Study of valence mixing in SmB_6 by x-ray photoelectron spectroscopy

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Clean single-crystal surfaces of samarium hexaboride (SmB₆) have been investigated by x-ray photoelectron spectroscopy. The results confirm the existence of a mixed configuration of Sm in this compound. Comparison of the valence-band spectrum with that of LaB₆ allows an accurate determination of the Sm 4*f* contribution, and a direct comparison with theoretical Sm²⁺ and Sm³⁺ 4*f* spectra. The effective Coulomb interaction is found to be 7.0 ± 0.2 eV; the lifetime broadening of the Sm³⁺ 4*f* spectrum is as large as 1.0 eV, which is one order of magnitude larger than that of the Sm²⁺ 4*f* spectrum. The ratio of Sm²⁺ to Sm³⁺ from the 4*f* photoemission intensities is 0.4 in good agreement with the value deduced from earlier susceptibility and Mössbauer experiments. The investigation of the Sm 4*d* core levels provides additional evidence for the mixed valence state. The background contribution to the Sm 4*d* spectrum is determined accurately by comparison with the "tail" associated with the narrow B 1*s* line; after background correction, a quantitative comparison with Sm²⁺ and Sm³⁺ 4*d* spectrum. Our results are discussed in connection with other data on more complex mixed-configuration systems.

I. INTRODUCTION

Recently, there has been renewed interest in various "homogeneous" mixed-valence rare-earth compounds and alloys in which the rare-earth ion has a nonintegral number of 4f electrons. Examples of such compounds are CeAl₃, metallic SmS, TmSe, YbB₄.¹

Samarium hexaboride, SmB_6 , is also a "homogeneous" mixed-valence compound, with physical properties at atmospheric pressure very similar to those of metallic SmS above 6.5 kbar. Mössbauer-effect studies of SmB_6 showed an anomalous Sm isomer shift, intermediate between the values expected for the $\rm Sm^{2+}$ and $\rm Sm^{3+}$ configurations.^2 Earlier magnetic-susceptibility data showed a leveling off of the susceptibility at low temperature,³ analogous to the one reported for the highpressure phase of SmS.⁴ This rules out the possibility of nonequivalent Sm²⁺ and Sm³⁺ sites, because in this case the Sm³⁺ sublattice should order magnetically. No quantitative theory of the mixedvalence state has yet been worked out, although it is now agreed that the ground state involves a mixed configuration,⁵⁻⁷ a somewhat surprising fact at first, because it implies that the 4f electrons contribute to the Fermi surface. This ground state can be viewed either as a partially filled band with a small width $\Delta \sim 0.01$ eV, or as a fluctuating state between the 2+ and the 3+ configurations, with characteristic fluctuation time \hbar/Δ .

X-ray photoelectron spectroscopy (XPS) is a powerful tool in the study of mixed-valence compounds, because the effective Coulomb interaction $U_{\rm eff}$ is much larger than Δ ; in other words

the "characteristic time" of the XPS process is much shorter than \hbar/Δ . Hence, the XPS spectrum is well resolved into the 2+ and 3+ components. Separate informations can be extracted from these two sets of photoemission lines and the effective Coulomb interaction $U_{\rm eff}$ is measured directly.

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m SmB}_6$ had previously been studied by the XPS technique, but only using air-exposed powder and low-energy resolution.⁸ We report here XPS studies on single-crystal surfaces using mono-chromatized Al $K\alpha$ radiation. For purpose of comparison we have also investigated LaB₆. A short report of these studies will appear else-where.⁹

II. EXPERIMENTAL

 SmB_6 was synthesized by the reaction $2\text{Sm}_2\text{O}_3$ + $30\text{B} \rightarrow 4\text{SmB}_6 + 3\text{B}_2\text{O}_2$. The reaction product was then melted in an argon-arc furnace. At this stage slight amounts of surface oxides were removed and the melting procedure stopped when crystal regions (~4 × 3 mm) emerged at the surface. X-ray analysis of the samples gave a lattice constant of 4.133 ± 0.001 Å, which confirms the good stoichiometry of our crystals.¹⁰

XPS data were obtained in an HP 5950 A spectrometer with 0.55-eV full-width-at-half-maximum resolution. The surfaces were cleaned by abrasion with a diamond file in a vacuum better than 10^{-8} Torr. The sample was then introduced into the main chamber of the spectrometer where the vacuum was in the 10^{-9} -Torr range, without exposure to the atmosphere. The state of the surface was monitored by the O 1s and C 1s XPS lines. The

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use of diamond for scraping was required because of the extreme hardness of SmB_6 . Earlier attempts to cleave or scrape with a tungsten carbide blade failed to give a good surface, because large amounts of tungsten were left on the sample.

From measurements of the O 1s spectrum, an upper limit can be derived for the percentage of samarium ions present in the form of surface oxides. For the present spectra this upper limit is 10%.

In the following we discuss the results obtained for selected lines in the XPS spectrum. All electron states with binding energy in the range 0-500eV were investigated, but most of them result in broad lines which are difficult to analyze in detail. We have, therefore, limited our study to the Sm 4f, B 1s, and Sm 4d levels.¹¹ In addition we have studied in detail the valence-band region of LaB₆.

A. Sm 4f spectrum

The Sm 4f spectrum, shown in the upper part of Fig. 1, is composed of two well-resolved nonoverlapping parts. The first part lies just at the Fermi energy. It is clearly similar to the Sm^{2+} 4f spectra in the samarium monochalcogenides.¹² The second part of the spectrum consists of a broad line, which lies above 6-eV binding energy; although the structure of this line is obscured by its width, it can be related to the Sm^{3+} 4f spectra observed in SmSb,¹³ and Sm metal.¹⁴ This provides additional, spectroscopic evidence for a mixed-valence configuration of the ground state of samarium in SmB₆.

In order to obtain more quantitative information from this spectrum, the contributions of the valence bands generated by B 2sp states with some covalent mixture of Sm 5*d* states must be identi-



FIG. 1. High-resolution x-ray photoemission spectra of the valence band and 4f region of SmB₆ and of metallic "trivalent" LaB₆.

fied. Although the theoretical ratio¹⁵ of the cross sections, $6\sigma_{B_{2s}}/\sigma_{Sm 4f}$, is only about $\frac{1}{6}$, the valence bands might contribute some additional structure. To check this point we have investigated the closely related compound LaB_6 , which does not have occupied 4f states. The valence band spectrum of this material is found to be almost featureless, see the lower part of Fig. 1. It can be used to remove the B sp contribution from the SmB₆ spectrum. Before performing this subtraction, the SmB_6 and LaB_6 spectra were normalized to equal counting time. It was also verified that with such normalization, the area under the boron 1s core line is nearly the same for the two samples. This provides a good check on the reproducibility of the experimental conditions, and supports the validity of the subtraction whose result is shown in the upper part of Fig. 2.

The resulting Sm 4f spectrum can then be directly compared with theory. It is known that when an electron is photoexcited from a partially filled $4f^n$ shell, the remaining (n-1) 4f electrons are left in the various possible multiplet states of the final $4f^{n-1}$ configuration, which appear at different energies. Their intensities are given by the squares of the *coefficients of fractional parentage*, calculated as the projections of the initial electron state onto products of the various (n-1) electrons



FIG. 2. Upper curve: difference curve of the data of Fig. 1; below: theoretical curve calculated using the intensity of final-state multiplets after Cox, Ref. 16.

final states and the one-electron outgoing wave function. These coefficients have been tabulated by Cox.¹⁶ In the case of the Sm²⁺ spectrum, the energies of the Sm³⁺ multiplet final states are found in the literature, either from optical data or from calculations.¹⁷ For the Sm³⁺ spectrum, the final state is Sm^{4+} which is a $4f^4$ configuration. The corresponding multiplet levels can be approximated by those of the Pm³⁺ ion, provided a scaling factor is used to take into account the difference in ionic charge.¹³ From data in various rare-earth materials, it is generally found that a unit increase in Z results in a (7-15)% increase in splitting.¹⁸ In the present case after examination of the SmSb and Sm metal spectra, we have found that the appropriate scaling factor is 1.13.

By using the multiplet energies and the squared coefficients of fractional parentage, theoretical Sm^{2+} and Sm^{3+} 4*f* spectra have been generated numerically, see Fig. 2 lower part. The line shapes were assumed to be of the Doniach-Sunjic type.¹⁹ The asymmetry parameter α was assumed to be the same for Sm^{2+} and Sm^{3+} , but the lifetime widths were allowed to be different. The best fit is shown in Fig. 2. It reproduces all the features of the experimental spectrum rather accurately. A small misfit in the 5-eV region is possibly due to some oxide contamination (i.e., a few percent of the Sm ions). The value of α is well determined by the fit to the Sm²⁺ spectrum to be ≈ 0.25 .

The most striking results of the fit are the very different values of the lifetimes required to fit the Sm^{2+} and Sm^{3+} spectra. For Sm^{2+} the lifetime width used in Fig. 2 is 0.08 eV. This must be regarded as an average value for the various multiplet components. As can be seen from Fig. 2, the experimental ${}^{6}P$ line is noticeably broader than the one in the generated spectrum. In contrast, the multiplet ${}^{6}H_{5/2}$, which lies right at the Fermi level, is hardly distinguishable from the shape of the instrumental resolution function and its natural width might be appreciably smaller than 0.08 eV. This can be easily understood because the corresponding final state is a component of the mixedvalence ground state. Consequently, the lifetime width of this line would be expected to be of the order of the mixing width Δ , i.e., typically 0.01 eV. Despite the good experimental resolution, this is still well beyond our capabilities of data analysis.

For Sm^{3+} , the lifetime width used in Fig. 2 is as large as 1.0 eV. In order to understand this unusually large broadening, we have investigated the 4*f* spectra in other rare-earth hexaborides. A more detailed account of these experiments will appear elsewhere.²⁰ The main result is that other rare-earth hexaborides exhibit comparable broadening of the 4*f* spectrum. This can be ascribed to an Auger recombination mechanism. Such a process is highly favored by the large number of boron bands, which provide many channels for the excitation of the Auger electron. The probability of excitation, however, goes to zero with decreasing hole-binding energy; this is the reason, we believe, for the narrowness of the shallowest lines of the Sm²⁺ 4*f* spectrum.²⁰

From our fit we can evaluate the relative areas of the Sm^{2+} and $Sm^{3+} 4f$ spectra; the corresponding ratio of the concentrations can be deduced, taking into account the fact that the XPS cross sections are in the ratio 5/6, due to the different number of f electrons in the initial states. The result is $r = C_{\rm Sm^{2+}}/C_{\rm Sm^{3+}} \approx 0.4$, which corresponds to an average valence of 2.7. This is in good agreement with the earlier estimations from Mössbauer and susceptibility measurements. However, the uncertainties on the present estimate are large. The main difficulty is that the area under the Doniach-Sunjic lines is not integrable unless a cutoff is imposed. The cutoff is determined by the width of the conduction band which is not known for SmB_6 . As a result the theoretical estimate of r contains some uncertainties.²¹

A most interesting aspect of the XPS technique when applied to mixed-valence materials is the direct measurement of the energy shift between the two final-state configurations. From Fig. 2 we deduce that the shift, U_{eff} , between the fundamental lines of the two configurational states, ${}^{6}H_{5/2}$ for the Sm²⁺ spectrum and ${}^{5}I_4$ for the Sm³⁺ spectrum, is 7.0 ± 0.2 eV. This value is about 1 eV larger than that measured in the case of the metallic phase of SmS.^{12,20} We attribute this difference to the screening, which depends upon the nature of the ligands and the band structure of the material.

B. Boron 1s line

The B 1s line was initially investigated as a test for the success in surface preparation. In oxidized samples a secondary peak appears in the spectrum, about 5 eV to the high-energy side of the main line which can be of comparable height for a fully oxidized surface. After diamond scraping in ultrahigh vacuum, the oxide peak was reduced by at least two orders of magnitude and became comparable to the noise.

The B 1s line measured under good conditions is shown in Fig. 3. It is well fitted by a single Doniach-Sunjic line shape, convoluted with the instrumental resolution function. The lifetime width is 0.23 eV and the asymmetry parameter $\alpha \approx 0.13$. This value of α is significantly smaller than that used to fit the Sm 4f spectrum. This is not sur-

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FIG. 3. XPS spectrum of the B 1s level in SmB₆. The upper curve is the experimental spectrum. The lower curve is a theoretical fit, using a Doniach-Sunjic line ($\alpha = 0.13$; lifetime width, 0.23 eV) convoluted with the experimental resolution function.

prising, since it is known that many-body effects in photoemission from compounds have "local character,"²² because the conduction-electron wave functions have different weights on the Sm and the B sites.

C. Fit of the Sm 4d spectrum

The Sm 4d spectrum, shown in the upper part of Fig. 4 is spread over 15 eV and exhibits a largely unresolved complicated structure. Unlike the 4f spectrum, this structure is not readily analyzed on a theoretical basis, because the number of final states produced by the multiplet coupling of a d-core hole to the unfilled 4f configuration is large.

However, examples of Sm^{2*} and $\text{Sm}^{3*} 4d$ spectra can be separately obtained by observing this level in SmTe and SmSb, respectively. These spectra are shown in Fig. 3, together with the corresponding spectrum in SmB₆. The energy scales have been shifted to align the corresponding peaks. It is clear that the SmB₆ spectrum may be represented by a combination of the two others, with some additional broadening. The peak on the low-energy side, together with two small bumps on the side of the broad line, corresponds to the Sm²⁺ configuration. The remainder of the broad line, which exhibits three main structures, is ascribable to Sm³⁺.

In order to get quantitative information from the 4d spectrum, the first step is to determine the tailing background of inelastic excitations. This problem is particularly complicated here, because the spectrum is very broad and its height is of the same order of magnitude as the tail itself. Two methods have been widely used in the past: the first is the linear background approximation; the second rests on the assumption that the background



FIG. 4. Sm 4d spectra in SmB_6 , SmSb, and SmTe. The energy scale is valid for SmB_6 ; for positions of the SmSb and SmTe spectra have been slightly shifted to line up the corresponding peaks. The backgrounds drawn under each of these spectra were calculated as explained in the text.

associated with a δ -function line is a step-function tail on the high-energy side. Both methods involve a high degree of arbitrariness and are hardly supported by any physical model. The results obtained in both cases are often unsatisfactory; for example, the model of the step-function tail is unable to account for the rise of the background well beyond the line, as is observed in our spectrum.

In SmB_6 , however, the background problem can be solved in a rather simple way because the elementary tail associated with a δ -function line turns out to be a function almost directly accessible by experiment. For this purpose we consider the B 1s line, which is narrow and does not interfere with other lines. In this case the tail and the line itself can be separated (see Fig. 5): the line shape in the region of the peak fits very well with a Doniach-Sunjic line shape, convoluted with our instrumental resolution function. The excess tail in the higher-energy region gives a good measure of the contribution of inelastic excitations. The difference between the observed spectrum and the theoretical line shape, divided by the area of the theoretical line, gives the elementary tail associated with a δ -function line (i.e., a narrow line of unit area).²³ This tail vanishes at the center of the



FIG. 5. XPS spectrum of the B 1s level in SmB_6 on a 50–eV scale. The points correspond to the experimental spectrum. The continuous line is the calculated curve (see Fig. 3). The difference between these two quantities gives a measure of the tailing background of inelastic excitations. This elementary tail was used to calculate the background for the Sm 4*d* spectrum in SmB₆.

line; it increases monotonically up to the first plasmon peak 20 eV below, then decreases weakly with a secondary peak about 30 eV from the center of the line.

If the shape of the elementary tail for a δ function is called f(E), then the tailing background associated with any line g(E) in the spectrum is simply the convolution of f and g. The main assumptions are that the tail is dominated by the extrinsic plasmons and does not depend strongly on the kinetic energy of the outgoing electron, which is probably a good approximation. This allows us to use an iterative procedure to determine the background from the experimental data. This was done for the Sm 4d spectrum by taking as a zero-order approximation for the spectrum a Gaussian line of 10-eV width and about 30000 counts per channel height. The convergence was found to be very fast; no change was discernible beyond the second iteration. The calculated background fits very well with the rising tail observed experimentally (see Fig. 4). No adjustable multiplicative factor is involved in our fit, since the elementary tail has been obtained for a line of unit area. Therefore, the agreement in the absolute magnitude in the highenergy limit is a further check of the validity of our method. The difference between the experimental spectrum and this background is shown in the upper part of Fig. 7.²⁴

Unfortunately, the same procedure cannot be applied to the Sm 4d spectra in SmTe and SmSb,

due to the lack of an isolated narrow line in the XPS spectra of these compounds. By analogy with the elementary tail obtained in SmB_6 , a model tail was assumed which is sketched in Fig. 6. This function is zero at the center of the line; it increases linearly up to the plasmon energy (12 eV in SmTe, 14 eV in SmSb)²⁵ and then levels off. Although somewhat arbitrary, this model tail exhibits the main features which are expected from any physical model, i.e., vanishing at zero excitation energy, and a characteristic rise up to the plasmon energy. The linear shape is merely a convenient assumption; the resulting background is not expected to be very sensitive to the exact functional dependence of f(E). However, in this case we have no information on the absolute magnitude of the tail. Consequently, the background determination involves an adjustable parameter, which is determined by matching the height of the high-energy side.

After these three background corrections were performed, the Sm 4*d* spectrum in SmB₆ could be compared quantitatively with the superposition of Sm²⁺ and Sm³⁺. Their proportions were allowed to vary, and a further lifetime broadening was provided, which might be different from Sm²⁺ and Sm³⁺. The best fit is shown in Fig. 7. The areas of Sm²⁺ and Sm³⁺ spectra are in a ratio about 1 to 3, but this is very sensitive to the choice of the background for SmTe and SmSb, and this number must not be taken too seriously. The lifetime broadening was found to be very different for Sm²⁺ and Sm³⁺, being 0.2 and 0.7 eV, respectively. If one takes into account the original lifetimes in SmTe and SmSb, the overall lifetime widths in



FIG. 6. Model tail associated with a δ -function line. $\hbar \omega_p$ is the plasmon energy. This model tail was used to calculate the inelastic background of the Sm 4*d* spectrum in the case of SmTe and SmSb, where no measurement of the elementary tail is possible.

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FIG. 7. Fit of the Sm 4d spectrum in SmB_6 . The upper part shows the experimental spectrum, after background correction. The lower part shows the calculated spectrum, obtained by using the Sm 4d spectra of SmTe and SmSb (see text).

 SmB_6 are about 0.3 eV for Sm^{2+} and 0.8 eV for Sm^{3+} . This behavior is strikingly similar to that observed for the 4*f* spectra, and moreover the large broadenings of $\text{Sm}^{3+} 4f$ and $\text{Sm}^{3+} 4d$ are the same within 30%. This might suggest that the recombination $4d^9 - 4d^{10}$ in the case of Sm^{3+} involves as a first step a capture in the 4*f* levels $4d^94f^5$

 $-4d^{9}4f^{6}$, this transition being favored by the highly efficient Auger processes.

III. CONCLUSION

XPS measurements in SmB₆ provide further support for a model invoking a mixed-configuration ground state. The simple electronic structure of the hexaborides, coupled to a very favorable ratio of photoelectric cross sections, $\sigma_{\text{Sm 4f}}/6\sigma_{\text{B 2s}} \sim 6$, allows us to obtain quantitative data for the analysis of the 4f photoemission line shape. This gives a valence mixing ratio $r = C_{\text{Sm}^{2+}}/C_{\text{Sm}^{3+}} \approx 0.4$ in agreement with the average valence deduced from Mössbauer and magnetic-susceptibility measurements. The effective Coulomb interaction U_{eff} , is found to be ≈ 7.0 eV which is larger than in "chemically" collapsed phase of SmS. This evidences, we believe, the dependence of the screening upon the ligands.

The experiment also gives a clear-cut evidence for a very large lifetime broadening of the Sm^{3+} spectrum. This can be ascribed to an Auger recombination mechanism, whose high efficiency stems from the large number of bands in the hexaborides.

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and the choice of the cutoff is therefore not critical. ²⁴This procedure is similar to Van Cittert deconvolution: the response function of the system, taken as a δ function plus a tail, is unfolded from the experimental spectrum. Note that this result could be attained by a simpler, though less general method: scanning *E* from lower to higher binding energy, and calculating

$$g(E) = g_0(E) - \int g(E - E') f(E') dE'$$

where g_0 is the original spectrum and f the elementary tail, would yield directly the corrected spectrum g in a single step. This is made possible by the peculiar form of the response function.

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