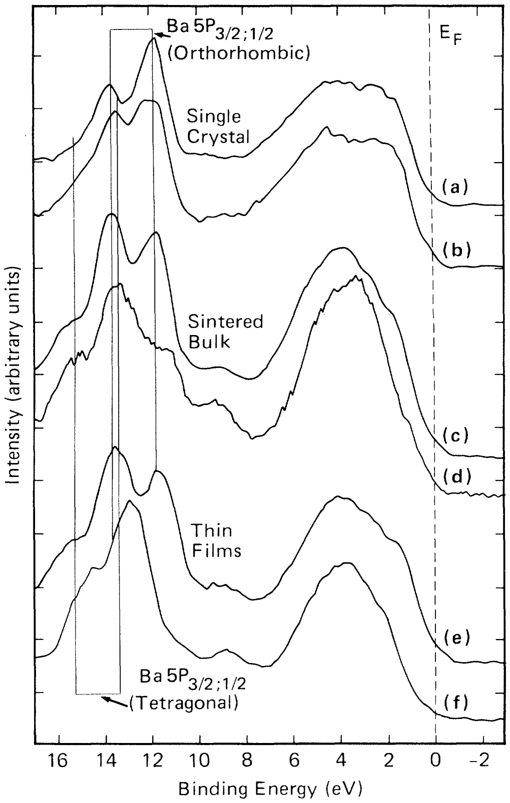

FIG. 2. Ba $5p$ and valence-band spectra equivalent to the spectra of Fig. 1. Though more complex than the $3d_{5/2}$ spectra, the BE shifts between orthorhombic and tetragonal-phase-spectral components are essentially the same as for the $3d_{5/2}$ spectra. This is not completely true for trace (f), where the dominant $5p_{3/2;1/2}$ components are at slightly lower-BE values than the tetragonal phase. This is because the sample was prepared *ex situ* and exhibits significant contributions from $Ba(OH)_2$ and $BaCO_3$ on the surface (Ref. 2).

The local interactions of Ba with O in Y-Ba-Cu-O are studied by means of *ab initio* cluster calculations using the Sr atom as a model. We have replaced the Ba atom with a Sr atom to reduce the amount of computational effort needed to obtain the cluster wave functions. We believe that the features of the Ba-O interactions of interest to us are adequately represented by the Sr-O interactions because we are concerned with calculating shifts in core-level BE's when bond length changes and not with absolute values of BE's. However, since the ionic radius of Sr^{2+} is 0.19 Å smaller than that of Ba^{2+}, we have appropriately reduced the Sr—O bond distances in our clusters. We have used 2.57 and 2.79 Å for the in-plane and out-of-plane metal-oxygen distances;[13] in Y-Ba-Cu-O (tetragonal) these distances are 2.76 and 2.98 Å, respectively.

For the cluster wave functions we performed *ab initio*

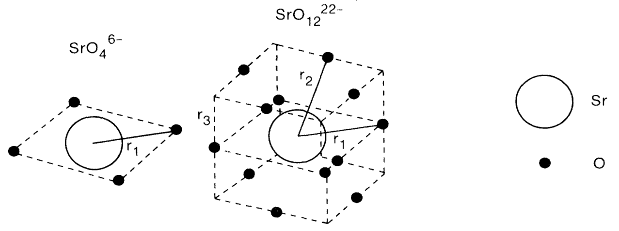

FIG. 3. Geometry of the $[SrO_4]^{6-}$ and $[SrO_{12}]^{22-}$ clusters used for *ab initio* electronic structure calculations. The Sr-O distances are reported in the text.

self-consistent-field (SCF) Hartree-Fock nonrelativistic calculations. Two cluster arrangements were chosen to represent the local Ba-O interactions in Y-Ba-Cu-O. The first is an $[SrO_4]^{6-}$ unit in which the Sr atom is bound to the four nearest-neighbor O atoms in the Sr-O plane (see Fig. 3) with this cluster surrounded by 134 point charges (PC's) simulating the remainder of the crystal and providing an approximation to the Madelung potential. The total entity, cluster plus PC's is neutral. The second cluster replaces the point charges in the second shell by oxygen atoms, giving an $[SrO_{12}]^{22-}$ unit embedded in further point charges (see Fig. 3). The total entity is again neutral. For these calculations, we have modified the Y-Ba-Cu-O geometry so that the clusters, including the PC's, have C_{4V} symmetry. This was done to simplify the calculations and only involves changes of the positions of the atoms in the CuO sheets.

All-electron SCF wave functions were obtained for both the $[SrO_4]^{6-}$ and $[SrO_{12}]^{22-}$ clusters, and the molecular orbitals were expanded in terms of basis sets centered on the Sr and O atoms. Two basis sets were used, denoted set *A* and set *B*. Basis set *A* is reasonably large and gives flexible descriptions for both Sr (Ref. 14) and O (Ref. 15). Basis set *B* was a smaller set centered on Sr and a minimal basis set, with two functions to represent the 1*s* and 2*s* orbitals and one to represent the 2*p* orbital, optimized for the O^{2-} anion. The results for basis sets *A* and *B* have been compared for the $[SrO_4]^{6-}$ cluster, and qualitatively similar results are obtained with both sets. For the larger $[SrO_{12}]^{22-}$ cluster, only basis set *B* has been used.

To interpret the differences in the experimental XPS BE's the cluster core-level orbital energies, ε_i, were used. The calculated shifts were essentially the same for all core levels, so we report here only those of the 3*s* level. The orbital energies represent unrelaxed ionizations potentials (Koopmans' theorem,[16] KT), which are much greater than the observed experimental values because of final-state relaxation effects, which screen the core hole. Nevertheless, when considering *variations* in the experimental BE's with changes in coordination, bond length, or chemical environment, there is a great deal of evidence, based on the explicit calculations of final-state relaxation energies, to show that the major source of the shifts are contained in the initial-state KT variations. This is the case for molecules and for cluster models of extended systems.[17,18]

TABLE I. $[SrO_4]^{6-}$ 3*s* core-level BE decreases ΔE_b, and total energy changes, ΔE_{tot}, caused by contractions of the Sr-O distance in the Sr-O plane.

Basis set	*r*(Sr-O) (Å)	ΔE_{tot} (eV)	ΔE_b (eV)
A	2.573	0.0	0.0[a]
	2.563	0.16	−0.15
	2.473	1.85	−1.5
B	2.573	0.0	0.0[b]
	2.563	0.10	−0.1
	2.473	1.58	−1.1

[a] $\varepsilon_{3s}=334.3$ eV.
[b] $\varepsilon_{3s}=337.7$ eV.

Calculations for the $[SrO_4]^{6-}$ cluster have been performed with basis sets *A* and *B* in order to determine the effect of contraction of the Sr-O distance (representative of the change in going from tetragonal to orthorhombic Y-Ba-Cu-O) on the orbital energies and the total energy of the system (Table I). A contraction of the in-plane Sr-O distance of only 0.01 Å (0.4%) results in a significant 0.15-eV shift of the Ba core levels to lower BE and a 0.16-eV change in the total energy (Table I). For the smaller basis set, *B*, the O^{2-} ions are less spatially diffuse, and the same shrinkage of the metal-O distance induces only a 0.10-eV decrease in the BE's (Table I), an underestimate of $\simeq 50\%$. The difference between the results for basis sets *A* and *B* are smaller for the total energy changes, ΔE_{tot}.

The $[SrO_{12}]^{22-}$ cluster should give a more realistic representation of Ba atom local environment in Y-Ba-Cu-O. Other types of lattice changes can also be considered in addition to the Sr-O in-plane contractions. Consider, for instance, displacement of the Sr ion normal to the SrO_4 plane or a uniform contraction of the SrO_{12} lattice. Unfortunately the $[SrO_{12}]^{22-}$ calculation can only be done with the more restricted basis set *B*, so the effects on BE's will be underestimated by about 50%. Table II shows the results of the three types of lattice modifications for a range of bond-length changes. The Sr-O in-plane contractions produces a 0.16-eV decrease in BE for a 0.01-Å contraction (compared to 0.1 eV for the $[SrO_4]^{6-}$ cluster using basis set *B*, Table I). The Sr-ion displacement out of the SrO_4 plane requires very large movements to produce significant core-level shifts; a 0.2-Å motion produces only a +0.1-eV BE positive shift. Since the observed BE shift is both small and in the wrong direction, we dismiss this type of distortion as a possible explanation for the observed Ba core-level shifts. Uniform lattice contractions produce the largest effects on the BE, as might be expected, since more O ions are involved in effecting the change. A uniform contraction of 0.01 Å produces a decrease of 0.4 eV. The real lattice contraction between tetragonal and orthorhombic Y-Ba-Cu-O depends on the stoichiometry and is not completely uniform. It falls in the 0.01–0.02-Å range[19] for significant stoichiometry differences, for which the basis set *B* calculations on the

TABLE II. $[\mathrm{SrO}_{12}]^{22-}$ calculated $3s$ core-level BE decreases, ΔE_b, caused by various types of lattice contraction. Basis set B is used throughout.

Type of contraction	r(Sr-O) (Å)	ΔE_b (eV)
Sr-O in plane	2.573	0.0[a]
	2.563	−0.16
	2.473	−1.6
Sr displacement out of Sr-O plane	2.573	0.0
	2.580[b]	+0.1
Uniform Sr-O	2.573	0.0
	2.563	−0.35
	2.473	−2.9

[a] $\varepsilon_{3s}=341.1$ eV.

[b] This corresponds to an out-of-plane displacement of the Sr ion by 0.2 Å.

$[\mathrm{SrO}_{12}]^{22-}$ cluster predict a BE decrease of 0.4–0.8 eV. Given that basis set B underestimates the effect by $\sim 50\%$, it appears that decreases of 0.6–1.1 eV are easily accounted for by such lattice contraction effects. This is qualitatively in agreement with the $\simeq 1.5$-eV difference found between the tetragonal and orhorhombic phases, which is all that can be expected considering that Sr has been substituted for Ba and that Cu and Y ions are represented entirely by point charges.

Table II shows that the decrease in BE with uniform lattice contractions is quasilinear with Sr-O distance. The Ba core-level spectra[8] of the "good quality" orthorhombic single crystals show a shoulder at high BE in some regions of the cleave: Figs. 1(b) and 2(b). The shoulder may represent tetragonal Y-Ba-Cu-O present at the surface caused either by the simple presence of the solid/vacuum interface, or by the mechanical damage due to the cleaving process, or possibly by tetragonal bulk inclusions that lie in the cleavage plane. The BE shift, however, is smaller than that for bulk or thin-film tetragonal Y-Ba-Cu-O, being about 1 eV instead of 1.5 eV (see Fig. 1). It is quite possible then that smaller lattice expansions occur in the surface region of cleaved orthorhombic Y-Ba-Cu-O than are representative of the formation of the tetragonal phase and that they give rise to smaller BE shifts. In this regard it is interesting to note that the *smoothest* regions of cleavage give spectra showing the *largest* intensities of the high-BE component, whereas rough, heavily stepped regions give almost pure orthorhombic spectra.[8] We suggest that in the latter regions the orthorhombic surface may be stabilized against distortions.

Yang, Schrott, and Tsuei[20] have reported small Ba core-level BE increases for the orthorhombic phase of Y-Ba-Cu-O as a function of δ. For $\mathrm{YBa_2Cu_3O_{7-\delta}}$, where δ increases from 0 to 0.4, Ba shifts of 0.0–0.5 eV were detected. The authors propose an explanation involving changes in the Ba $5d$–O $2p$ covalency effects. Our calculations with the smaller basis set B indicate that the electrostatic contribution is dominant, since it allows only very restricted covalency and yet it reproduces a large fraction of the observed BE shift. We do, however, see *larger* BE shifts using the more flexible basis set A, which allows covalency to play a greater role, and therefore it is certainly possible that covalency changes might also contribute to the BE shifts. In any case, both these effects, electrostatic and covalent bonding, involve BE changes that may be related to the metal-oxygen bond distance.

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