

Calculation of surface core-level shifts in $\text{Sm}_{1-x}\text{Y}_x\text{S}$

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We present a simple microscopic theory for the surface core-level shift in mixed-valence systems. In the case of a not fully screened final state, the core-level shift consists of an electronic and a Madelung-energy contribution. The electronic contribution is determined by the assumption of a rectangular d -band density of states. The Madelung-energy contribution is calculated with the use of reasonable assumptions for the screening of the ionic interactions. Using this theory we obtain results for the surface-energy shifts of the $4f$ state in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ as a function of the Y concentration. The numerical results agree well with recent photoemission data.

I. INTRODUCTION

Surface core-level spectroscopy has proved very useful in providing microscopic insight into surface properties of various materials. For example, in the case of transition metals and their alloys the observed surface core-level shifts have been related to the surface structure¹ and the heat of surface segregation.^{2,3} Similarly, one expects from studying the surface core-level shifts of mixed-valent compounds that one learns about the electronic structure of such systems. In particular, one may learn whether the valence at the surface is different from that in the bulk,⁴⁻⁷ whether the Sm and Y d electrons in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ share a common band, and how the semiconductor-metal transition in mixed-valent systems is reflected in the surface core-level shift.

Whereas surface core-level shifts have been calculated successfully for the case of metals, no such calculations have been performed for mixed-valent systems showing a metal-semiconductor transition. In such systems one expects the screening capacity of itinerant d electrons to be limited and to depend in a very sensitive way on the alloy concentration. The purpose of this paper is to present a theory for the surface core-level shift in mixed-valent systems using a simple model for the electronic contribution to the surface core-level shift. In addition to the electronic contribution there results a contribution arising from Madelung-type energy shifts. Both contributions will depend on the electronic charge transfer between the core-excited atoms and

their surroundings. We use this theory to explain the recently observed⁸ surface core-level shifts in $\text{Sm}_{1-x}\text{Y}_x\text{S}$.

In Sec. II we outlined the general theory for surface core-level shifts Δ_c^s in mixed-valent systems. In Sec. III this theory is applied to $\text{Sm}_{1-x}\text{Y}_x\text{S}$ and numerical results are presented for $\Delta_c^s(x)$. Finally, we discuss our theory and numerical results in Sec. IV.

II. THEORY FOR THE SURFACE CORE-LEVEL SHIFTS IN MIXED-VALENT SYSTEMS

The surface core-level shift of the atom Z is given by²

$$\Delta_c^s(Z) = E_c^S(Z) - E_c^B(Z), \quad (2.1)$$

which is the difference of the core-electron binding energies (as measured in photoemission) at the surface and in the bulk. These binding energies can be expressed in terms of total energies as follows:

$$E_c(Z) = E_f(Z^*) - E_i(Z), \quad (2.2)$$

where $E_f(Z^*)$ is the final energy of the core-excited atom Z^* after a photoelectron is emitted, and $E_i(Z)$ is the initial energy. Equation (2.1) can be rewritten as

$$\Delta_c^s(Z) = [E_S(Z^*) - E_B(Z^*)] - [E_S(Z) - E_B(Z)], \quad (2.3)$$

where $E_{B(S)}(Z)$ denotes the binding energy⁹ of an

atom with atomic number Z in the bulk (at the surface). In the case of pure metals, where the conduction electrons screen the core-hole completely, the core-excited atomic state Z^* has been successfully approximated by a $(Z+1)$ atom.¹⁰ On the other hand, in an insulator the excited atom can rather be thought of as an ion with a nuclear charge increased by one. Therefore, in the case of solids with semiconductor-metal transitions, all energy shifts result from electron redistribution and from the changes in the Coulomb fields of the ions. Thus, in $\text{Sm}_{1-x}\text{Y}_x\text{S}$, which shows a metal-insulator transition as a function of Y concentration x , we expect contributions to the Sm binding energy $E(\text{Sm})$ that result from changes in electronic bond energies E_e and from changes in Madelung energy E_M .

Therefore, we write

$$E(Z) = E_e(Z) + E_M(Z). \quad (2.4)$$

Consequently,

$$\Delta_c^s(Z) = \Delta_e(Z) + \Delta_M(Z). \quad (2.5)$$

First, we consider the electronic part of the core-level shift. Within the one-electron picture, which has proven useful in explaining cohesion in metals, the binding energy of a Z atom in its ground state can be given as

$$E_e(Z) = \sum_i \int_{-\infty}^{E_F} dE (E - E_0^i) g^i(E), \quad (2.6)$$

where the summation i is taken over all occupied bands and where $g^i(E)$ and E_0^i denote the local electronic density of states and center of gravity of the i th band, respectively. Note that owing to the term $E - E_0^i$, this formula approximately includes, as commonly assumed,¹¹ contributions to the Coulomb interaction energy. Nonzero contributions to the binding energy will arise only from partially filled bands, which in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ are the $5d$ and $4f$ bands of the alloy. As will become clear later on, the $4f$ contribution to the binding energy is negligible due to the small $4f$ bandwidth.¹² Thus, only the $5d$ electrons contribute to Eq. (2.6). Note that in the alloys under consideration the number of $5d$ electrons per atom never exceeds 1. Therefore, only the lower-lying t_{2g} part of the crystal-field-split $5d$ band will be partially occupied. In order to estimate the value of the integral in Eq. (2.6), we describe this electronic subband t_{2g} by a rectangular density of states. Such an approximation was previously used to calculate the cohesive energy of transition metals.¹³ From Eq.

(2.6) one finds now for the bulk

$$E_{e,B}(Z) = \int_{-\infty}^{E_F} dE (E - E_{0,B}) g_B(E). \quad (2.7)$$

Here, the local t_{2g} electron density of states in the bulk $g_B(E)$ is normalized to

$$\int_{-\infty}^{\infty} dE g_B(E) = 6. \quad (2.8)$$

An expression analogous to Eq. (2.7) will arise also for the surface. Because of the reduced coordination number z_S at the surface compared to z_B in the bulk, the surface t_{2g} subbandwidth W_S can be related to the corresponding bulk bandwidth W_B as

$$W_S = \sqrt{z_S/z_B} W_B. \quad (2.9)$$

This result follows from using the tight-binding approximation. Denoting by $N_{B(S)}$ the occupation number of the alloy t_{2g} subband per metal atom in the bulk (at the surface), the electronic part of the binding energy terms for the Z atom in Eq. (2.3) can be written as

$$\begin{aligned} \Delta E_e(Z) &= E_{e,S}(Z) - E_{e,B}(Z) \\ &= \frac{1}{2} W_B \left[\left(\frac{z_S}{z_B} \right)^{1/2} N_S \left(\frac{N_S}{6} - 1 \right) \right. \\ &\quad \left. - N_B \left(\frac{N_B}{6} - 1 \right) \right] + E(4f). \quad (2.10) \end{aligned}$$

$E(4f)$ is the contribution due to the $4f$ band. The expression for $E(4f)$ is exactly of the same form as that obtained for the d band where W_B, N_B, N_S are replaced by the corresponding quantities for the $4f$ electrons. Obviously, $E(4f)$ is proportional to the $4f$ bandwidth, which is very small¹² compared to the d bandwidth. Thus $E(4f)$ is much smaller than the d band contribution to $\Delta E_e(Z)$ and will be neglected in what follows. An expression similar to Eq. (2.10) can be given for the Z^* state, replacing $N_{B(S)}$ by $N_{B(S)}^*$. Hence, the electronic part of the core-level shift is given by

$$\Delta_e(Z) = \Delta E_e(Z^*) - \Delta E_e(Z), \quad (2.11)$$

where $\Delta E_e(Z^*)$ and $\Delta E_e(Z)$ are given by Eq. (2.10).

In the following we consider the Madelung-energy contribution $\Delta_M(Z)$ to the core-level shift. The bulk Madelung binding energy of a Z ion¹⁴ with effective charge $Q(Z)$ can be given by¹⁵

$$E_{M,B}(Z) = -\alpha \frac{Q(Z)Q(A)}{r} \left[1 - \frac{1}{m} \right], \quad (2.12)$$

where α is the Madelung constant and $Q(A)$ and r are the nearest-neighbor anion charge and distance, respectively. In the case of $\text{Sm}_{1-x}\text{Y}_x\text{S}$, one has $Q(\text{Sm})=2e$ and $Q(\text{S})=-2e$. The term $1/m$ describes the core repulsion between Z and surrounding A atoms and can be related¹⁵ to the experimentally accessible bulk modulus by

$$m = 1 + \frac{18Br^4}{\alpha Q(Z)Q(A)}. \quad (2.13)$$

The Madelung binding energy at the surface has been estimated to be 20% smaller than in the bulk,¹⁶ assuming the same electronic configuration. Using this argument, the Madelung binding-energy terms for the Z atom can be combined in analogy to Eq. (2.10) as

$$\begin{aligned} \Delta E_M(Z) &= E_{M,S}(Z) - E_{M,B}(Z) \\ &= 0.2\alpha \frac{Q(Z)Q(A)}{r} \left[1 - \frac{1}{m} \right]. \end{aligned} \quad (2.14)$$

Note that for the excited atom, the surface and bulk charge $Q_S(Z^*)$ and $Q_B(Z^*)$ are different. An expression similar to Eq. (2.14) can be given for the Z^* site. One finds

$$\begin{aligned} \Delta E_M(Z^*) &= \alpha \frac{Q_B(Z^*)Q(A)}{r^*} \left[1 - \frac{1}{m_{B^*}} \right] \\ &\quad - 0.8\alpha \frac{Q_S(Z^*)Q(A)}{r^*} \left[1 - \frac{1}{m_{S^*}} \right], \end{aligned} \quad (2.15)$$

where

$$m_{B(S)}^* = 1 + \frac{18B^*r^{*4}}{\alpha Q_{B(S)}(Z^*)Q(A)}. \quad (2.16)$$

Here, variables marked by an asterisk refer to the core-excited state. Finally, the Madelung contribution $\Delta_M(Z)$ to the surface core-level shift is given by

$$\Delta_M(Z) = \Delta E_M(Z^*) - \Delta E_M(Z). \quad (2.17)$$

The parameters that have not been specified are the t_{2g} subband occupation numbers $N_{B(S)}$, $N_{B(S)}^*$ and the ionic charges $Q_B(Z^*)$, $Q_S(Z^*)$ of the excited state. Furthermore, information about the bulk bandwidth W_B , the nearest-neighbor distance r , and the bulk modulus B is needed. Provided that these parameters are known, the surface core-level shift $\Delta_c^s(Z)$ can easily be calculated from Eq. (2.5).

III. NUMERICAL RESULTS FOR $\text{Sm}_{1-x}\text{Y}_x\text{S}$

Expressions for the electronic and the Madelung contribution to the core-level shift presented in the preceding section are now applied to calculate the surface core-level shift $\Delta_c^s(\text{Sm})$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$. The required input parameters are determined as follows.

First, consider the Y-concentration-dependent d band occupation numbers $N_B(x)$ and $N_S(x)$ used in Eq. (2.10). In $\text{Sm}_{1-x}\text{Y}_x\text{S}$, due to the $4f$ - $5d$ hybridization, a $4f$ -to- $5d$ charge transfer occurs, changing the valence v of Sm. We assume now for the Sm and Y d electrons a common d band in the alloy. Then the d band occupation N coming from an originally divalent Sm will be $v-2$. On the other hand, each Y atom is expected to supply one electron to the d band. Then the average occupation numbers are given by

$$N_B(x) = (1-x)[v_B(x)-2] + x, \quad (3.1a)$$

$$N_S(x) = (1-x)[v_S(x)-2] + x. \quad (3.1b)$$

Experimental data¹⁷ for the bulk valence $v_B(x)$ are shown in Fig. 1(a).

At the surface of Sm metal, the $4f$ level has

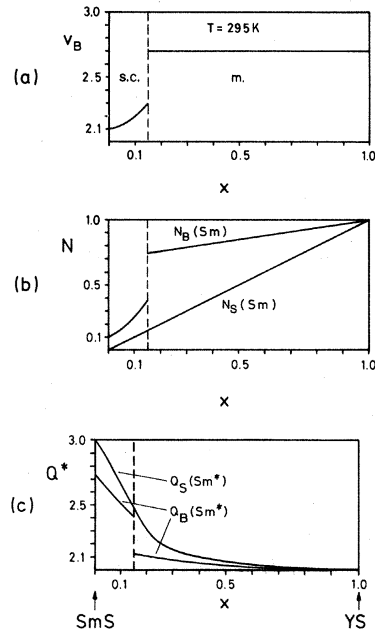


FIG. 1. (a) Experimental values for the Sm bulk valence $v_B(x)$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ from Ref. 17 (room-temperature data). (b) Ground-state t_{2g} subband occupation $N_{S(B)}$ (Sm) at the surface (in the bulk) as calculated using Eqs. (3.1a) and (3.1b). (c) Surface (bulk) ionic charge of core-excited Sm atoms $Q_{S(B)}(\text{Sm}^*)$ obtained from Eqs. (3.4a) and (3.4b).

been reported to shift towards higher binding energy. This suggests strongly that the surface of metallic Sm is divalent.^{4-6,16} The same $4f$ -level shift has been observed⁵ in SmS and SmYS at low Y concentrations and we assume therefore a divalent Sm surface here as well. Consequently, the filling $N_S(x)$ of the d band at the surface would only result from the Y atoms.

The t_{2g} occupation numbers $N_B(x)$ and $N_S(x)$, calculated from Eqs. (3.1a) and (3.1b), are shown in Fig. 1(b).

Consider now the core-excited Sm^* atom, where the ejected $4f$ photoelectron leaves a hole behind. Due to the low conductivity, practically only the d electrons already present at the Sm^* site will partially screen the hole. These electrons can be trapped in a localized state, which may be exciton-like, or these electrons may partially occupy the $4f$ hole. In both cases, the resulting d band occupation is zero:

$$N_B^*(x) = N_S^*(x) = 0. \quad (3.2)$$

Thus, the electronic part of the core-level shift in Eq. (2.11) will approximately reduce to

$$\Delta_e(\text{Sm}) = -\Delta E_e(\text{Sm}). \quad (3.3)$$

We assume here that Eq. (2.10) can also be applied, at least approximately, if locally $N_{B(S)} \rightarrow 0$. For the (100) surface of $\text{Sm}_{1-x}\text{Y}_x\text{S}$, we use the coordination numbers $z_S = 5$ and $z_B = 6$ in Eq. (2.10).

The above-mentioned localized electronic charge, which disappeared from the d band, will try to screen the core hole in the excited state. Owing to $N_{B,S} < 1$ this screening is incomplete. Hence, the resulting charge of the excited Sm^* atom $Q(\text{Sm}^*)$ will be larger than the positive ground-state ionic charge. Thus, one has

$$Q_B(\text{Sm}^*) = Q(\text{Sm}) + S_B(1 - N_B)e, \quad (3.4a)$$

$$Q_S(\text{Sm}^*) = Q(\text{Sm}) + S_S(1 - N_S)e. \quad (3.4b)$$

The positive surplus charge $(1 - N_{B,S})e$ that occurs is still expected to be partially screened by some itinerant d electrons from the immediate local neighborhood. This fact is described by the screening factors $S_{B,S}$ and will be discussed further in Sec. IV. Note that for an insulator $S_B = S_S = 1$. In the other extreme case of a metal, no unscreened surplus charge will occur, and $S_B = S_S = 0$.

As there is no simple way to determine S_B and S_S , we use them as the only free parameters to fit the experimental data.⁸ This procedure, however, does not define S_B and S_S uniquely. Note, howev-

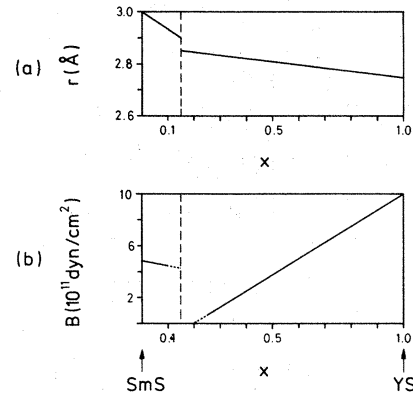


FIG. 2. (a) Nearest-neighbor distance $r(x)$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ from Ref. 17. (b) Bulk modulus $B(x)$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ from Ref. 18.

er, that the effective ionic charges $Q_{B,S}(\text{Sm}^*)$, calculated from Eqs. (3.4) and plotted in Fig. 1(c), are not greatly affected by the uncertainty in S_B and S_S because in those equations they are only weighting the small values $(1 - N_{B,S})e$.

Experimental data for the concentration-dependent bulk modulus¹⁸ $B(x)$ and the nearest-neighbor distance¹⁷ $r(x)$ in the ground state are shown in Fig. 2. For one core-excited Sm^* in the $\text{Sm}_{1-x}\text{Y}_x\text{S}$ host we do not expect a change of the nearest-neighbor distance or the bulk modulus. Therefore, we use

$$r^*(x) = r(x) \quad (3.5)$$

and

$$B^*(x) = B(x). \quad (3.6)$$

The width of the t_{2g} subband for $\text{Sm}_{1-x}\text{Y}_x\text{S}$ was obtained from linear interpolation between those of SmS (1.75 eV) and YS (3.0 eV) as done previously.¹⁹

Using the formulas of the preceding section with the above-described parameters, the surface core-level shift $\Delta_c^s(\text{Sm})$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ has been calculated as a function of the Y concentration and the results are presented in Fig. 3(a). To demonstrate the dependence of Δ_c^s on the surface valence of Sm, we show in Fig. 3(c) results for Δ_c^s as a function of the Sm surface valence v_S .

IV. DISCUSSION

The surface core-level shift Δ_c^s in mixed-valence systems has been studied. In general there are electronic and Madelung contributions to Δ_c^s . In cal-

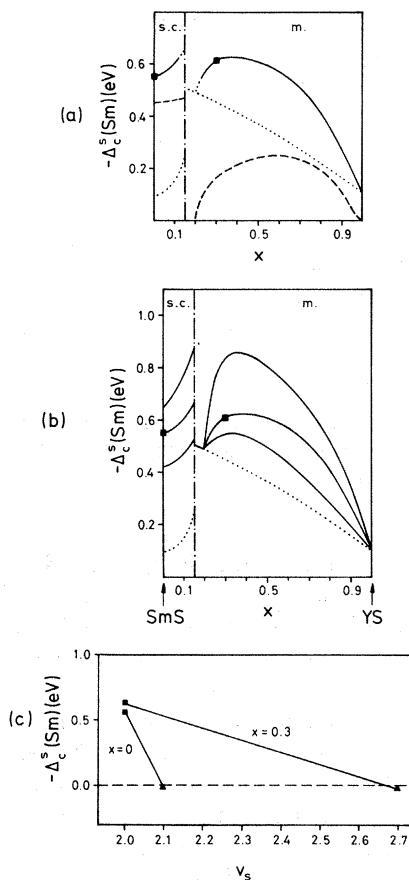


FIG. 3. (a) Numerical results for the surface core-level shift $\Delta_c^s(\text{Sm})$ in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ (solid line), the electronic contribution Δ_e (dotted line), and the Madelung contribution Δ_M (dashed line). Closed squares refer to experimental data for the $4f$ -level shifts; see Ref. 8. (b) $\Delta_c^s(\text{Sm})$ for three different sets of screening parameters $S_{B,S}$ (solid lines). The curve fitting the experimental data is taken from (a). The electronic shift Δ_e (dotted line) does not depend on the choice of $S_{B,S}$. (c) Dependence of $\Delta_c^s(\text{Sm})$ on Sm-surface valence v_s taken as a free parameter. The screening parameters $S_{B,S}$ have been kept constant for each of the Y concentrations. Closed squares and triangles refer to experimental data from Ref. 8 and to points of equal surface and bulk valence, respectively.

culating the electronic contribution Δ_e we assume atoms with an average valence v rather than an alloy of atoms with integer valence V and $(V+1)$. This should be valid if $\delta/W < 1$, where W is the d bandwidth and δ the electronic energy change due to fluctuations in the number of d electrons per atom. Our numerical results refer to Δ_c^s of Sm atoms in the Sm^{2+} state. Figure 3(a) indicates that the electronic and the Madelung contribution to the total surface core-level Δ_c^s are comparable in

magnitude. The shape of Δ_c^s , however, is predominantly determined by the variation of Δ_M . The relatively small Δ_e for small x can be attributed to the small occupation of the common d band; see Fig. 1(b). The results for Δ_e in the whole concentration range are expected for a d band which is occupied by less than one electron. For example, this may be seen from the contribution of d electrons to the cohesion of transition metals. On the other hand, Δ_M is determined by the ionic bond energies which in the case of relatively poor screening are more than one order of magnitude larger than the electronic energy.

In Fig. 3(a) we observe abrupt changes in Δ_e and Δ_M at $x=0.15$. These are caused by discontinuities in the input parameters at the metal-semiconductor transition point; see Figs. 1 and 2. However, note that these discontinuities, in particular for B , are experimentally not too well known [which is indicated by the dashed part of the B curve in Fig. 2(b)]. Thus, close to the critical concentration our results would change if these discontinuities are weaker or replaced by continuous changes. We also observe an increase in magnitude of Δ_e for increasing Y concentration when crossing the transition point. This results from the increasing d band occupation. The slight decrease of Δ_e for the $x > 0.15$ is caused by a decreasing difference in the surface and bulk d band occupation; see Fig. 1(b) and Eq. (2.10).

The Madelung part Δ_M experiences a more irregular behavior. For $x < 0.15$, the decrease in the nearest-neighbor distance $r(x)$ [see Fig. 2(a)] compensates the decrease of the bulk modulus $B(x)$ in Eqs. (2.14) and (2.15). For $0.2 < x < 0.4$ the increase in magnitude of Δ_M is caused by both the increase of $B(x)$ and decrease of $r(x)$ (see Fig. 2), which turns out to be more important than the increasingly better screening of the ionic charge; see Fig. 1(c). When the explosive metal-semiconductor transition takes place at $x=0.15$ at room temperature, the bulk modulus may vanish and may then cause an abrupt drop to zero of the Madelung shift Δ_M . This discontinuity is also reflected in the total core-level shift Δ_c^s . It is of interest to check experimentally this behavior near the critical point $x=0.15$. For $x > 0.4$ the surface core-level shift is expected to decrease continuously and, eventually when x is close to 1, to be determined by its electronic contribution Δ_e . As can be inferred from Fig. 3(a), this behavior is mainly due to the strong decrease of the Madelung part Δ_M which even vanishes for $x=1$. This limiting case corresponds to

the situation when finally only few Sm ions are left as substitutional impurities in a YS host crystal. According to its electronic transport properties YS behaves as a simple monovalent metal,²⁰ so that for our screening parameters we have to take $S_B = S_S = 0$ which means full metallic screening. For higher Y concentrations the Δ_c^s curve was evaluated by making a linear interpolation for the screening parameters between $x = 0.3$ (highest x value for which Δ_c^s has been measured so far) and the limiting concentration $x = 1$. This means that for higher Y concentrations the proposed Δ_c^s curve should be understood from a more qualitative than quantitative point of view.

The dependence of our numerical results on the screening capacity of the d electrons is of particular interest. In the present calculation it has been assumed that Sm and Y d electrons share a common d band. A feeling for the dependence of the core-level shift on this assumption is obtained as follows. As a limiting case we assume that Y keeps its d electrons and only induces internal lattice pressure due to its smaller atomic size. Then in Eqs. (3.1a) and (3.1b) the last terms must be omitted in order to obtain the appropriate values for the d band occupation numbers. No other modifications are necessary except for keeping the bandwidth constant at its SmS value. Using the same values for the screening parameters S_B, S_S as above, only a very minor deviation is obtained from our result in Fig. 3(a). From a physical point of view we can think that the Y atom contribution to the binding energy of Sm in $\text{Sm}_{1-x}\text{Y}_x\text{S}$ will be the same at the surface and in the bulk and will approximately cancel in the difference in Eq. (2.3). Hence, the electronic properties of Y seem to be only of minor importance for the surface core-level shift of Sm in $\text{Sm}_{1-x}\text{Y}_x\text{S}$, at least for Y concentration lower than 0.5. The qualitative features of $\Delta_c^s(\text{Sm})$ as a function of x are determined rather by the $4f-5d$ hybridization at the Sm site and the changes in the interatomic distance than by the influence of Y on the electronic structure.

Taking the curve in Fig. 3(a) as a reference we further show in Fig. 3(b) how the values of Δ_c^s change if the screening of the core hole is approximately half as strong (upper curve) or twice as efficient (lower curve) as in Fig. 3(a). Further experiments, however, are needed to learn more about the screening of the core hole at Sm^* .

Another important point is the dependence of $\Delta_c^s(\text{Sm})$ on the surface valence of Sm. Following Lang and Williams²¹ the surface core-level shift

can be decomposed into a chemical, relaxational, and configurational part. This last contribution arises because of the different electronic configurations (here, different valence) for surface and bulk atoms. We can investigate the importance of the configurational surface core-level shift by artificially changing the valence v_S of the surface Sm atoms towards their bulk valence v_B . The results for $\Delta_c^s(\text{Sm})$ as a function of v_S are presented in Fig. 3(c). In this calculation v_S has been treated as the only free parameter which varies between 2 and v_B for a given concentration. Note, that we expect only a very small surface core-level shift if the surface valence were equal to the bulk valence. Thus, we conclude that the observed core-level shift is dominated by its configurational part. Hence, if the exact values for the screening parameters $S_{B,S}$ were known in our theory, it should be possible to extract the surface valence from photoemission data. This means a new promising application of the core-level shift spectroscopy.

In the following some critical remarks are made concerning the approximations used in setting up our theory. Consider first the choice of parameters in the Madelung shift Δ_M . We have already pointed out the possibly irregular behavior of B near the metal-semiconductor transition point at $x = 0.15$ and discussed the consequences for the surface core-level shift in Fig. 3(a). The bulk modulus $B(x)$ enters in the core-repulsion terms $1/m(x)$ and $1/m^*(x)$ of the Madelung energy and affects Δ_M , especially for small values. For a large atomic number such as that of Sm, the core repulsion is not expected to change much in the excited state with one core hole. Therefore, the bulk modulus $B^*(x)$ in the excited state is believed to keep its ground-state value $B(x)$ even locally [Eq. (3.6)]. Another critical remark refers to the nearest-neighbor distance $r^*(x)$ in the excited state. Clearly, for an unscreened final state the trivalent Sm^{3+} ion would prefer a distance to nearest-neighbor sulfur which is smaller than for the divalent Sm^{2+} . We neglect, however, such a lattice relaxation, as the photoemission process is several orders of magnitude faster compared to typical phonon frequencies. Therefore, as a good approximation we set $r^*(x)$ equal to $r(x)$. Further we discuss the screening parameters S_B and S_S , which are obtained from fitting the experimental data⁸. Although their proper choice is somewhat arbitrary, the values for $S_{B,S}$ for $x < 0.5$ are found to be in the physically plausible region between 1 and 0.3, decreasing with enhanced metallic character of the

compound. Also, for a given Y concentration, the ratio S_B/S_S is approximately constant, increasing from 0.8 at $x=0$ to 0.95 at $x=0.3$. This points to a better screening of the core-hole at the surface towards the metallic regime. As has been mentioned earlier, $S_{B,S} < 1$ accounts for a possible charge transfer to the Sm^* atoms from neighboring metal atoms. This supplementary negative charge is supposed to screen the hole in addition to the d band electrons which are locally available at the excited atoms. From another point of view $S_{B,S} < 1$ can be taken as phenomenological parameters describing the increasing polarizability of the electron gas in case of higher Y concentrations. A point of great importance in the discussion of the Madelung shift Δ_M is the dependence of the binding energy of surface atoms on the surface structure. While the empirical rule¹⁶

$$E_{M,S}(Z) = 0.8E_{M,B}(Z) \quad (4.1)$$

has proven useful in calculating the Madelung energy at a general surface, minor deviations from 0.8 may be expected for well-defined single-crystal surfaces.

Finally, we make some comments concerning the electronic shift Δ_e . Clearly, Δ_e depends not only on the bandwidth and the occupation number, but also on the actual band shape which we approximated by a rectangle. It is, however, instructive to note that similar calculations, performed for a parabolic (t_{2g} subband) and a fourth-order parabolic (whole d band) density of states, differed from the rectangular approximation by typically less than 0.1 eV. This is indeed much less than the observed $\Delta_c^s(\text{Sm})$ values. At this point we also want to stress again that the $4f$ band contribution to the electronic binding energy in Eq. (2.10) can be safely neglected as compared to the $5d$ contribution. Even near the metal-semiconductor transition, where the f electron contribution should be maximal, this would be 2 orders of magnitude smaller than the corresponding d band contribution to Δ_e .

Our last remark concerns a possible change in Δ_e caused by a charge transfer from the neighboring metal atoms towards the excited site which we mentioned while discussing the screening parameters $S_{B,S}$. These supplementary d electrons are expected to be confined to localized bound states below the Fermi-level rather than to populate the d band which furthermore remains empty. Thus, we

still expect zero electronic contribution to the binding energy for the core-excited atom.

Until now we have been discussing surface core-level shifts only for SmYS , which is one of the few mixed-valent systems studied fairly completely. However, it is evident that our theory is quite general so that it should be applicable to other mixed-valent materials as well. For those systems where the photoexcited $4f$ final states are not fully screened, one expects a considerable Madelung-type contribution to the surface core-level shift. This is certainly the case if the initial-state occupation numbers N_B, N_S per metal atom for the d conduction band are smaller than one and should be the case for rare-earth monochalcogenides²² such as $\text{Sm}_{1-x}\text{R}_x\text{S}$ ($R = \text{Ce, Pr, Gd, Tb, Dy, Ho}$) which show similar behavior as $\text{Sm}_{1-x}\text{Y}_x\text{S}$. Also for Sm monopnictides (e.g., $\text{SmS}_{1-x}\text{As}_x$ and $\text{SmS}_{1-x}\text{P}_x$), and for the Tm pnictide $\text{TmTe}_{1-x}\text{Se}_x$ we expect significant Madelung-type contributions. In these and similar systems bulk and surface valence changes can be induced by varying the sample's stoichiometry. In mixed-valent systems with considerable ionicity in their binding character, such as $\text{CeN, SmB}_6, \text{TmSe}$, the Madelung contribution to the surface core-level shift should be particularly large. In contrast, in mixed-valent alloys such as YbAl_2 , etc., we assume that the electronic contribution to the surface core-level shift is dominant.

In summary, we presented a simple microscopic theory for the surface core-level shifts in mixed-valent systems which we applied to $\text{Sm}_{1-x}\text{Y}_x\text{S}$. We obtain good agreement with experimental results. Our calculations can also be applied to other mixed-valent compounds. This work should be extended to a parameter-free calculation which would allow to determine the surface valence from photoemission data.

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