

Chemical and surface core-level shifts of barium studied by photoemission

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Polycrystalline Ba films are prepared on an Al(111) substrate with thickness ranging from monolayer to about ten layers. The clean and oxidized films are investigated by uv photoelectron spectroscopy using synchrotron radiation in the energy range $20 \text{ eV} \leq \hbar\omega \leq 120 \text{ eV}$. Besides the conduction-band region of bulk Ba the $5p$ and $4d$ levels are studied, both showing surface core-level shifts of 0.48 eV to higher binding energies. At E_F and extending down to 0.7 eV, d states are identified in the bulk conduction band. For the bulk, oxidation introduces negative (towards E_F) chemical shifts of the core levels and a very sharp O^{2-} peak in the valence-band region. It is argued that these oxygen- $2p$ -derived states, and not the Ba $5d$ states, are responsible for the negative chemical shift. For the Ba monolayer the chemical shift is positive and no O^{2-} state is found, in agreement with the new interpretation of the chemical shifts for bulk Ba.

I. INTRODUCTION

With regard to their electronic structure, the heavier alkaline earth metals (Ca, Sr, Ba) differ from simple metals such as Na, K, or Al. There are only a few photoemission studies on the alkaline earth metals and several observations have so far not been explained, among them being the large satellite intensity of the core levels,¹⁻⁵ the occupation number of the Ba $5d$ states near E_F (Refs. 6, 2, and 7), and the negative (i.e., towards E_F) shifts of the Ba binding energies in BaO.^{4,5,8} Ley *et al.*¹ have shown that the satellite intensity follows the loss function $\text{Im}(-1/\epsilon)$ and concluded that these excitations are "collective in nature in the sense that they are characteristic for the metal and not for the atom." Others^{2,3} have argued that intensity and line shapes² point to a more atomiclike final-state multiplet including the $3d$, $4d$, and $5d$ state for Ca, Sr, and Ba, respectively. The question as to whether or not the Ba $5d$ states are empty in the ground state is also controversial. There are indications for partly filled conduction-band d states^{2,6,7} but others assume the d states to be completely empty as in the atom.^{3,8} Recently, the Ba $5d$ states have been used to explain the unusual, negative chemical shift of the Ba core levels in BaO.⁸ Also, in connection with the surface core-level shifts, which we shall discuss, the energy of the Ba $5d$ states above or below E_F is of importance.

In this contribution we present ultraviolet photoemission (UPS) results on thick Ba films and Ba monolayers prepared on an Al(111) substrate. By using synchrotron radiation in the range between 20 and 120 eV we have measured the conduction-band states as well as the $5p$ and $4d$ core levels of Ba with high-energy resolution. Most important is the evidence given for the existence of surface core-level shifts observed for the $5p$ and $4d$ levels for the first time. This result will strongly influence the discussion of the line shape and loss structure of these levels.

In addition, we have measured the chemical shifts during oxidation for the same levels. The shifts are opposite for the bulk metal and the monolayer. The arguments in explaining the negative (towards E_F) shifts of the levels between bulk Ba metal and Ba oxide are critically reviewed. Finally we conclude that not the Ba $5d$ states but the O- $2p$ -derived states are responsible for this shift.

II. EXPERIMENT

Angle-resolved uv photoelectron spectroscopy was performed using a hemispherical electrostatic energy analyzer (ADES 400, VG Scientific). The UHV system, operated with a base pressure of 5×10^{-11} Torr, was equipped with standard surface-analytical tools. The photon source was the TGM-4 (toroidal grating monochromator) beam line at the Berlin Electron Storage Ring for Synchrotron Radiation (BESSY). Photon energies were chosen in the range $20 \text{ eV} \leq \hbar\omega \leq 120 \text{ eV}$. The energy analyzer was set for a pass energy of 5 eV thus contributing 100 meV to the resolution. The overall energy resolution including energy analyzer and monochromator for the light was chosen as 100 meV at $\hbar\omega = 25 \text{ eV}$, 250 meV at 40 eV, and ~ 500 meV at 120 eV. The angle of incidence of the light was fixed at 45° with respect to the surface normal. All spectra were taken at normal emission ($\pm 1.5^\circ$). The calibration of the monochromator setting for a photon energy $\hbar\omega$ was performed by measuring the Al $2p$ level of the uncovered substrate by means of higher-order lines ($2\hbar\omega$, $3\hbar\omega$, or $4\hbar\omega$). The binding energy of the $\frac{3}{2}$ component of the Al $2p$ core line was found at E_B^F (Al $2p_{3/2}$) = (72.6 ± 0.2) eV with a spin-orbit split of 0.40 eV, in very good agreement with literature values.⁹⁻¹¹ The binding energies of the Ba levels refer to the above Al $2p$ energy.

The Ba films were prepared by evaporation from a Knudsen cell filled with Ba metal pieces. The oven had to be operated for several minutes with residual pressure below 10^{-8} Torr to prepare clean films. The cleanliness was judged from the features in the valence-band region

which are known to be very sensitive for *s* metals such as Ba. The layer thickness was estimated from the weakening of the Al 2*p* core level from the clean Al(111) substrate.

III. RESULTS

For an overview Fig. 1 shows energy distribution curves (EDC's) for the clean bulk Ba surface and after dosing with 0.2 and 2.4 L of O₂ (1 L $\equiv 10^{-6}$ Torr). The origin of the different peaks is indicated. The exact values for the peak positions measured with better resolution are given in Table I. Near 15 and 17 eV the Ba 5*p*_{1/2,3/2} doublet and at 30 eV the Ba 5*s* can be seen. After oxygen dosing a narrow peak develops at 4.65 eV which is O-2*p* derived. Besides this the O 2*s* level at 20 eV evolves. During oxidation the Ba 5*p*, 5*s*, and also 4*d* levels, the latter not shown in Fig. 1, are shifted in energy. These chemical shifts are discussed in greater detail below.

Several other features can be observed in Fig. 1. At and near E_F (i.e., at 0 eV) in curve (a) one recognizes a sharp structure, which is already nearly quenched after an exposure of 0.2 L O₂. Furthermore, from the O₂ dosing we conclude that the peak at 4.65 eV in the clean spectrum is likely to be due to a small oxygen residue from the preparation of the Ba film. This residual oxygen contribution is small since it contains only about $\frac{1}{3}$ of the intensity found for an oxygen dose of 0.2 L in curve (b). Therefore, we believe that this residue does not influence our conclusions. What is not understood so far is the peak at 8.8 eV in the clean spectrum. From its sharpness one could speculate that it may also be due to a *p*-electron-derived state of an impurity, like the oxygen residue at 4.65 eV. This interpretation, however, does not fit with its very strong quenching by the 0.2-L oxygen dose.

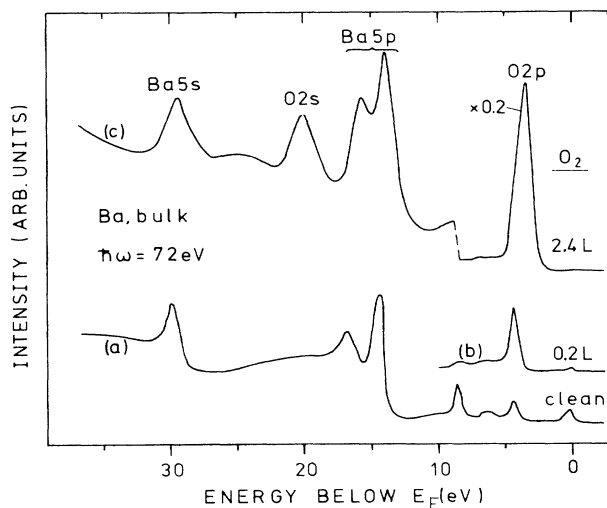


FIG. 1. Photoelectron energy distribution curves (EDC's) for a thick Ba film evaporated onto an Al(111) substrate. The photon energy is 72 eV. Besides the spectrum for the clean surface (a), the spectra for oxygen doses of 0.2 L (b) and 2.4 L (c) are shown. The oxygen dose is given in units of langmuir (1 L $\equiv 10^{-6}$ Torr).

We must say that the origin of this peak is not clear at the moment, but it is believed not to influence the conclusions drawn from the measurements. Finally, from Fig. 1 it becomes evident that there is a step in the background connected with the Ba 5*p* as well as the 5*s* emission for the clean sample. This step is well known¹ and has been attributed to intrinsic losses connected with the excitation of the respective core hole. Its explanation is still under discussion, as we will see.

In Fig. 2 the Ba 5*p* levels are shown for a Ba monolayer (a) and a thick film (b). One clearly recognizes that in the case of the bulk the 5*p*_{1/2} and 5*p*_{3/2} spin-orbit split doublet is further split into two contributions separated by 0.48 eV for both components. The background intensity was estimated from overview spectra as shown in Fig. 1 and is indicated by a solid line. The data shown are taken and reproduced here in such a way that the relative intensities can be compared. Therefore, one recognizes that the intensity in the single line is higher for the monolayer than for the bulk. This shows, in addition to the considerations about the background, how much of the intensity lies in the intrinsic losses for the bulk sample.

A similar result is found for the 4*d* core levels at a photon energy of 120 eV. The 4*d* spectrum is not shown separately here but can be seen from Fig. 4 below in the context of the oxidation study. The doubling of the 4*d*_{3/2} and 4*d*_{5/2} spin-orbit-split peaks is clearly indicated. It is not as well resolved as for the 5*p* levels of Fig. 2 due to the limited resolution in photon energy. But there is no

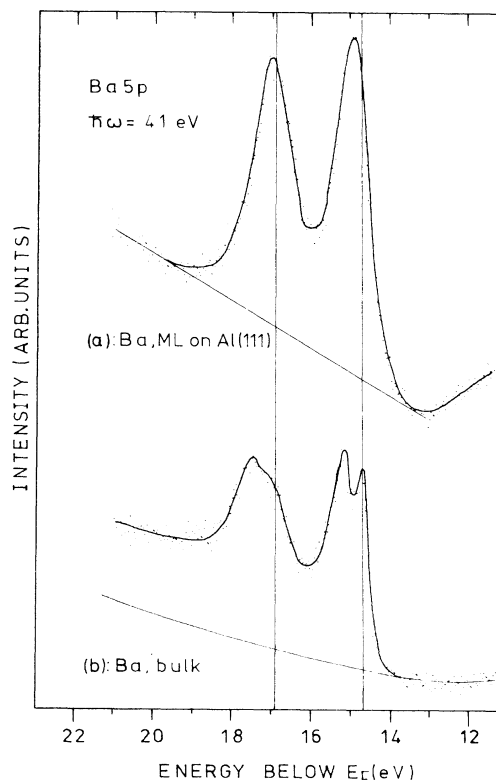


FIG. 2. EDC's of the Ba 5*p*_{1/2,3/2} doublet for the monolayer (a) and the bulk (b).

question that there are two components split by the same amount of 0.48 eV as in the case of the $5p$ levels.

In Fig. 3 the emission near the Fermi edge is compared for differently prepared surfaces. The main result is the strong increase of intensity for the bulk Ba samples. Curve (a) on top shows that the Fermi edge falls to zero between ± 100 meV. This sharpness is due to the good energy resolution of the monochromator at $\hbar\omega = 25$ eV and the low temperature. The given value of 20 K is a conservative estimate and the actual value may lie well below this value. It is this curve (a) which indicates that there is no peak just below E_F but that a smooth band is filled until E_F . For our polycrystalline Ba sample such a density-of-states interpretation of the EDC instead of a direct transition model may be appropriate here, being further substantiated by the fact that there is no change seen by changing $\hbar\omega$ as in curve (b).

Figure 4 shows the changes of the Ba $4d$ peak position, peak shape, and background during oxidation. We have indicated the bulk position for the clean surface, and one can recognize that the peaks are shifted to smaller binding energy with increasing amounts of oxygen. For a very small dose the surface core-level shift vanishes. For the 2.4-L curve the whole intensity is confined to the two spin-orbit components and no intensity is in the loss area, as indicated by the hatches in Fig. 4.

For the same run of the experiment Fig. 5 gives the Ba $5p$ spectra. One recognizes very similar trends for the changes of the peak position, peak shape, and background as for the $4d$ levels. Again the surface core-level shifts vanish at 0.2 L of oxygen. The main difference to the result for the $4d$ levels is the reduced shift of $5p_{3/2}$ component.

The binding energies for the largest coverages are also given in Table I, including the values for the Ba mono-

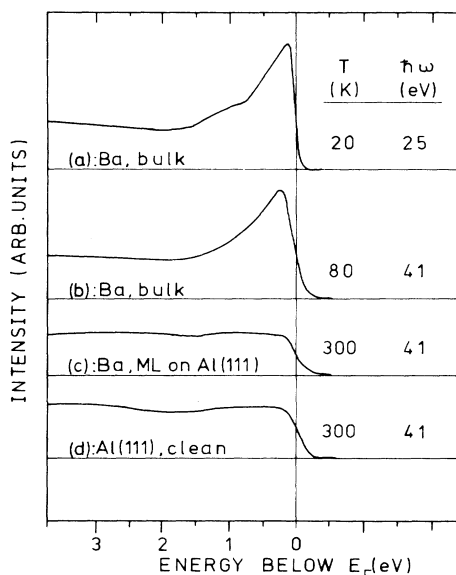


FIG. 3. EDC's for the clean Al(111) substrate and different Ba films on top of it. The sample temperature T and photon energy $\hbar\omega$ are given.

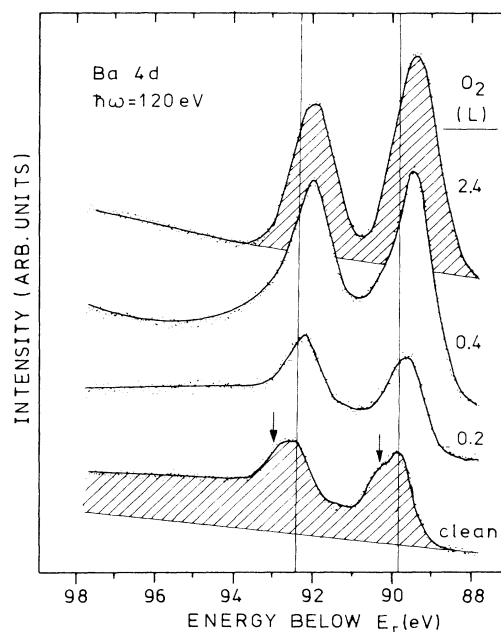


FIG. 4. EDC's for a clean thick bulklike Ba film in the $4d$ region and the changes after dosing oxygen in different amounts as indicated. The arrows indicate the surface core level.

layer. For the Ba monolayer the chemical shift during oxidation is to higher binding energies, i.e., into the opposite direction compared to bulk Ba. The photoemission from the Ba monolayer differs strongly from the bulk one. This was demonstrated already for the loss region of the $4d$ and $5p$ levels and the direction of the chemical shift

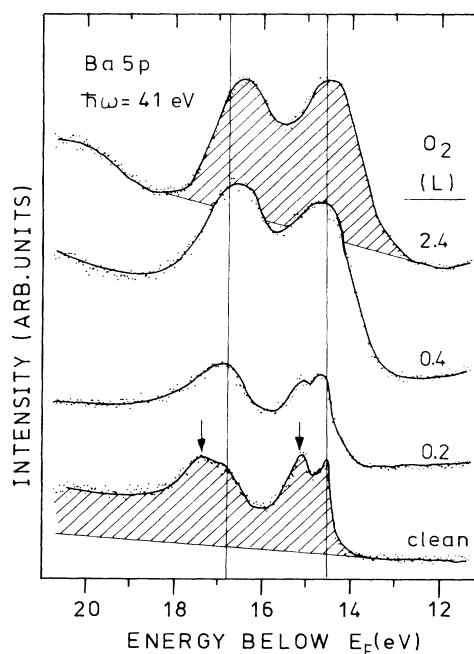


FIG. 5. EDC's for a clean thick bulklike Ba film in the $5p$ region and the changes after dosing oxygen in different amounts. The arrows indicate the surface core level.

and is also true for the valence-band region during oxidation. Instead of a very sharp peak at 4.65 eV, a very broad peak develops with its maximum at 6.2 eV and a shoulder at 3.8 eV.

The attack of the oxygen can also be monitored from the Al 2*p* core level of the substrate. Figure 6 shows the Al 2*p* level for the bare surface and two difference curves for the oxidized state. One recognizes that the first dose of 0.2 L O₂ does not interact with the Al substrate. Only the relatively high dose of 1.0 L attacks also the substrate showing mainly a chemical shift of 1.4 eV to higher binding energy.

IV. DISCUSSION

A. Clean barium

Our data confirm that for bulk Ba there are filled 5*d* states extending down to 0.7 eV below E_F . There are two experimental observations for this assignment. First, the cross section is of the same order of magnitude as for O 2*p* or Ba 5*p* states as seen from Fig. 1, i.e., larger than for the Al *sp* band. Secondly, our spectra at 20 K clearly demonstrate that the Fermi edge cuts into the lower part of a strong band. Besides these observations, our measurements agree perfectly with the band calculation of Johansen⁷ which indicates that the *d* band extends down to 0.7 eV and that the bottom of the *s* band lies at 2.5 eV below E_F . Our spectra are also in very good agreement with those of Kress and Lapeyre⁶ and Fujimori *et al.*² who all interpret the strong intensity near E_F as belonging to *d* states. It seems that, so far, not enough attention has been given to these results (e.g., Refs. 3 and 2).

We explain the structure found for the 5*p* as well as the 4*d* levels of bulk Ba by a surface core-level shift (SCLS) to

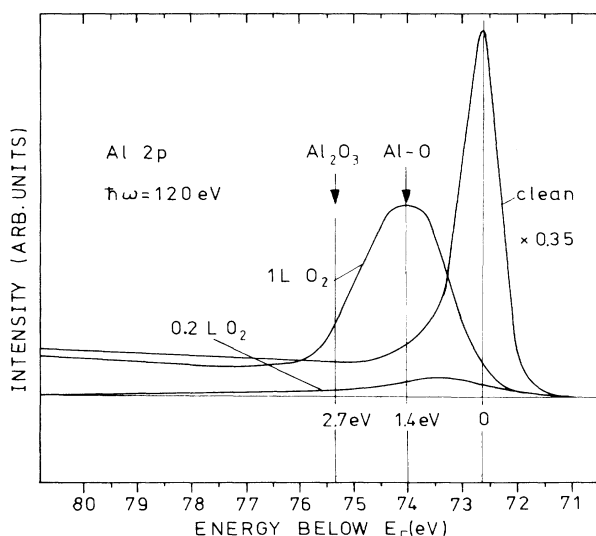


FIG. 6. EDC for the Al 2*p* core level of the clean Al(111) substrate. At this photon energy the spin-orbit split 2*p*_{1/2,3/2} components are not resolved. Given are also two difference curves (oxidized spectrum—clean spectrum) for two different oxygen doses. The positions of the chemical shifted level are also given according to Ref. 11.

higher binding energies for the atoms of the surface. The structure in the 5*p* levels as observed by Fujimori *et al.*² agrees with our measurements but is not as well resolved. A first argument in favor of our interpretation is the fact that this shift is exactly the same for both the 5*p* and 4*d* levels and also for each of the spin-orbit components. This is not the case for a final-state multiplet interpretation (e.g., 5*p*⁵5*d*¹ for the 5*p* level),² which is also not in agreement with another aspect of our measurements. If the atomic picture of multiplet final state were correct, then it should be even more appropriate for the monolayer, which is not at all the case, as can be seen from our measurements.

It should be noted that also the Ba 5*s* level shows an asymmetry which seems to point to two levels. We have not studied this level with better resolution than in Fig. 1. Last but not least, the observed surface core-level shifts are in very good agreement with experimental results on the transition elements as summarized in Refs. 12 and 13 and with model calculations¹² and qualitative arguments.¹³

For these theoretical models our confirmation of the existence of a *d* band near E_F filled by probably less than one electron is now essential. Johansson and Mårtensson (JM, Ref. 12) have calculated a SCLS of +0.48 eV for Yb which is exactly the same value that we find for Ba. We can compare Ba with Yb quite well because for the atom the only difference is the filled 4*f* shell in the case of Yb. For their semiquantitative calculation JM used a Born-Haber cycle to connect the electronic binding energy in the gas phase and the difference of surface cohesive energy of the *Z* and *Z* + 1 atom. The basic assumptions are a fully screened final state and the (*Z* + 1) approximation for the screening valence charge distribution around the core-ionized site. By this method JM have been able to reproduce the change of sign in the middle of the 5*d* transition-metal series from Yb to Bi. The change of sign and the positive shift (i.e., to higher binding energies) at the Ba surface can be understood qualitatively as follows: For the beginning of the transition series the screening charge sits in the lower, i.e., the bonding, part of the *d* band. Therefore, the bonding is stronger in the final state, i.e., more electrons including the shielding electron are in the *d* band than in the initial state. Due to the larger coordination number of the bulk this gain in bonding in the final state is larger in the bulk than at the surface. This gain of energy is transferred to the outgoing photoelectron thus reducing its binding energy more for the bulk than for the surface atom. For the heavier atoms in the transition series the situation reverses since now the upper (nonbonding) part of the *d* band is filled by the shielding electron. Citrin and Wertheim,¹³ on the other hand, come to the conclusion that the SCLS is predominantly an initial-state effect. They consider the narrowing of the conduction band for a surface layer of atoms which is hypothetically separated from the bulk. If one fills in the same number of conduction electrons as for the bulk, the position of E_F has to move up. Connecting then the surface layer to the bulk, the Fermi levels have to be aligned, which shifts all levels in the surface layer downwards in energy. This shift explains the greater binding

TABLE I. Binding energies in eV with reference to the Fermi level. Values for the spin-orbit split (SOS) are also given. The surface core-level shift for the clean bulk Ba is 0.48 eV.

		Bulk				
Al	$2p_{3/2}$	72.6				
	$2p_{1/2}$	73.0				
	SOS	0.40				
		Bulk	Surface	Ref. 9	2.4 L O ₂	8.4 L O ₂
Ba bulk	$5p_{3/2}$	14.6	15.1	14.6	14.5	14.2
	$5p_{1/2}$	16.8	17.3	16.8	16.5	16.2
	SOS	2.28	2.28		1.96	1.9
	$5s$	30.4		30.1	29.9	
	$4d_{5/2}$	89.8	90.3	90.0	89.2	
	$4d_{3/2}$	92.5	93.0	92.6	91.9	
	SOS	2.68	2.68		2.68	
O in BaO _x	$2p$	4.65 ^a			3.7	3.7
	$2s$				20.3	20.2
		Clean			1 L O ₂	
Ba mono- layer	$5p_{3/2}$	14.7			15.4	
	$5p_{1/2}$	16.6			17.3	
	SOS	1.94			1.9	
	$4d_{5/2}$	89.8			90.4	
	$4d_{3/2}$	92.5			93.1	
	SOS	2.6			2.6	

^aResidual amount of O in a bulk Ba film.

energies of the surface core levels for a metal with a nearly empty conduction band.

This interpretation also explains the change in sign of the shift in the middle of the transition series. Our measurements do not argue in favor of either one of these explanations. Therefore, we have mentioned them both. In a full theory certainly both aspects have to be incorporated.

With regard to high loss intensity we mainly confirm the view of Ley *et al.*¹ It is a property of the bulk metal, vanishing for small oxygen doses and for the Ba monolayer. A fully developed conduction band seems to be essential. It is interesting to note that in our spectra the Ba $5s$ level exhibits nearly the same loss intensity as each spin-orbit component of the $5p$ and $4d$ levels. This finding can qualitatively be recognized from Fig. 1 and was quantitatively checked by deconvolution of the different parts of our spectra. It makes the results of Ley *et al.*¹ even more consistent since one expects the loss function to be rather independent for the different core levels.

B. Oxidation of barium

For the first very small oxygen doses, i.e., for 0.2 L in our examples presented above, a very sharp peak at 4.65 eV develops which was attributed to an O- $2p$ -derived state of O²⁻.⁶ The narrow width was taken as an indication for the completely filled O $2p$ shell. The spectral shape is very different from that of oxygen adsorbed on most of the metal surfaces. It is typical for alkali or alkaline earth metals, i.e., the interaction with a highly

electropositive metal is essential for the filling of a complete $2p$ shell. A dose as small as 0.2 L has a great influence on the other spectral features from bulk Ba films.

(a) The surface component of the $5p$ and $4d$ levels vanishes almost completely.

(b) The metallic $5d$ states at the Fermi edge become empty.

(c) Part of the loss intensity is lost.

(d) The $4d$ levels are chemically shifted.

We know from the weakening of the Al $2p$ level that the Ba films we studied are 5–10 layers thick. Such a thick film can hardly be influenced by oxygen residing at the surface; instead, the oxygen seems to penetrate immediately into the bulk, withdrawing electrons from a whole next-neighbor shell thus influencing a large number of atoms in the bulk. At higher doses the O- $2p$ -derived state broadens somewhat into a narrow band with its maximum shifting slightly to smaller binding energies.

From the spectral shape and binding energy well below E_F we conclude that this is mainly O- $2p$ derived and contains no Ba $5d$ contributions. This has some implication in the interpretation of the core levels, as we will now see. The chemical shifts during oxidation are summarized in Table I and for the $5p$ level also in Fig. 7. For the oxidation of Ba in the thick film we confirm the direction of the chemical shift towards E_F as found by others.^{4,5} For the $4d$ level Verhoeven and van Doveren have measured a chemical shift of 0.2 eV which they corrected later to 0.6 eV (Ref. 14) in very good agreement with our result. Lampert *et al.*⁵ claim negative

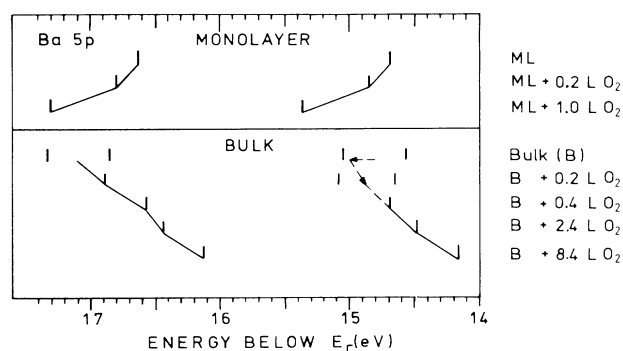


FIG. 7. Peak positions below E_F for the Ba $5p$ states for the monolayer and the bulk during oxidation.

shifts as well but report also on charging problems with their sample. For the Ba monolayer they found the same shift direction as for the bulk which is opposite to our finding. We believe that their result may be due to either their charging problems or their monolayer preparation.

The negative chemical shift (to smaller binding energies) is very unusual. Normally, during the compound formation from a metal into a metal oxide the core levels of the cation (metal) are shifted to larger binding energies. There are two mechanisms which lead to positive shifts when a metal atom is transformed into a positive compound ion: First, the withdrawal of charge reduces the screening charge in the region of the core, thus increasing the binding energies of the core levels. Second, in the final state the screening changes. In the metal it is done by shifting of conduction electrons, whereas in the oxide it is done by polarization of the neighboring anions. For the oxide both initial- and final-state effects normally increase the binding energy as measured by photoemission.

Recently, Wertheim pointed to a possible explanation for the negative shifts in BaO.⁸ He considered the flow of charge into orbitals with smaller spatial extent during the transition from the metallic into the cationic state within a compound. For the transition from Ba metal to BaO this means a redistribution from $6s$ into $5d$, e.g., from $6s^{25}d^0$ for the metal into $6s^{2-x}5d^x$ for the oxide. From such a redistribution of charge a stronger shielding of the core levels would follow, as seen by a shift to smaller binding energies.

Our measurements are in contradiction to this, in principle, reasonable model for the interpretation of the negative shifts in BaO. We do not see any filled $5d$ states in BaO. The opposite is true: During oxidation filled Ba $5d$ states are emptied, that means our measurements indicate a valence-state configuration of $6s^{2-x}5d^x$ for the Ba metal and $O2p^6Ba\ 6s^05d^0$ for BaO. It is very unlikely that there is a $5d$ contribution in the sharp peak at 4.65 eV localized at Ba. So far there is agreement that this sharp peak is a purely O- $2p$ -derived O^{2-} state.

A final-state interpretation of the negative shift in BaO including the $5d$ states is also not possible since for both Ba metal and Ba oxide there are localized $5d$ states available to accept the shielding electron in the photoemission final state. This shielding is normally found to be much

more effective in the metal than in the oxide.

If it is not the special $6s \rightarrow 5d$ redistribution which explains the negative shift of binding energies in BaO, there must be another explanation. To find it, we obtain some clues by comparing Ba with Cs, its neighbor in the Periodic Table. For Cs it is clear that the $5d$ states are empty in the atom, in the metal, and in any compound, and that they do not play a role in the final-state shielding since there is always an empty $6s$ level available. On the other hand, the oxidation of Cs is very similar to that of Ba: There is a very narrow peak at 2.5 eV below E_F due to O^{2-} , the sticking coefficient of oxygen is very high, and the number of Cs atoms influenced is large, all indicating a penetration of the O into the bulk.¹⁵ Finally, and most important for the comparison, the chemical shift is negative, i.e., towards E_F , as for Ba. Therefore, it is this special O^{2-} state which seems to be responsible for the negative chemical shift for both Ba and Cs. We could imagine that these O states are highly polarizable, thus shielding very effectively in the final state.

The buildup of the O^{2-} state improves from Mg, Ca, Sr, to Ba. From Ca to Sr the positive chemical shift becomes smaller and turns to negative values for Ba.¹⁶ Typical is the small energy width of this band. This is well reproduced in recent band calculations.¹⁷ For MgO the O band is more than 5 eV wide, in agreement with x-ray photoemission spectroscopy results,¹⁶ and is reduced to about 3 eV for SrO. For SrO this calculation gives a mainly O- $2p$ -derived valence band and hybridized Sr $4d$ and $5s$ states in the conduction states. This fits well into our scheme.

There is another very important experimental finding which supports our interpretation. In the Ba monolayer no sharp O^{2-} state is found but a rather broad structure similar to chemisorbed O on Al.¹⁸ The chemical shift of the Ba levels is positive, demonstrating the interconnection between the O^{2-} state and a negative chemical shift for bulk Ba.

Finally, we discuss an interesting observation which connects the results for bulk Ba and BaO. In Fig. 7 the chemical shifts of Ba $5p$ levels are reproduced. One notices that the spin-orbit split (SOS) found as 2.28 eV for bulk Ba reduces to 1.96 eV in BaO. This value is also found for the atom. Ley *et al.*¹ have already discussed that, quite obviously, the metallic state of the rare-earth metals shows high loss intensity and a SOS greater than the SOS for the atom. They have noticed the connection between these findings. For the SOS they have posed the argument that the $5p_{3/2}$ component overlaps more with the $6s$ state than does the $5p_{1/2}$ component resulting in a better shielding. If the shielding is more effective for the $\frac{3}{2}$ component than for the $\frac{1}{2}$ component, then the SOS increases. Figure 7 is intended to show that the first oxygen dose, which, as shown above, reduces the $6s^{2-x}5d^x$ emission remarkably, does not give a chemical shift for the $5p_{3/2}$ opposite the $5p_{1/2}$ component. This missing shift can be understood in terms of a compensation between a reduction of the SOS by reducing the extra shielding for the $5p_{3/2}$ component and a chemical shift similar to that of the $5p_{1/2}$ component according to the selected oxygen dose. This is indicated in Fig. 7 by the dashed line.

V. CONCLUSION

There is experimental evidence for a $6s^{2-x}5d^x$ occupation of the bulk Ba conduction band where the bottom of the d part lies 0.7 eV below E_F , in excellent agreement with the band calculation⁷ and experiment.^{6,2} For the Ba monolayer no filled d states can be found, indicating that overlap into all three space directions is necessary to develop the Ba conduction band. This band not only needs overlap into three directions but also can be distorted easily by small amounts of oxygen incorporated as an O^{2-} species. The clean bulk Ba surface shows the core levels of the surface atoms shifted by 0.48 eV to greater binding energy. The direction and amount of this SCLS is in very good agreement with semiquantitative predictions.^{12,13}

Experimental evidence is given that the negative chemical shift (towards E_F) for bulk BaO cannot be understood

by special bonding or shielding properties of the Ba $5d$ orbitals. It is shown that the arguments given for this explanation hold for both Ba and BaO and therefore cannot be used to explain the positive shift.

Instead, we propose that the special O^{2-} species in the bulk is responsible for the anomalous chemical shift. This is supported by the facts that Ba is the most electropositive among the rare-earth elements and that Cs, for which the $5d$ states play certainly a minor role, shows the same chemical shift.

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