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# Ba 4*d* core-level spectroscopy in the $YBa_2Cu_3O_{6.9}$ high-$T_c$ superconductor: Existence of a surface-shifted component

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Two sets of spin-orbit split Ba 4*d* core-level photoemission peaks were observed in a crystal of $YBa_2Cu_3O_{6.9}$. From constant final-state measurements taken as a function of kinetic energy, the low-binding-energy doublet is identified as a surface component. Possible origins of the surface shift are discussed.

## I. INTRODUCTION

We report here clear evidence of a Ba 4*d* surface core-level shift in $YBa_2Cu_3O_{6.9}$, cleaved *in situ* at 20 K.

The existence of an extra component in the Ba core-level spectra of this material was shown by several authors previously,[1,2] but the interpretations of the extra component have been quite diverse. Steiner *et al.*[1] obtained a rather broad spectrum. They interpreted the additional features as an indication of different Ba core-hole screening caused by oxygen vacancies. This interpretation is doubtful because the changes of screening should be continuous, since the oxygen vacancies are distributed randomly, or nearly so, in the sample. Other possibilities are also present. For instance, the extra component might result from hybridization between valence electrons and the Ba 4*f* final states, which is the case for many La and Ce compounds.

Stoffel *et al.*[2] interpreted their data as a surface core-level shift, but they assigned the spin-orbit doublet at higher binding energy to the surface component which is in the opposite direction from what we observed. Moreover, the two-component structure was not clearly resolved in their data, possibly due to lack of a well-defined surface.

Since photoemission is a surface-sensitive probe, a good surface is essential for obtaining reliable data. It was realized very early that oxygen loss near the surface is quite common for these oxide superconductors, and it was recently emphasized by List and co-workers[3,4] that the freshly cleaved surface of $EuBa_2Cu_3O_{6.7}$ is unstable in vacuum at and above 55 K. Therefore, cleaving the sample *in situ* at low temperature is very important in producing a surface which retains the bulk stoichiometry.

## II. EXPERIMENTAL DETAILS

The $YBa_2Cu_3O_{6.9}$ single crystal was grown at Argonne National Laboratory. The oxygen stoichiometry is inferred from the midpoint of the superconducting transition temperature as measured by the diamagnetic susceptibility. More details on the sample are given in Ref. 5.

The measurements were done on the Ames-Montana beamline at the Synchrotron Radiation Center, Stoughton, Wisconsin. The combined ERG-Seya monochromator[6] gave access to energies from 10 to 1000 eV. The spectra were taken with the angle-integration provided by a double-pass cylindrical mirror analyzer. The overall instrument resolution was about 200 meV for the core-level spectra. The chamber base pressure was $5\times10^{-11}$ Torr for all the measurements.

The sample was attached to the cold finger of a He refrigerator, and was cleaved at 20 K without contact with any room-temperature object. Most of the measurements were done at 20 K.

## III. RESULTS

The energy distribution curve (EDC) taken at 130-eV photon energy is shown in Fig. 1. It can be seen that there are two sets of spin-orbit split doublets, shifted 1.2 eV relative to each other.

In order to clarify whether this extra component results from a surface shift, we made constant final-state (CFS) measurements at different kinetic energies. There are several reasons to use the CFS mode instead of the EDC mode. First, in a CFS, the kinetic energy of the photoelectron is constant, while the photon energy is scanned. Therefore, the degree of surface sensitivity is the same for all the peaks in the spectrum. On the contrary, in an EDC, the kinetic energy is scanned while the photon energy is held constant. The degree of surface sensitivity is then different for each peak. Second, in the photon energy range from 100 to 110 eV, there is an Auger peak superimposed on the Ba 4*d* peaks, preventing one from going to low photon energies for higher bulk sensitivity. However, the CFS spectrum is a superposition of primary and secondary electrons, and the background secondary elec-

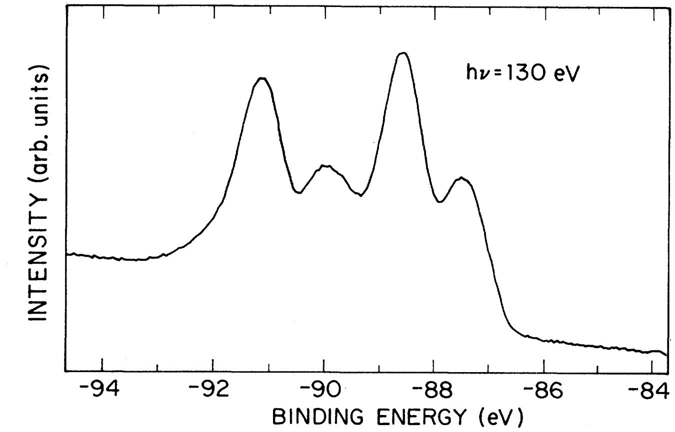

FIG. 1. EDC taken at 130-eV photon energy.

tron spectrum reflects the optical-absorption coefficient. Therefore, a CFS feature represents the density of initial states only if the optical-absorption coefficient has no structure in the photon energy region being scanned. We measured the absorption coefficient by measuring very-low-energy secondary electrons. We found that it is featureless in the photon energy range used.

The CFS spectra are shown in Fig. 2. From top to bottom, the three curves are taken at kinetic energies of 20, 30, and 50 eV, respectively. The curves are scaled to give comparable intensity. The decrease in escape depth with increasing kinetic energy in this range indicates that the least bound doublet is the surface component, and the more deeply bound pair is the bulk contribution.

However, in view of the anomalous energy dependence of the escape depth in Ba metal,[7] additional measurements were made to verify this assignment. First, the peak intensities were normalized to the incident flux. The strength of the surface peak was independent of kinetic energy, while the strength of the bulk peak dropped with increasing kinetic energy in the expected manner.

Second, when we dosed with 0.1 L of oxygen at 20 K, the surface component was suppressed, and when we removed the adsorbed oxygen by heating the sample to 100 K, the surface component was restored. (The fact that the oxygen only physisorbed on the surface and can be easily removed by heating was reflected in the changes in the valence band.) After the sample was kept at room temperature for a long time (several hours), all the observed features were broadened and smeared out, but the surface component can still be seen [Fig. 3(b)]. The broadening is probably due to oxygen loss, and the attendant changes of the Ba-oxygen coordination.

After sputtering the sample with 1-keV argon ions, the surface component totally disappeared as expected, since the surface was damaged after sputtering [Fig. 3(c)]. The remaining doublet was severely broadened and the peak position shifted towards higher binding energy. The shift results from a metal-to-insulator transition occurring at the surface during sputtering, as identified from the changes in the valence-band spectra. The broadening was also due to the changes of the Ba-oxygen coordination caused by oxygen loss.

From the deterioration of the spectra after the sample was warmed to room temperature or sputtered, it is clear

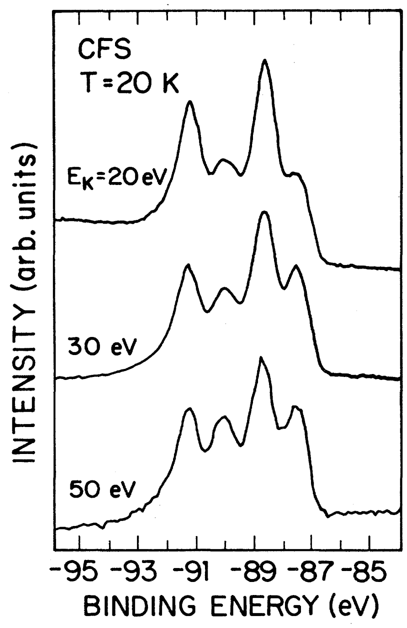

FIG. 2. CFS spectra, taken at a kinetic energy of, from top to bottom, 20, 30, and 50 eV. The curves are scaled to give comparable intensity. For all three spectra, the sample was at $T=20$ K.

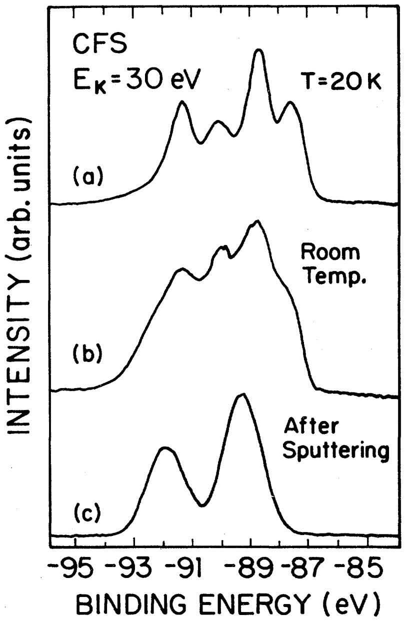

FIG. 3. (a) CFS taken at $T=20$ K. (b) CFS taken at room temperature. (The sample had been at room temperature for several hours.) Note that all the features are broadened. (c) CFS taken after the sample was sputtered by high-energy argon ions. Note that only one spin-orbit split doublet appears, and the peak position is shifted. For all three spectra, $E_k=30$ eV.

that the quality of the spectra depends very much on the condition of the sample surface. Therefore, the spectra could very likely be deceptive if the surface was not well-defined.

## IV. DISCUSSION

As we think about the origin of the surface shift, we note that the dimension of the unit cell in the $c$ direction normal to the cleavage plane for $YBa_2Cu_3O_{6.9}$ is large, 11.68 Å. In the energy range used, the average escape depth is only about 10 Å. Therefore, the information we obtained is extracted from only the first few unit cells. We also looked at core levels of the other elements (O 1$s$, Y 4$p$, 3$d$, Cu 3$p$), and no evidence of a surface shift was found. Therefore, we believe that the sample cleaves at a Ba plane, and the cause of the surface core-level shift is the altered surface environment of the Ba atoms. A number of effects can lead to a surface core-level shift. Among them are an altered Ba cation charge on the surface because of the change of oxygen coordination, the change of Madelung potential at the surface, and the change of core-hole relaxation of the final state. It is hard to determine which effect dominates. The argument that Ba at the surface has more screening electrons in the initial state, because it may have a smaller cation charge due to reduced oxygen coordination, gives the correct sign of the shift.

The main peaks in Fig. 1 are quite symmetric, suggesting that the Ba at and near the surface may not be embedded in a metallic environment, even though a clear Fermi edge appeared in valence-band spectra. In order to see how the change of Madelung potential at the unreconstructed surface would affect the core-level binding energy, we calculated the bulk and surface Madelung potential for $YBa_2Cu_3O_7$ by the Ewald method.[8] The lattice parameters are from Le Page *et al.*[9] For the charge assignment of each ion, we assumed an extreme ionic case for the compound, although this compound may be covalent in many aspects. This gives an upper bound for the effect of the Madelung potential. The assigned charges were $+3$ for Y, $+2$ for Ba and Cu, $-1$ for the O in the Cu-O chain, and $-2$ for O at the other sites. The charge on O in the Cu-O chain was assigned as $-1$ to obtain a neutral unit cell. The surface potential is obtained by constructing a slab with the $c$ axis normal to the slab, assuming no structural relaxation or reconstruction and no charge redistribution on the surface.

We note that although the two Ba atoms in the bulk structure occupy equivalent sites, cleavage within the unit cell makes the two Ba planes at the surface inequivalent, as shown in Fig. 4. The difference in the surface Madelung potential for the two cases is striking. Table I lists the results of the Madelung potentials at the Ba sites in and near the surface, for both cleavage planes. We see that the surface Madelung potential is smaller than the bulk in one case, and larger in the other. In reality, if the sample can cleave at one plane, it should also cleave at the other bulk equivalent plane. In both cases, the magnitude of the calculated surface-to-bulk potential difference is quite large. This suggests that the surface so obtained is unstable and is likely to relax or reconstruct. In case 1, the Madelung potential at the Ba sites in the surface is greater than zero, which means the atoms would leave the surface. Reduced ionic charge and surface reconstruction may bring this potential below zero.

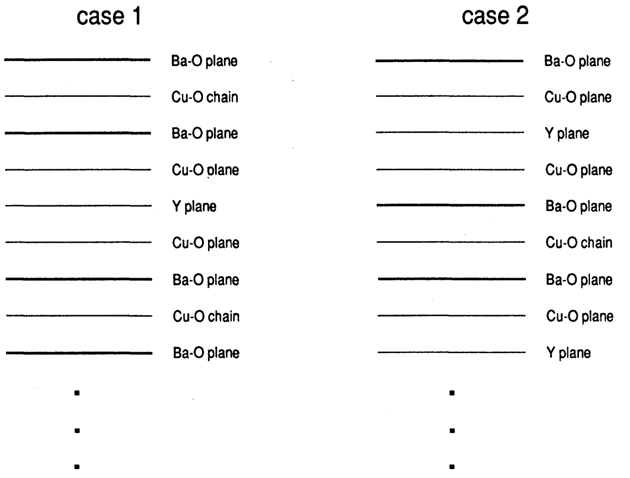

FIG. 4. Schematic diagram of the two cleavage cases with different Ba-O planes as the outermost layer on the surface.

If we assume no structural relaxation or reconstruction, another problem arises: the Madelung potential at the O sites on the Ba-O plane would change by about the same amount as on the Ba sites. But no O core-level shift was observed. This again suggests the possibility of surface reconstruction.

In conclusion, the results of the Madelung potential calculation show that a simple termination of the bulk crystal at either of the two Ba planes without surface relaxation or reconstruction is unlikely, and the Ba 4$d$ core-level surface shift cannot be accounted for by the change of Madelung potential at the surface alone. To allow the surface to relax or reconstruct, and also allow the surface charge to redistribute, a self-consistent quantum-mechanical treatment is required.

TABLE I. Madelung potentials at Ba sites in and near an unreconstructed surface, assuming two kinds of surface with different Ba-O planes as the outermost layer. In the table, case 1 and case 2 refer to the schematic diagram shown in Fig. 4. The listed distances of sites from the face are approximate. The refined lattice parameters (Ref. 9) were used in the calculation. The Madelung potential at Ba sites in the bulk is $-16.89$ eV.

| Distance of site from face | Case 1 (eV) | Case 2 (eV) |
|---|---|---|
| 0 | +3.03 | −36.48 |
| $\frac{1}{3}c$ | −7.43 | · · · |
| $\frac{2}{3}c$ | · · · | −22.64 |
| $c$ | −14.88 | −19.07 |
| $\frac{4}{3}c$ | −16.26 | · · · |
| $\frac{5}{3}c$ | · · · | −17.18 |
| $2c$ | −16.83 | −16.96 |

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