PHYSICAL REVIEW B VOLUME 26, NUMBER 6 15 SEPTEMBER 1982

Valence instability of the samarium metal surface

Anders Rosengren
Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

Börje Johansson
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 28 December 1981)

The stability of the surface of the samarium and thulium metals against a divalent state is investigated within the pair-bonding model. Thereby it is found that a divalent surface is favored in samarium and close to becoming stable in thulium. The position of the surface divalent samarium f^6 level relative to the Fermi energy is calculated and compared with experiments. Also the surface core-level shifts for the europium and ytterbium metals are considered. Finally some interesting possible physical consequences of the divalent samarium surface layer are pointed out.

I. INTRODUCTION

The rare-earth elements and their compounds have been studied intensively during the last decade. One reason for this is the discovery of a new type of ground state, the so-called mixed- or intermediate-valence state. This state has now been observed in many rare-earth systems, of which SmS probably is the most well-known example.[1] The fundamental origin of this state is that two configurations $4f^{n+1}V^2$ and $4f^nV^3$ of the rare-earth atom (where V stands for the valence electrons), depending on the chemical surroundings, may be brought so close in energy that the ground state has to be described quantum mechanically as a superposition of these configurations. One popular way to probe this "mixed" state has been to use x-ray photoelectron spectroscopy (XPS). The spectra so obtained show peaks originating from both divalent (f^{n+1}) and trivalent (f^n) initial configurations and the intensities of these peaks are often used to derive a value of the degree of valence mixing for the material in question. The phenomenon of mixed valence was only detected in compounds and alloys[2] and it therefore caused some excitement when the $4d$ spectrum of Sm metal showed peaks attributable to both Sm^{2+} and Sm^{3+},[3(a)] and claims were made that Sm metal was in a mixed-valence state (see, e.g., Ref 4). However, the question remained whether the observed divalent signal originated from bulk or surface samarium atoms.[3(a)]

In view of the facts that the trivalent metallic state of samarium is energetically favored relative to the divalent state by about 6 kcal/mol,[5,6] and that the bulk properties of samarium closely follow those of the other trivalent rare-earth metals and intra-rare-earth alloys,[5] the interpretation that bulk samarium metal is in a mixed-valence state seemed unlikely. It was therefore suggested[7] that the presence of the divalent peak in the XPS spectrum was exclusively a *surface effect,* i.e., at the surface the conditions are such that the divalent state is favored. This conjecture was subsequently strongly supported by new, surface-sensitive XPS measurements by Wertheim and Crecelius,[8] who studied both the $3d$, the $4d$, and the conduction-band region. By tilting the surface normal of the sample away from the direction of electron collection they could from the $3d$ and $4d$ spectra show that the Sm^{2+} signal originated from the surface region. However, the question then arose whether this divalent samarium signal was an initial-state surface feature of a final-state, charge-transfer satellite. This latter discrimination can be made on basis of the $4f$ spectra, since they are not accompanied by satellites.[3(a),3(b)] The presence of the $4f^6V^2$ initial state near E_F (the Fermi energy) was only detected in Ref. 8 by a uniform increase of the intensity of the valence-band region relative to the $+3$ intensity with increasing takeoff angle. A somewhat safer identification of the presence of divalent samarium atoms at the surface was made by Allen *et al.*,[9,10] who compared partial-yield spectra of different surface sensitivities to a bulk absorption spectrum. The energetics of the samarium surface was also investigated theoretically[11] and it was demonstrated that a divalent surface layer should be favored relative to a trivalent one. A direct XPS observation of the $4f^6 \rightarrow 4f^5$ transition at the surface was then reported by Lang and Baer.[12] They found the binding energy of the $4f^6$ level to be 0.77 ± 0.25 eV relative to the Fermi energy, which is in good agreement with the value of 0.65 eV measured by Allen *et al.*[10] Lang and Baer also reported BIS (bremsstrahlung isochromate spectroscopy) experiments for the reverse transition $f^5 \rightarrow f^6$ for bulk atoms, and obtained that the energy position for the unoccupied f^6 level is 0.46 ± 0.2 eV above the Fermi level. In the first papers concerning this problem for the samarium surface it was believed that the surface atoms were in an intermediate-valence state.[8,9] However, the later found large value for the binding energy of the divalent f^6 component makes this unlikely. From the measured angular dependence of the relative ratio between the intensities of the divalent and trivalent $3d_{5/2}$ levels, Wertheim and Crecelius[8] concluded that only about 40% of the surface atoms were in a divalent phase. With the recent finding of the strong binding of the divalent samarium f^6 level this would now imply an *inhomogeneous* valence mixture at the surface.[10,12] It should be noted, however, that the divalent samarium atoms are considerably larger than the trivalent ones. Thus the number of divalent samarium atoms needed to cover the same surface area as covered by trivalent atoms is quite significantly reduced (by about 25%), which to some extent might explain the observed relatively low intensity of the divalent surface signal. However, and probably more important, in the experiments the surface was obtained by evaporating samarium onto a substrate[8] and therefore the surface is likely to have been rather rough and the experimental results might not faithfully reflect the properties of an atomistically planar surface. In the surface-sensitive experiments by Allen *et al.*[10] an (inhomogeneous) valence mixture with an average valence of about 2.7 was derived. In this case a photoemission spectrum taken at 135 eV was compared with a corresponding one for SmB_6. Assuming that the surface valence state of SmB_6 is the same as in the bulk, namely 2.7, the valence value for the samarium-metal surface was obtained. However, in view of the drastic disturbance produced by a surface, the assumption of the same valence mixture at the surface as in the bulk for SmB_6 seems unjustified.[13] Furthermore, in these experiments SmB_6 was a polycrystalline sample while for the samarium metal an evaporated film was used. Therefore, also here, it is not clear to what extent the results are fully representative for an ideal samarium surface. (See *Note added in proof.)*

It is rather surprising that the divalent f^6 configuration is situated so far below the Fermi level (~ 0.7 eV). This position seems to imply that the divalent state has become very stabilized at the surface. In fact, at first sight, a homogeneously mixed-valence state might have appeared to be more likely, i.e., a state where the f^6 level coincides with the Fermi energy. As already mentioned, from the BIS experiment it was found that the energy for the bulk $f^5 \rightarrow f^6$ transition is about 0.5 eV. This in conjunction with the XPS surface measurement implies a surface core-level shift (SCS) of the f^6 level of about $0.5 + 0.7 = 1.2$ eV towards higher binding energy (notice that we here consider the shift between an *unoccupied* f^6 bulk level and an *occupied* f^6 surface level). This SCS is about a factor of 2 larger than expected theoretically for a normal surface core-level shift.[14] There is, however, a distinct difference between the present case of samarium and a normal type of surface core-level shift, namely that for the samarium surface there is a macroscopic number of atoms which have turned over into the divalent state. Therefore the surface $f^6 \rightarrow f^5$ transition (XPS) occurs in an environment which is very different from that of a bulk samarium atom on which the $f^5 \rightarrow f^6$ transition (BIS) takes place. Thus, rather than to show a normal value for the SCS (i.e., of about $0.5 - 0.6$ eV), which would have given an f^6 level close to the Fermi energy and a possiblity for a homogeneously mixed-valence state, the transition at the samarium surface seems instead to be of the first-order type.

The main purpose of the present work, besides demonstrating the stability of the divalent samarium surface, is to investigate how the phase change at the surface influences the energy position of the divalent f^6 level and to try to rationalize its experimentally found high binding energy, i.e., to account for the abnormally large SCS of the f^6 level. In this connection we also study the corresponding valence problem for thulium. There are two essential assumptions underlying the theoretical treatment performed. The first one is that if an f electron is photoemitted, the final state will be completely screened. This means, e.g., that in case the f electron is emitted from a Sm^{2+} ion we can treat the final state as a fully screened Sm^{3+} ion. This *impurity* picture of the final state was used by us in an investigation of the occurrence of mixed valence in europium metal under pressure,[15,16] and has been successfully applied for calculating both XPS and BIS excitation energies for all the rare-earth metals,[17,18] for calculating the shift in binding energy of core electrons in metals relative to the free atom,[14] and for calculating the shift in binding energy of core electrons for surface atoms relative to bulk atoms (surface core-level shifts).[14,19,20] The impurity picture has also been used to derive surface heat of segregation from surface core-level shifts[21,22] and also to obtain the heat of formation of alloys from chemical shifts.[23,24] The other assumption, or rather approximation, we have used is that the total configurational energy of our system can be written as a sum of interaction energies between nearest-neighbor atom pairs only. The reason we resort to a pair-bonding approach, instead of using direct information from thermochemical data, is that in the present case we would need thermodynamic entities not presently known experimentally. What we have in mind are, for example, different kinds of heats of solutions which a pair-bonding approach allows us to relate to each other. Furthermore, the simplicity of the pair-bonding model provides a rather direct and straightforward picture of the physics involved, namely the interplay between on one hand the gain of bonding energy in the trivalent state relative to the divalent one, and on the other the gain of binding energy of the localized nonbonding f electron in the divalent state.

In Sec. II we introduce the model. The calculations for samarium are presented in Sec. III, where the surface valence of thulium is also investigated. The surface core-level shifts in europium and ytterbium are treated in this section as well. The last section, Sec. IV, contains a discussion and some remarks on certain aspects of the unique properties of samarium metal and its surface.

II. THE MODEL

As was stated in the Introduction, the assumption of a fully screened final state in the XPS and BIS experiments is essential for the following treatment. This is what allows us to treat, e.g., the final f^6 state in a bulk samarium BIS experiment as a divalent samarium impurity dissolved in an otherwise trivalent host. The use of the pair-bonding approach gives us the possibility to go beyond the treatment undertaken by Herbst *et al.*[18] and Johansson[17] in that those papers only compare energies between completely trivalent and completely divalent metals. Therefore they neglect the last step which has to be taken to arrive at the BIS experiment final state, namely the solution of a divalent metal impurity in the trivalent host, although this impurity effect was discussed by Johansson.[17]

The total configuration energy in the pair-bonding model may be written as a sum of interaction energies of nearest-neighbor atom pairs. In our calculation we will deal with two kinds of atoms, Sm^{2+} and Sm^{3+} (called A and B, respectively, for brevity in the equations). We consider a semi-infinite system, the surface of which is assumed to be atomistically planar. This system is divided into layers parallel to the planar surface, the layers being numbered with the index λ ranging from zero to infinity, with $\lambda=0$ being the surface layer. If we let $N_{ij}^{\lambda\mu}$ be the total number of nearest-neighbor (NN) pairs in which an atom of type i lies in the λth layer and an atom of type j in the μth layer and if ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} are the bond enthalpies for NN pairs of A and/or B atoms, the total configuration energy can be written as[25]

$$\begin{aligned}U=\sum_{\lambda=0}[&\epsilon_{AA}(N_{AA}^{\lambda\lambda}+N_{AA}^{\lambda\lambda+1})\\&+\epsilon_{AB}(N_{AB}^{\lambda\lambda}+N_{AB}^{\lambda\lambda+1}+N_{BA}^{\lambda\lambda+1})\\&+\epsilon_{BB}(N_{BB}^{\lambda\lambda}+N_{BB}^{\lambda\lambda+1})]\ .\end{aligned}\tag{1}$$

Numerical values for the bond-energy parameters ϵ_{AA} and ϵ_{BB} are obtained from cohesive energies. For the hypothetical divalent samarium metal we can with high accuracy use the cohesive energies for barium, europium, and ytterbium[26] for interpolation and thereby we obtain 43.0 kcal/mol for its divalent cohesive energy. In the pair-bonding scheme the bond enthalpy for trivalent samarium has the trivalent atomic state as reference level and the corresponding appropriate cohesive energy is 105 ± 1 kcal/mol.[27] Thus ϵ_{AA} and ϵ_{BB} are simply obtained from the relations (in units of kcal/mol)

$$\begin{aligned}(Z/2)\epsilon_{AA}&=-43\ ,\\(Z/2)\epsilon_{BB}&=-105\ ,\end{aligned}\tag{2}$$

where Z is the bulk coordination number. Using the value of 55.7 kcal/mol for the excitation energy[27] of the divalent (A) atom f^6s^2, to the appropriate trivalent atomic state (B) f^5ds^2, we find for the energy difference between the hypothetical bulk divalent samarium metal and the actual trivalent one, $\Delta H_{\mathrm{II,III}}$, the value

$$\Delta H_{\mathrm{II,III}}=43+55.7-105\simeq-6.3\ ,\tag{3}$$

in units of kcal/mol. Thus the trivalent state is stable by 6.3 kcal/mol relative to the divalent metal.

In order to arrive at ϵ_{AB}, which is related to the heat of solution of an A impurity in a B host, we could in principle resort to the empirical scheme of Miedema and coworkers,[28,29] because experimental data are lacking in this case. But since the uncertainty of this scheme is unknown for the present case, we have instead chosen to use the BIS experiment for determining ϵ_{AB}. In the BIS experiment for bulk samarium one starts from the B metal and from the complete screening picture of the excitation one ends up with a final state where one B atom (f^5) has been transformed into an A atom (f^6). This gives immediately the following relation (using 1 eV/atom $=23.05$ kcal/mol):

$$-Z\epsilon_{BB}-55.7+Z\epsilon_{AB}=0.46(23.05)\ , \tag{4}$$

where 0.46 ± 0.2 eV is the value for the BIS excitation measured by Lang and Bear.[12] Thus we find $Z\epsilon_{AB}=-143.7$ kcal/mol. The left-hand side of Eq. (4) can be written in a more transparent form as

$$\begin{aligned}-Z\epsilon_{BB}-55.7+Z\epsilon_{AB}&=-(Z/2)\epsilon_{BB}+(Z/2)\epsilon_{AA}+Z[\epsilon_{AB}-(\epsilon_{AA}+\epsilon_{BB})/2]-55.7\\&=E_{\text{coh}}(B)-E_{\text{coh}}(A)-E_A^{\text{imp}}(B)-55.7\ ,\end{aligned} \tag{5}$$

where $E_{\text{coh}}(B)$, $E_{\text{coh}}(A)$, and $E_A^{\text{imp}}(B)$ are the cohesive energy of trivalent samarium metal (relative to the appropriate trivalent atomic configuration), the cohesive energy of hypothetical divalent samarium, and the energy of dissolving a divalent (A) samarium metallic impurity in the trivalent (B) host, respectively. From this we find that $E_A^{\text{imp}}(B)=4.3$ kcal/mol. The positive value here means that A will not dissolve in B, which is gratifying since it is known that the divalent rare-earth metals europium and ytterbium do not form solid solutions or alloys with the trivalent rare earths.

It should be noted, however, that the BIS experiment refers to a vertical excitation, i.e., there is no relaxation of the lattice positions of the surrounding atoms. In a thermodynamic situation the neighboring atoms of the A atom impurity will adjust their positions in order to minimize the energy. This means that the corresponding value for the thermodynamic ϵ_{AB} bond will be somewhat smaller (more negative) than the one derived from the BIS experiment.

Having defined the model and its parameters we will in the next section consider various physical situations of interest in the present context of the samarium surface. At the same time we will also investigate the corresponding surface problem for the thulium metal. The other rare-earth metals are much less likely to show a valence change in their most stable surface planes.[11]

III. CALCULATIONS

A. Stability of a divalent surface

We now first turn to the question if a completely trivalent samarium crystal is energetically stable against a crystal state where the surface layer consists of divalent samarium and the rest of the system remains trivalent. A fact which has to be recognized is that the divalent samarium ions are considerably larger than the trivalent ones, meaning that the surface-layer density will be *lower* than the bulk-layer density. Thus the number of surface atoms for a divalent surface will be less than it is for the corresponding trivalent one. Therefore if we want to make an energy comparison of the two states defined above, this means that for the case of a divalent surface layer we have to transport the "missing" surface atoms to the bulk, since the energy comparison has to be made with the total number of atoms fixed. If we denote the number of atoms in the surface layer and in a bulk layer by N_2 and N_3, respectively, their ratio α is (assuming the divalent surface-layer density will be the same as for hypothetical pure divalent samarium metal),

$$\alpha=N_2/N_3=(19.95/30.0)^{2/3}\approx0.76\ , \tag{6}$$

where 30.0 cm^3/mol is the atomic volume interpolated for hypothetical divalent samarium and 19.95 cm^3/mol is the experimental atomic volume for trivalent samarium metal.[5]

Another question related to this difference in atomic size between divalent and trivalent atoms is how to define the number of bonds between the divalent surface layer and the trivalent first layer N_{AB}^{01}. Since the surface layer due to this size difference is incommensurate with the underlying bulk layers, we face a problem. If Z_{LL} and Z_{IL} denote the number of nearest neighbors of an atom in the same layer and in the underlying layer, respectively, it is clear that the $N_{ij}^{\lambda\mu}$'s of Eq. (1), except for N_{AB}^{01}, can be expressed in terms of N_2, N_3, Z_{LL}, and Z_{IL}, e.g., N_{AA}^{00} for the divalent surface is equal to $N_2Z_{LL}/2$. The problem we have to consider in the incommensurate or nonregister situation is how to define the number of "vertical" nearest neighbors, or rather a mean value of this quantity. In the commensurate situation, i.e., with the divalent atoms squeezed so much together that their lattice parameters in the surface plane exactly fit those of the underlying layer, N_{AB}^{01} is simply equal to $N_3 Z_{IL}$.

In order to obtain an estimate of the value for N_{AB}^{01} in the incommensurate situation, we first represent the point density in the plane $\lambda=0$ by a function h_0 to be specified below. Each atom in plane $\lambda=0$ has in plane $\lambda=1$ (in the commensurate situation) three NN situated at the corners of an equilateral triangle, the center of gravity of which is situated right below the atom considered in plane $\lambda=0$. This center-of-gravity point density in plane $\lambda=1$ is represented by a function h_1. For the case of an fcc (111) surface we chose h_0 and h_1 to have the following forms:

$$\begin{aligned} h_0 &= \cos^2(\pi x/a_2)\cos^2(\pi y/a_2\sqrt{3}) \\ &\quad + \cos^2[\pi(x+a_2/2)/a_2] \\ &\quad \times \cos^2[\pi(y+a_2\sqrt{3}/2)/a_2\sqrt{3}]\,, \\ h_1 &= \cos^2(\pi x/a_3)\cos^2(\pi y/a_2\sqrt{3}) \\ &\quad + \cos^2[\pi(x+a_3/2)a_3] \\ &\quad \times \cos^2[\pi(y+a_3\sqrt{3}/2)/a_3\sqrt{3}]\,. \end{aligned} \tag{7}$$

Here $a_2\sqrt{2}$ and $a_3\sqrt{2}$ are the fcc lattice cube edges for the surface and the first layer, respectively. Thus h_1 has now been generalized to the incommensurate case. The fact that we have chosen to perform the calculations for an fcc (111) surface will be commented upon later. In case we have the first situation with the planes $\lambda=0$ and $\lambda=1$ commensurate, we can get a measure of the number of nearest-neighbor pairs consisting of A atoms in layer 0 and B atoms in layer 1, by performing the "overlap" integral I_C,

$$\begin{aligned} I_C &= \int_0^{a_3(N_3)^{1/2}} dx \int_0^{a_3(N_3)^{1/2}3^{1/2}} dy\, h_0 h_1 \\ &= \int\int dx\, dy\, h_0^2\,, \end{aligned} \tag{8}$$

where in the last step we have utilized, the fact that for this case, h_1 is identical to h_0. In the incommensurate case we have instead to perform the integral in Eq. (8) with h_0 and h_1 as defined in Eq. (7). This integral will then be denoted by I_{IC}. For the commensurate integral I_C we immediately get the result $I_C=(\frac{5}{16})N_3 a_3^2\sqrt{3}$. That is, I_C divided by a_3^2, which is a measure of the width of cosine density distribution peaks, is proportional to $N_3 Z_{IL}$. Evaluation of the incommensurate integral gives

$$I_{IC}=(\tfrac{1}{4})N_3 a_3^2\sqrt{3}=(\tfrac{1}{4})\sqrt{N_2 N_3}\,a_2 a_3\sqrt{3}\,,$$

where in the last step we have used the fact that the surface area is proportional to $N_3 a_3^2$ or $N_2 a_2^2$ with the same proportionality constant, i.e., it holds that $\sqrt{N_3}a_3=\sqrt{N_2}a_2$. Once again dividing by an appropriate measure of the widths of the cosine peaks $a_2 a_3$ and multiplying with the proportionality constant derived from the commensurate case gives $N_{AB}^{01}=(\frac{4}{5})\sqrt{N_2 N_3}Z_{IL}$. At first sight it might seem somewhat astonishing that the integral I_{IC} is independent of the difference in phase between the two surface planes. Instead, one might have suspected that a small difference in phase would have resulted in a higher value of this integral than with a larger difference in phase, and that when the phase difference becomes smaller and smaller the value of the integral would approach its value for the commensurate phase. This very sharp distinction between the commensurate and the incommensurate situations, and the independence of phase difference, can, however, be understood when one considers the fact that the integrals are extended over an infinite surface. Therefore, when the phase difference is small, the large regions, where the two lattices are "almost" commensurate, will be compensated by equally large regions, where the two lattices are "almost" completely out of phase.

Thus we find that the quantity N_{AB}^{01} is reduced in the incommensurate situation by the factor

$$\beta=I_{IC}/I_C=(\tfrac{4}{5})\sqrt{N_2/N_3}$$

relative to its value of the commensurate case $N_3 Z_{IL}$, the latter being the situation usually encountered in applications of pair-bonding theory.

Now having defined N_{AB}^{01} we return to the question we first addressed; namely, if a pure trivalent samarium crystal is energetically stable against a samarium crystal with a top layer of divalent samarium atoms. The energy of the completely trivalent crystal will be called U_0 and the energy of the samarium crystal with the divalent top layer will be denoted by U. From Eq. (1) we can write the energy difference $U-U_0$ as (remembering that the total number of atoms in both situations has to be the same)

$$U-U_0=\epsilon_{AA}N_{AA}^{00}-\epsilon_{BB}N_{BB}^{00}+\epsilon_{AB}^{IL}N_{AB}^{01}-\epsilon_{BB}N_{BB}^{01}-N_2(55.7)+(N_3-N_2)\epsilon_{BB}(Z/2)$$

$$=\epsilon_{AA}N_2(Z_{LL}/2)-\epsilon_{BB}N_3(Z_{LL}/2)+\epsilon_{AB}^{IL}\beta N_3Z_{IL}-\epsilon_{BB}N_3Z_{IL}-N_2(55.7)+(N_3-N_2)\epsilon_{BB}(Z/2)\ . \qquad (9)$$

The last term in this expression originates from the fact that the surface layer for the divalent surface contains only N_2 atoms, due to the larger size of these atoms. Therefore, in order to compare with the trivalent surface with N_3 atoms, and keeping the total number of atoms fixed, the system with a divalent surface must instead contain N_3-N_2 more bulk atoms. The factor β is the reduction factor for the number of vertical NN bonds for the incommensurate situation as derived above. Equation (9) can be understood as follows: If we start from the completely trivalent crystal, the second and fourth terms describe the energy it will cost to take away the topmost layer of metallic B (trivalent) atoms and separate them into free B atoms with an appropriate trivalent atomic configuration ($4f^5 5d^1 6s^2$). The term preceding the last term accounts for the gain in energy when we let N_2 of these N_3 free B atoms change their atomic configuration from $4f^5 5d^1 6s^2$ to $4f^6 6s^2$. The so obtained N_2 (divalent) A atoms are then brought to crystallize on top of the crystal; the gain in energy of this process is described by the first and the third term in Eq. (9). After this we let the remaining N_3-N_2 free B atoms (with the atomic configuration $4f^5 5d^1 6s^2$) crystallize as B metallic bulk atoms, gaining the energy described by the last term of Eq. (9).

Since the number of vertical bonds are reduced for the divalent surface by the factor β, there will be a tendency to somewhat compensate for this by making the remaining bonds stronger. Therefore we renormalize the vertical AB bonds in this case by

$$\epsilon_{AB}^{IL}=\epsilon_{AB}(1+\delta_{AB}^{IL})\ ,$$

where $\delta_{AB}^{IL}=0.1$ should be a reasonable choice. The last entities to be specified in Eq. (9) are now Z_{LL}, Z_{IL}, and Z. We perform here the calculation for the most densely packed surface of the fcc structure, the (111) surface, where Z_{LL}, Z_{IL}, and Z are 6, 3, and 12, respectively. In reality, samarium crystallizes in a hexagonal-type structure[30] but we note here that for the hcp (0001) surface with an ideal axial ratio the different Z numbers will be the same as for the fcc (111) plane. Since for the samarium crystal structure the effective c/a axial ratio is 1.61, this is a most reasonable substitution. Also the functions h_0 and h_1 of Eq. (7) will be the same. That we use the most dense surface fcc (111) or hcp (0001) is natural since they have the lowest surface energies. Equation (9) can now be rewritten as

$$U-U_0=N_3\alpha\{3[\epsilon_{AA}+\epsilon_{AB}(1+\delta_{AB}^{IL})\beta\alpha^{-1}]-55.7-6\epsilon_{BB}\}\ . \qquad (10)$$

With the bond parameters defined in Sec. II we find that

$$(U-U_0)/N_3=-0.28$$

in units of eV/atom. This means that a divalent surface on top of the trivalent samarium crystal is stable against the completely trivalent samarium crystal.

B. Position of the f^6 level

We now turn to the question of the position of the f^6 level, i.e., the energy of the $4f^6V^2 \rightarrow 4f^5V^3$ transition at the surface. The initial state, with energy U, is the trivalent bulk crystal covered with a divalent layer. The final state, with energy U', is the same except for that one of the divalent atoms in the surface layer is replaced by a trivalent atom. Straightforward application of Eq. (1) leads to

$$U'-U=Z_{LL}(\epsilon_{AB}-\epsilon_{AA})+Z_{IL}[\epsilon_{BB}-\epsilon_{AB}(1+\delta_{AB}^{IL})]\beta\alpha^{-1}+55.7\ . \qquad (11)$$

This gives $U'-U=0.65$ eV, which is in good agreement with the experimental values 0.77 ± 0.25 eV (Ref. 12) and 0.65 eV.[10] The main point here is that the reconstruction at the surface to a divalent layer brings the f^6 level far down below the Fermi energy. The performed calculation corresponds to an average situation. For the (rare) occasion that a divalent atom in the surface plane occupies a correct commensurate position, we calculate the excitation energy to the trivalent state to be 0.45 eV. A similar deviation from the average value, but in the opposite direction, is found for an atom in a position totally out of phase with the underlying trivalent layer. Even for these extreme (and rare) cases do we find a substantial binding of the f^6 surface level.

C. Hypothetical cases

In order to see more clearly how the $f^6 \rightarrow f^5$ transition energy is influenced by the reconstruction of the surface, and the accompanying reduction of the number of surface atoms, one could, for comparison, consider a hypothetical case where the divalent surface attains the same lattice parameters as the bulk layers. This would mean that the divalent surface atoms have to be considerably compressed. Since the energy difference between divalent and trivalent samarium is small, such a compression would strongly favor the trivalent state. This rules out the possiblity of having a divalent commensurate surface layer with the same density as the bulk layers.

Another extreme case to consider would be "isolated" divalent samarium atoms in the surface plane. In this case the divalent atoms are surrounded by only trivalent atoms both within the surface plane and down in the bulk. For this situation we find for the position of the f^6 level, $U'^{\mathrm{isol}} - U^{\mathrm{isol}}$, the following expression:

$$U'^{\mathrm{isol}} - U^{\mathrm{isol}} = (Z_{LL} + Z_{IL})(\epsilon_{BB} - \epsilon_{AB}) + 55.7 \,. \tag{12}$$

When evaluated, this gives 0.26 eV, which is rather close to the Fermi level compared with the experimental values and our calculation above. This illustrates the importance of the surface reconstruction for obtaining a high binding energy of the divalent f^6 surface level.

D. Surface core-level shift for a completely trivalent Sm metal

In order to investigate further the influence of the surroundings on the surface core-level shift of the BIS process $f^5 \rightarrow f^6$, we consider now the hypothetical case of a trivalent samarium metal with a trivalent surface. For the process in the bulk we have [compare Eq. (4)]

$$U''^{\mathrm{bulk}} - U_0 = -Z\epsilon_{BB} - 55.7 + Z\epsilon_{AB} = 0.46 \tag{13}$$

in units of eV, where U''^{bulk} is the total energy for the trivalent metal with one divalent bulk impurity. On the surface we find (the meaning of U''^{surf} being obvious)

$$U''^{\mathrm{surf}} - U_0 = (Z_{LL} + Z_{IL})(\epsilon_{AB} - \epsilon_{BB}) - 55.7 \;\; (= -0.26) \tag{14}$$

in units of eV. Thus, the surface (BIS) shift is found to be 0.46+0.26=0.72 eV. This value is of a reasonable magnitude as shown in Ref. 14. A direct interpretation of the negative value in Eq. (14) is, of course, that the surface is unstable against a divalent configuration. The relatively low value for the position of the unstable surface level might suggest that a homogeneously mixed-valence state should not be totally ruled out at the surface, or at least that the reverse (XPS) excitation $f^6 \rightarrow f^5$ at the surface should be quite low in energy. This, however, neglects the effect of the surface reconstruction and, as seen above in Sec. III B, this reconstruction in fact causes the f level to become displaced quite far from the Fermi level.

E. Surface core-level shift for a completely divalent Sm metal

The surface core-level shift of the (XPS) $f^6 \rightarrow f^5$ transition for a hypothetical divalent samarium metal can be used as an independent test of the present pair-bonding approximation. This is so since although divalent samarium does not exist, we can directly compare our calculated value with experiment on europium, the divalent neighbor element of samarium in the Periodic Table. In this case the initial state is the fully divalent samarium metal, and its energy will be denoted by U_0^{II}. The final state is a trivalent *bulk* samarium impurity and a trivalent *surface* impurity, respectively. If the total energies of these two final states are called U_B and U_S, respectively, the surface core-level shift Δ_c^S, is immediately obtained as

$$\Delta_c^S = (U_S - U_0^{II}) - (U_B - U_0^{II}) = U_S - U_B = (\epsilon_{AA} - \epsilon_{AB}) Z_{IL} \,. \tag{15}$$

From this, we calculate the surface core-level shift to be 0.63 eV. This is in nice agreement with the experimental value for europium metal, 0.63±0.02 eV.[31] Now it should be recalled that europium crystallizes in the bcc structure and that the calculation above has been performed for the fcc structure. We notice, however, that Eq. (15) may be rewritten as

$$\Delta_c^S=[E_{\rm coh}(B)-E_{\rm coh}(A)-E_B^{\rm imp}(A)]Z_{IL}/Z\ . \tag{16}$$

For the densest surface for fcc and bcc, i.e., fcc (111) and bcc (110), the ratio Z_{IL}/Z is the same, which means that within the present pair-bonding model Δ_c^S is identical for the two surfaces.

F. Stability of the thulium surface

Among the rare earths the next element to come in focus for a surface instability is thulium.[11] In this subsection we treat the same surface problem for thulium as above for samarium.

The main difference between samarium and thulium is that the appropriate excitation energy from the divalent atom to the trivalent one is significantly lower in thulium, namely 47.2 kcal/mol (Ref. 27) instead of 55.7 kcal/mol for samarium. Thus the divalent state is somewhat less favored in thulium than in samarium. Regarding the other parameters in our model, they will only be slightly modified in thulium as compared to samarium. Thus the appropriate trivalent cohesive energy is 103 kcal/mol (Ref. 27) and the hypothetically divalent one is interpolated to be 37.8 kcal/mol. As for samarium, we obtain the ϵ_{AB} parameter from the BIS experiment on thulium, where it was found[32] that the f^{13} level is situated 1.10 ± 0.2 eV above the Fermi level. From the same type of relation as in Eq. (4), this gives $\epsilon_{AB}=-11$ kcal/mol. Finally, the parameter α $(=N_2/N_3)$ is equal to 0.81 for thulium.

Using these values for the parameters we calculate the energy difference between the thulium metal with a divalent layer, on the one hand and, on the other hand, the completely trivalent metal as [Eq. (10)]

$$(U-U_0)/N_3=0.15 \tag{17}$$

in units of eV. Thus we find that the trivalent surface layer is stable in thulium, which is in agreement with experiments, where no indication of a divalent surface component has been found.[9,33] The calculation still serves to show that the divalent state is close to become stable at the thulium surface.

For the *hypothetical* divalent thulium surface we calculate from Eq. (11) the energy position of the f^{13} level to be 0.22 eV below the Fermi level. Thus from the point of view of a one-atom-excitation process the divalent surface state should be stable. This points to the collective nature of the surface transition within our model.

Finally, as a partial check on our approach we calculate the surface core-level shift of the f^{13} level for the hypothetical completely divalent thulium metal.[34] Here we can compare with the recent experimental results for ytterbium. From Eq. (15) we directly find Δ_c^S [Tm(II)] $=0.63$ eV. This is in good agreement with the experimental value 0.63 ± 0.03 eV for ytterbium[35-37] and also the value (0.56 eV) calculated in Ref. 14.

IV. DISCUSSION

From the given analysis and that in Ref. 11 it seems clear that a trivalent samarium surface is unstable against a valence change, a finding which is strongly supported by the experimentally observed features in Refs. 8–10. It is, however, also clear that as a consequence of this valence change an extremely complicated physical situation is created. First of all, due to the divalency, the accompanying atomic expansion causes a matching problem between the trivalent bulklike second layer and the divalent topmost layer. Furthermore, since hypothetical bulk divalent samarium is expected to attain a bcc crystallographic structure, it might be that the most favorable divalent surface layer should be the bcc (110) surface. Thus, two different structures could meet at the samarium surface, which would complicate the situation even more. Still it may be that this latter bulk ↔ surface interfacial structure problem is of less importance for the following reason: In ytterbium the bulk bcc and fcc phases are very close to each other energetically and therefore they would be expected to be rather close also in hypothetical divalent bulk samarium. Thus *if* the bulk layers of samarium were of (trivalent) fcc type, this underlying bulk structure might very well be able to *induce* the fcc phase for the divalent Sm surface layer. In practice the crystal structure of samarium is of the so-called hexagonal closed-packed Sm-type, rhombohedral, but since its effective c/a ratio is 1.61, i.e., close to the ideal ratio, the atomic ordering in the surface region will be very similar to that of an fcc (111) surface plane. Therefore it seems reasonable to expect that the bulk Sm-type structure will be able to determine also the surface structure of the divalent layer. Even so the problem remains that the bulk and surface structures are noncommensurate due to the larger lattice constant of divalent samarium. In this situation a lot of complications might be envisioned, such as, i.e., inhomogeneous island formations of various types.

In the present communication we have simplified the problem and treated the surface layer as a rigid divalent fcc (111) surface on top of an underlying fcc (111) trivalent layer and applied the pair-bonding model. Thereby we met the difficult problem of how to define the number of bonds between two noncommensurate layers with different numbers of atoms, N_2 and N_3, respectively. This was treated here by deriving an average number of bonds between the two layers, but admittedly, the applied method is by no means unique.[38] Still, the most serious approximation in our treatment is probably the neglect of the possibility of various deformation, such as an induced buckling of the surface layer.

From the above-mentioned difficulties it is clear that what is presently most needed is an experimental surface structure determination of samarium. The experimental indication that only 40% of the surface atoms are divalent is another feature which needs further clarification. This possible complication has been totally neglected in our analysis. (See *Note added in proof.*)

Besides demonstrating the plausibility of a divalent samarium surface, the main task of the present work was to account for the experimentally observed high binding energy of the divalent f^6 level at the surface. In our treatment we have argued that the reason for this is due to a surface reconstruction, such that at the surface there will be a macroscopic number of divalent atoms. Therefore a divalent surface samarium atom will to a large extent be surrounded by other divalent atoms which greatly influences on the f^6 binding energy. As a partial check on the general validity of our treatment we also calculated the surface core-level shift for the europium and ytterbium metals and found a very good agreement with experiment. Also the valence state of the surface of thulium was investigated and in agreement with the experimental indications we found that the trivalent state is stable. It should, however, be noted that the divalent state is calculated to be close in energy.

As a final remark we want to stress that for an elemental metal a most unique physical situation is met with in samarium, namely that it has a surface with very different characteristics than its interior parts. This should affect several physical properties. For example, one might expect that the divalent surface metal should melt at a considerably lower temperature than the bulk metal. It is then of interest to speculate about the possibility that this early surface melting could have some influence on the bulk melting temperature. In this respect we notice that the experimental melting temperatures for the lanthanide metals[39] do indicate a somewhat anomalously low melting temperature for samarium (Fig. 1). Clearly, samarium metal deserves increased experimental and theoretical attention. Regarding the other rare earths, we have already mentioned that the thulium metal surface seems stable against a valence change. However, at high temperatures the situation is less clear, especially so since the energy margin by which the thulium surface retains its trivalent state is small.[40] Whether or not this possibility of a valence change of the thulium surface at elevated temperatures has anything to do with the slightly anomalous melting temperature of thulium (see Fig. 1) can for the moment only remain speculative. But it is certainly remarkable that the two lanthanide metals which are most likely to have a divalent surface both show anomalous melting temperatures.

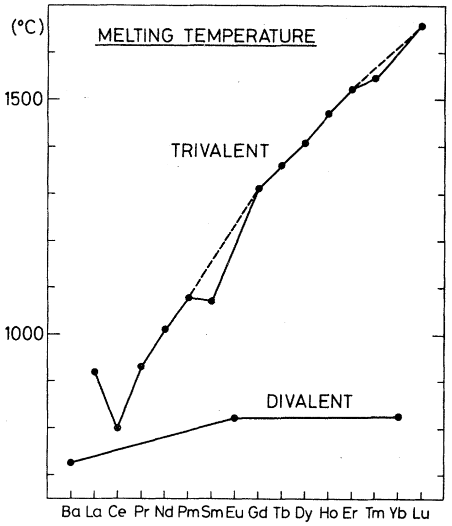

FIG. 1. Experimental (Ref. 39) melting temperatures for the lanthanide metals and barium. The slightly anomalous melting temperatures of cerium *and* lanthanum relative to the other lanthanides are of no concern in the present context.

Note added in proof. Very recently, new surface-sensitive UPS spectra were recorded for Sm metal [F. Gerken, J. Barth, R. Kammerer, L. I. Johansson, and A. Flodström, DESY Report No. SR-81/11 (unpublished) and unpublished]. It was established that there is *no* observable surface shift of the *trivalent* component of the spectrum, and therefore it could be concluded that at the surface there are at most 10% trivalent samarium atoms. This supports the validity of our assumption that the surface is composed of only divalent samarium atoms.

ACKNOWLEDGMENTS

One of the authors (A. R.) would like to thank the Swedish National Science Research Council for financial support and also the Nordic Institute for Theoretical Atomic Physics for financing a stay at the University of Aarhus.

---

[1] A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B 9, 2513 (1974).

[2] It is commonly claimed that the α phase of cerium is a mixed-valence state. This interpretation has, however, been refuted in B. Johansson, Philos. Mag. 30, 469 (1974).

[3] (a) C. K. Wertheim and M. Campagna, Chem. Phys. Lett. 47, 182 (1977). (b) An exception to this has recently been found in γ-cerium metal [N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. 41, 573 (1982)]. Here a weak $4f$ feature is observed close to the Fermi energy, while the main $4f$ line is located at 2 eV. The $4f$ peak close to the Fermi energy can be understood as a $4f$ shakedown satellite. A similar interpretation has also been proposed by S. Hüfner (private communication).

[4] D. A. Shirley, *Topics in Applied Physics* (Springer, Berlin, 1978), Vol. 27, p. 165.

[5] B. Johansson and A. Rosengren, Phys. Rev. B 11, 2836 (1975).

[6] B. Johansson and A. Rosengren, Phys. Rev. B 11, 1367 (1975).

[7] B. Johansson, in *Rare Earths and Actinides,* edited by W. D. Corner and B. K. Tanner (IOP, London, 1978), Chap. 3, p. 39.

[8] G. K. Wertheim and G. Crecelius, Phys. Rev. Lett. 40, 813 (1978).

[9] J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagström, Phys. Rev. Lett. 41, 1499 (1978).

[10] J. W. Allen, L. I. Johansson, I. Lindau, and S. B. M. Hagström, Phys. Rev. B 21, 1335 (1980).

[11] B. Johansson, Phys. Rev. B 19, 6615 (1979).

[12] J. K. Lang and Y. Baer, Solid State Commun. 31, 945 (1979).

[13] Since Allen *et al.* (Ref. 10) found the samarium divalent f^6 surface component of SmB_6 at 0.6 eV below the Fermi energy they concluded an inhomogeneous mixture existed at the surface. It is difficult to find any physical reason for why this inhomogeneous mixture has to have the same valence mixture as the bulk homogeneously mixed-valence state.

[14] B. Johansson and N. Mårtensson, Phys. Rev. B 21, 4427 (1980).

[15] A. Rosengren and B. Johansson, Phys. Rev. B 13, 1468 (1976).

[16] B. Johansson and A. Rosengren, Phys. Rev. B 14, 361 (1976).

[17] B. Johansson, Phys. Rev. B 19, 6615 (1979); see also B. Johansson, J. Phys. F 4, L169 (1974).

[18] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 17, 3089 (1978).

[19] A. Rosengren and B. Johansson, Phys. Rev. B 22, 3706 (1980).

[20] A. Rosengren, Phys. Rev. B 24, 7393 (1981).

[21] A. Rosengren and B. Johansson, Phys. Rev. B 23, 3852 (1981).

[22] P. Steiner and S. Hüfner, Solid State Commun. 37, 279 (1981).

[23] P. Steiner and S. Hüfner, Solid State Commun. 37, 79 (1981).

[24] N. Mårtensson, R. Nyholm, H. Calén, J. Hedman, and B. Johansson, Phys. Rev. B 24, 1725 (1981).

[25] V. Kumar, D. Kumar, and S. K. Joshi, Phys. Rev. B 19, 1954 (1979).

[26] L. Brewer, Lawrence Berkeley Laboratory LBL Report No. LBL3720 (unpublished).

[27] B. Johansson (unpublished).

[28] A. R. Miedema, F. R. de Boer, and P. F. de Chatel, J. Phys. F 3, 1558 (1973).

[29] A. R. Midemea, J. Less-Common Met. 46, 67 (1976).

[30] J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974).

[31] R. Kammerer, J. Barth, F. Gerken, A. Flodström, and L. I. Johansson, Solid State Commun. 41, 435 (1982).

[32] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F 11, 121 (1981).

[33] L. I. Johansson, J. W. Allen, and I. Lindau, Phys. Lett. 86A, 442 (1981).

[34] In this connection it is also of interest to consider the surface core-level shifts of the trivalent rare-earth metals within the present pair-bonding model. As we have noticed, the core-level shift is practically identical for the two divalent elements, europium and ytterbium, and an essentially constant shift is expected also for the trivalent lanthanides. Therefore it suffices to consider just one element and we choose lutetium. For the shift we use the expression given in Eq. (16), where B now stands for the hypothetical tetravalent state of lutetium. The corresponding tetravalent cohesive energy can be substituted by the experimental cohesive energy of hafnium. Furthermore, we neglect the $E^{\text{imp}}(A)$ term since it will only give a relatively small contribution. From this we obtain Δ_c^S (lutetium)$=(148.4-102.2)(\frac{1}{4})$ kcal/mol$=0.50$ eV/atom, a value which should also be representative for the SCS

of the other trivalent rare-earth metals when a NN pair-bonding model is applied.

[35] S. F. Alvarado, M. Campagna, and W. Gudat, J. Electron Spectrosc. Relat. Phenom. 18, 43 (1980). In this work the observed surface shift was interpreted as due to an (unknown) contamination at the surface. However, Johansson and Mårtensson (Ref. 14) argued that, instead, this shift was an inherent property of the ytterbium surface, which now has been confirmed by the more recent experimental work in Refs. 36 and 37.

[36] M. Hecht, L. I. Johansson, J. W. Allen, S. J. Oh, and I. Lindau, Proceedings of the VI Vacuum Ultraviolet Conference, Charlottesville, 1980 (unpublished), p. I-64.

[37] L. I. Johansson, A. Flodström, S.-E Hörnström, B. Johansson, J. Barth, and F. Gerken, Solid State Commun. 41, 427 (1982).

[38] If, e.g., the number of bonds between the divalent and trivalent layers is defined as $\min(N_2,N_3)Z_{IL}$, the calculated excitation energies remain essentially unchanged.

[39] F. H. Spedding, *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, Ohio, 1970), p. B-253.

[40] This expected close neighborhood of the divalent state is not only shown from our model calculations, but can also be inferred from available experimental data. For samarium the measured shift between the unoccupied bulk f^6 level and the occupied surface f^6 level is about 1.2 eV (see text). Since the unoccupied bulk f^{13} level in thulium is at 1.1 eV above the Fermi energy (Ref. 32), the expected similarity of the shifts for samarium and thulium gives that at a *reconstructed* divalent thulium surface the f^{13} level should be 0.1 eV below the Fermi level, and thus be stable in the divalent state. As discussed in the text, this is a necessary but not a sufficient condition for the stability of a divalent surface. Still, it strongly indicates that the divalent surface state must be almost stable in the thulium metal. A monolayer (or less) of thulium on an ytterbium crystal will most likely be divalent. Experimentally this situation might be difficult to attain since trivalent thulium droplets might be formed instead.