Inverse photoemission of mixed-valence compounds and $4f$ inner-well stability

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We present the inverse photoemission spectra of compounds which unambiguously display either homogeneous or inhomogeneous mixed valence, TmSe, and oxidized SmS. The spectra show two $4f$ peaks, $4f^n$ and $4f^{n+1}$, arising from the $4f^{n-1}$ and $4f^n$ ground-state configurations. These data, along with inverse photoemission spectra on clean SmS, show that the $4f$ inner potential well is stable enough to contain one more $4f$ electron than in the divalent, atomic ground state. The valence deduced from the TmSe bremsstrahlung isochromat spectrum agrees well with that obtained from other spectroscopic studies.

I. INTRODUCTION

Because of their unusual and interesting electronic, magnetic, and lattice properties, mixed-valence rare-earth materials are currently studied heavily.[1-3] In these materials, typically compounds of Sm, Eu, Tm, and Yb, the rare-earth ions can fluctuate in the ground state between the $4f^n$ and $4f^{n-1}$ configurations with corresponding compensation of conduction electrons, $4f^n \rightleftharpoons 4f^{n-1}+e$. The occurrence of two valence states is shown clearly by the $4f$ electron-*removal* spectrum, obtained by x-ray photoemission spectroscopy (XPS),[4-6] which contains two sets of $4f$ multiplets, one set corresponding to $4f^{n-1}$ final states $(4f^n + h\nu \rightarrow 4f^{n-1}+\text{photoelectron})$ and the other set corresponding to $4f^{n-2}$ final states $(4f^{n-1}+h\nu \rightarrow 4f^{n-2}+\text{photoelectron})$. Implicit in this picture is the expectation that the electron-*addition* spectrum, which is measured by inverse photoemission[7,8] or bremsstrahlung isochromat spectroscopy (BIS), will also display two peaks corresponding to $4f^n \rightarrow 4f^{n+1}$ and $4f^{n-1} \rightarrow 4f^n$ transitions. In spite of its being an intrinsic part of the entire mixed-valence concept, this expectation has never been confirmed experimentally. To date, BIS data have only been reported for single-valence metallic rare-earth materials[8] and for some anomalous cerium compounds[9] whose valency is still a controversial subject.[1-3,9-11]

Apart from the simple need to confirm the most basic elements of the mixed-valence model, there are two other motivations for obtaining BIS spectra in systems well documented for displaying mixed valence. The first motivation follows from the fact that for the anomalous cerium materials, with nominally one $4f$ electron per cerium, more than 90% of the $4f$ spectral weight occurs in the BIS spectrum, and, furthermore, that only the BIS spectrum displays more than one valence peak. We have found[12] that the spectral weights of the two BIS peaks in some cerium compounds imply a different valence than what is deduced from other spectroscopic measurements, and so it is important to establish that the BIS technique has no intrinsic failings in application to mixed-valence materials, i.e., to give a calibration of the method.

The second motivation concerns the well-known fact that the potential seen by rare-earth $4f$ electrons has two wells and that the inner well is potentially unstable against partial or complete transfer of the $4f$ wave function to the outer well.[13-15] It has been proposed that this instability,[16] or a modified version of it,[17] plays a role in the behavior of cerium materials, and even in the transition to mixed valence in SmS.[18] A stringent test of the stability of the well for n electrons is to examine experimentally the consequences of inserting yet another electron. However, as discussed below, most of the BIS spectra to data do not actually provide new stability information because the BIS final states have the same number of $4f$ electrons as in the stable atomic ground states. Only in systems that are completely or partially divalent can the number of $4f$ electrons be increased beyond a number known already to be stable.

In this paper, we present the electron-addition spectrum of TmSe. This compound is accepted as an archetypal mixed-valence material with $4f^{12}$ and $4f^{13}$ configurations in the ground state, probably homogeneous,[6,19] and the valence-band XPS spectrum is known.[5,6] As in the XPS spectrum, which shows both $4f^{12} \rightarrow 4f^{11}$ and $4f^{13} \rightarrow 4f^{12}$ structures, we find that the inverse photoemission spectrum also shows signatures of both $4f$ configurations, giving two peaks corresponding to the transitions $4f^{12} \rightarrow 4f^{13}$ and $4f^{13} \rightarrow 4f^{14}$. We also show the inverse photoemission spectra for divalent SmS and for partially oxidized SmS, the latter as an example of inhomogeneous mixed valence.

II. EXPERIMENTAL METHODS

The apparatus used is a Vacuum Generators ES-CALAB, factory modified for BIS measurements. The BIS system is similar to the one described in Ref. 8, detecting x-ray photons at an energy of 1486.6 eV while scanning the kinetic energy of incoming electrons. From Ag Fermi edge spectra, the BIS resolution was determined to be 0.5 and 0.8 eV for the operating conditions used to obtain spectra on clean and oxidized samples, respectively. For the materials studied, high-resolution XPS spectra are available in the literature, and so the total data acquisition time was reduced by taking XPS spectra with a nonmonochromatized Mg source, yielding approximately 1.0 eV
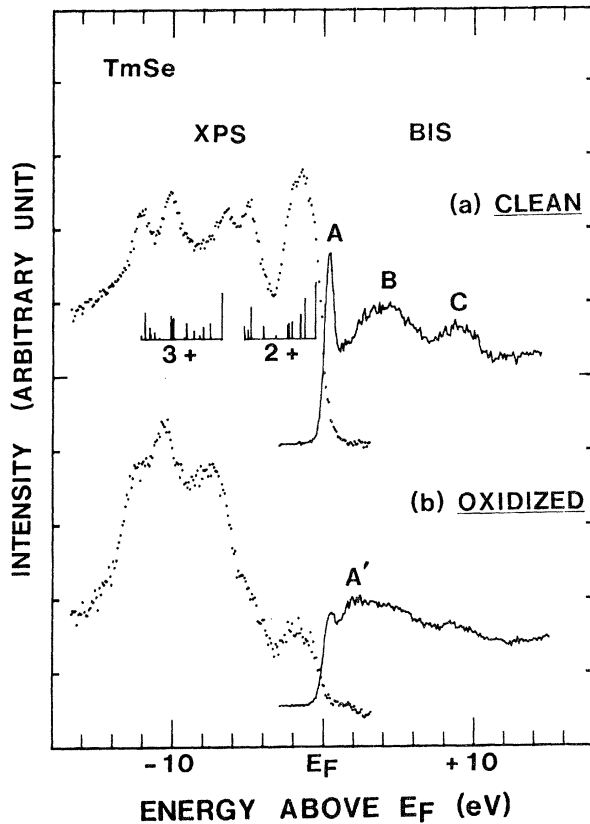
FIG. 1. XPS and BIS spectra of (a) clean and (b) oxidized TmSe. The resolution of BIS spectra is 0.5 eV for (a) and 0.8 eV for (b). Calculated relative energies and intensities of XPS final-state multiplets (Ref. 6) for the divalent Tm(2 +) and trivalent Tm(3 +) components are shown with bars. The ratio of XPS to BIS weight was chosen to approximate the ratio of electrons to holes in the $4f$ shell.

FIG. 2. YS BIS spectrum. The energy resolution is 0.5 eV.

resolution. The samples used were single crystals of TmSe, YS, and SmS, all of which have the rocksalt structure. The TmSe sample has also been studied by soft-x-ray resonant photoemission, to be reported elsewhere,[20] and its lattice constant, measured by x-ray diffraction to be 5.715 ± 0.004 Å, shows it to be nearly stoichiometric. The samples were cleaved along the (100) plane *in situ* under vacuum better than 5×10^{-11} Torr, and the pressure while taking data was less than 1×10^{-10} Torr. A typical XPS-BIS data acquisition time is 3–4 h, and sample contamination, monitored by oxygen and carbon $1s$ core-level signals, was negligible over this time. All the data were taken at room temperature.

III. EXPERIMENTAL DATA AND INTERPRETATION

Figure 1(a) shows combined XPS and BIS spectra of clean TmSe. Apart from differing resolutions, the valence-band spectrum is as reported previously,[5,6] showing two sets of $4f^{12}$ and $4f^{11}$ multiplets arising from the $4f^{13}$ and $4f^{12}$ ground-state configurations. The binding energy of the lowest $4f^{12}$ multiplet is less than the experimental resolution. The BIS spectrum consists of three
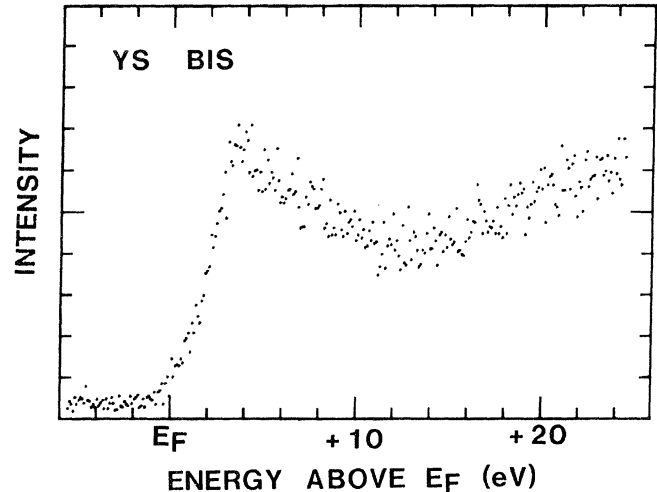
peaks, labeled A, B, and C. Peak B is the s-d conduction-band density of states, as shown by comparison with the BIS spectrum in Fig. 2 for YS, which has no $4f$ electrons. We then identify peak A as $4f^{12}\rightarrow4f^{13}$ spectral weight, and peak C as $4f^{13}\rightarrow4f^{14}$ spectral weight. The lack of multiplet structure in peak C is expected because the $4f^{14}$ final state is a singlet, while for peak A a calculation of coefficients of fractional parentage has shown that essentially all the BIS weight for the $4f^{13}$ final state is in a single $^2F_{7/2}$ multiplet.[8]

Several aspects of the TmSe BIS spectrum merit discussion. Peak A is remarkably sharp, its width and distance from E_F being determined entirely by the instrumental resolution. This is consistent with TmSe displaying homogeneous mixed-valence, since the simplest expectation in this case is that the $4f^{12}\rightleftharpoons4f^{13}$ spectral weight is exactly at E_F, where there are no decay channels. The valence v of TmSe can be deduced from the ratio of the areas A_{12} and A_{13} under peaks A and C, respectively, from the formula $v=2+(1+2A_{13}/A_{12})^{-1}$, where the factor of 2 accounts for the differing number of $4f$ holes in the two initial states. The BIS valence determination is somewhat more straightforward than that from the XPS spectrum because the $4f$ weight lies in well-separated peaks devoid of multiplet structure. To extract the peaks for area measurement, the YS BIS data were scaled to match peak B in the TmSe BIS spectrum and then subtracted. The valence obtained from this procedure is 2.6 ± 0.08, in good agreement with the value $v\simeq2.55$ deduced from the valence-band XPS spectrum,[6] the L_{III} x-ray absorption edge,[21] magnetic properties,[21] and a soft-x-ray photoemission study,[22] which distinguished the bulk and surface valences. This value, however, is somewhat smaller than that implied by a linear interpolation of lattice constants ($v\simeq2.72$). The electron correlation energy U, defined as the lowest energy difference between multiplets of the $4f^n\rightarrow4f^{n-1}$ (XPS) and $4f^n\rightarrow4f^{n+1}$ (BIS) spectral weights, is 6.3 eV for the $4f^{12}$ configuration and 8.7 eV for the $4f^{13}$ component. The U value for the $4f^{12}$ config-
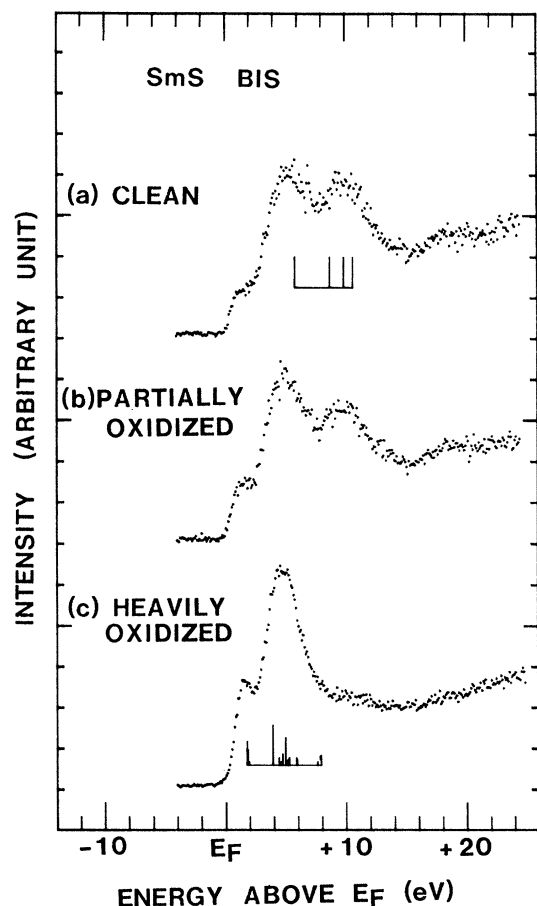
FIG. 3. BIS spectra of (a) clean SmS, (b) partially oxidized SmS, and (c) heavily oxidized Sm_2O_3. The energy resolution is 0.5 eV for (a) and (b), and 0.8 eV for (c).

uration has been deduced from the TmSe valence-band XPS spectrum,[6,22] but this is the first determination of the electron correlation energy for the $4f^{13}$ configuration.

In Fig. 1(b) we show the change of spectra of TmSe as we oxidize it. The effect of oxidation in the XPS valence-band spectrum is to increase the $4f^{12} \to 4f^{11}$ spectral weight relative to the $4f^{13} \to 4f^{12}$ peak. The new weight has slightly higher binding energy than that in the clean spectrum. This can be understood as oxygen converts homogeneously mixed-valence thulium sites into stable single-valence $4f^{12}$ sites, making Tm_2O_3 or $(TmO)_2Se$. The corresponding change in the BIS spectrum is that *both* peak A and peak C decrease in intensity, while a new peak A' appears. It is therefore clear that both peaks A and C arise from the mixed-valence site of TmSe, whereas peak A' arises from $4f^{12} \to 4f^{13}$ transitions of the oxidized, trivalent thulium site. The peak A' is ~ 1.5 eV above the Fermi level, and U for the oxidized Tm site is larger than that of the $4f^{12}$ configuration of the mixed-valence Tm site. This increase of U is probably due to the lack of local screening charges around the site in the oxide.

As an example of inhomogeneous mixed valence, where

two inequivalent sites exist, one in the $4f^n$ configuration and the other in the $4f^{n-1}$ configuration, we show the BIS spectrum of partially oxidized SmS. SmS is a divalent Sm compound (Sm $4f^6$),[23] which upon oxidation is converted to the trivalent Sm_2O_3 (Sm $4f^5$). Our XPS core-level and valence-band spectra confirm this fact, and agree with published SmS and Sm_2O_3 data.[23,24] Figure 3 shows BIS spectra on (a) clean SmS, (b) an intermediate stage of oxidation, and (c) SmS heavily oxidized to Sm_2O_3. The clean SmS spectrum shows features at energies corresponding to $4f^7$ multiplets, as expected for $4f^6 \to 4f^7$ transitions. The relative energies of the $4f^7$ multiplets, shown with bars in the figure, are estimated from Tb metal XPS ($4f^8 \to 4f^7$), reduced by 38% to account for three less nuclear charges.[6,8] A coefficient-of-fractional-parentage analysis has not been done, so the bar heights do not indicate relative intensities. The oxidized spectrum in (c) shows peaks corresponding to $4f^5 \to 4f^6$ transitions, in fair agreement with calculated relative energies and intensities[8] of the $4f^6$ multiplets. The emission at 3—7 eV above E_F is stronger than expected, probably due to the underlying s-d conduction-band states. In the intermediate stage of oxidation (b), both peaks $4f^6 \to 4f^7$ and $4f^5 \to 4f^6$ coming from two different sites can be seen, and upon more oxidation the latter peak grows at the expense of the former peak. This is in contrast to the TmSe case, where, upon oxidation, the two $4f$ spectral weights of the mixed valence sites decrease *together*.

IV. STABILITY OF THE INNER POTENTIAL WELL

The BIS spectra of most rare-earth metals show clearly the $4f^n \to 4f^{n+1}$ multiplet structure,[8] indicating that the additional $4f$ electron in the final state remains localized. This is not surprising, since most rare-earth metals have one less $4f$ electron than for their atomic ground states, and therefore the BIS final states have the same number of $4f$ electrons as the stable atomic states. An exception is Eu, which has the $4f^7$ configuration in both metallic and atomic states, and its BIS spectrum with the $4f^8$ final state is extremely broad.[8] This breadth has been interpreted[8] as large lifetime broadening associated with the energy being very high above the Fermi level so that there are many channels available for decay. Because the issue of inner-well stability has been raised[16-18] both for cerium materials and for SmS, it is important to consider the alternate possibility that the width signals some delocalization of the electron in the $4f^8$ configuration because the atomic $4f$ well is not strong enough to hold one more electron than the atomic ground state.

Our BIS spectra are then relevant to this question of the stability of the inner atomic well because, like Eu metal, Sm in SmS has the same number of $4f$ electrons as does atomic Sm, and the same is true for the $4f^{13}$ state of Tm in TmSe. From the observation that the BIS spectrum for SmS shows the appropriate $4f^7$ final-state multiplet structure we conclude that the additional $4f$ electron goes into the inner well of the $4f$ atomic potential and remains localized. That is, the $4f$ inner well of Sm is stable enough to hold one more electron than in the atomic ground state. From the $4f^{13} \to 4f^{14}$ peak in the TmSe BIS data, which

has the expected weight in spite of being somewhat broad, the same conclusion can be drawn for Tm as well.

For the particularly interesting case of cerium, available evidence shows the stability of the inner well. Atomic calculations show that the transfer of wave function from the outer to the inner well actually occurs[14] between Ba and La, and[25] that the modified double-well picture[17] is suspect. Consistent with these theoretical results, BIS spectra show, well above E_F, stable $4f^1$ states in La (Ref. 8) and stable $4f^2$ states in cerium materials.[8,9,12]

V. CONCLUSIONS

In conclusion, we have reported the first BIS spectra for rare-earth compounds that are unambiguously mixed valent. These data show that (1) in accordance with the basic picture of mixed valence, the inverse photoemission spectra of mixed-valent compounds display signatures of both $4f$ occupation configurations, (2) the lower-energy $4f$ peak in the BIS spectrum of TmSe is very sharp and within experimental resolution lies at the Fermi level, supporting its homogeneous mixed valency, (3) the relative weights of the two Tm BIS peaks yield a valence consistent with that obtained from other spectroscopic measurements, and (4) the $4f$ inner potential well, even for divalent rare earths, is stable enough to bind yet one more electron than in the ground state.

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