

**Alkaline Earth Core Level Photoemission Spectroscopy of High
Temperature Superconductors**

R. P. Vasquez

Center for Space Microelectronics Technology

Jet Propulsion Laboratory, California Institute of Technology

Pasadena, California 91109-8099 USA

(Received April 9, 1993)

Abstract

Photoemission measurements of the alkaline earth core levels of high temperature superconductors and related materials are reviewed. Models which seek to explain the large negative chemical shifts observed relative to the corresponding alkaline earth metals are discussed and critically examined. The effect of lattice site disorder on the core level spectra and the presence or absence of intrinsic surface peaks are also reviewed.

Introduction

Although the alkaline earth core levels have not been the focus of as much attention as the valence bands or the O 1s and Cu 2p core levels in photoemission studies of high temperature superconductor (HTS) materials, nevertheless there has been considerable controversy regarding their interpretation. Initially the controversy involved the identification of the intrinsic signals since, as in the O 1s region, the measured features in the alkaline earth core level regions depend sensitively on the level of surface contaminants. In the earliest photoemission measurements from $\text{La}_{2-x}(\text{Sr,Ba})_x\text{CuO}_4$ (LSCO) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO, or Y-123) sintered pellets, the alkaline earth core level signals consisted of two components separated by -1.5- 2 eV. The intensity of the higher binding energy component was shown to be dependent on the sample quality and the surface preparation, and was also shown to be surface related in variable angle and variable photon energy measurements. Since it was always present, even on surfaces freshly exposed in vacuum, the higher binding energy component was often interpreted as being at least partially intrinsic, possibly associated with oxygen defects which resulted in less efficient core hole screening (e.g. see [1-3]). These measurements [1-3] are among the highest quality of the earliest measurements, and include some of the first measurements of a clear Fermi edge in the valence band region of LSCO [2], and also some of the first measurements of the O 1s regions of both LSCO and YBCO in which the low binding energy signals are dominant [2,3], both of which are characteristic of high quality surfaces (see the discussion in [4], and references therein). However, despite these indicators of high quality surfaces, subsequent studies of both LSCO [5] and YBCO [6-8] show that the high binding energy components of the alkaline earth core levels measured from high quality surfaces are either negligible or much less intense than was observed earlier. It is now known that the high binding energy signals originate from extrinsic contaminant phases, especially alkaline earth carbonates, either from unreacted material in grain boundaries or from reaction products of clean HTS surfaces with water vapor and/or carbon dioxide, even the trace amounts present in ultrahigh vacuum chambers (see the discussion of HTS surface stability in [4]).

More recently, studies have focused on the presence or absence of an intrinsic shifted surface component, the effect of inequivalent alkaline earth lattice sites in some materials, and factors affecting the binding energies, which are significantly lower than those of the corresponding metals. This review will primarily consider those studies for which clear evidence of high quality surfaces, such as the detection of the Fermi edge or a low intensity of high binding energy signals in the O 1s region, are reported. These include studies of LSCO [1,2,5], YBCO [5-11], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO, or Bi-2212) [12-18], $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ (TBCCO, or

Tl-2212) [19,20], $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x \sim 0.25$, BPBO) [21-24], $\text{Ba}_{1-x}(\text{K,Rb})_x\text{BiO}_3$ ($x \sim 0.4$, BKBO) [25,26], as well as related nonsuperconducting compounds and superconductors with differing stoichiometry or doping. In this review, each of the areas of study mentioned above will be critically examined, and where possible a resolution of conflicting interpretations will be offered based on the currently available evidence.

Alkaline Earth Core Level Binding Energies

Table 1 summarizes alkaline earth core level binding energy measurements from a variety of HTS materials and related nonsuperconducting compounds. Measurements from alkaline earth metals [27,28] and oxides [28] are included in Table 1 for comparison. Equivalent measurements from the metals have been reported in studies from many laboratories, but reported measurements from the oxides vary in studies from different laboratories and for different methods of oxide preparation and treatment (e.g. see [31]). The oxide binding energies in Table 1 are those measured in this laboratory [28].

It is clear from Table 1 that the alkaline earth core level binding energies measured from the HTS materials are lower than those measured from the corresponding metals or oxides. The negative binding energy shifts are evident in the Ba $3d_{5/2}$, Sr $3d$, and Ca $2p$ spectra shown in Figs. 1, 2, and 3, respectively. The negative binding energy shifts are largest for the Ba core levels of YBCO, -3 eV. These binding energy shifts are in the opposite direction of those observed for most other elements. Initial state charge transfer to the anions in a compound increases the electrostatic potential for the remaining cation core electrons, and thus should increase the cation core level binding energies. Final state relaxation, which is larger in the metal due to the more efficient metallic screening compared to the polarization screening in compounds, is an additional contribution to a positive chemical shift. The unusual negative binding energy shifts of Ba compounds, especially the oxide, have therefore been the subject of study and controversy for several years. Several explanations of the negative shifts have been proposed, all of which in some form have also been suggested to explain the negative shifts observed in measurements from the HTS materials. Factors which have been proposed to explain the observed binding energies include (i) covalent bonding involving the alkaline earth d orbitals, (ii) final state screening involving either the alkaline earth d orbitals or highly polarizable ligands, (iii) binding energy referencing effects, such as pinning of the Fermi level by defects or Fermi level variation resulting from band filling with doping, and (iv) the effect of the

initial state electrostatic potential. In the discussions below, each of these models and the relevant supporting and conflicting evidence will be briefly presented and critically examined.

Initial State Covalency Effects

The possibility that the low lying alkaline earth d orbitals may play a part in final state screening (discussed in the next section) or initial state chemical bonding in the oxides was first suggested as an explanation for small or negative binding energy shifts nearly a decade ago [33]. Since the nd orbitals ($n = 3, 4, \text{ and } 5$ for Ca, Sr, and Ba, respectively) are spatially more compact than the $(n+1)s$ orbitals, lower core electron potentials, and hence lower binding energies, are possible if there is increased initial state occupation of d orbitals in the compounds compared to the metals. For the graphite intercalation compound BaC_6 , there is in fact both theoretical [34] and experimental [35] evidence that the Ba 5d orbitals may be occupied in the initial state. Similarly, Ba 5d - 0 2p hybridization in covalent Ba-O bonds has more recently been suggested to explain the Ba core level binding energies observed in measurements from YBCO and related materials with rare earth substitutions [36,37].

The above interpretation has been disputed on several grounds. First consider the situation for simple alkaline earth compounds. Partial occupation of d orbitals in the initial state has been observed in several studies of the alkaline earth metals [38-40]. However, the d states are absent in measurements from the oxidized metal surfaces [38,40]. Band structure calculations for alkaline earth fluorides and chalcogenides also show the d orbitals to be unoccupied (see the discussion and works cited in [28]). These findings are inconsistent with this model's requirement for increased initial state d orbital occupancy for compounds. In fact, the opposite situation appears to be more common, i. e. the alkaline earth d orbitals may be partially occupied in the metals, but are unoccupied in the simple ionic compounds. It is also well-known that alkaline earth compounds are nearly ideally ionic (e.g. see [41]), so significant covalency involving ligand hybridization with alkaline earth d orbitals seems unlikely.

Findings for the more complex HTS materials are similar to those for the simpler alkaline earth compounds. Band structure calculations for YBCO [42,43], BSCCO [44,45], TBCCO [46], BPBO [47,48], and BKBO [49] show that the alkaline earth d orbitals are well above the Fermi level and hence unoccupied. Resonant inverse photoemission measurements provide experimental verification that the alkaline earth d orbitals of YBCO [50,51], BSCCO [52], TBCCO [19], and BKBO [25] are $\sim 7-13$ eV above the Fermi level, and are therefore unoccupied. In fact, the densities of states from the band structure calculations show little contribution from alkali, alkaline earth, or rare earth orbitals of any type. These electropositive elements can thus

to a good approximation be regarded as ions embedded in a covalently bonded matrix of the other elements. The intensities of the backgrounds on the high binding energy side of the alkaline earth core level signals in Figs. 1-3 for the HTS materials are also much more similar to those of the corresponding signals from the ionic oxides than they are to those of the covalently bonded metals. This observation is consistent with the alkaline earths being present as ions in the HTS materials.

Finally, other ionic compounds for which no initial state d orbital occupancy is expected, such as alkali compounds, also exhibit negative cation core level chemical shifts (see the discussion and works cited in [28]). Nearly all K, Rb, and Cs compounds exhibit chemical shifts which are in the range -1 to -2.5 eV, while Na compounds exhibit chemical shifts which are in the range $\sim +0.5$ to -1 eV [53]. Among HTS materials, the K $2p_{3/2}$ signal occurs at 292.1 eV for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ [25], compared to 294.4 -294.7 eV for K metal [53,54], while the Rb $3d_{5/2}$ signal occurs at 108.6 eV for $\text{Ba}_{0.6}\text{Rb}_{0.4}\text{BiO}_3$ (estimated from Fig. 1 in [26]), compared to 111.5 -111.8 eV for Rb metal [53,55]. These negative shifts are comparable in magnitude to those observed for the alkaline earth core levels in HTS materials. Negative or small positive chemical shifts are also observed for Cu^{+1} , Ag^{+1} , Zn^{+2} , and Cd^{+2} compounds, all of which have filled d shells [56]. A cause and effect relationship between additional initial state d orbital occupancy in compounds relative to metals and negative chemical shifts therefore is not possible for these compounds, and appears unlikely for HTS materials and alkaline earth compounds in general.

Final State Screening Effects

Two models based on final state screening have been proposed, one based on screening by electrons in the alkaline earth d orbitals [33], and the other based on screening by highly polarizable ligands [40]. Since many of the arguments for the first model are similar to those outlined above, this model will be considered first. Although this model has not been suggested to apply specifically to HTS materials, it has been suggested for alkaline earth compounds in general, and is therefore considered here. The justification for this model is based on the $Z+1$ (or equivalent cores) approximation, in which the photoionized core of an atom of atomic number Z is approximated as the core of an atom of atomic number $Z+1$ (e.g. see [57]). Full screening of the core hole then produces a valence electron configuration appropriate for the $Z+1$ atom. For example, a core ionized Ba atom in Ba metal which is fully screened would have the valence configuration of $\text{La}^0, [\text{Xe}]5d6s^2$, while a core ionized Ba^{2+} ion which is fully screened would have the valence configuration of $\text{La}^{2+}, [\text{Xe}]5d$. Similar considerations yield similar results for

Ca and Sr. This model can alternately be formulated as the core hole causing an increase in the potential, resulting in a conduction band state being pulled below the Fermi level.

Several problems have been pointed out with the model discussed above [28]. First, both Ba^0 and Ba^{2+} are screened by a 5d electron. In order for Ba in a compound to have significantly higher final state d orbital occupancy than Ba^0 , the initial state would have to be close to Ba^{1+} so that the fully screened core hole would have the valence electron configuration of $La^{1+}, [Xe]5d^2$ [33], i.e. there would have to be significant covalency in the Ba-ligand bonding. Similar considerations apply for Ca and Sr. However, as mentioned in the previous section, alkaline earth compounds are nearly ideally ionic, so this possibility seems unlikely. Another problem is that band structure calculations show that the lowest lying conduction band states in the alkaline earth fluorides have primarily cation s character [58-60]. Even though the alkaline earth core holes may not be screened by d electrons in the fluorides, negative chemical shifts are still observed [28]. A third problem is that, as noted in the previous section, negative chemical shifts are also observed for alkali and other compounds, for which final state screening by additional d electrons is less likely or, in the case of Na, Group Ib, and Group IIb compounds, impossible. Finally, the final state relaxation energies have been estimated from the Auger parameters [61] for simple Ba salts [28] and for TBCCO and YBCO in both the superconducting orthorhombic (o-YBCO) and oxygen-deficient semiconducting tetragonal (t-YEICO) phases [8]. No correlation with the Ba core level binding energies is observed, and in fact the final state relaxation energies for the compounds are smaller than that for the metal, which is opposite to the requirement for this model.

Some of the problems with initial state or final state d orbital occupancy, noted above and in the previous section, prompted the alternative suggestion that the negative alkaline earth core level shifts observed for the oxides were due to final state polarization screening by highly polarizable O^{2-} ligands [40]. This model has also been considered as a possibility in some early studies of HTS materials (e.g. see [13]). The final state relaxation energies of the Ba halides and chalcogenides are in fact observed to increase with increasing ligand polarizability [28], as one might expect. However, as noted above, there is no correlation between the estimated final state relaxation energies and the observed alkaline earth core level binding energies for either simple salts [28] or for HTS and related materials [8]. Initial state effects must therefore be dominant in determining the alkaline earth core level binding energies.

Binding Energy Referencing Effects

In a study of **Ba** oxides with various preparation and treatment conditions, it has been found that the **Ba** core level chemical shift could be varied from +0.45 to -1.6 eV [31]. Since the valence band and all the core levels were found to be rigidly shifted, it was suggested that the negative chemical shift of **BaO** observed in many studies resulted from the pinning of the Fermi level by defect states in the band gap. It was also suggested that, by considering the HTS materials to be doped alkaline earth oxides, the same explanation could account for the negative alkaline earth core level shifts in these materials [31].

As a general explanation for the negative chemical shifts, two objections to this model have been raised. One objection is that for some materials the negative chemical shifts are so large that a “normal” positive chemical shift cannot be obtained even when the Fermi level is pinned near the conduction band edge [28]. Even the maximum chemical shift of +0.45 eV observed for **BaO** [31] is extraordinarily small for a doubly ionized cation. For comparison, the Si 2p chemical shift observed for **SiO₂** (cation charge +2.04 [62]) is +4.5 eV, or +2.2 eV/electron [62].

The second objection to this model is that in comparing measurements from o-YBCO and t-YBCO, the 1.0 eV binding energy difference in the 13a core levels is not accompanied by a rigid shift of the other core levels or of the valence band [8]. On the contrary, the valence band spectra differ primarily in shape, consistent with a differing distribution of states. In the oxygen stoichiometry range where YBCO remains orthorhombic and superconducting, a trend towards higher alkaline earth core level binding energies with increasing oxygen deficiency is also apparent in Table 1. However, even these core level shifts are not accompanied by rigid shifts in the valence band region. The primary effects of oxygen deficiency in the valence band region are a loss of states near the Fermi level and changes in the band shape [63]. These findings are consistent with changes in the distribution of states, rather than changes in the Fermi level position. Clearly effects other than Fermi level shifts are therefore significant for YBCO.

Fermi level shifts of a few tenths of an eV may be observable as a function of doping in 13 SCCO, however. Rigid shifts of the core levels and valence band of -0.15-0.2 eV have been reported in a study of BSCCO with varying oxygen stoichiometry [64]. Similarly, rigid shifts as large as ~0.7 eV have been reported for $0 \leq x \leq 1$ in **Bi₂Sr₂Ca_{1-x}Y_xCu₂O_{8+δ}** [65]. However, in studies of the same material another group reports rigid shifts of -0.1-0.2 eV only for $x \leq 0.2$, but not for larger values of x [66-68]. While chemical potential variations thus appear to be detectable in at least some HTS materials, the effect on the core level binding energies is at most a few tenths of an eV. This effect thus does not appear to be sufficient by itself to account for the large negative chemical shifts of the alkaline earth core levels observed in HTS materials.

Recently, a different type of binding energy referencing problem has been suggested for alkaline earth compounds in general, though not for HTS materials specifically. In studies of alkaline earth metals and simple ionic salts, it was found that the chemical shifts of the compounds were positive if the core levels of both the metals and compounds were referenced to the C 1s peak at 285 eV, but negative if the metal core levels were referenced to the Fermi level [69,70]. These findings prompted the suggestion that the negative chemical shifts claimed for alkaline earth compounds were an artifact of choosing different binding energy references for the metals and the compounds. It is useful to recall that the commonly used method of correcting the core level binding energies of insulators to the C 1s signal originated from measurements of the same signal from the conducting surfaces of metals. The assumption is that the adventitious hydrocarbon contaminants on the different surfaces have C 1s core level binding energies that are sufficiently similar that they can be used as a standard to reference to the Fermi level of the spectrometer. However, on reactive surfaces this may not be a valid assumption. On alkaline earth metal surfaces, this assumption is in fact demonstrably invalid. Ba metal is known to react with some hydrocarbons and with common background gases in ultrahigh vacuum systems, such as CO, to form BaC₂ [71]. Since the C 1s binding energy for BaC₂ is significantly lower than that observed for hydrocarbons [71], the choice of the C 1s signal as the binding energy reference in this case results in two different binding energy references for the metal and the compounds. The suggestion that the negative chemical shifts are artifacts related to differences in binding energy referencing therefore appears to be erroneous.

Initial State Electrostatic Effects

Electrostatic models in which the ionization energy and lattice potential (Madelung energy) are the primary determinants of core level binding energies are among the oldest models which have been applied to ionic compounds. Modifications to the simplest point charge model to correct for the effects of polarization (final state relaxation), internuclear repulsion, the work function, etc., are common, but these effects nearly offset each other so that the net effect of the corrections is small. The point charge model has been applied to ionic materials such as alkali compounds [72,73], Group Ib and IIb compounds [56], alkaline earth compounds [28,74], and metal oxides [75], and has been found to be most effective for cations with closed shell electronic configurations in low formal oxidation states (+3 or lower) [75], conditions which the alkaline earth cations satisfy. Studies of the cation core levels in Group Ib and IIb compounds [56] and in alkaline earth compounds [28] concluded that negative chemical shifts result primarily from initial state effects, where the positive shift expected with ionization is more than offset by large

lattice electrostatic potentials at the cation sites. A similar conclusion can be drawn from an earlier study of alkali halides [73], though the issue of negative chemical shifts was not specifically addressed. More recently, a similar conclusion was reached in a study of alkaline earth oxides [76] using a more sophisticated model, utilizing *ab initio* Hartree-Fock self-consistent field wavefunctions for metal oxide clusters, which were surrounded by point charges to reproduce the lattice potential in the vicinity of the cluster.

The qualitative success of a simple point charge model in explaining negative cation core level chemical shifts in simple ionic alkaline earth salts prompted the suggestion that lattice potential effects may also be responsible for the negative chemical shifts observed for the alkaline earth core levels of HTS materials [8,28]. A more quantitative basis for establishing that electrostatic effects may be important in determining the Ba core level binding energies of YBCO is found in the results of *ab initio* calculations [77]. In that study [77], it was found that the difference in the initial state electrostatic potential resulting from the 13a-O bond length difference was the dominant cause of the 13a core level binding energy difference observed between o-YBCO and t-YBCO.

The importance of electrostatic effects has been disputed, based on 13a core level binding energy measurements in the systems $Y_{1-x}Pr_x-123$, $Y_{1-x}Eu_x-123$, and $Eu_{1-x}Pr_x-123$ [36,37]. The argument was that the Ba core levels in $Y_{1-x}Pr_x-123$ and $Eu_{1-x}Pr_x-123$ showed similar shifts with Pr substitution, but the Ba-O bond length changes are not comparable. In addition, $Y_{1-x}Pr_x-123$ and $Y_{1-x}Eu_x-123$ exhibit similar Ba-O bond length changes with x, but the Ba core levels of $Y_{1-x}Pr_x-123$ shifted to higher binding energy with increasing x, while those of $Y_{1-x}Eu_x-123$ did not. Since no correlation was observed between Ba core level binding energies and Ba-O bond lengths, it was concluded that electrostatic effects were not dominant [37]. The explanation favored in these studies [36,37] was that the dominant factor affecting the Ba core level binding energies is initial state Ba 5d-O 2p covalency, which for reasons discussed previously does not seem likely.

The reasoning outlined above is open to question. While it is true that the Ba-O bond lengths increase with increasing x in both $Y_{1-x}Pr_x-123$ and $Y_{1-x}Eu_x-123$, the magnitude of the increase is not comparable. The shortest Ba-O distances, in the Ba-O plane, increase by 0.01 Å in $Y_{1-x}Eu_x-123$ when x is increased from 0 to 1, while the comparable Ba-O distances increase by 0.03 Å in $Y_{1-x}Pr_x-123$ [78]. The fact that the Ba core levels are observed to shift to higher binding energy by 0.4 eV when x is increased from 0 to 0.8 in $Y_{1-x}Pr_x-123$ [36] and not to shift with Eu substitution in $Y_{1-x}Eu_x-123$ [37] is therefore not contradictory with the findings of [77]. In addition, the observation of a Ba core level shift with increasing Pr substitution in $Y_{1-x}Pr_x-123$ is itself in question, since a recent study reported no such shift [79]. Preliminary measurements

in this lab are in agreement with the findings of [79], in that no significant difference in the Ba core level binding energies is observed between Y-123 and Pr-123, as shown in Fig. 4. The reason for these differing findings is most likely differences in surface quality. The Ba 4d doublets in the spectra measured in [37] are poorly resolved, indicating significant surface contamination and/or damage due to scraping [4]. As noted in [37], variations in the intensities of the high binding energy components could result in apparent core level shifts. The reported binding energies in [37] were therefore based on decomposition of the line shapes using least squares fitting, which may give nonunique solutions and is certainly not as reliable as binding energies determined from well-resolved spectra such as those in Fig. 4.

The spectra in Fig. 4 also appear to be contradictory to expectations based on the findings of [77], since the difference in Ba-O distances between Y-123 and Pr-123 is nearly identical to the difference between o-YBCO and t-YBCO [78,80], yet in the former case no Ba core level shift is observed while in the latter case a core level shift of 1 eV is observed [8]. While this observation appears to argue against bond length variations as the major determinant of the Ba core level binding energies, it does not rule out other electrostatic effects. Other factors include the difference in Ba-O coordination between o-YBCO and t-YBCO, the possible effect of Pr 4f-02p hybridization, etc.

It is clear from the discussion above that there is no consensus on an explanation of the observed alkaline earth core level binding energies measured from either simple salts or from the more complex HSC materials, and this remains an active area of research and debate. At this time, initial state electrostatic effects appear to be the most likely dominant determinants of the binding energies, in the opinion of the author.

Lattice Site Occupancy & Disorder Effects

Some alkaline earth core level spectra measured from WIS materials clearly exhibit two components even when there is little or no evidence of contaminants in the other core level and valence band spectra. This is especially noticeable in the Ca 2p spectra measured from both BSCCO [5,13,14,16-18] and TBCCO [19,20] when the signal to noise ratio is sufficiently high, as exemplified in Fig. 5. Two components are visually less obvious in the Sr 3d spectra measured from BSCCO, and are inferred from least squares fitting [13,15-18]. As shown in Fig. 2, the Sr 3d lineshapes measured from a BSCCO single crystal and SrO are similar, the difference being that the signal from BSCCO exhibits a marked asymmetry towards higher binding energy. The line width (-1.2. eV) is also significantly larger than that observed from a

SrTiO₃ single crystal (0.95 eV) [28]. Two Ba signals have also been reported in a study of Tl-2223 [19], though another study of Tl-2212 with lower contaminant levels [20] found a greatly reduced intensity of the higher binding energy component, suggesting that only the lower binding energy component is intrinsic. A comparison of the Ba 4d signals measured from YBCO and Tl-2212 is shown in Fig. 6. The lineshapes are very similar except for a more pronounced asymmetry towards higher binding energy for the signal from Tl-2212, which corresponds to an additional signal at -1 eV higher binding energy than the main doublet. This high binding energy component corresponds closely to signals measured from bulk Ba(OH)₂ and BaCO₃ [28], again suggesting an extrinsic origin.

The presence of two components in the alkaline earth core level spectra discussed above has been interpreted as resulting from cation disorder [5,13-20], since the alkaline earth ions in the ideal crystals occupy inequivalent sites with differing coordination to oxygen and hence differing lattice potentials. In the case of BSCCO, Ca-Sr disorder is a physically reasonable expectation. The ionic radii of Ca²⁺ (Pauling radius 0.99 Å) and Sr²⁺ (1.13 Å) are reasonably close to each other, and consequently solid solutions are obtained over the entire composition range with no miscibility gap in simple ionic salts such as Ca_{1-x}Sr_xO [81], as well as in more complex mixed metal oxides such as the perovskite Ca_{1-x}Sr_xTiO₃ [81]. Ca-Sr disorder in BSCCO has indeed been inferred from high resolution transmission electron microscopy (HRTEM) [82] and from x-ray and neutron diffraction measurements ([18], and references therein). It therefore seems probable that the two components observed in the alkaline earth core level spectra measured from BSCCO do in fact originate from Ca-Sr disorder.

In the case of TBCCO, significant Ca-Ba disorder seems less likely. The ionic radius of Ba²⁺ (1.35 Å) is much larger than that of Ca²⁺. As a result, a miscibility gap covering virtually the entire composition range is observed in simple ionic salts such as Ca_{1-x}Ba_xO [81] and Ca_{1-x}Ba_xF₂ ([83], and references therein), and the miscibility gap in the perovskite Ca_{1-x}Ba_xTiO₃ covers most (-70% at 1200° C) of the composition range [81,84]. In addition, as previously mentioned, since the high binding energy Ba core level signals correspond closely to the binding energies measured from contaminant phases and the intensities also are minimized for higher quality surfaces, a predominantly extrinsic origin for these signals is likely. Tl-Ca disorder is more likely, since the ionic radius of Tl³⁺ (0.95 Å) is close to that of Ca²⁺. Tl-Ca disorder has in fact been observed in HRTEM measurements [85], and has also been inferred at a level of - 10% from Rietveld refinement of x-ray diffraction data [86]. However, this level of disorder is insufficient to account for the Ca 2p signals observed in [19,20] and in Fig. 5. There is also little or no evidence of multiple signals in the Tl 4f region [19,20,87], as might be expected if Tl were occupying different lattice sites. An alternative explanation might be that

one of the Ca signals originates from intergrowth defects [85]. Additional research is necessary to resolve these issues.

Surface Core Level Shifts

The possibility of a chemically shifted surface peak in the Y-123 Ba 4d core level region which is intrinsic, rather than due to extrinsic contaminant phases, was first suggested in [10]. Two Ba 4d doublets separated by 1.2 eV were observed [10] from surfaces of Y-123 single crystals cleaved in vacuum at 20 K. These same surfaces exhibited clear Fermi edges [88] and a single O 1s signal at 528 eV [89]. The low binding energy doublet was identified as the surface peak based on factors such as the dependence of the intensity on the photoelectron kinetic energy. The origin of the two Ba signals was suggested to be the difference in oxygen coordination for bulk and surface Ba atoms for a surface terminated with the 13a-O plane, obtained by cleaving between the Ba-O plane and either the adjacent Cu-O plane or Cu-O chain layer.

A subsequent study of cleaved Y-123 single crystals [7] showed the high binding energy Ba 4d doublet to be the surface signal, based on reinterpretation of the energy-dependent intensity data, angle-resolved measurements, and the fact that high quality surfaces could be prepared with no high binding energy component apparent. The single component Ba spectra seemed to correlate with measurements from stepped surfaces, while the double component spectra originated from smooth surfaces. Examination of the published O 1s spectra [7] from these two types of surfaces reveals little variation, in agreement with the earlier studies' finding that the multiple Ba signals [10] were not accompanied by obvious multiple O signals [89]. The surface Ba signal was interpreted as originating from extrinsic phases [7], either from impurities in the crystal or possibly from mechanical damage during cleavage. "his interpretation would require the impurity/damaged surface phase to have nearly the same O 1s binding energy as o-YBCO.

A study of chemically-etched Y-123 epitaxial thin films also found single component Ba signals [8] for both o-YBCO and t-YBCO, as shown in Fig. 7. The two-component spectra from cleaved single crystals [7,10] look essentially like the sum of the two spectra in Fig. 7. The single Ba signal observed in this study [8] was attributed to the termination of the chemically-etched surface in Cu-O planes [90,91], so that Ba only occurs in a bulk environment. The surface stability compared to cleaved single crystals was also attributed to the Cu-O plane surface termination, so that the reactive Ba was only occupying subsurface sites. The chemically

shifted Ba signals observed in the earlier studies of cleaved single crystals [7,10] were attributed to the **Ba-O** surface termination obtained by cleaving the weak bond between the **Ba-O** plane and the adjacent **Cu-O** plane [8]. Cleavage between the **Ba-O** plane and the **Cu-O** chain layer was considered much less likely due to the strength of this bond.

It is important to note that with the proposed **Ba-O plane/Cu-O plane** cleavage, **inequivalent** surfaces are obtained. On a surface with steps (i.e. a real surface) the intensity ratio of the **surface/bulk Ba** signals can therefore vary depending on the fraction of the surface area with **Ba-O** plane termination. It has also recently been suggested that cleavage can occasionally occur between **Cu-O** planes [92], producing a surface which would not result in a surface **Ba** signal. The surface termination of **YBCO** is discussed in detail elsewhere in this issue [93]. With at least two surface terminations possible, only one of which would produce a surface **Ba** signal, it is therefore not surprising that the surface 13a signal intensity is observed to vary at different locations on a cleaved crystal surface [7]. However, at this time an extrinsic origin for the surface 13a signal cannot definitively be ruled out, and additional research on this issue is required.

Most recently, it has been suggested that chemically-etched **o-YBCO** is terminated with a surface layer of **t-YBCO** [11], based on the presence of a surface **O 1s** signal at the same binding energy as that observed for **t-YBCO**. This suggested surface phase should also result in an observable surface **Ba** signal, since the signals for **o-YBCO** and **t-YBCO** differ by 1 eV [8], as shown in Fig. 7. However, as also shown in Fig. 7, the **o-YBCO** signal seems consistent with a single component. The lack of a surface **Ba** signal is emphasized in angle-resolved measurements of the more surface-sensitive **Ba 3d** signal, as shown in Fig. 8. Even at a grazing photoelectron emission angle of 20°, only a slight difference in lineshape is observed, verifying that there is no significant surface **Ba** signal for chemically-etched surfaces.

Conclusions

The alkaline earth core level signals measured from HTS materials occur at significantly lower binding energies than those from the corresponding metals, the negative chemical shift being as large as -3 eV for the **Ba** signals from **YBCO**. Signals at -1.5-2 eV higher binding energy are also often observed, but are due to extrinsic contaminant phases. In the case of the bismuthates, the alkaline earth core level binding energies for the doped superconducting materials do not appear to differ significantly from those of the undoped parent compounds, but for the cuprates the observed binding energies are lower than any other material measured to

date. The cause of the large negative shifts is a matter of ongoing research and debate, but the evidence available at this writing appears to favor initial state electrostatic effects as the dominant factors, though chemical potential variations also appear to play a smaller, but detectable, role.

Alkaline earth lattice site disorder seems to be well-established for BSCCO, resulting in two intrinsic signals separated by -1 eV in both the Ca 2p and Sr 3d core levels. Two Ca 2p signals separated by -1 eV are also observed for TBCCO, but only the lowest binding energy Ba signals are unambiguously identifiable as intrinsic. At this time, Tl-Ca disorder seems more likely than Ca-Ba disorder, but does not seem sufficient to explain the observed intensity ratio of the Ca 2p signals. Further work is necessary to resolve this issue.

Two Ba core level signals separated by -1 eV are also usually observed for cleaved YBCO single crystals, with only the low binding energy signal being intrinsic to the bulk. The higher binding energy signal is not accompanied by a high binding energy O 1s signal, and thus has also been interpreted as being intrinsic to Ba-O terminated surfaces, though an extrinsic origin cannot be definitively ruled out at this time. On chemically-etched YBCO surfaces, which are terminated in Cu-O planes, surface Ba signals are absent and only the low binding energy component intrinsic to the bulk is observed.

Acknowledgements

The writing and publication of this paper were supported by the Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, and were jointly funded by the National Aeronautics and Space Administration, Office of Advanced Concepts and Technology, and by the Strategic Defense Initiative Organization, Innovative Science and Technology Office.

References

1. P. Steiner, J. Albers, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner and C. Politis, *Z. Phys. B*, 66 (1987) 275.
2. P. Steiner, R. Courths, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner and C. Politis, *Appl. Phys. A*, 44 (1987) 75.
3. P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner and C. Politis, *Z. Phys. B*, 67 (1987) 19.
4. R. P. Vasquez, *J. Electron Spectrosc. Relat. Phenom.*, this issue.
5. H. M. Meyer III and J. H. Weaver, in D. M. Ginsberg (Ed.), *Physical Properties of High Temperature Superconductors 11*, World Scientific Publishing, Singapore, 1990, p. 369.
6. H. M. Meyer III, D. M. Hill, T. J. Wagener, Y. Gao, J. H. Weaver, D. W. Capone 11 and K. C. Goretta, *Phys. Rev. B*, 38 (1988) 6500.
7. D. E. Fowler, C. R. Brundle, J. Lerczak and F. Holtzberg, *J. Electron Spectrosc. Relat. Phenom.*, 52 (1990) 323; C. R. Brundle and D. E. Fowler, unpublished.
8. R. P. Vasquez, M. C. Foote, L. Bajuk and B. D. Hunt, *J. Electron Spectrosc. Relat. Phenom.*, 57 (1991) 317.
9. R. S. List, A. J. Arko, Z. Fisk, S-W. Cheong, S. D. Conradson, J. D. Thompson, C. B. Pierce, D. E. Peterson, R. J. Bartlett, N. D. Shinn, J. E. Shirber, B. W. Veal, A. P. Paulikas and J. C. Campuzano, *Phys. Rev. B*, 38 (1988) 11966.
10. R. Liu, C. G. Olson, A.-B. Yang, C. Gu, D. W. Lynch, A. J. Arko, R. S. List, R. J. Bartlett, B. W. Veal, J. Z. Liu, A. P. Paulikas and K. Vandervoort, *Phys. Rev. B*, 40 (1989) 2650.
11. A. Hartmann, G. J. Russell and K. N. R. Taylor, *Physics C*, 205 (1993) 78.
12. P. Steiner, S. Hufner, A. Jungman, S. Junk, V. Kinsinger, I. Sander, W. R. Thiele, N. Backes and C. Politis, *Physics C*, 156 (1988) 213.
13. H. M. Meyer III, D. M. Hill, J. H. Weaver, D. L. Nelson and C. F. Gallo, *Phys. Rev. B*, 38 (1988) 7144.
14. F. U. Hillebrecht, J. Fraxedas, L. Ley, H. J. Trodahl, J. Zaanen, W. Braun, M. Mast, H. Peterson, M. Schaible, L. C. Bourne, P. Pinsukanjana and A. Zettl, *Phys. Rev. B*, 39 (1989) 236.
15. A. Fujimori, S. Takekawa, E. Takayama-Muromachi, Y. Uchida, A. One, T. Takahashi, Y. Okabe and H. Katayama-Yoshida, *Phys. Rev. B*, 39 (1989) 2255.
16. S. Kohiki, T. Wada, S. Kawashima, H. Takagi, S. Ushida and S. Tanaka, *Phys. Rev. B*, 38 (1988) 8868.
17. R. P. Vasquez and R. M. Housley, *Physics C*, 175 (1991) 233.

18. K. Tanaka, H. Takaki and S. Mizuno, *Jpn. J. Appl. Phys.*, 31 (1992) 2692.
19. H. M. Meyer III, T. J. Wagener, J. H. Weaver and D. S. Ginley, *Phys. Rev. B*, 39 (1989) 7343.
20. R. P. Vasquez and W. L. Olson, *Physics C*, 177 (1991) 223.
21. G. K. Wertheim, J. P. Remeika and D. N. E. Buchanan, *Phys. Rev. B*, 26 (1982) 2120.
22. H. Sakamoto, H. Namatame, T. Mori, K. Kitazawa, S. Tanaka and S. Suga, *J. Phys. Soc. Jpn.*, 56 (1987) 365.
23. C. L. Lin, S. L. Qiu, J. Chen, M. Strongin, G. Cao, C.-S. Jee and J. E. Crow, *Phys. Rev. B*, 39 (1989) 9607.
24. Z.-X. Shen, P. A. P. Lindberg, B. O. Wells, D. S. Dessau, A. Borg, I. Lindau, W. E. Spicer, W. P. Ellis, G. H. Kwei, K. C. Ott, J.-S. Kang and J. W. Allen, *Phys. Rev. B*, 40 (1989) 6912.
25. T. J. Wagener, H. M. Meyer III, D. M. Hill, Yongjun Hu, M. B. Jest, J. H. Weaver, D. G. Hinks, B. Dabrowski and D. R. Richards, *Phys. Rev. B*, 40(1989) 4532.
26. R. Itti, I. Tomeno, K. Ikeda, K. Tai, N. Koshizuka and S. Tanaka, *Phys. Rev. B*, 43 (1991) 435.
27. J. C. Fuggle and N. Mårtensson, *J. Electron Spectrosc. Relat. Phenom.*, 21 (1980) 275.
28. R. P. Vasquez, *J. Electron Spectrosc. Relat. Phenom.*, 56 (1991) 217.
29. T. J. Wagener, H. M. Meyer III, Y. Hu, M. B. Jest, J. H. Weaver and K. C. Goretta, *Phys. Rev. B*, 41 (1990) 4201.
30. H. M. Meyer III, D. M. Hill, J. H. Weaver, K. C. Goretta and U. Balachandran, *J. Mater. Res.*, 6 (1991) 270.
31. D. M. Hill, H. M. Meyer III and J. H. Weaver, *Surf. Sci.*, 225 (1990) 63.
32. R. P. Vasquez, in J. J. Pouch, S. A. Alterovitz, R. R. Romanofsky, and A. Hepp (Eds.), *Synthesis and Characterization of High Temperature Superconductors*, Trans Tech Publications Ltd., Aedermannsdorf, Switzerland, 1993, Materials Science Forum Vol. 130-132 (in press).
33. G. K. Wertheim, *J. Electron Spectrosc. Relat. Phenom.*, 34 (1984) 309.
34. N. A. W. Holzwarth, D. P. DiVincenzo, R. C. Tatar and S. Rabi, *Int. J. Quantum Chem.*, 23 (1983) 1223.
35. M. E. Preil, J. E. Fischer, S. B. DiCenzo and G. K. Wertheim, *Phys. Rev. B*, 30 (1984) 3536.
36. I.-S. Yang, A. G. Schrott and C. C. Tsuei, *Phys. Rev. B*, 41 (1990) 8921.
37. I.-S. Yang, A. G. Schrott, C. C. Tsuei, G. Bums and F. H. Dacol, *Phys. Rev. B*, 43 (1991) 10544.

38. K. A. Kress and G. J. Lapcyre, *Phys. Rev. Lett.*, 28 (1972) 1639.
39. A. Fujimori, J. H. Weaver and A. Franciosi, *Phys. Rev. B*, 31 (1985) 3549.
40. K. Jacobi, C. Astaldi, B. Frick and P. Geng, *Phys. Rev. B*, 36 (1987) 3079.
41. B. F. Levine, *J. Chem. Phys.*, 59 (1973) 1463.
42. S. Massidda, J. Yu, A. J. Freeman and D. D. Koelling, *Phys. Lett. A*, 122 (1987) 198.
43. B. Szpunar and V. H. Smith, Jr., *Phys. Rev. B*, 37 (1988) 7525.
44. M. S. Hybertson and L. F. Mattheis, *Phys. Rev. Lett.*, 60 (1988) 1661.
45. H. Krakauer and W. E. Pickett, *Phys. Rev. Lett.*, 60 (1988) 1665.
46. J. Yu, S. Massidda and A. J. Freeman, *Physics C*, 152 (1988) 273.
47. L. F. Mattheis and D. R. Hamann, *Phys. Rev. B*, 28 (1983) 4227.
48. K. Takegahara and T. Kasuya, *J. Phys. Sot. Jpn.*, 56 (1987) 1478.
49. L. F. Mattheis and D. R. Hamann, *Phys. Rev. Lett.*, 60 (1988) 2681.
50. T. J. Wagener, Y. Gao, J. H. Weaver, A. J. Arko, B. Flandermeyer and D. W. Capone II, *Phys. Rev. B*, 36 (1987) 3899.
51. T. J. Wagener, Y.-J. Hu, M. B. Jest and J. H. Weaver, *Phys. Rev. B*, 42 (1990) 1041.
52. T. J. Wagener, Y. Hu, Y. Gao, M. B. Jest, J. H. Weaver, N. D. Spencer and K. C. Goretta, *Phys. Rev. B*, 39 (1989) 2928.
53. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Eden Prairie, MN, 1992 (and references cited therein).
54. L.-G. Petersson and S.-E. Karlsson, *Physics Scripts*, 16 (1977) 425.
55. J. A. Leiro and E. E. Minni, *Phys. Rev. B*, 31 (1985) 8248.
56. S. W. Garenstroom and N. Winograd, *J. Chem. Phys.*, 67 (1977) 3500.
57. B. Johansson and N. Mårtensson, *Phys. Rev. B*, 21 (1980) 4427.
58. J. P. Albert, C. Jouanin and C. Gout, *Phys. Rev. B*, 16 (1977) 4619.
59. R. A. Heaton and C. C. Lin, *Phys. Rev. B*, 22 (1980) 3629.
60. N. C. Amaral, B. Maffeo and D. Guenzburger, *Phys. Status Solidi B*, 117 (1983) 141.
61. C. D. Wagner, *Faraday Discuss. Chem. Sot.*, 60 (1975) 291.
62. R. N. Nucho and A. Madhukar, *Phys. Rev. B*, 21 (1980) 1576.
63. B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, J. C. Campuzano, C. Olson, A.-B. Yang, R. Liu, C. Gu, R. S. List, A. J. Arko and R. Bartlett, *Physics C*, 158 (1989) 276.
64. Z.-X. Shen, D. S. Dessau, B. O. Wells, C. G. Olson, D. B. Mitzi, L. Lombado, R. S. List and A. J. Arko, *Phys. Rev. B*, 44 (1991) 12098.

65. M. A. van Veenendaal, R. Schlattmann, G. A. Sawatzky and W. A. Green, *Phys. Rev. B*, **47** (1993) 446.
66. T. Kusunoki, T. Takahashi, S. Sate, H. Katayama-Yoshida, K. Kamiya and H. Inokuchi, *Physics C*, 185-189 (1991) 1045.
67. T. Watanabe, T. Takahashi, S. Suzuki, S. Sato and H. Katayama-Yoshida, *Phys. Rev. B*, **44** (1991) 5316.
68. T. Takahashi, T. Watanabe, T. Kusunoki and H. Katayama-Yoshida, *J. Phys. Chem. Solids*, **52** (1991) 1427.
69. M. I. Sosulnikov and Yu. A. Teterin, *J. Electron Spectrosc. Relat. Phenom.*, **59** (1992) 111.
70. V. G. Yarzhemsky, Yu. A. Teterin and M. I. Sosulnikov, *J. Electron Spectrosc. Relat. Phenom.*, **59** (1992) 211.
71. J. Verhoeven and H. van Doveren, *J. Vat. Sci. Technol.*, **20** (1982) 64.
72. C. S. Fadley, S. B. M. Hagstrom, M. P. Klein and D. A. Shirley, *J. Chem. Phys.*, **48** (1968) 3779.
73. P. H. Citrin and T. D. Thomas, *J. Chem. Phys.*, **57** (1972) 4446.
74. H. Franzen, J. Merrick, M. Umaña, A. S. Khan, D. T. Peterson, J. R. McCreary and R. J. Thorn, *J. Electron Spectrosc. Relat. Phenom.*, **11** (1977) 439.
75. J. Q. Broughton and P. S. Bagus, *J. Electron Spectrosc. Relat. Phenom.*, **20** (1980) 261; **21** (1980) 283.
76. P. S. Bagus, G. Pacchioni, C. Sousa, T. Minerva and F. Parmigiani, *Chem. Phys. Lett.*, **196** (1992) 641.
77. F. Parmigiani, G. Pacchioni, C. R. Brundle, D. E. Fowler and P. S. Bagus, *Phys. Rev. B*, **43** (1991) 3695.
78. R. M. Hazen, in D. M. Ginsberg (Ed.), *Physical Properties of High Temperature Superconductors II*, World Scientific, Singapore, 1990, p. 121.
79. O. Cohen, F. H. Potter, C. S. Rastomjee and R. G. Egdell, *Physics C*, **201** (1992) 58.
80. J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus and W. K. Kwok, *Phys. Rev. B*, **41** (1990) 1863.
81. W. Kwestroo and H. A. M. Paping, *J. Am. Ceram. Soc.*, **42** (1959) 295.
82. S. Horiuchi, H. Maeda, Y. Tanaka and Y. Matsui, *Jpn. J. Appl. Phys.*, **27** (1988) L1 172.
83. P. W. Sullivan, R. F. C. Farrow and G. R. Jones, *J. Crystal Growth*, **60** (1982) 403.
84. R. C. DeVries and R. Roy, *J. Am. Ceram. Soc.*, **38** (1955) 145.
85. B. Raveau, C. Michel, M. Hervieu and D. Groult, in T. A. Vanderah (Ed.), *Chemistry of Superconductor Materials*, Noyes Publications, Park Ridge, NJ, 1992, p. 106.

86. M. A. **Subramanian**, J. C. **Calabrese**, C. C. **Torardi**, J. **Gopalakrishnan**, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. **Chowdhry** and A. W. **Sleight**, *Nature*, 332 (1988) 420.
87. T. Suzuki, M. Nagoshi, Y. **Fukuda**, Y. **Syono**, M. Kikuchi, N. Kobayashi and M. **Tachiki**, *Phys. Rev. B*, 40(1989)5184.
88. A. J. Arko, R. S. List, R. J. Bartlett, S.-W. **Cheong**, Z. Fisk, J. D. Thompson, C. G. Olson, A.-B. Yang, R. Liu, C. Gu, B. W. **Veal**, J. Z. Liu, A. P. **Paulikas**, K. **Vandervoort**, H. Claus, J. C. **Campuzano**, J. E. Schirber and N. D. Shinn, *Phys. Rev. B*, 40 (1989) 2268.
89. A. J. Arko, R. S. List, R. J. Bartlett, S. W. **Cheong**, C. G. Olson, A.-B. Yang, R. Liu, C. Gu, B. W. Veal, J. Z. Liu, A. P. **Paulikas**, K. Vandervoort, H. Claus and J. C. **Campuzano**, in J. D. Jorgenson, K. **Kitazawa**, J. M. **Tarascon**, M. S. Thompson and J. B. Torrance (Eds.), *High Temperature Superconductors: Relationships Between Properties, Structure, and Solid-State Chemistry*, MRS Symposium Proceedings No. 156, Materials Research Society, Pittsburgh, 1989, p. 159.
90. A. T. Fiery, A. F. Hebard, R. H. Eick, P. M. Mankiwich, R. E. Howard and M. L. **O'Malley**, *Phys. Rev. Lett.*, 65 (1990) 3441.
91. A. T. Fiery, A. F. Hebard, R. H. Eick, L. F. Schneemeyer, J. V. Wasczak and H.-J. **Gossman**, *Appl. Phys. Lett.*, 58 (1991) 777.
92. N. Schroeder, R. **Böttner**, S. Ratz, E. Dietz, U. Gerhardt and Th. Wolf, *Phys. Rev. B*, 47 (1993) 5287.
93. C. **Calandra** and F. **Manghi**, *J. Electron Spectrosc. Relat. Phenom.*, this issue.

Table 1. Alkaline earth core level binding energies (eV) of the metals, oxides, and high temperature superconductors and related materials.

Material	Ba 3d _{5/2}	Ba 4d _{5/2}	Ba 5p _{3/2}	Sr 3d _{5/2}	Ca 2p _{3/2}	References
13a	780.2-780.4	89.9-90.0	14.8			[27,28]
BaO	779.2	88.8				[28]
BaBiO ₃	779	88.4	13.5 ^a			[21,24]
BaPb _{1-x} Bi _x O ₃ (0 ≤ X ≤ 0.6)			13-13.5			[21-24]
Ba _{0.6} K _{0.4} BiO ₃	779.3		13			[25]
Ba _{0.6} Rb _{0.4} BiO ₃	779					[26]
La _{1.85} Ba _{0.15} CuO ₄	779 ^b					[2]
EuBa ₂ Cu ₃ O _{6.7}		87.3 & 88.2	12.6			[99]
EuBa ₂ Cu ₃ O _{<6.5}		87.8 & 89.0				[9]
YBa ₂ Cu ₃ O _{7-δ} δ=0.1		87.4 & 88.6 ^b				[10]
&-o	777.4 & 778.6 ^c	87.0 & 88.3 ^c	12.0			[7]
δ~0	777.6	87.2	12.0			[8]
δ=0.25	778.2		12.3			[11]
δ~0.5	778.3		12.5			[5,6] ^d
δ=0.7			12.6			[11]
δ~1	778.6	88.2	12.9			[8]
Ca					346.4	[27,28]
CaO						[28]
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	778.3 & 779.2				~345 ^{b,e}	[19]
Tl ₂ Ba ₂ CaCu ₂ O ₈	778.3	87.9			344.7 & 345.7	[20]
Sr				134.0-134.2		[27,28]
SrO				132.6		[28]
Bi ₂ Sr ₂ CaCu ₂ O ₈				132.2	345.3	[12]
				131.8 & 133.15	344.7 & 345.6	[13]
				132.25	345.1 & 346.1	[14]
				131.7 & 132.6 ^b		[15]
				131.7 & 132.9	344.7 & 345.9	[16]
				131.8 & 132.6	344.8 & 345.8	[17]
				132.0 & 133.1 ^b	345.1 & 346.1 ^b	[18]
La _{1.85} Sr _{0.15} CuO ₄				132.3 ^b		[5]
La _{1-x} Sr _x CuO ₄ (x = 0.075 & 0.20)				132.3		[11]

Notes for Table 1:

aThe position of **14.4 eV** reported in [24] is the average of the spin-orbit split components. Half of the spin-orbit splitting of **1.9 eV** has been subtracted to yield the value in the table.

bThe peak positions are not stated in the **text**, and are estimated from the published spectra.

cThe high binding energy component is a surface peak which is not observed on stepped surfaces.

dMeasurement of the Fermi edge is presented in [29]; the oxygen stoichiometry is estimated in [30].

eTwo components (binding energies not reported) separated by **~1 eV** are discussed in [19].

Figure Captions

1. Comparison of the **Ba 3d_{5/2}** signals measured from **Ba** metal, BaO, and YBCO, scaled to the same integrated intensities (from [32]).
2. Comparison of the Sr 3d signals measured from Sr metal, SrO, and BSCCO, scaled to the same signal maxima (from [32]).
3. Comparison of the **Ca 2p** signals measured from **Ca** metal, CaO, and BSCCO, scaled to the same signal maxima (from [32]). The peak near 357 eV in the spectrum from BSCCO is the Sr 3s signal.
4. Comparison of the **Ba 4d** signals measured from chemically-etched epitaxial thin film surfaces of (a) Pr-I 23, and (b) Y-123.
5. Ca 2p spectrum measured from a chemically-etched epitaxial thin film surface of T1-2212, shown with two doublets obtained from least squares fitting.
6. Comparison of the **Ba 4d** signals measured from chemically-etched epitaxial thin film surfaces of YBCO (from [8]) and 'H-2212 (from [20]).
7. Comparison of the **Ba 4d** signals measured from chemically-etched epitaxial thin film surfaces of o-YBCO and t-YBCO (from [8]).
8. Comparison of the **Ba 3d_{5/2}** signals measured from a chemically-etched epitaxial thin film surface at photoelectron emission angles 70° and 20° relative to the sample surface.

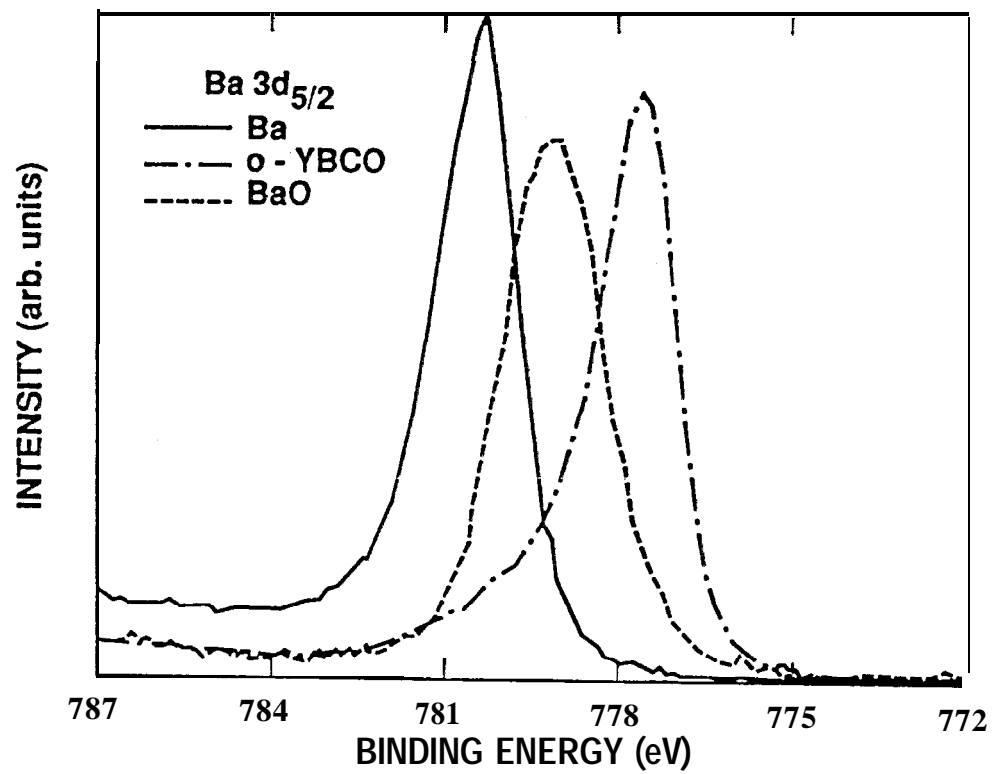


Fig 1

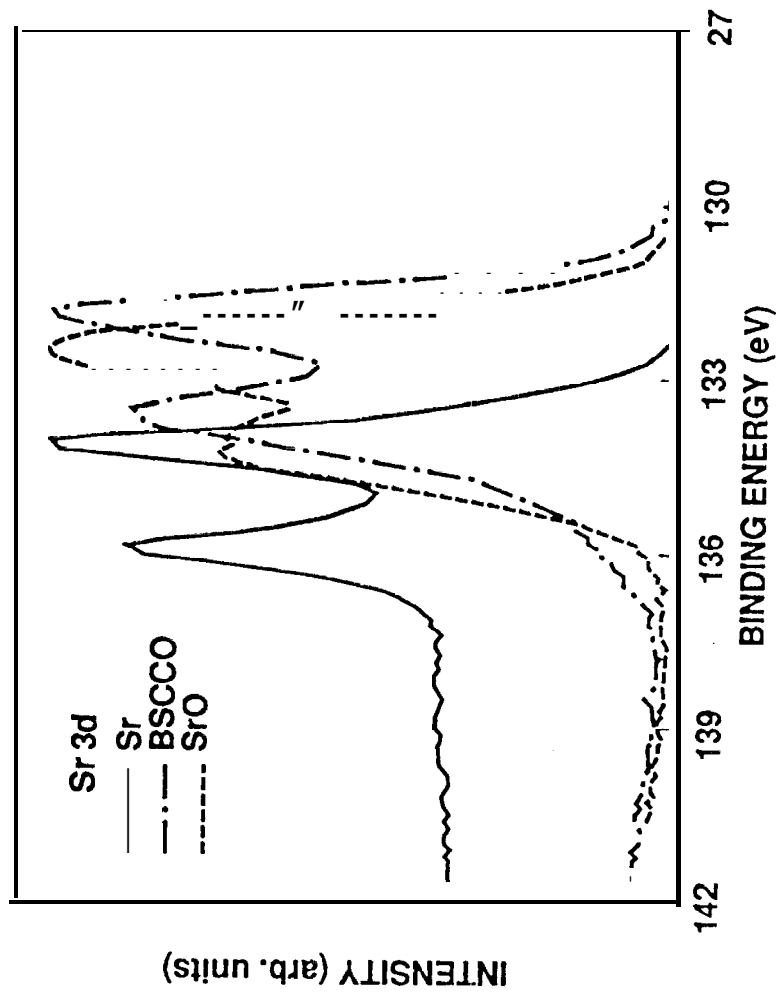


Fig. 3

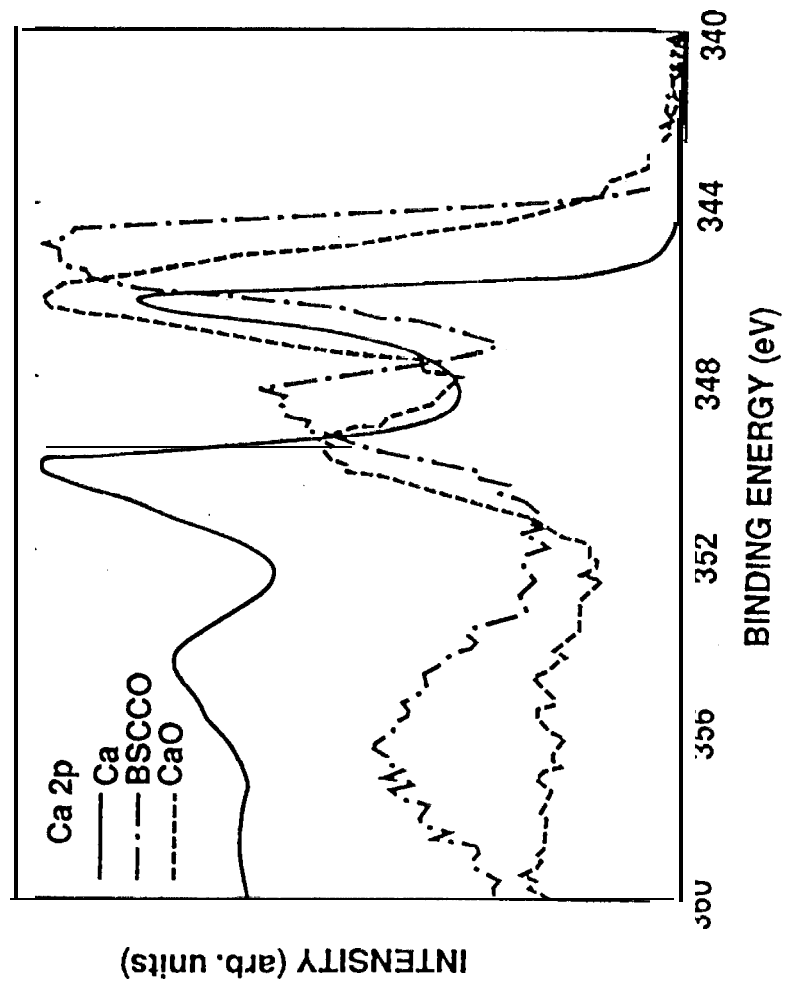


Fig. 3

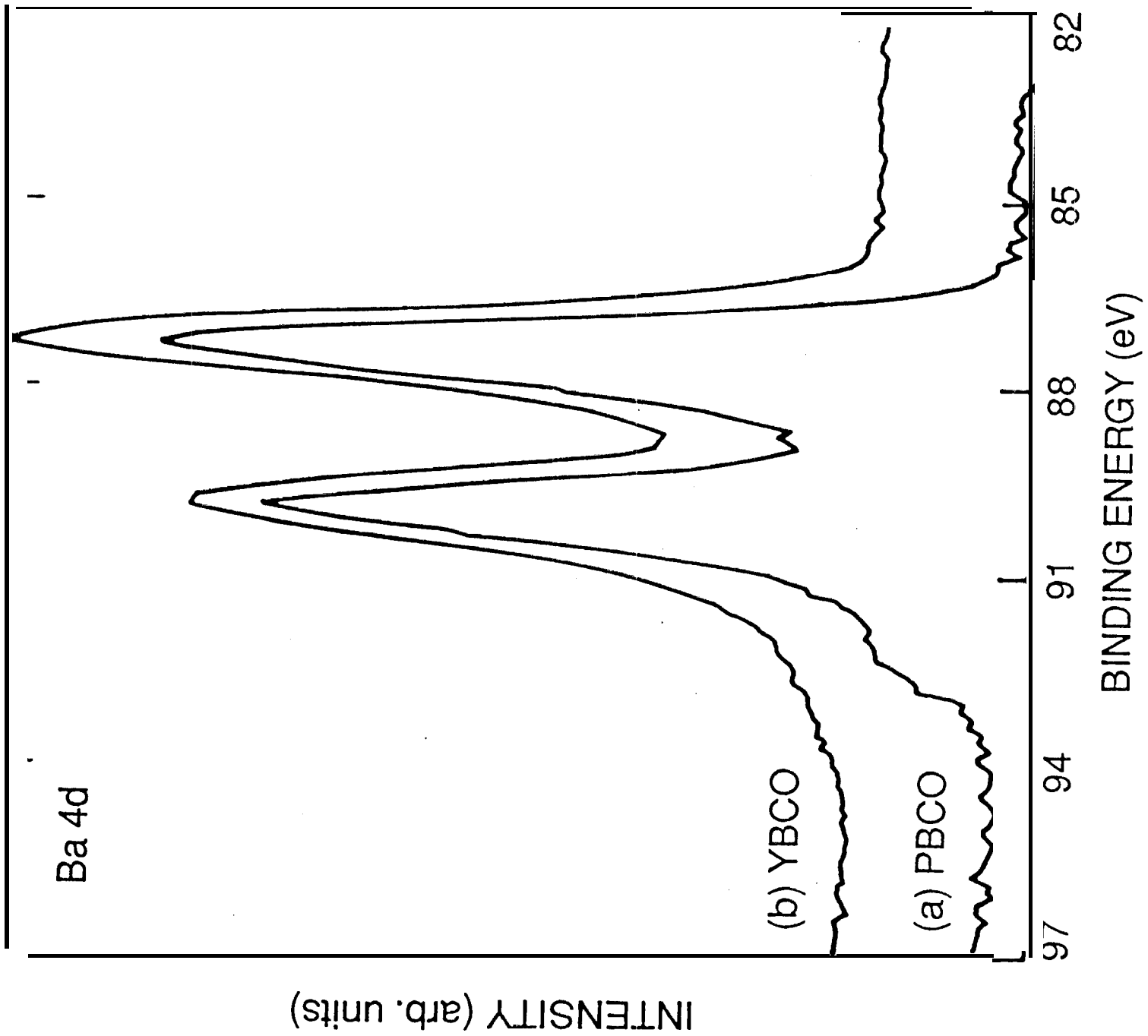


Fig. 4

TBCCO
Ca 2p

INTENSITY (arb. units)

352

350

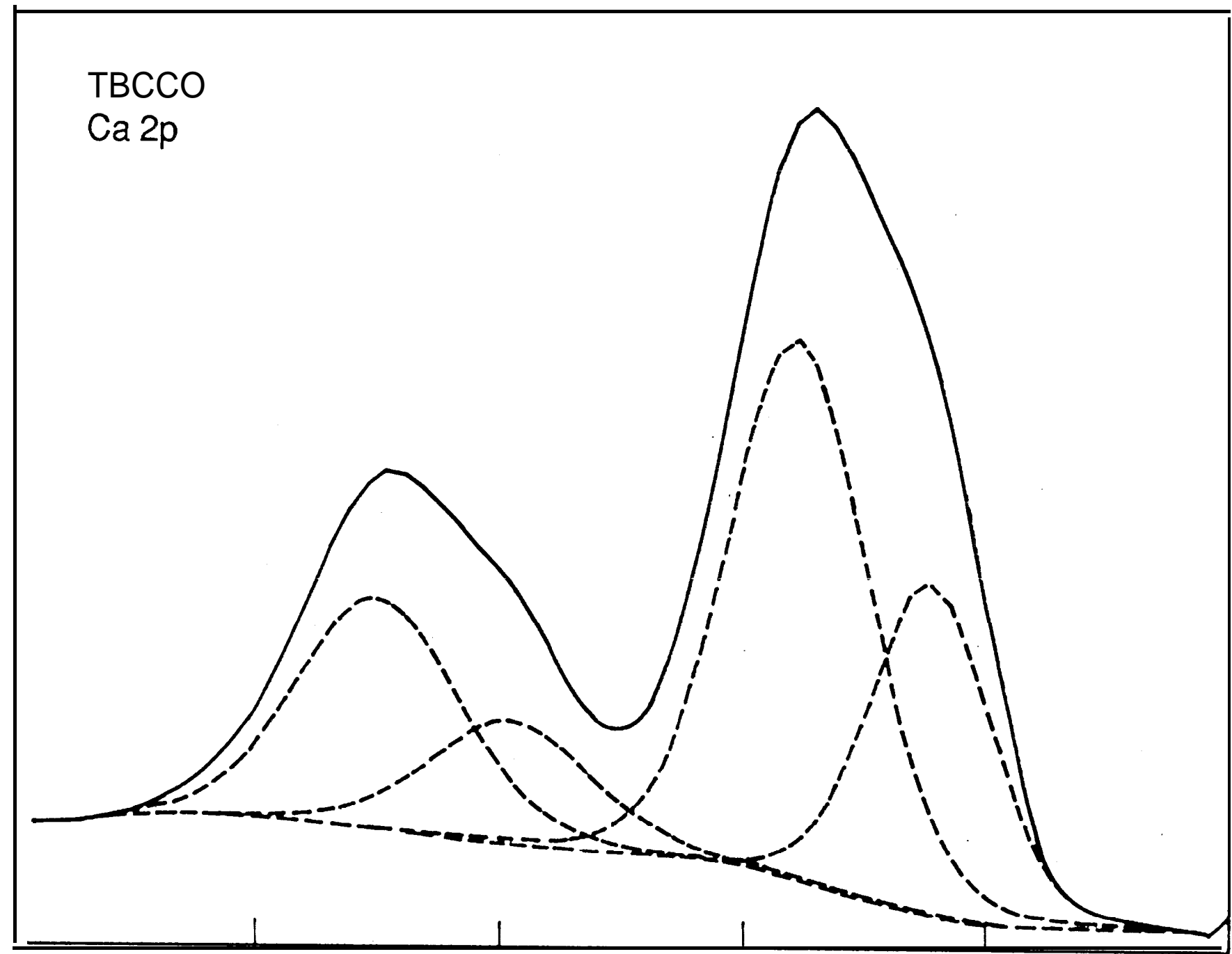
348

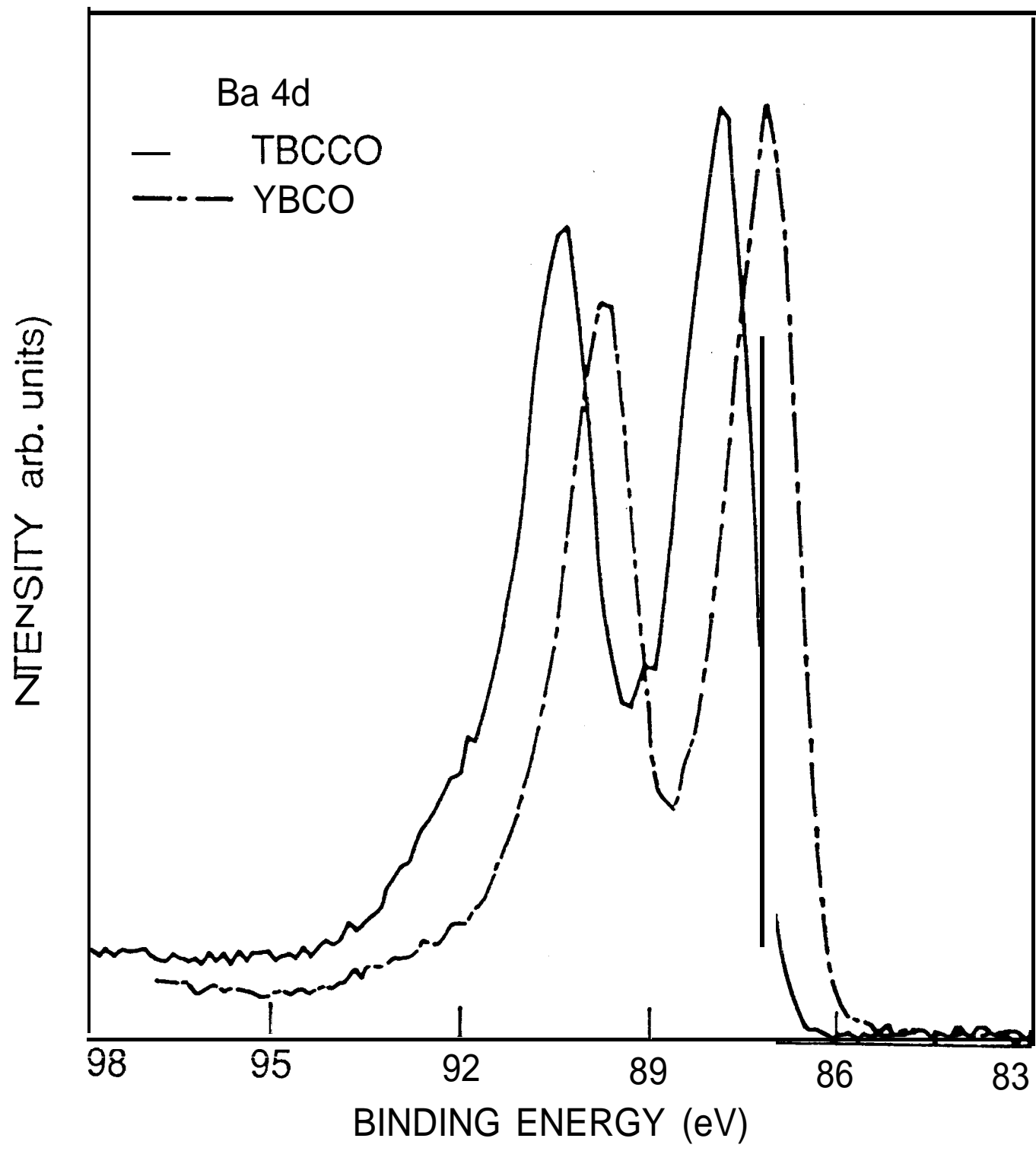
346

344

342

BINDING ENERGY (eV)





Ba 4d

— o-YBCO
- - - t-YBCO

INTENSITY (ARB. UNITS)

96

94

91

88

85

82

BINDING ENERGY (eV)

