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Surface mixed valence in Sm and SmB_6

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Surface-sensitive photoelectron measurements reveal bulk-to-surface shifts of the Sm $4f^6$ level which imply inhomogeneous valence mixing on the surface of Sm and SmB_6. The surface valence fraction is estimated to be the same for both materials. The measurements take advantage of a large resonant enhancement of $4f$ electron emission due to $4d \rightarrow 4f$ photon absorption, and detailed spectra showing this phenomena are presented. It is shown that the $4d$ hole in the $4d \rightarrow 4f$ absorption process stabilizes the $4f$ state by ~ 4–7 eV. Exposure of Sm films to oxygen is found to eliminate, rather than increase, the emission from the surface $4f^6$ state, showing that the $4f^6$ state does not arise from oxygen contamination. Observed variations in Sm film spectra are described, including the finding in some films of an unexplained photoemission peak 2.4 eV below the Fermi level. SmB_6 also displays a broad band of Auger emission when a boron $1s$ core hole is created, and this is ascribed to electrons in the boron $2p$ bonding band. Various trends in $4d$ and $4f$ binding energies for Sm and SmB_6 are pointed out and discussed.

I. INTRODUCTION

X-ray photoemission spectroscopy (XPS) has proved to be a valuable source of information about the $4f$ shell valence states of rare earth metals and compounds because emission from a particular valence state $4f^n$ has a characteristic spectrum due to the multiplet structure of the $4f^{n-1}$ final state.[1] In mixed valent materials the characteristic emission of two valence states is observed, such as $4f^5$ and $4f^6$ in SmB_6.[2] If the material is homogeneously mixed valent, the separation of the two spectra is the Coulomb energy U of adding one electron to a $4f^n$ shell and the state with highest n is expected to occur just at the Fermi level.

This paper describes the results of photoemission measurements performed at the Stanford Synchrotron Radiation Laboratory on Sm and SmB_6 (Ref. 3) using photon energies between 50 and 250 eV, much lower than is typical for XPS. There are two principal differences between using these photon energies and higher ones. The first is that the escape depth for unscattered electrons with kinetic energies ~150 eV is very short, ~4 Å, so that great surface sensitivity is achieved in measurements collecting elastic electrons.[4] The second is that very intense $4d \rightarrow 4f$ photon absorption occurs in this energy range. An important finding of the present work is that a large enhancement of the $4f$ state emission is obtained from this absorption.[5,6]

These two attributes of rare-earth photoemission in this energy range are particularly well suited for probing surface $4f$ valence states. Recently, Wertheim and co-workers have presented evidence that the surface of Sm has both $4f^5$ and $4f^6$ Sm atoms, although the bulk has only $4f^5$ atoms. Wertheim and Campagna[7] pointed out that the XPS $3d$ and $4d$ core level spectra of Sm were very similar to those of SmB_6, which is known to be mixed valent and whose $4f$ and other core level spectra have been shown to consist of both $4f^5$ and $4f^6$ components. They commented that the XPS valence-band spectrum of Sm showed emission near the Fermi level that was larger and more structured than is seen in other rare earth metals, but pointed out that the characteristic $4f^6$ spectrum, which would be expected near the Fermi level in the event of mixed valence, could not be unambiguously identified. Subsequently, Wertheim and Crecelius[8] showed by varying the takeoff angle in Sm XPS measurements that the spectral features ascribed to Sm $4f^6$ atoms increase in intensity relative to those of the Sm $4f^5$ atoms as the surface sensitivity of the XPS measurement is increased. As briefly reported previously,[5] the present work is important in identifying both $4f^5$ and $4f^6$ surface valence states by a clear spectroscopic "fingerprint" obtained in a direct surface-sensitive probe of the $4f$ electrons themselves. A discussion of the energetics of $4f$ state bulk-to-surface shifts has been given recently by Johansson,[9] who concludes that the $4f^6$ state of Sm should be stabilized on the surface, as is observed.

Section II of this paper summarizes briefly the previously published photoemission data on Sm, and then reports other interesting results, including the effect of Sm film aging and deliberate oxygen exposure. The latter studies clearly show that the surface $4f^6$ state is intrinsic and not the result of contamination. In Sec. III photoemission data on bulk-mixed-valent SmB_6 are presented for comparison and contrast with that from surface mixed valent Sm. Section IV points out evidence that the valence mixing on the surface of both Sm and SmB_6 is inhomogeneous, estimates the fractional valence, compares the threshold energies for $4d$ photoemission and $4d \rightarrow 4f$ photon absorption, and discusses certain binding energy trends.

II. Sm RESULTS

Sm films were prepared *in situ* by evaporation onto various substrates, including SmB_6 as described in the next section. The source was outgassed by a number of slow evaporations, and then a sample was prepared by rapid evaporation. The chamber pressure was $\leq 2 \times 10^{-8}$ Torr during evaporation, dropped immediately to 2×10^{-9} Torr after the evaporation, and then dropped further to the base pressure of 5×10^{-10} Torr in about 2 mins. As discussed further below, the films show certain signs of contamination, either during preparation of after ageing, which then requires that another film be made.

The experiments were performed on the 4° branch[10] of beam line I at the Stanford Synchrotron Radiation Laboratory. The electron kinetic energy was analyzed using a double-pass cylindrical-mirror energy analyzer operated to give between 0.2- and 0.4-eV resolution. The energy resolution ΔE of the radiation used is given[11] by $\Delta E = 16 \times 10^{-6} E^2$, where E is the photon energy in eV, which gives 0.36 eV at 150 eV.

Figure 1 compares the Sm valence-band kinetic energy distribution curves (EDC's) obtained with x rays[12] and 150-eV photons. Both spectra show $4f^5$ emission beginning at 5-eV binding energy, and the 150-eV spectrum clearly shows near the Fermi level spectral structure known to be characteristic of $4f^6$ emission.[2] This $4f^6$ emission can also be seen in the XPS spectrum, although considerably obscured by the bulk ($5d$-$6s$) emission at the Fermi level. The clear observation of the $4f^6$ emission in the surface-sensitive 150-eV spectrum is consistent with the hypothesis that the $4f^6$ atoms lie on the Sm surface.

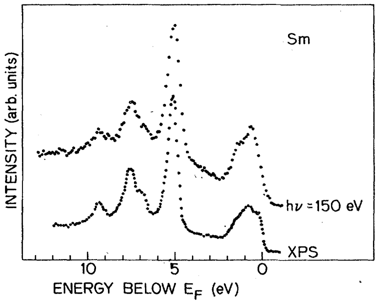

FIG. 1. Valence-band photoelectron energy distribution of Sm excited with 150-eV photons. Final-state multiplets of both $4f^5$ and $4f^6$ emission appear. Also shown is the Sm valence-band spectra excited at 1487 eV, from Ref. 12.

Figure 2 shows constant-initial-state (CIS) spectra with the initial state chosen in the valence band EDC $4f^5$ and $4f^6$ peaks closest to the Fermi level, and a constant-final-state (CFS) spectrum with kinetic energy fixed at 60 eV. The CFS spectrum has been shown[5] to be identical to the bulk Sm photon absorption[13,14] and is ascribed to $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ absorption. The $4f^6$ CIS spectrum has a distinctly different spectral character than the CFS spectrum and was assigned[5] to $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ transitions. This assignment can now be confirmed by comparison to recent measurements[15] of the CFS spectrum of SmS, in which Sm is known to be $4f^6$. The $4f^5$ CIS spectrum is mainly like that of the CFS spectrum, but has a small contribution of the $4f^6$ absorption spectrum due to inelastic scattering of electrons emitted from $4f^6$ states. That the CFS spectrum matches the bulk photon absorption is expected since many inelastically scattered electrons coming from deeper in the solid are collected. The CIS spectra are obtained by collecting mostly elastically scattered electrons, the

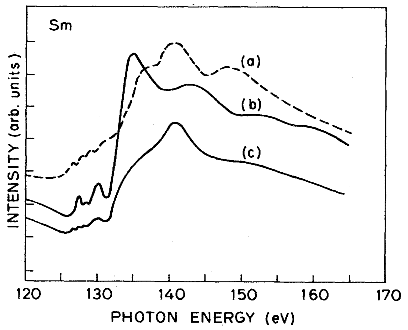

FIG. 2. Curve (a): $4d \rightarrow 4f$ photon absorption measured by partial yield with 60-eV kinetic-energy window. The spectrum is identical to the bulk $4d^{10} 4f^5 \rightarrow 4d^9 4f^6$ photon absorption spectrum. Curve (b): $4d \rightarrow 4f$ photon absorption given by constant-initial-state yield with the initial state set in the valence-band $4f^6$ structure. The spectrum is assigned to $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ absorption. Curve (c): $4d \rightarrow 4f$ photon absorption given by constant-initial-state yield with the initial state set in the valence-band $4f^5$ structure. The spectrum is that of curve (a) with a contribution from curve (b) due to inelastically scattered electrons. The vertical scales of the three curves are arbitrary, different, and offset from zero.

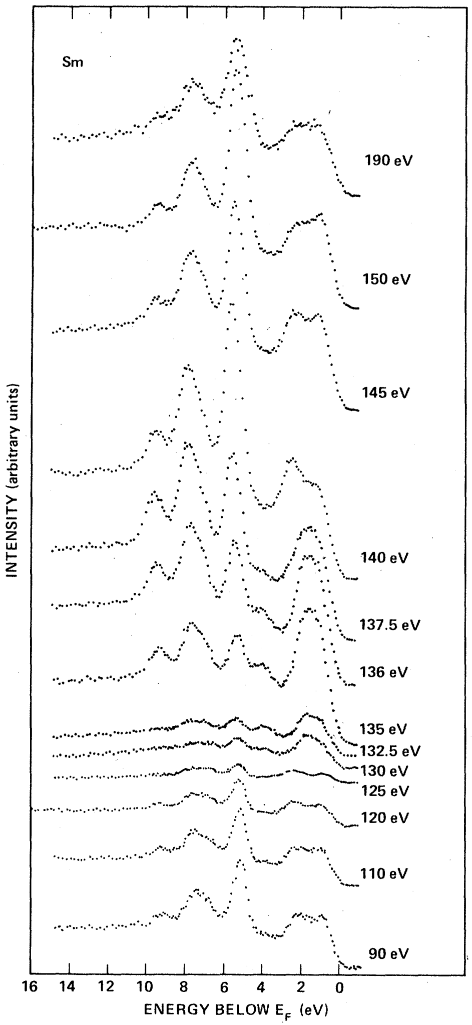

FIG. 3. Valence-band photoelectron energy distribution of Sm excited at various photon energies between 90 and 190 eV. The spectra have been normalized with respect to variations in incident photon flux and electron analyzer efficiency. The relative intensity of the $4f^5$ peaks varies with photon energy and a Fano minimum occurs around 125 eV. The $4f^6$ emission is particularly evident in the 135-eV spectrum. The valence-band feature at 2.4 eV is not present in the spectra of Fig. 1, and does not occur in all Sm films.

more so the closer is the initial state to the Fermi level, and hence are expected to be surface sensitive. Thus the three spectra of Fig. 2 provide firm evidence that the Sm surface has both $4f^5$ and $4f^6$ atoms, while the bulk has only $4f^5$ atoms.

The CIS spectra imply that the EDC spectra will display great intensity variations as a function of photon energy and this is confirmed by the sequence of spectra shown in Fig. 3. Three features are particularly notable. The first is the spectacular enhancement of $4f^6$ emission relative to $4f^5$ emission obtained with 135-eV photons, this energy being precisely at the peak of the $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ absorption. The second is the pronounced reduction in intensity of the 125–130-eV spectra. The reduction in intensity occurs because the $4d \rightarrow 4f$ absorption spectra have a dip in this energy range, preceding the large absorption maxima. Such a dip, and the very asymmetric shape of the absorption peak, are typical of a Fano line shape,[16] which arises from absorption to a sharp state, here a $4d^9 4f^{n+1}$ multiplet, that is degenerate with and coupled to a continuum, here the $4d^{10}4f^{n-1}$ ϵ_k states, where ϵ_k is the state of the emitted electron. The coupling is the super-Koster-Kronig[17] decay process $4d^9 4f^{n+1} \rightarrow 4d^{10}4f^{n-1}\epsilon_k$, which proceeds via the Coulomb interaction. Detailed line-shape analysis of the spectra is complicated by the presence of many sharp lines, all of which should be treated simultaneously,[18] and will not be pursued here. The third feature of interest is that the relative enhancement of different final state multiplets varies with photon energy. This is most clearly seen for the $4f^5$ emission, but also occurs for the $4f^6$. The implication is that the Coulomb matrix elements for the decay process differ for $4f^{n-1}$ multiplets of $4d^{10}4f^{n-1}\epsilon_k$ depending on the particular $4d^9 4f^{n+1}$ multiplet excited by the photon, but there have been no theoretical tests of this hypothesis.

Another feature to be noted in Fig. 3 is the emission at about 2.4 eV below E_F, seen most prominently in the 140-eV spectrum. This emission is not present in all films, as shown, for example, by comparison of the 150-eV spectrum of Fig. 3 with that of Fig. 1, which was taken with a different sample and in which the emission at 2.4 eV is clearly absent. Although this feature occurs in the general spectral range of $4f^6$ emission, it has no correspondence with any of the standard structure of the $4f^6$ spectrum, and is absent for photon energies which enhance the $4f^6$ emission. In fact, as shown by the CIS spectrum of Fig. 4, the new feature is enhanced by $4d \rightarrow 4f$ absorption of $4f^5$ atoms. This fact, coupled with the sharpness of the feature, suggests that it could be the first least-binding-energy peak of a weak $4f^5$ spectrum displaced by about 2.9 eV to lower binding energy from the main $4f^5$ spectrum. But at present it is not clear how to assign this feature, or what aspect of film preparation causes it. Although contamination is the probable cause, it does not seem to be due to the most common contaminant, oxygen, as is described in the next paragraph.

The major effect of aging and oxygen exposure is to decrease the $4f^6$ emission, showing that the $4f^6$ emission is not caused by contamination and is

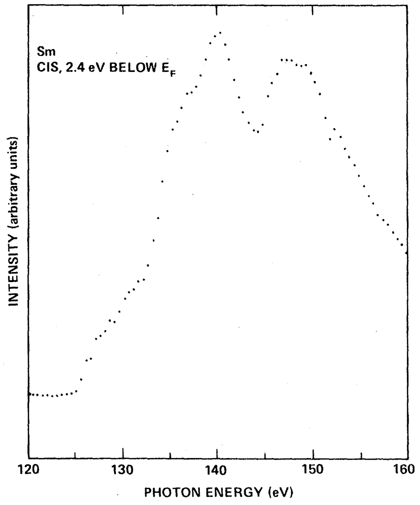

FIG. 4. Constant-initial-state yield spectrum for the 2.4 eV valence-band feature of Fig. 3. General features are characteristic of $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ absorption.

intrinsic. Figure 5 shows the effect on the 150 eV spectrum of 6 h of aging followed by a very small uncalibrated exposure to oxygen, for a sample also displaying the extra 2.4-eV emission. The 2.4-eV emission becomes more prominent in the sequence, but this is because the $4f^6$ emission near the Fermi level decreases, rather than because the 2.4-eV emission is increased. Figure 6 shows the effect of calibrated oxygen exposures on the 135-eV spectrum, where the $4f^6$ emission is most enhanced. A 10 Langmuir dose essentially eliminates the $4f^6$ emission, leaving a small peak at about 2.8 eV. The CIS spectrum for the peak has the spectral features of Fig. 4, suggesting that oxygen exposure has shifted the 2.4 eV feature to slightly higher binding energies. Increasing oxygen exposure shifts this feature further and reduces its intensity nearly to zero, leaving a spectrum consisting of oxygen emission around 6 eV and greatly broadened $4f^5$ emission. It also appears that the $4f^5$ emission has shifted to higher binding energies to produce the increased emission at about 11 eV, as would be expected due to charge transfer from samarium to oxygen atoms.

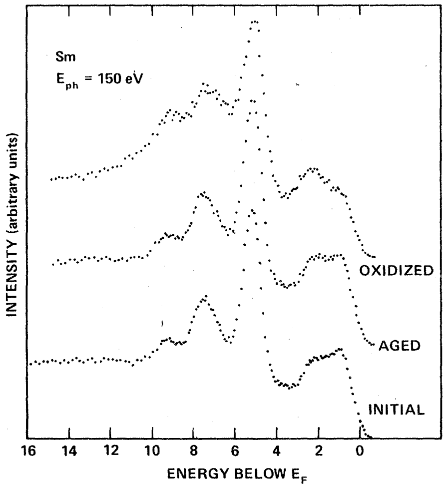

FIG. 5. 150-eV valence-band spectra of Sm, showing effect of 6 h aging and very small uncalibrated exposure to oxygen. The $4f^6$ emission is decreased, but the 2.4-eV feature is nearly constant in the sequence.

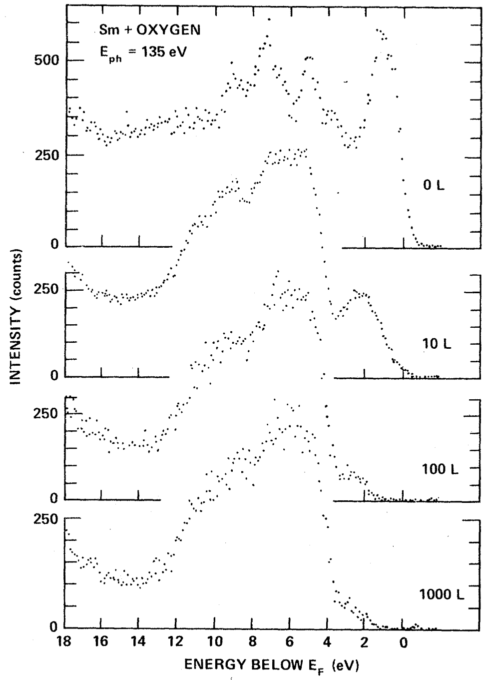

FIG. 6. 135-eV valence-band spectra of Sm, showing effect of large calibrated exposures to oxygen. The $4f^6$ emission and ultimately the extra 2.4-eV emission are eliminated.

III. SmB_6 RESULTS

The SmB_6 sample used was a polycrystalline solid prepared from powder by melting in a triarc furnace and slow cooling. We are indebted to J. C. Mikkelsen of the Xerox Palo Alto Research Center for providing this sample. Measurement of the temperature dependence of the resistivity of the sample shows that the bulk has (2–3)% Sm vacancies,[19] typical of samples prepared this way. A flat shiny surface was prepared by mechanical polishing, and residue from the polishing was removed by ultrasonic cleaning in acetone. After degreasing, the sample was placed in the photoemission chamber, where the surface was cleaned by argon ion sputtering for 2 min using a 2-keV accelerating potential, followed by heating for 10 min at 700 °C to anneal away surface damage and drive argon from the surface. Photoemission from the boron $1s$ core level was found to give a single unshifted line, indicative of no oxygen contamination.[2] In order to compare Sm and SmB_6, with a calibrated Fermi level for both, a gold film was subsequently evaporated on the SmB_6, and after recording the gold valence band and $4f$ core level spectra, a Sm sample film was evaporated over the gold.

Figure 7 compares the valence-band emission of Sm and SmB_6 for a photon energy of 135 eV, and shows the expected final state multiplet structure for $4f^5$ and $4f^6$ emission by vertical bars. The heights of the bars are based on the usual coefficient-of-fractional-parentage analysis,[20] and hence may not agree with the experiment due to the different effects of the super-Koster-Kronig decay matrix elements. As found in XPS studies, SmB_6 displays $4f^5$ emission beginning about 7 eV below E_F.[2] The $4f^5$ peak at highest binding energy is somewhat enhanced in the 135-eV spectrum, enabling it to be seen a little more clearly than in the XPS or 150-eV spectra, where it is obscured by overlapping boron $2p$ state emission. Near E_F there is $4f^6$ emission. In contrast with Sm, previous XPS studies[2] of SmB_6 clearly showed this emission, consistent with SmB_6 being mixed valent in the bulk. There is a small difference between the binding energies of the $4f^6$ peaks in the present spectra and the XPS spectra, however, and this is discussed further in Sec. IV. As expected, the $4f^6$ emission is greatly enhanced in the 135-eV spectra, and except for the different binding energies of the $4f^5$ peaks, there is a great similarity between the Sm and SmB_6 results at 135 eV.

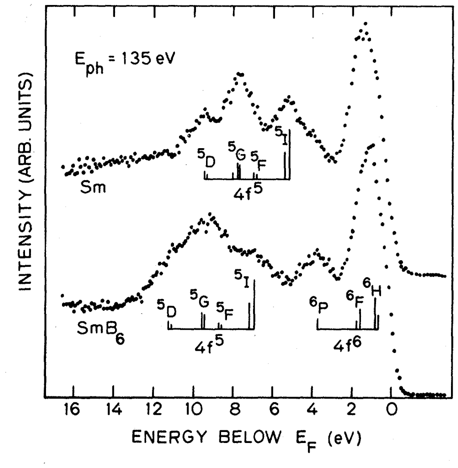

FIG. 7. 135-eV valence-band spectra of Sm and SmB_6 compared. The $4f^6$ emission lies below the Fermi level about 0.65 eV for both. Drawing vertical lines on the figure aids comparison.

Given the highly localized and atomic character of the $4d \rightarrow 4f$ absorption, it would be expected that the CIS and CFS spectra of Sm and SmB_6 would be very similar and this is so, as shown in Fig. 8. There is, however, one difference expected but not clearly observed. It was argued above for Sm that the CFS spectrum showed only $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ absorption because the CFS spectrum is bulk sensitive and Sm is not mixed valent in the bulk. By this reasoning, SmB_6, which is mixed valent in the bulk, should show both $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ and $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ absorption in its CFS spectrum. In fact there is very little difference in the Sm and SmB_6 CFS spectra, and in particular, neither show appreciable evidence of the 135-eV edge which is characteristic of the $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ absorption. CFS spectra taken with a kinetic energy of 6 eV are essentially identical to those of Fig. 8, taken with the kinetic energy at 60 eV. It would appear that either the CFS spectra are not so bulk sensitive as previously believed, or that the $4d^{10}4f^6 \rightarrow 4d^9 4f^7$ absorption is weaker in the CFS spectrum than that due to $4d^{10}4f^5 \rightarrow 4d^9 4f^6$ transitions. This is a problem which will require further study.

A search was also made for resonant photoemission due to excitation of the boron $1s$ core level, but this does not occur. For photon energies greater than the threshold for producing a $1s$ hole, electrons are emitted in a broad band of kinetic energy which does not change with photon energy, showing that the $1s$ hole decays by an ordinary Auger process. Band structure calculations for several hexaborides predict that the boron $2p$ states produce broad bonding and antibonding bands separated by a gap.[21] For LaB_6, the Fermi level lies near the bottom of the antibonding band, which is hybridized with other states in this energy range. For SmB_6, because it is mixed valent, E_F will be somewhat lower. It is then reasonable to attribute the photon absorption to transitions from the $1s$ core level to the unoccupied states with fractional antibonding $2p$ character, and to attribute the Auger emission to a process in which the $1s$ core hole is filled by an electron from the bonding $2p$ states, while another bonding $2p$ electron is emitted.

If the Coulomb interaction between the two $2p$ holes is neglected, the Auger emission can be analyzed to obtain the location and width of the bonding $2p$ states, which is useful since emission from these states is mixed with $4f$ emission in the valence-band EDC's. It is straightforward to show that if the $2p$ bonding band begins at an energy A below the Fermi level, and has width W, then A and W are given by

$$W = \tfrac{1}{2}(E_{K\,\max} - E_{K\,\min}) , \quad (1)$$

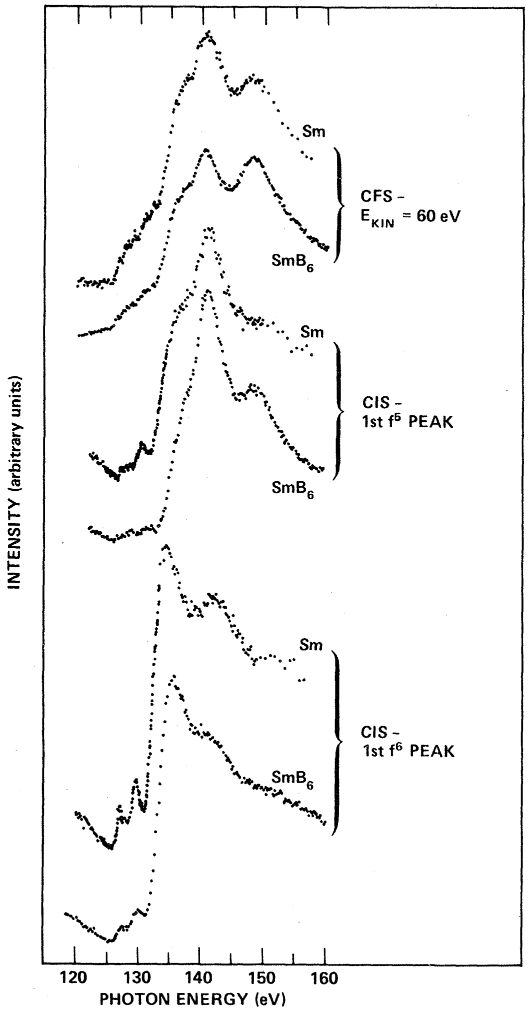

FIG. 8. Constant-final-state and constant-initial-state spectra of Sm and SmB_6 compared. "1st" means smallest binding energy.

$$A = \tfrac{1}{2}(E_{1s} - E_{K\max} - \varphi) , \qquad (2)$$

where $E_{K\max}$ and $E_{K\min}$ are the maximum and minimum kinetic energies of the emission, respectively, E_{1s} is the 1s binding energy, and $\varphi = 4.6$ eV is the work function of the electron analyzer. Using the experimental values $E_{1s} = 187.9$ eV, $E_{K\max} = 178$ eV, and $E_{K\min} = 160$ eV yields $A = 2.6$ eV and $W = 9$ eV. These values compare fairly well with the values estimated from the theoretical partial density of 2*p* states,[21] $A = 3$ eV and $W = 11$ eV. The neglect of the Coulomb interaction between the two 2*p* holes may be justified by the large bandwidth, which may also account for the fact that the photon absorption edge and photoemission binding energy of the 1s level are identical.

IV. DISCUSSION

A. Homogeneous versus inhomogeneous surface valence mixing

For homogeneous mixed valence it is expected that both the occupied and unoccupied $4f^6$ levels will lie just at the Fermi level. (By "unoccupied $4f^6$ level" is meant the energy for adding an electron to $4f^5$ to produce $4f^6$.) This has been found to be true, within experimental resolution, for the occupied $4f^6$ level observed in the XPS spectrum of SmB_6, which is homogeneously mixed valent in the bulk. For inhomogeneous mixed valence it is expected that the occupied $4f^6$ level will lie below the Fermi level and that the unoccupied $4f^6$ level will lie above the Fermi level. Thus in the inhomogeneous case there are energy barriers against fluctuations of electrons between the conduction band and the 4*f* states, or vice versa, and the valence mixing is static, with inequivalent rare earth sites. Also, the energy separation of occupied $4f^5$ and $4f^6$ states can not be interpreted as the Coulomb energy *U*.

Figures 9 and 7 provide evidence of inhomogeneous valence mixing on the surfaces of SmB_6 and Sm. Figure 9 shows a comparison of the XPS and 135-eV spectra for SmB_6, from which it is apparent that the separation of the $4f^5$ and $4f^6$ emission is 0.7 eV less in the 135 eV spectrum than the XPS spectrum. This decrease is due partly to a very small shift of the $4f^5$ emission to lower binding energy, but mostly to an ~0.65-eV shift of

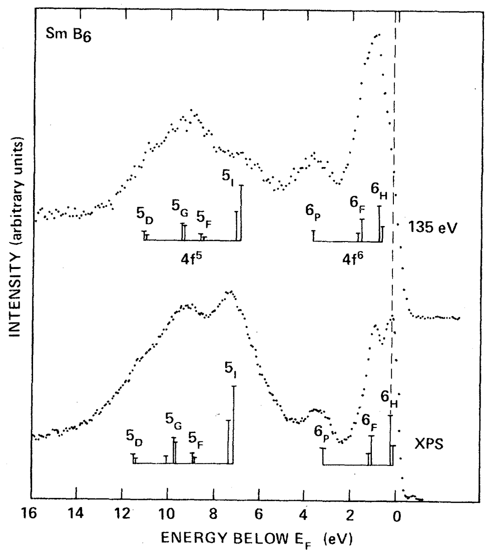

FIG. 9. XPS and 135-eV valence band spectra of SmB_6 compared. The $4f^6$ strucutre in the 135-eV spectrum is broadened and shifted to larger binding energy by ~0.65 eV. Drawing vertical lines on the figure aids comparison.

the $4f^6$ emission to higher binding energy, so that it does not occur at the Fermi level. The shape of the spectrum also suggests some weak emission at the energy observed in the XPS spectrum. These comparisons are most easily seen by drawing a series of vertical lines in Fig. 9 at strategic energies. Taking account of the much greater surface sensitivity of the 135-eV spectrum, one infers that a surface shift of the $4f^6$ state has occurred so that the surface is inhomogeneously mixed valent. The possibility that this situation is due to the surface preparation cannot be excluded, but an intrinsic surface shift is certainly plausible in view of the fact that the $4f^6$ state in Sm metal must shift from being above E_F in the bulk to being at or below E_F on the surface. In fact, the data of Fig. 7 show that the $4f^6$ emission observed for Sm metal occurs below the Fermi level by an amount about the same as for SmB_6 (again, drawing vertical lines on the figure will aid the comparison), leading to the conclusion of inhomogeneous surface valence mixing for both.

The magnitude of the surface shift of the $4f^6$ level for Sm metal can be deduced from bremsstralung isochromat spectra,[23] which show that the unoccupied $4f^6$ state in the bulk is ~0.4 to 0.6 eV above the Fermi level, implying a surface shift of ~1.05 to 1.25 eV. This can be compared to SmB_6, for which the surface shift is 0.65 eV. These fairly small shifts (~1 eV) are of a reasonable magnitude when regarded as the energies of the lattice distortions that must accompany the occurrence of inequivalent lattice sites, a process which is facilitated by the extra degree of freedom at the surface.

The finding of inhomogeneous valence mixing raises the question of whether the surface of Sm and SmB_6 could be valence ordered. To pursue this question entails making surface-sensitive structural measurements like low-energy electron diffraction (LEED) on single-crystal surfaces. It is thus extremely interesting to note a brief report of superlattice spots in the LEED pattern of a single crystal surface of SmB_6.[24] Further work on this subject is merited.

B. Surface valence fraction

The data of Fig. 7 allow in principle a comparison of the fractional valence of Sm and SmB_6, by comparing the integrated intensity of $4f^5$ and $4f^6$ emission. Although error due to underlying boron $2p$ emission in the SmB_6 spectrum should be rather small, since the boron $2p$ emission is not enhanced by the Sm $4d \rightarrow 4f$ absorption, the comparison is still rather crude because it is necessary to separate the areas under the $4f^5$ and $4f^6$ emission from each other and from the inelastic background. Such an analysis of the data of Fig. 7 shows that the ratio of $4f^5$ area to $4f^6$ area is the same for the Sm and SmB_6 spectra, implying the same fractional valence on the surface. If the fractional valence for SmB_6 on the surface is ~2.7, as in the bulk,[2] then one concludes that for the surface of Sm the fractional valence is also ~2.7, in fair agreement with the value of 2.6 deduced by Wertheim and Crecelius[8] from their XPS data.

C. 4*d* photoemission and photoabsorption thresholds

It is known that the energy of empty $4f$ states can be stabilized several eV by a $3d$ core hole, which acts very much like an extra proton in the nucleus.[25] Comparison of the $4d$ photoemission and photoabsorption data for Sm atoms in Sm metal and SmB_6 shows the same effect for a $4d$ core hole. In the absence of this effect the minimum energy of a $4d \rightarrow 4f$ transition would be the sum of the minimum $4d$ binding energy and the minimum energy to populate an unoccupied $4f$ state above the Fermi level, these minimum energies corresponding to the lowest lying multiplet of the configuration excited. The $4d$ energies can be obtained from $4d$ XPS spectra.[7] The unoccupied surface $4f^6$ state in both Sm and SmB_6 must lie very near the Fermi level, and for the present discussion it suffices to take the value for the unoccupied $4f^6$ state in the bulk of Sm, which is ~0.5 eV above the Fermi level. The unoccupied $4f^7$ state is estimated from known $4f$ valence separations[2,23] to lie ~6 eV above the occupied $4f^6$ states, or ~5.5 eV above E_F for both Sm and SmB_6. The error in these estimates is not likely to be so large as to invalidate the conclusions to be drawn. Table I summarizes the relevant numbers for both $4f^5$ and $4f^6$ Sm atoms in Sm and SmB_6. Some uncertainty in these numbers due to surface-to-bulk energy shifts and the different probe depths of the techniques used must be acknowledged. The Δ values are the energies by which the observed photoabsorption edge energy is less than the value estimated from independent electron addition and removal energies, and is the shift in the $4f^6$ and $4f^7$ binding energy due to the $4d$ hole.

The $\Delta(4f^6)$ values for both Sm and SmB_6 are very nearly the same as the values of the Coulomb energy $U(4f,4f)$ deduced from the separation in energy of the $4f^5$ and $4f^6$ states in each material, ~5.7 and ~7 eV, respectively.[2,23] Since Δ is a Coulomb energy of the type $U(4f,4d)$, this confirms that $U(4f,4d) \sim U(4f,4f)$, as deduced previ-

TABLE I. Comparison of $4d \to 4f$ photoabsorption energy (a), (e) with independent $4d$ electron removal (b), (f) and $4f$ electron addition (c), (g) energies. Removal and addition energies are relative to the Fermi energy. Δ is the shift deduced in the $4f^6$ or $4f^7$ energy due to $4d$ hole. All energies are in eV. (a), (e) $4d \to 4f$ absorption, present work. (b), (f): Energy below E_F, from XPS $4d$ spectra, Ref. 7. (c), (g): Energy above E_F, estimated, see text.

	Process	Sm	SmB_6
(a)	$4d^{10}4f^5 \to 4d^9 4f^6$	125.5	125.5
(b)	$4d^{10}4f^5 \to 4d^9 4f^5$	129.6	132.4
(c)	$4d^{10}4f^5 \to 4d^{10}4f^6$	$\sim$0.5	$\sim$0.5
(d)	$\Delta(4f^6)$: (b) + (c) − (a)	4.6	7.4
(e)	$4d^{10}4f^6 \to 4d^9 4f^7$	126.0	126.0
(f)	$4d^{10}4f^6 \to 4d^9 4f^6$	124.3	124.3
(g)	$4d^{10}4f^6 \to 4d^{10}4f^7$	$\sim$5.5	$\sim$5.5
(h)	$\Delta(4f^7)$: (f) + (g) − (e)	3.8	3.8

ously[5] from the nearly identical onset energies of $4d \to 4f$ photon absorption for $4f^5$ and $4f^6$ atoms. Also the usual argument that $U(4f, 4f)$ is smaller in Sm than SmB_6 due to greater screening in the metal can be applied to the values of $\Delta(4f^6)$ $\sim U(4f, 4d)$ in Sm and SmB_6. The same trend is expected for $\Delta(4f^7)$ in Sm and SmB_6, but cannot be confirmed in the absence of experimental energies for the $4f^7$ levels.

Charge-transfer satellites, in which an electron is transferred from the valence band to the $4f$ shell during the $4d$ photoemission event could occur in the $4d$ XPS spectra with threshold energies nearly the same as the photoabsorption thresholds because the final $4d$-$4f$ configurations (although not the valence-band configurations) are the same for the two processes. But this does not appear to occur; the existing assignments of the structure in the $4d$ spectra are well based on comparison to known spectra.

D. Trends

Here certain energy level trends are pointed out, as follows.

(a) The $4d \to 4f$ photon absorption energies are the same in Sm and SmB_6, and there is no evidence that they differ for atoms of the same valence in the bulk or on the surface. This is probably a consequence of there being only inner-shell wave functions involved in the process. As discussed previously[5] the absorption edge energy is nearly the same for $4f^5$ and $4f^6$ atoms because a shift of the two edges would be due to differences of Coulomb energies, notably $U(4f, 4f)$ and $U(4f, 5d)$, which are nearly equal.

(b) The $4f^5$ binding energies are not much changed between the surface and the bulk, but are about 2 eV greater in SmB_6 than Sm. Similarly the $4d$ binding energy of $4f^5$ atoms is about 2.8 eV greater for SmB_6 than Sm. The shifts between Sm and SmB_6 are in the proper direction to be ascribed to charge transfer from samarium to boron states, leaving Sm positively charged in SmB_6. That the shifts are similar for the $4d$ and $4f^5$ binding energies is consistent with the fact that core levels tend to shift together due to a change in chemical environment and the supposition that the $4f^5$ state behaves essentially like a core level.

(c) The $4f^6$ binding energies have a reverse trend from those of the $4f^5$. There is a bulk-to-surface increase of $\sim$0.65 and $\sim$1.25 eV for SmB_6 and Sm, respectively. However the difference between the Sm and SmB_6 values is very small for the bulk and nearly zero for the surface. There is a tendency for the $4f^6$ level to "stick" near the Fermi level, making mixed valence likely. Also the $4d$ binding energies of the $4f^6$ atoms are identical for Sm and SmB_6, in contrast to those for the $4f^5$ atoms, but consistent again with the chemical shifts of the $4d$ and $4f$ levels tracking together.

V. SUMMARY

Photoemission measurements on evaporated Sm films and polycrystalline SmB_6 using photon energies between 50 and 250 eV have revealed bulk-to-surface shifts of the $4f^6$ level which imply that Sm changes from being single valent in the bulk to inhomogeneously mixed valent on the surface, and that SmB_6 changes from being homogeneously mixed valent in the bulk to inhomogeneously mixed valent on the surface. The surface valence fraction is estimated to be the same for Sm and SmB_6. These studies are aided by a large enhancement of $4f$ emission due to $4d \to 4f$ absorption, leading to considerable intensity variation of the $4f$ structure with photon energy. It can be deduced that the $4d$ hole in this absorption process stabilizes the $4f^6$ and $4f^7$ states by amounts between $\sim$4.6 and $\sim$7.4 eV. It is also found that some Sm films exhibit, at about 2.4 eV below the Fermi level, extra emission, the origin of which is not known, but which is resonantly enhanced by $4d \to 4f$ absorption of $4f^5$ atoms. Oxidation experiments on Sm show that the surface $4f^6$ state is not induced by oxygen contamination, but is, in fact, eliminated by it. Finally, boron $2p$ band Auger emission can be crudely analyzed to be in fair agreement with the $2p$ partial density of states from band calculations for the hexaborides.

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