PHYSICAL REVIEW B VOLUME 20, NUMBER 4 15 AUGUST 1979

Energy position of $4f$ levels in rare-earth metals

Börje Johansson
Department of Physics, Section 214, FOA 2, National Defense Research Institute, S-104 50 Stockholm, Sweden

(Received 17 January 1979)

The energy position of the occupied and unoccupied $4f$ levels relative to the Fermi energy is studied for the rare-earth metals. This is done by treating the excited state as an impurity in an otherwise perfect crystal. This picture is first considered in the complete screening approximation. In this approximation thermochemical data can be used directly to give energy values for the unoccupied f levels which are accurate to ±0.05 eV; for the occupied f levels the uncertainty is somewhat larger. The obtained values are then compared with recent x-ray photoemission spectroscopy (XPS) and Bremsstrahlung isochromat spectroscopy (BIS) data. The deviations found are discussed in terms of impurity effects left out in the complete screening approximation. When these effects are included a general good agreement with experiment is obtained. The consistency found in the XPS results is utilized for an improved estimation of the fourth ionization energy of the rare earths.

I. INTRODUCTION

The rare-earth elements, characterized by the gradual filling of the $4f$ shell, have during the last decade or so been extensively studied by spectroscopic methods. This is true both for the free atoms and ions[1] as well as for the metallic state.[2,3] Also reliable thermochemical data for the pure metals have been accumulated in the same period.[4] Therefore, the time now seems apt to let these data confront each other, not just qualitatively, but on a direct quantitative level. In this paper we will focus our attention to the x-ray photoemission spectroscopy (XPS) results for the rare-earth metals by Lang *et al.*[5] As will be apparent, these measurements have reached a level of accuracy and internal consistency that they now can be trustfully employed for theoretical considerations. What we especially have in mind is the position of the $4f$ level relative to the Fermi energy.

In the metallic state the open $4f$ electron shell retains an integral occupation number and gives rise to a well-defined localized magnetic moment. The electronic structure of the f shell in the free ion or atom remains essentially intact when the metallic state is formed. Thus there are two types of electronic states in the rare-earth metals; (a) a normal conduction band state of (sd) type and (b) a localized f state. Because of its localized nature the energy position of the $4f$ level cannot be obtained from a conventional band-structure calculation.[6] Then in order to go beyond the inappropriate one-particle scheme the following picture of the position of the $4f$ level relative to the Fermi energy appears to be more adequate[7,8]: namely, (for the case of a trivalent metal) that it is the *energy difference* between, on one hand, a trivalent metallic host with *one* of its rare-earth ions in the tetravalent ionic state, and on the other hand, the perfect crystal composed of only trivalent rare-earth ions. Thus in the excited state one of the $4f$ electrons of a particular ion has been promoted to the conduction band leaving behind it a tetravalent ion at that site. This new ionic state is assumed to be in its ground state. Also the original conduction electrons plus the extra excited one are assumed to be in a *completely relaxed state* relative to the new ionic configuration of the whole crystal. This means that the excited state is composed of a tetravalent *impurity* placed in a trivalent metallic host.[9] Therefore, hypothetically, this excited state may be obtained by the following two step process; first the trivalent atomic site is converted to a tetravalent atomic site (as it should be in a tetravalent environment, i.e., if the whole metal was made tetravalent) costing an energy $\Delta E_{\mathrm{III,IV}}$, and only thereafter this tetravalent cell is left free to adjust itself to the trivalent environment, this involving the energy $E_{\mathrm{IV}}^{\mathrm{imp}}(\mathrm{III})$. Thus the $4f$ excitation energy, $\epsilon(f \rightarrow \epsilon_F)$, can be written

$$\epsilon(f \rightarrow \epsilon_F) = \Delta E_{\mathrm{III,IV}} + E_{\mathrm{IV}}^{\mathrm{imp}}(\mathrm{III}) \quad . \qquad (1)$$

In the present paper we will concentrate on the first part of this process, $\Delta E_{\mathrm{III,IV}}$, since this gives by far the most important contribution to the excitation energy. However, we will later argue that the solution energy of the impurity, $E_{\mathrm{IV}}^{\mathrm{imp}}(\mathrm{III})$, may also be of some significance.

In a series of papers Herbst *et al.*[10-12] have introduced and applied what they refer to as the "complete screening" picture for describing the photoionization process of an f electron in a metal. For a free atom, photoejection of an electron gives an ion as a final state. On the other hand, for the same process in a metal, the conduction electrons will in the final state screen the excited atomic site. The "complete screening" picture is meant to correspond to the case that the excited atomic cell attain charge neutrality. In the words of Herbst *et al.*[11] "The principal assumption is the *complete screening approximation* employed in calculating the energy of a cell in the metal excited by photoejection of a $4f$ electron; charge neutrality is maintained by describing the excited cell with a band structure appropriate to a configuration having one fewer $4f$ and one more conduction electron". Thus, in their treatment, the position of the $4f$ state is obtained from a calculated energy difference between the excited state and the ground state of the atomic cell. This means that Herbst *et al.* put the main emphasis to the energy difference $\Delta E_{\text{III,IV}}$ and (like we do for the main part of this work) neglect to a first-order approximation the impurity term. In what follows we find it convenient to let the complete screening picture be synonymous with the first term in Eqs. (1) and (2). In the actual computations Herbst *et al.* applied the renormalized-atom method[13] combined with experimental atomic spectroscopic data. The calculated energy change was then compared with XPS measurements and a comparatively good general agreement was found. Still it is difficult to assess to what extent the "complete screening" assumption is justified because of the various types of approximations necessary in the numerical treatment. However, the obtained agreement is most encouraging and justifies a further investigation of the validity of the complete screening assumption. This is essentially the main program of the present paper.

Bremsstrahlung isochromat spectroscopy (BIS),[14] has recently been utilized by Lang *et al.* to study the unoccupied $4f$ levels (residing above the Fermi level) for the rare-earth metals.[5] Also here the complete screening picture can be applied and now it corresponds to an electron being taken from the Fermi level and injected *into* the f shell of a specified ion. Evidently, in this case the metallic site is converted into a site with a *lower* integral valence state. Also here it is of interest to fully investigate to what extent the complete screening picture can account for the BIS experiments. The completely screened and relaxed model gives the energy position of the unoccupied $4f$ level relative to the Fermi energy (for a trivalent metal) as

$$\epsilon(\epsilon_F \to f) = -\Delta E_{\text{II,III}} + E_{\text{II}}^{\text{imp}}(\text{III}) \quad , \tag{2}$$

where $\Delta E_{\text{II,III}}$ is the energy difference between the divalent and trivalent metallic states. $E_{\text{II}}^{\text{imp}}(\text{III})$ is the solution energy of the appropriate divalent impurity in the trivalent host.

Now, it turns out to be possible to obtain very accurate numbers for the quantities $\Delta E_{\text{II,III}}$ and $\Delta E_{\text{III,IV}}$. The accuracy is in fact about ~0.05 eV, which is more accurate than the experimental accuracy of ±0.2 eV for the XPS and BIS experiments. This is true for the case of the unoccupied f levels (corresponding to the BIS experiments). For the occupied f levels, involving a transition from a trivalent site to a tetravalent one, the uncertainty is somewhat larger. However, in this case, after having fixed the position of the f level for one element (as a tie-point), the relative uncertainty for the neighboring elements is again small. That this possibility of getting accurate numbers for the complete screening picture exists was already pointed out in Ref. 15. With the BIS experiments available, it now seems worthwhile to reinvestigate the subject, although it means that at some stages we have to repeat the arguments already given in Ref. 15. Further, the energy difference between the trivalent and the (hypothetical) tetravalent cerium metal is now known more accurately than when Ref. 15 was written. Also, some rather new spectroscopic results for the free ions permit us to make additional refinements which were not possible before. Therefore we will in this paper also reinvestigate the XPS measurements.

As a final comment in this Introduction, we want to emphasize that almost all the numbers we are going to present in this paper can be obtained from just a few "canonical" values. These are the free atomic excitations $f^{n+1}s^2 \to f^n ds^2$ and $f^n ds^2 \to f^{n-1} d^2s^2$ and the regular values of the cohesive energy of di-, tri- and tetravalent metals (the II A–IV A elements of the Periodic Table). Thus, for example, in a trivalent metal, the position of the occupied f level relative to the Fermi energy, ϵ_F, is essentially the energy of the atomic reaction $f^n ds^2 \to f^{n-1} d^2s^2$ renormalized by about 2 eV.

The organization of this paper is as follows: In Sec. II we derive the energy difference between the divalent and trivalent metallic states of the rare-earth metals. Some experimental atomic excitation energies are compared in Sec. III to demonstrate the close relationship between various excitations of type $f^{n+1} \to f^n$. The experience gained from this is then applied to derive the energy for the transition of the trivalent metal to the tetravalent metal. In Sec. III we also compare this energy with recent XPS measurements. Having demonstrated the remarkably good consistency in the XPS measurements we then show that they can be utilized to give improved estimations of the fourth ionization energy of the lanthanides (Sec. IV). In Sec. V we consider the BIS experiments. Corrections to the complete screening picture, i.e., the impurity effects, are discussed in Sec. VI. Some comments on the theoretical calculations by Herbst and co-workers are given in Sec. VII. Section VIII contains some concluding remarks. In the Appendix we give the derived $\Delta E_{\text{II,III}}$ and $\Delta E_{\text{III,IV}}$ values explicitly.

II. ENERGY DIFFERENCE BETWEEN THE DIVALENT AND TRIVALENT METALLIC STATES OF THE RARE-EARTH ELEMENTS

Since we want to study total energy differences between different metallic valence states it is natural that we should consider cohesive energies. In Fig. 1 we give cohesive energies[16] for some elements relevant for the present study. From this figure it is immediately clear that di-, tri- and tetravalent metals have cohesive energies of about 40, 100, and 145 kcal/mol, respectively. (Such a regular behavior of the cohesive energy in the Periodic Table is not limited to just these elements but has a much wider applicability.[17]) This regularity together with experimental atomic spectroscopic levels could in fact have been used throughout this paper to give results practically identical to those we now will derive in a somewhat different way. We choose, however, this different route in order to make a more direct contact with experimental thermochemical data.

As free atoms, most of the rare earths have a divalent atomic configuration, $4f^{n+1}6s^2$. Only lanthanum, cerium, gadolinium, and lutetium are different in this respect holding a trivalent configuration; $4f^0 5d6s^2$, $4f^1 5d6s^2$, $4f^7 5d6s^2$, and $4f^{14} 5d6s^2$, respectively. However, as is well known, in the metallic phase most of the rare earths are found in a trivalent configuration. There is a simple explanation to this, based on the *f* electrons being nonbonding, and the property that II A and III A elements have a cohesive energy of about 40 and 100 kcal/mol, respectively. This means that in the divalent metal a promotion of one *f* electron of all the atoms to the bonding metallic ($5d6s$) state gives an additional binding energy of about 100-40=60 kcal/mol. However, this gain of binding energy must be balanced against the energy required to excite the *f* electron to the (ds) state. From atomic spectroscopic levels[1] it is then immediately clear that it is only for europium and ytterbium that this promotion energy is more costly than the gain of binding energy. This is the fundamental reason why Eu and Yb are divalent metals in contrast to all the other lanthanides. Note that we here only compare total energies and do not invoke a single-particle picture with a level crossing.

Sr s^2 39.7	Y ds^2 100.8	Zr d^2s^2 144.2				
Ba s^2 43.7	La ds^2 103.0	Ce fds^2	Ln-series	Yb s^2 37.1	Lu ds^2 102.2	Hf d^2s^2 148.4
Ra s^2 38.2	Ac ds^2 ?	Th d^2s^2 142.9				

FIG. 1. Cohesive energies (Ref. 16) for some elements relevant for the lanthanide series.

As stressed already in the Introduction, the *f* states are localized and accordingly, do not belong to an energy-band description. Therefore, in the many published descriptions of valence transitions as a level crossing, it must be understood that the *f*-level position relative to the conduction band must not be taken from a normal one-particle picture. Instead, its position must be considered as the total energy difference between having and not having the *f* electron placed in the conduction band.

A tetravalent metal (IV A-type) has a cohesive energy of about 145 kcal/mol (compare Fig. 1). Thus if a trivalent rare-earth metal is made tetravalent by promoting an *f* electron of every atom into the conduction band, a binding energy of about 145-100=45 kcal/mol is gained. However, for all the rare-earth elements the promotion energy of the *f* electron is much too high to permit such a transition.[18,19] This is the fundamental reason why *none* of the rare earths is found in a tetravalent metallic state.

We will now derive the energy difference between the divalent and trivalent metallic state of the same rare-earth element. The cohesive energies of barium, europium, and ytterbium are known experimentally.[16] Therefore, a smooth interpolation between these values gives an accurate estimate of the (hypothetical) divalent metallic cohesive energy for the rest of the lanthanides relative to their $f^{n+1}s^2$ atomic states. As is immediately clear from Fig. 2(a) the difference between such an interpolated value and the one actually measured gives directly $\Delta E_{\mathrm{II,III}}$ for most of the lanthanides. Only for La, Ce, and Gd do we have to take into account the atomic excitation $E(f^n ds^2 \rightarrow f^{n+1}s^2)$ before we can obtain $\Delta E_{\mathrm{II,III}}$. This is illustrated in Fig. 2(b). To give a comprehensive survey we show in Fig. 3 the experimental

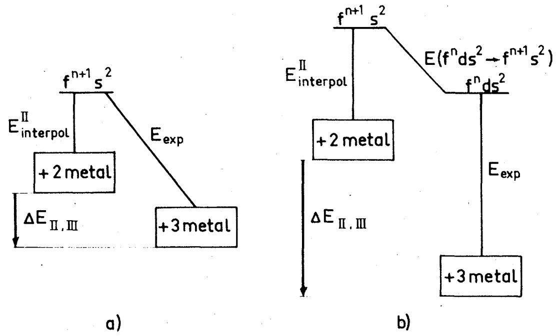

FIG. 2. Illustration of how the quantity $\Delta E_{\mathrm{II,III}}$ is derived. For a lanthanide with a divalent atomic configuration this involves the difference between the experimental cohesive energy, E_{exp}, and the interpolated value, E_{interpol}, (a). For a lanthanide with a trivalent atomic state we have to include the atomic excitation, $E(f^n ds^2 \rightarrow f^{n+1}s^2)$, before $\Delta E_{\mathrm{II,III}}$ can be obtained, (b).

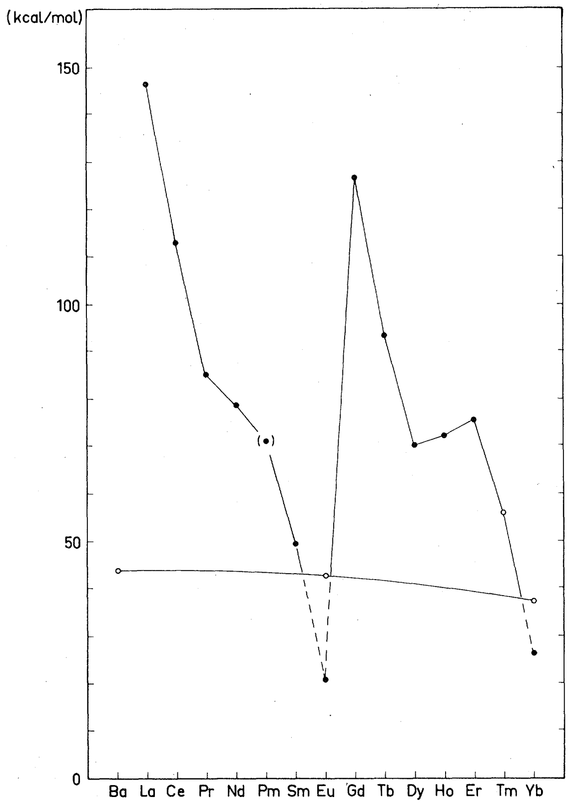

FIG. 3. Cohesive energy of the lanthanides as measured relative to their divalent atomic configuration, $f^{n+1}s^2$, (filled circles). For europium and ytterbium the filled circles correspond to the hypothetical trivalent metallic state. The open circles refer to the divalent metals and the smooth line gives interpolated cohesive energies for the lanthanides in their hypothetical divalent metallic state (relative to their divalent atomic configuration).

cohesive energy[16] for all the lanthanides relative to the divalent atomic configuration $f^{n+1}s^2$. The difference between this value and the smoothly interpolated divalent cohesive energy curve in Fig. 3 gives immediately $-\Delta E_{\mathrm{II,III}}$ for most of the lanthanides. The experimental cohesive energies are generally determined with an accuracy better than 1 kcal/mol. This means that the derived values of $\Delta E_{\mathrm{II,III}}$ have an accuracy of about 1 kcal/mol or 0.05 eV/atom. It is only for europium and ytterbium that a different procedure must be utilized to obtain $\Delta E_{\mathrm{II,III}}$. This has been discussed by Gschneidner in Ref. 20, where he, for example, compares the heat of formation of $\mathrm{EuCl_3}$, in which compound Eu has clearly become trivalent, with that of its neighbor element, $\mathrm{GdCl_3}$. The formation of $\mathrm{EuCl_3}$ can be thought of as taking place in two steps in which the divalent europium metal is first transformed to the trivalent metal and only then the trichloride is formed. For the latter process, the heat of formation of $\mathrm{EuCl_3}$ will be very similar to that of $\mathrm{GdCl_3}$. Therefore, the difference in the experimental values of the heat of formation for $\mathrm{EuCl_3}$ and $\mathrm{GdCl_3}$ corresponds directly to $\Delta E_{\mathrm{II,III}}$. Naturally the heat of formation of other compounds where Eu is trivalent can be used for the same purpose. The same type of procedure can also be applied for Yb. A somewhat different method, but still closely related to the one used by Gschneidner, was applied in Ref. 21 to get the $\Delta E_{\mathrm{II,III}}$ numbers for Eu and Yb. The most consistent values for $\Delta E_{\mathrm{II,III}}$ appears to be 23 and 11 kcal/mol for Eu and Yb, respectively.

Since none of the rare earths form a tetravalent metal, it is somewhat more difficult to obtain accurate values for $\Delta E_{\mathrm{III,IV}}$. However, from Fig. 1 it is quite clear that cerium as a tetravalent metal should have a cohesive energy close to 145 kcal/mol relative to its tetravalent atomic state d^2s^2. For the tetravalent element after lutetium in the Periodic Table, i.e., hafnium, the experimental cohesive energy is 148.4 kcal/mol.[16] Therefore all the rare earths should in their hypothetical tetravalent metallic state have a cohesive energy of about 145–148 kcal/mol relative to the proper tetravalent atomic state. This means that if the atomic excitations $f^n ds^2 \rightarrow f^{n-1} d^2s^2$ were known for the rare earths we could easily obtain accurate values for $\Delta E_{\mathrm{III,IV}}$. However, since these tetravalent levels are very high in energy, they have not yet been identified among the spectroscopic levels. (In fact for most of the lanthanides the $f^{n-1} d^2s^2$ level is above the first ionization potential.) Still, even if this atomic excitation was known for only one element, there are quite reliable methods available from which the $f^n ds^2 \rightarrow f^{n-1} d^2s^2$ excitation energies for the rest of the rare earths could be estimated. This was actually the procedure employed in Ref. 15 to derive $\Delta E_{\mathrm{III,IV}}$. In the present paper we will use a somewhat different approach in order to get $\Delta E_{\mathrm{III,IV}}$, although this method is essentially equivalent to the one used before. This will be done in Sec. III.

III. ENERGY DIFFERENCE BETWEEN TRIVALENT AND TETRAVALENT METALLIC RARE-EARTHS AND COMPARISON WITH XPS EXPERIMENTS

In Sec. II we obtained $\Delta E_{\mathrm{II,III}}$ for the rare earths. Here we will show that these data can be used directly to give $\Delta E_{\mathrm{III,IV}}$ through the series, provided that this value is known for at least one of the elements. The method we will use is well known in atomic spectroscopy and is called the "horizontal analysis" method. Originally this method was applied to the 3*d* series,[22] but more recently it has been used for the rare-earth atoms by Jørgensen.[23] A more refined and a much more extensive treatment has been given by Vander Sluis and Nugent,[24] again for the rare earths.

The basis is that the $f^{n-1}-f^n$ difference can be expressed as[25]

$$U_f-(n-1)E^0-g(S_{n-1}-S_n+\tfrac{1}{2})E^1 +y[(L,U)_{n-1},(L,U)_n]E^3 \ , \qquad (3)$$

where U_f, E^0, E^1, and E^3 are known as the Racah parameters and the coefficients in Eq. (3) depend on certain group quantum numbers.[26] The Racah parameters are assumed to be equal for the two configurations f^n and f^{n-1}. Therefore, if the Racah parameters are known for all the lanthanides and the $f^{n-1}-f^n$ difference is known for one element, then the expression in Eq. (3) can be used to give an estimation of the $f^{n-1}-f^n$ difference for the rest of the lanthanides.

An alternative method of making predictions, due originally to Racah,[27] is also available and is known as the "vertical analysis" method. This can simply be stated as follows: A plot of, for example, the following promotion energies for the same element $f^{n+1}s^2\rightarrow f^n ds^2$, $f^{n+1}s\rightarrow f^n ds$, and $f^{n+1}\rightarrow f^n d$ through the lanthanide series will give three essentially parallel curves. Therefore if one of the mentioned excitations is known for all the elements, the other two may be obtained by a vertical displacement of this curve. This is illustrated in Fig. 4 for the excitations $f^n s\rightarrow f^{n-1}s^2$ and $f^n\rightarrow f^{n-1}s$. As can be seen the expected parallellity is well borne out. We should observe that the Racah method applies for the $f^n\rightarrow f^{n-1}$ excitation for the same element, but at different ionization stages. However, in the present paper we want to compare the excitation $f^n\rightarrow f^{n-1}$ for neighboring elements, i.e., $\mathrm{Ln}(A,f^n\rightarrow f^{n-1})$ and $\mathrm{Ln}(A+1,f^n\rightarrow f^{n-1})$, where A is the atomic number. If the Racah parameters E^1 and E^3 were the same for $\mathrm{Ln}(A)$ and $\mathrm{Ln}(A+1)$ we would again expect a parallel behavior of this $f^n\rightarrow f^{n-1}$ excitation energy (when plotted as a function of n), except for a possible (but relatively small) linear deviation, i.e.,

$$\mathrm{Ln}(A+1,f^n\rightarrow f^{n-1}) =\mathrm{const}+\mathrm{Ln}(A,f^n\rightarrow f^{n-1})+B(n-1) \ . \qquad (4)$$

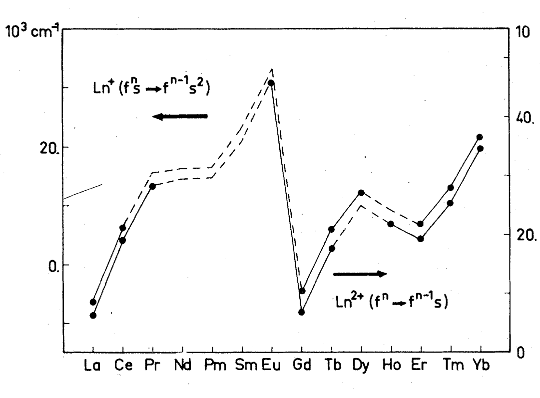

FIG. 4. Comparison between the atomic excitations $\mathrm{LnII}(f^n s\rightarrow f^{n-1}s^2)$ and $\mathrm{LnIII}(f^n\rightarrow f^{n-1}s)$ for the rare earths. Note the displacement between the scale to the left and the scale to the right.

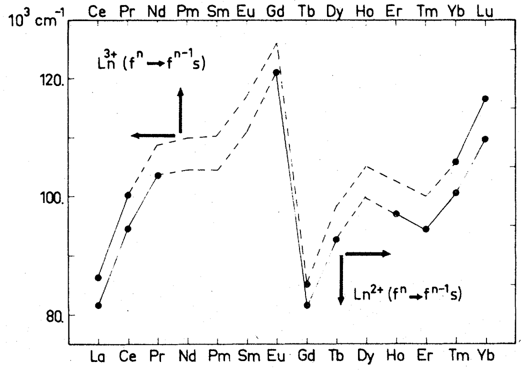

FIG. 5. Comparison between the atomic excitations $\mathrm{LnIII}(f^n\rightarrow f^{n-1}s)$ and $\mathrm{LnIV}(f^n\rightarrow f^{n-1}s)$ for the rare earths. Note the displacements of scales and the displacement of elements for the upper and lower curve.

In Fig. 5 we have plotted the excitation energies $\mathrm{LnIII}(A,f^n\rightarrow f^{n-1}s)$ and LnIV $(A+1,f^n\rightarrow f^{n-1}s)$ as a function of n. As can be seen, an essentially parallel behavior is found. However, it is certainly true that the Racah parameters are not exactly equal for $\mathrm{LnIII}(A)$ and $\mathrm{LnIV}(A+1)$. Therefore there should be a correction to Eq. (4) and we write

$$\mathrm{Ln}(A+1,f^n\rightarrow f^{n-1}s)=\mathrm{const}+\mathrm{Ln}(A,f^n\rightarrow f^{n-1}s) +\Delta(n)+B(n-1) \ . \qquad (5)$$

From Fig. 5 we find, if $\Delta(n=1)$ is put equal to zero, that the value of the constant is $80.2\times 10^3\ \mathrm{cm}^{-1}$. Further, it is also quite clear from Fig. 5 that the $\Delta(n)$ and $B(n-1)$ corrections are only of secondary importance.

From the discussion above it is obvious that we can obtain the $\Delta E_{\mathrm{III,IV}}$ energy differences for the lanthanides from the following relation:

$$\Delta E_{\mathrm{III,IV}}(A+1,f^n\rightarrow f^{n-1})=\mathrm{const}' +\Delta E_{\mathrm{II,III}}(A,f^n\rightarrow f^{n-1}) +\Delta(n)+B(n-1) \ . \qquad (6)$$

We will for the moment neglect the last two terms, but return to them at a later stage. Then it remains to determine the value of the constant. In order to do that we need to know the value of $\Delta E_{\mathrm{III,IV}}$ for one of the rare-earth elements. From the regularities in the cohesive energies of the metallic elements this quantity was found to be about 48 kcal/mol in the case of cerium.[18] In a study of the heat of formation of tetravalent cerium compounds, i.e., from a determination of the deviation between the experimental value and the one expected for tetravalent metallic cerium, $\Delta E_{\mathrm{III,IV}}$ was found to be about 40 kcal/mol. In this paper we choose 45 kcal/mol as a relatively appropriate value. An error in this value will give the same vertical displacement of all the other lanthanide $\Delta E_{\mathrm{III,IV}}$ values. Since

$$\Delta E_{\mathrm{II,III}}(\mathrm{La}) = -103 \text{ kcal/mol}$$

we immediately obtain const' = 148 kcal/mol. From this we can now obtain values for $\Delta E_{\mathrm{III,IV}}$ for the rest of the lanthanides. These values are given in Fig. 6 as filled circles. In this figure we have also included the XPS data for the position of the $4f$ level relative to the Fermi energy.[5,28] The derived values for $\Delta E_{\mathrm{III,IV}}$ reproduce the experimental trends in a quite acceptable way. Some embarrassing features should be noted, however, as for example a too low value for gadolinium and a too high value for terbium. As we will see below, the reason for this can actually be found in the term $\Delta(n)$, which we so far have neglected.

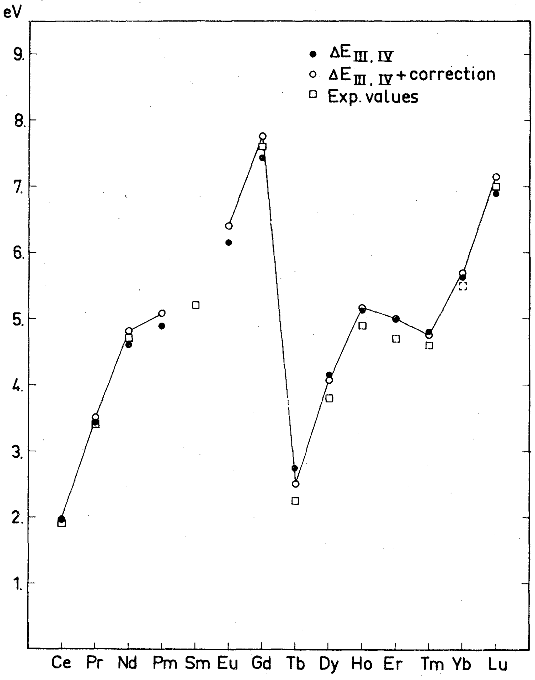

FIG. 6. Experimental XPS data (Ref. 5) for the position of the $4f$ level relative to the Fermi level. For cerium we use the exp value given in Ref. 28. These experimental data are denoted by squares. The filled circles are the derived values of $\Delta E_{\mathrm{III,IV}}$ and the open circles correspond to $\Delta E_{\mathrm{III,IV}}$ corrected by the function $\Delta(n)$. Since we lack exp data on the cohesive energy of Pm, we cannot obtain an accurate value of $\Delta E_{\mathrm{III,IV}}$ for Sm. For Yb the dotted square is used to show that this is not an experimental value but is derived from its fourth ionization energy, as described in Sec. IV.

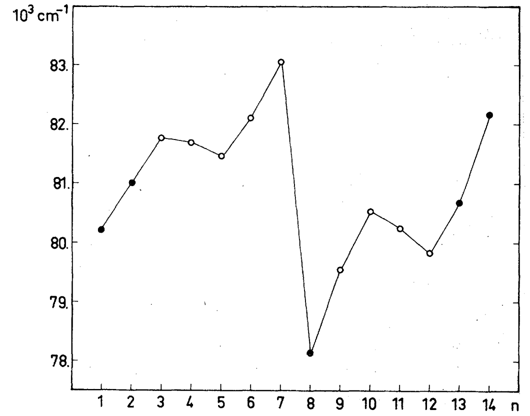

FIG. 7. Difference between the atomic excitations LnIV($f^n \rightarrow f^{n-1}s$) and LnIII($f^n \rightarrow f^{n-1}s$). Filled circles are experimental values and open circles are "interpolated" values as described in the text. The variation of this difference relative to the $n = 1$ case gives the $\Delta(n)$ function.

In Fig. 7 we plot the difference between the atomic LnIV($A+1, f^n \rightarrow f^{n-1}s$) and LnIII($A, f^n \rightarrow f^{n-1}s$) excitation energies. Considering the scale in the figure, it is true that the difference between these excitation energies is essentially constant. [This property has in fact been utilized in estimations of atomic spectroscopic levels[29] and can be referred to as a constant system difference (SD) change.] However, upon this large constant difference, there is a small but significant variation. This variation undoubtedly has as its origin the change of the Racah parameters in going from LnIII(A) to LnIV($A+1$). If the excitation energies themselves are given by the expression in Eq. (3) then their difference must again be given by Eq. (3) only that the Racah parameters for this difference are given by their change, i.e, ΔE^1 and ΔE^3. Therefore also the difference between the excitations LnIV($A+1, f^n \rightarrow f^{n-1}s$) and LnIII($A, f^n \rightarrow f^{n-1}s$) will show the same familiar zigzag behavior as the excitation energies themselves, only at a much smaller scale. Realizing this we arrive at the "interpolated" values, shown as open circles in Fig. 7.[30] From this figure we immediately obtain the function $\Delta(n)$ [$\Delta(1)$ is put equal to zero]. Note, however, that the total variation in $\Delta(n)$ is only 5×10^3 cm^{-1} (0.6 eV). These corrections are included into the $\Delta E_{\mathrm{III,IV}}$ values shown as open circles in Fig. 6. It is immediately clear that corrected $\Delta E_{\mathrm{III,IV}}$ values reproduce the features of the XPS data exceedingly well.

In Fig. 8 we plot the difference between the experimental XPS values and $\Delta E_{\mathrm{III,IV}}$ both without (upper curve) and with (lower curve) the correction $\Delta(n)$. First of all it is evident that the experimental data are accurate enough to show the importance of the $\Delta(n)$ correction. This can be clearly seen from the upper

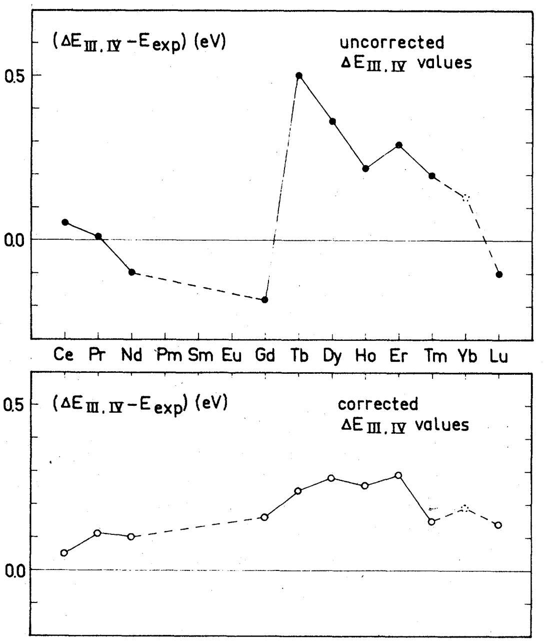

FIG. 8. Difference between $\Delta E_{\mathrm{III,IV}}$ and the experimental XPS data for the position of the $4f$ level relative to the Fermi energy. The lower curve corresponds to the case that the $\Delta E_{\mathrm{III,IV}}$ values have been corrected by the $\Delta(n)$ function. The dotted circle for ytterbium is used to show that the "experimental" value is derived from the fourth ionization energy (Sec. IV).

curve in Fig. 8, which closely resembles the $\Delta(n)$ curve in Fig. 7. Further, the experimental data seems to demonstrate that the neglected $B(n-1)$ term in Eq. (6) has very little importance (lower curve in Fig. 8).

IV. FOURTH IONIZATION ENERGIES OF THE RARE EARTHS

The first three ionization energies for most of the rare earths are known with a reasonably accuracy.[1] This is no longer true for the fourth ionization energy. Presently, it is only for the elements Ce, Pr, Tb, Yb, and Lu that I_4 is known with an accuracy better than 0.1 eV. Some years ago interpolation methods had suggested that the I_4 values for the other elements could be fairly well estimated.[31] This is still true, but the recent experimental fourth ionization value for Tb,[32] was found to be outside the error limit for the previous estimated value. Therefore, in general, the estimated values of I_4 are now ascribed an uncertainty of about ±0.7 eV. The reason for this can in fact be traced back to the assumption of a *constant* difference between the SD values for different ionization stages, which was used in the estimation of the fourth ionization energy. As we have seen in Sec. III, for the excitations of interest in the present context this assumption holds only with an accuracy of about ±0.6 eV. In fact, the deviation from a constant SD value was the basis for the $\Delta(n)$ corrections to $\Delta E_{\mathrm{III,IV}}$. Here we will utilize the XPS data to predict new rather accurate values for the fourth ionization energy. Since the accuracy of the XPS measurements is about ±0.2 eV, the derived I_4 values will be more accurate than those presently available.

That the XPS measurements for trivalent metals can be used for such a purpose is not so surprising since they really involve an ionization of a trivalent ion to a tetravalent one. In order to make the estimations we will study the difference D given by

$$D = I_4 - I_4^{\mathrm{XPS}}(\epsilon_F) \ . \tag{7}$$

Here I_4 is the ionization energy of the LnIV species and $I_4^{\mathrm{XPS}}(\epsilon_F)$ is the XPS result for the position of the f level relative to the Fermi energy. Since I_4 is rath-

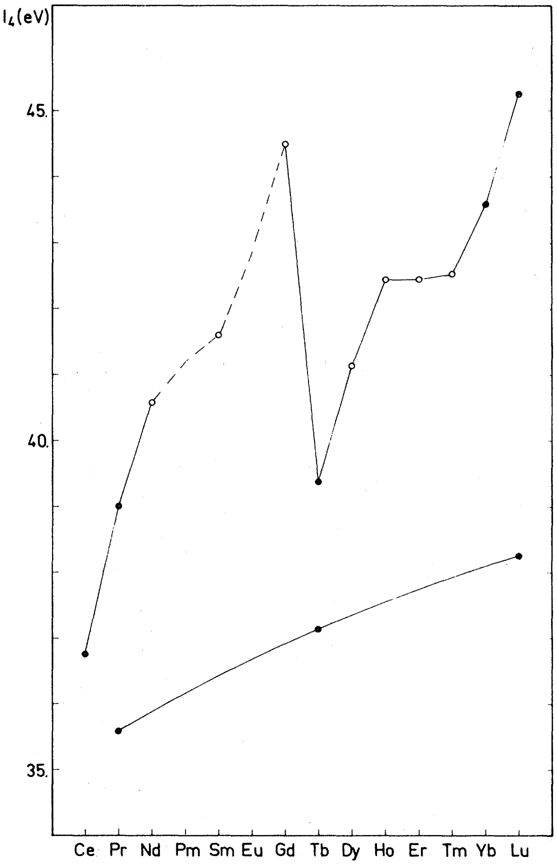

FIG. 9. Estimation of the fourth ionization energy of the lanthanides. Filled circles correspond to exp values (Ref. 1). The smooth curve is the interpolated D function discussed in Sec. IV.

TABLE I. Derived values of the fourth ionization energy for the rare-earth elements compared with earlier estimates. For completeness we also include the experimental values for Ce and Yb. (All energies are given in eV.)

	Exp values Ref. 1	Estimated values (this work)	Earlier estimations Ref. 1
Ce	36.758 ± 0.005		
Pr	38.98 ± 0.02		
Nd		40.6 ± 0.2	40.4 ± 0.4
Pm			41.1 ± 0.6
Sm		41.6 ± 0.2	41.4 ± 0.7
Eu			42.7 ± 0.6
Gd		44.5 ± 0.2	44.0 ± 0.7
Tb	39.37 ± 0.1		
Dy		41.1 ± 0.2	41.4 ± 0.4
Ho		42.4 ± 0.2	42.5 ± 0.6
Er		42.4 ± 0.2	42.7 ± 0.4
Tm		42.5 ± 0.2	42.7 ± 0.4
Yb	43.56 ± 0.1		
Lu	45.250 ± 0.025		

er accurately known for Pr, Tb, and Lu we will use the values of $D(\mathrm{Pr})$, $D(\mathrm{Tb})$, and $D(\mathrm{Lu})$ for a smooth interpolation through the series. Since the quantity D obviously should vary smoothly through the series we are in the favorable position that we know its value in the beginning, in the middle, and at the end of the series. This permits an accurate interpolation. The interpolated smooth D curve is shown in Fig. 9. From this interpolated curve we can now use Eq. (7) to derive I_4 for the other lanthanides. The obtained values are shown as open circles in Fig. 9. For completeness we also include in Fig. 9 the experimental I_4 values for Ce and Yb. For Eu and Yb we naturally lack XPS data for the trivalent state. The same is of course also true for Pm but for other reasons. In the case of Yb we may use the relation (7) in a reversed way, i.e., use the experimental value of $I_4(\mathrm{Yb})$ to predict the XPS value for the $4f$ excitation in the hypothetical trivalent Yb metal. From this we immediately find

$$I_4^{\mathrm{XPS}}(\epsilon_F)_{\mathrm{Yb(III-metal)}} = 5.5\ \mathrm{eV}\ .$$

In Table I we compare the so derived ionization energies with previous estimates. As can be seen, all the new values are within the error limits of the earlier estimations.

V. COMPARISON WITH THE BIS EXPERIMENTS FOR THE RARE EARTHS

In Fig. 10 we compare the experimental BIS data[5] for the rare earths with the $-\Delta E_{\mathrm{II,III}}$ values derived in Sec. II. The general features of the BIS data are certainly reproduced by the $\Delta E_{\mathrm{II,III}}$ values. Only for dysprosium do we have reasons to question the experimental value. The uncertainties in the $\Delta E_{\mathrm{II,III}}$ values are generally of the order of 0.05 eV. Therefore it is clear from Fig. 10 that there is a quite substantial deviation between the BIS data and the $-\Delta E_{\mathrm{II,III}}$ values, far greater than between the XPS data and $\Delta E_{\mathrm{III,IV}}$ for the trivalent metals. In Fig. 11 we plot the difference between the BIS experiments

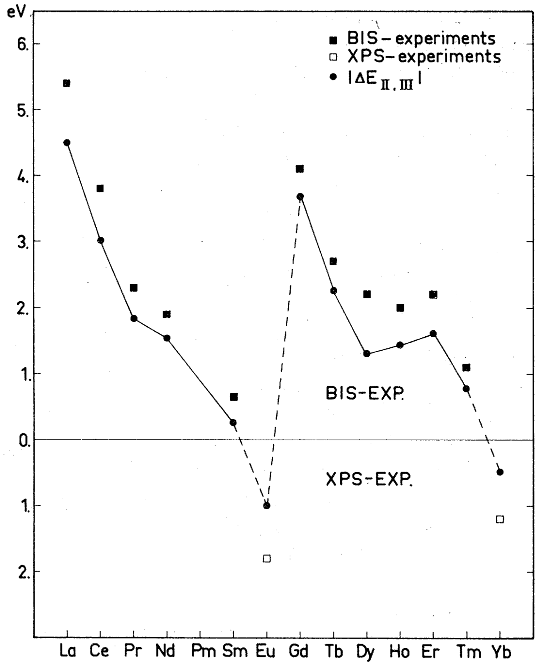

FIG. 10. Filled squares are the BIS data (Ref. 5) for the unoccupied $4f$ levels in the rare-earth series. The filled circles are the derived values of $\Delta E_{\mathrm{II,III}}$. Similarly, the open squares are XPS data for Eu and Yb (Ref. 5). Note that the upper part of the figure refers to BIS experiments, and that the lower part corresponds to XPS experiments.

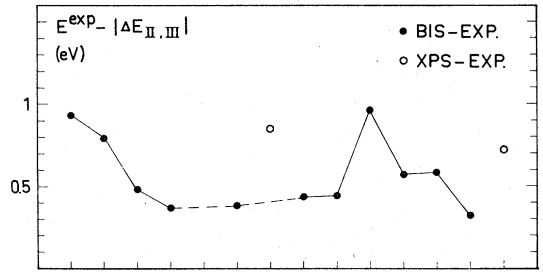

FIG. 11. Difference between on one hand the experimental BIS (Ref. 5) and XPS data (Eu and Yb) (Ref. 5) and on the other the derived values of $\Delta E_{\mathrm{II,III}}$. Filled circles correspond to the BIS case and open circles to the XPS case.

and the $-\Delta E_{\rm II,III}$ values. The slightly irregular behavior is unexpected, because even if there are deviations, these should vary smoothly through the series.

The finding that the $\Delta E_{\rm III,IV}$ values reproduce the XPS data quite well but that $-\Delta E_{\rm II,III}$ deviate substantially from the BIS data might lead one to suspect that these two types of experiments are not directly comparable. However, in Fig. 10 we have also included the XPS data for the two divalent metals europium and ytterbium[5] and also here we note quite a substantial deviation between experiment and $\Delta E_{\rm II,III}$. These deviations are plotted in Fig. 11 and are in fact even somewhat larger than the BIS data deviations. From this we conclude that it is rather the fact that we here are dealing with a divalent → trivalent or a trivalent → divalent transition instead of a trivalent → tetravalent transformation that cause the difference between the BIS and XPS results and not the experimental technique. We will return to this point in Sec. VI.

For the divalent metal europium, the BIS experiment involves a transition to a monovalent state. Therefore if we restrict ourselves to the "complete screening" picture we should study the quantity $-\Delta E_{\rm I,II}$, i.e., the energy difference between the divalent and monovalent metal. This may be obtained from the following steps of reaction;

$$\Delta E_{\rm I,II} = [(+1-\text{metal}) \rightarrow f^{n+2}s-\text{atom} \rightarrow f^{n+1}s^2-\text{atom} \rightarrow (+2-\text{metal})] \quad . \quad (8)$$

The first step corresponds to the cohesive energy of a monovalent metal, and should accordingly be about 20 kcal/mol. The last reaction in Eq. (8) is the experimental divalent cohesive energy. For the reaction involving the two atomic states there are no experimental data available. However, we have estimated the atomic excitation to be about

$$E(f^8s \rightarrow f^7s^2) = -7.6 \pm 0.5 \text{ eV} \quad .$$

Thus we obtain $-\Delta E_{\rm I,II} = 8.6 \pm 0.5$ eV which should be compared with the experimental value 8.7 eV.[5] The same arguments can be applied to the barium metal. In this case we find that the unoccupied 4*f* level should be situated at about 5.3 eV above the Fermi level. No experiments are yet available in this case. (See however note added in proof.)

Recent experiments have shown that there are divalent atoms present at the surface layer of samarium metal.[33] Therefore, if the BIS experiments are surface sensitive we could expect also a transition to a monovalent samarium ion at the surface. From the complete screening model, the position of the f^7 level [again using Eq. (8) and estimated spectroscopic data] would be at about 4.1 ± 0.4 eV above the Fermi energy.

VI. IMPURITY EFFECTS

In view of the obtained agreement between the XPS data and the complete screening picture (i.e., $\Delta E_{\rm III,IV}$), (the deviations being restricted to a range of about 0–0.25 eV, and the XPS experiments having an uncertainty of about 0.2 eV), it might seem a bit too ambitious to pay any further attention to the disagreements shown in the lower part of Fig. 8. On the other hand, the deviations all have the same sign and have about the same magnitude, which points to their being of some significance. Therefore we now turn to the impurity term in Eq. (1) which we have so far neglected.

Since a completely theoretical treatment of the energy term, $E^{\rm imp}$, is not yet feasible (at least not with an accuracy appropriate to the present problem), we turn instead to possible experimental information. What we actually are looking for is the solution energy of a tetravalent impurity in a trivalent host. This is in fact a quantity that can be determined experimentally. However, we are not aware of any such experiments for systems relevant in the present context. On the other hand it is known that thorium forms solid solutions with the rare-earth metals for all concentrations. This would imply that $E_{\rm IV}^{\rm imp}\,({\rm III})$ is negative. Further, over this complete range of solid solubility there is no predominant tendency to formation of well-defined compounds. This must mean that even though $E_{\rm IV}^{\rm imp}\,({\rm III})$ is negative, its magnitude should be comparatively small. Information on binary phase diagrams between rare-earth metals and zirconium (or hafnium) would also be helpful for the present problem, but to our knowledge very little is known about these systems. Even with this somewhat limited experimental background, it still seems possible to state with some confidence that $E_{\rm IV}^{\rm imp}\,({\rm III})$ in general will be negative, although only slightly so. If we add this effect to $\Delta E_{\rm III,IV}$ the agreement with XPS data would obviously improve (lower part of Fig. 8). Whether this impurity effect will vary with the lanthanide element or not is presently a too difficult question to answer. [Such a dependence could in fact have masked the small linear correction term $B(n-1)$ discussed in connection with Eq. (6).]

By applying the same ideas to the BIS experiments, we then deal with a divalent impurity in a trivalent host. Similarly, the XPS experiments for europium and ytterbium involve a trivalent impurity in a divalent host. Experimentally it is known that alkaline-earth metals and trivalent lanthanide metals do not form any solid solutions. This means that $E_{\rm II}^{\rm imp}\,({\rm III})$ and $E_{\rm III}^{\rm imp}\,({\rm II})$ are positive. Therefore the $|\Delta E_{\rm II,III}|$ curve in Fig. 10 should be subject to a correction upwards for the theoretical BIS values and downwards for the theoretical XPS values. Apparently this would improve on the agreement with the experiments. Using the Miedema semiempirical scheme[34] for this situation one finds that E^{imp} here might be of the order of 0.5 eV. This correction is in fact of about the right magnitude to give a good agreement for most of the lanthanides (compare Fig. 11) (we disregard the experimental value for Dy). It is only in the beginning of the lanthanide series that a somewhat larger effect is required before agreement with the BIS experiments can be obtained.

VII. COMMENTS ON THE CALCULATIONS BY HERBST *et al.*

Since we in the present work have obtained accurate results for the "complete screening" picture, it seems here appropriate to make some comments on the theoretical calculations by Herbst *et al.*[10–12] In their work they calculate *atomic* excitations of type $f^n d^{m-1} s \rightarrow f^{n-1} d^m s \; (m = 2, 3)$ and compare with experiments. Then they introduce a correlation parameter, which accounts for the deviation between calculated and measured values. In practice this means that they use the *experimental* spectroscopic levels as an input. Then the cohesive energies relative to the two spectroscopic levels ($f^n d^m s$ and $f^{n-1} d^{m+1} s$) remain to be calculated. Therefore, in principle, it is only here that our treatment deviates from theirs. In their latest work[12] Herbst *et al.* report explicitly on calculated cohesive energies for the divalent and trivalent lanthanide metals, which makes it possible for us to make a direct comparison. For lanthanum, gadolinium, and lutetium they calculate the cohesive energy to be 71, 48, and 60 kcal/mol, respectively. These values should be compared with the experimental values 103.1, 95.5, and 102.2 kcal/mol.[16] Similarly, for europium and ytterbium they obtain 14 and 10 kcal/mol; the experimental data are 42.8 and 37.1 kcal/mol,[16] respectively. Thus, for both the trivalent and divalent lanthanides, the calculations deviate considerably from experiments. However, since the quantity of interest involves a subtraction between the cohesive energies there will at least be a partial cancellation of errors. To what extent such a cancellation takes place is of course difficult to assess. But as an example we quote that for europium and ytterbium they obtain 44 and 25 kcal/mol for the position of the $4f$ level relative to the Fermi energy, while the more correct "complete screening" values are 23 and 11 kcal/mol, respectively. However, it so happens that in this case their calculated values almost completely agree with the XPS data for europium and ytterbium. Therefore it should be stressed that this agreement is somewhat fortuitous, and that effects beyond the $\Delta E_{\text{II,III}}$ term are not quite negligible for these two metals.

VIII. DISCUSSION

In the present paper we have studied the completely screened and relaxed final state picture of the XPS and BIS experiments for the $4f$ levels. For the XPS experiments it turned out that the main effect is already given by just the valence change of the site, $\Delta E_{\text{III,IV}}$, the further relaxation (the impurity effect) playing a relatively minor role; compare the lower part of Fig. 8. From atomic spectroscopy it has been noted that when comparing various excitations of the type $f^n \rightarrow f^{n-1}$ (by vertical or horizontal analysis), there might be a slight discontinuity for the $f^1 \rightarrow f^0$ excitation relative to the other excitation energies.[35,36] This is a bit unfortunate since we use cerium as the tie-point element for the $\Delta E_{\text{III,IV}}$ estimations, and here we just meet this $f^1 \rightarrow f^0$ case. However, it is only for cerium that the $\Delta E_{\text{III,IV}}$ value is known with a reasonable accuracy so there is no other choice. Another inaccuracy is found in the correction term $\Delta(n)$, which had to be estimated for many of the rare earths (Fig. 7). The estimations are somewhat more accurate for the heavier ($n > 7$) lanthanides than for the lighter elements, and this might account for the slightly asymmetric form of the deviation curve in the lower part of Fig. 8. If these two types of uncertainties could be avoided it might be that the so refined values for $\Delta E_{\text{III,IV}}$ will show a nearly constant shift relative to the XPS experiments. However, it must be stressed that this discussion is presently rather academic, since neither of these inaccuracies will be greater than the XPS experimental uncertainty (± 0.2 eV). If the accuracy of XPS experiments improve in the future, hopefully experimental values of $\Delta(n)$ for all the lanthanides will have become available from atomic spectroscopy to put more accurate $\Delta E_{\text{III,IV}}$ values at our disposal. Finally, the value of the constant in Eq. (6) is a bit uncertain, but a small change there will only result in a small rigid displacement of the $\Delta E_{\text{III,IV}}$ curve relative to the experimental values.

Another uncertainty, which was not discussed in Secs. II — VII is the possibility of a change of the f-state Racah parameters when going from the free atom to the solid (both having the same valence state). But from careful considerations of the cohesive energy through the trivalent lanthanide series no such effect could be discerned.[37] Therefore, this possible energy change of the f-level position could not exceed 0.05 eV. The same upper limit should also be expected for the divalent as well as the tetravalent metallic case. Therefore, for quantities like $\Delta E_{\text{II,III}}$ and $\Delta E_{\text{III,IV}}$, where a subtraction is made, this possible effect will be totally negligible.

In order to compare with the BIS experiments we have used the quantity $\Delta E_{\text{II,III}}$ which can be accurately determined. Thereby we found quite substantial deviations, much larger than the deviations between

XPS experiments and $\Delta E_{\rm III,IV}$. Further, we also noted that the BIS deviations and the XPS deviations were of opposite sign. In the present paper we have argued that these findings can be understood by means of the "impurity effect". This means that we have assumed that the final state consists of a charge neutral site and a completely relaxed electron density state. The obtained agreement with the experimental data seems to support this picture for these metallic systems. A somewhat contrasting case to this might be the semiconducting compound SmS, which we here will discuss very briefly. In recent XPS measurements for SmS the f level was found to be 0.9 eV below the Fermi energy.[38] Since SmS is known to readily transform into a mixed valence state (either by pressure or by chemical manipulation), this XPS result is a bit surprising since the f level is expected to be situated very close to the Fermi energy. Other experiments had in fact indicated a neighborhood of about 0.1 eV.[39] However, XPS experiments on $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$ (or $\mathrm{Sm}_{1-x}\mathrm{Gd}_x\mathrm{S}$) showed that the f level approaches the Fermi level rapidly with increasing x and several mechanisms were proposed in order to explain this behavior.[38] Among them we favor the picture of an incompletely screened final state, caused by SmS being not a metal but a semiconductor. Then by addition of YS or GdS, quite mobile d electrons become available to screen the final state more efficiently. Therefore, the f level position, as measured by XPS, will approach the Fermi level rapidly with increasing YS substitution.

The same approach as taken in the present paper can also be applied to metallic rare-earth alloys. In this connection we would like to mention Miedema's semiempirical thermodynamical investigation of the valence state of Eu in various alloys.[40] If we restrict ourselves to the complete screening picture of the XPS experiments (and thus neglect the impurity effect) we could use his derived values of $\Delta E_{\rm II,III}$ for comparison with XPS data for the 4f level (when such data will become available). From Miedema's treatment it follows that alloying may have a profound influence on the position of the 4f level and may in fact bring it up to the Fermi level. This is of course already clear from the experimental knowledge that Eu in some transition-metal compounds is found to be trivalent rather than divalent. Therefore, the "paradox", stated in the Appendix of Ref. 12, that in certain rare-earth systems some experiments indicate an immediate neighborhood of the f level to the Fermi level while XPS experiments would not support this, seems to us to be a somewhat too dramatized statement. To our knowledge such a paradoxial situation has not yet been established experimentally for any metallic systems. However, for semiconducting materials (like SmS), this is apparently the case, but here, as just mentioned, this is probably due to an incompletely screened final state in the XPS experiment and therefore this does not necessarily imply any fundamental contradiction.

Under high pressure both europium and ytterbium are expected to become trivalent. Then one may ask whether this valence transition will be continuous (passing through a pressure range with an intermediate valence) or discontinuous. Since the impurity effect of having a trivalent ion in a divalent host is energetically unfavorable, this would seem to favor a discontinuous change. However, high pressure has a tendency to equalize atoms, and therefore the impurity effect will decrease with pressure and maybe even to such an extent that a continuous transition will result. Another possibility is that the coherence energy associated with the interconfiguration fluctuation (ICF) state is prominent enough to give a continuous transition. The possibility of slightly different "impurity effects" in SmS, SmSe, and SmTe might be the cause of their different behavior under pressure.[41]

For a given series of trivalent rare-earth intermetallic systems, $\mathrm{Ln}_{1-x}M_x$ (x and M constant), the derived values of $\Delta E_{\rm III,IV}$ can be used to "linearize" the position of the f level through the series. What we mean by this is that if the experimental values of the f-level position is subtracted by $\Delta E_{\rm III,IV}$, a linear function through the series will result. Therefore, if the f-level position is known for one of the heavier and one of the lighter rare-earth intermetallic systems, then the position of the f level for the other rare-earth intermetallics (of the same type and composition) can be accurately determined from the $\Delta E_{\rm III,IV}$ values.

As we have seen in this paper the consistency between the measured cohesive energies, the XPS results and the atomic spectroscopic levels is very good. In fact this permitted us to use the XPS results for an improved estimation of the fourth ionization energy of the rare-earth elements.

Finally, we would like to comment on the position of the 4f level in cerium. From the internal consistency with the other rare-earth metals it follows immediately from the measured values of their f levels that the position of the 4f state in cerium should be expected at 1.9 ± 0.3 eV. This is in fact in agreement with the recent experiments by Platau and Karlsson[28] and by Johansson *et al.*[42] The implication of this for the understanding of the γ-α phase transition in cerium has been discussed elsewhere.[43]

Note added in proof: Recent experiments show that the unoccupied f level in barium is situated about 11 eV above the Fermi energy (P. O. Nilsson, private communication). This deviates considerably from our derived value of about 5 eV (Sec. V). This indicates that the 4f orbital in barium is far more extended than for the lanthanides and therefore very sensitive to changes in the (sd) electron density distribution. Thus the 4f electron in barium cannot be treat-

TABLE II. Derived values for $-\Delta E_{\mathrm{II,III}}$ and $\Delta E_{\mathrm{III,IV}}$ as described in the main text. The uncertainties of these values are discussed in the paper. The experimental XPS and BIS data for the $4f$ levels are also included (Ref. 5). (All energies are given in eV).

	$-\Delta E_{\mathrm{II,III}}$	BIS experiments[a]	$\Delta E_{\mathrm{III,IV}}$	corrected $\Delta E_{\mathrm{III,IV}}$	XPS experiments[a]
La	4.47	5.4			
Ce	3.01	3.8	1.95		1.9[b]
Pr	1.82	2.3	3.41	3.51	3.4
Nd	1.53	1.9	4.60	4.80	4.7
Pm	· · ·		4.89	5.07	
Sm	0.27	0.65	· · ·		5.2
Eu	−1.0	8.7	6.15	6.38	1.8
Gd	3.67	4.1	7.4	7.8	7.6
Tb	2.26	2.7	2.75	2.49	2.25
Dy	1.30	2.2	4.16	4.08	3.8
Ho	1.43	2.0	5.12	5.16	4.9
Er	1.62	2.2	4.99	4.99	4.7
Tm	0.78	1.1	4.80	4.75	4.6
Yb	−0.5		5.63	5.69	1.2
Lu			6.9	7.15	7.0

[a] Provisional values within ±0.2 eV (Ref. 5).
[b] Data given in Ref. 28.

ed as a core electron and therefore the approach of the present paper is no longer applicable.

ACKNOWLEDGMENT

We would like to express our gratitude to Dr. Y. Baer, Eidgenössische Technische Hochschule, Zürich for making his unpublished XPS and BIS data available to us prior to publication.

APPENDIX

In Table II we list the derived values of $-\Delta E_{\mathrm{II,III}}$ and $\Delta E_{\mathrm{III,IV}}$ together with experimental XPS and BIS data.

---

[1] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels - The Rare-Earth Elements,* Nat. Bur. Stand. (U.S.) Ref. Data Ser. 60 (U.S. GPO, Washington, D.C., 1978).

[2] Y. Baer, J. Electron. Spectrosc. Relat. Phenom. 5, 611 (1974).

[3] M. Campagna, G. K. Wertheim, and E. Bucher, *Structure and Bonding 30, Rare Earths* (Springer, Berlin, 1976), p. 99.

[4] C. E. Habermann and A. H. Daane, J. Chem. Phys. 41, 2818 (1964).

[5] J. K. Lang, Y. Baer, and P. A. Cox, Phys. Rev. Lett. 42, 74 (1979), and (unpublished).

[6] A. J. Freeman in *Magnetic Properties of The Rare-Earth Metals,* edited by R. J. Elliott (Plenum, New York, 1972), p. 245.

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

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

[9] When the single site $4f \rightarrow \epsilon_F$ excitation energy becomes very small, it seems likely that the given description should be replaced by a superposition of such one-particle excitations over the whole lattice. Thereby the $4f \rightarrow \epsilon_F$ excitation can go continuously over into the interconfiguration fluctuation (IFC) state. The formulation given in Refs. 7 and 8 happens to show this property.

[10] J. F. Herbst, D. N. Lowy and R. E. Watson, Phys. Rev. B 6, 1913 (1972).

[11] J. F. Herbst, R. E. Watson and J. W. Wilkins, Phys. Rev. B 13, 1439 (1976).

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

[13] L. Hodges, R. E. Watson and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972).

[14] J. K. Lang and Y. Baer, Rev. Sci. Instrum. (to be published).

[15] B. Johansson, J. Phys. F 4, L169 (1974).

[16] L. Brewer (unpublished).

[17] K. A. Gschneidner, Solid State Phys. 16, 275 (1964).

[18] B. Johansson, J. Phys. F 7, 877 (1977).

[19] B. Johansson, in *Proceedings of the 2nd International Conference on the Electronic Structure of the Actinides,* edited by J. Mulak, W. Suski, and R. Troc (Wroclaw, Ossolineum, 1977), p. 49.

[20] K. A. Gschneidner, J. Less-Common Metals 17, 13 (1969).

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

[22] M. A. Catalán, F. Rohrlich, and A. G. Shenstone, Proc. R. Soc. London Ser. A 221, 421 (1954); G. Racah, Bull. Res.

Counc. Isr. 3, 290 (1954).

[23] C. K. Jørgensen, Mol. Phys. 5, 271 (1962).

[24] K. L. Vander Sluis and L. J. Nugent, J. Opt. Soc. Am. 64, 687 (1974).

[25] For brevity we have in Eq. (3) neglected the rather important spin-orbit term. In the following when we refer to a change of the Racah parameters this is meant to include also a change of the coefficient for the spin-orbit term. When we later on in this paper "interpolate" values for the $\Delta(n)$-function the spin-orbit term has been included.

[26] W. C. Martin, Opt. Pur. Apl. 5, 181 (1972).

[27] See Ref. 26 for a review of these matters.

[28] A. Platau and S. E. Karlsson, Phys. Rev. 18, 3820 (1978).

[29] W. C. Martin, J. Opt. Soc. Am. 61, 1682 (1971).

[30] See the comment given under the heading of Ref. 25. Reasonable values for the change of the Racah parameters were initially assumed and then refined in order to fit the known experimental values of $\Delta(n)$, ($n = 1, 2, 8, 13$, and 14). From this the other values of $\Delta(n)$ can be "interpolated", compare Fig. 7.

[31] W. C. Martin, L. Hagan, J. Reader, and J. Sugar, J. Phys. Chem. Ref. Data 3, 771 (1974).

[32] N. Spector and J. Sugar, J. Opt. Soc. Am. 66, 436 (1976).

[33] G. K. Wertheim and G. Creselius, Phys. Rev. Lett. 40, 813 (1978); J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagström, Phys. Rev. Lett. 41, 1499 (1978).

[34] A. R. Miedema, J. Less-Common Metals 46, 67 (1976). In this semiempirical scheme, the energy effect on binary solid alloy formation is derived from a negative term from the difference in chemical potential, ϕ^*, for electrons at the two types of atomic cells, and a second term that reflects the discontinuity in the density of electrons, n_{ws}, at the boundary between dissimilar atomic cells. The parameters ϕ^* and n_{ws} are properties of the pure metals.

[35] K. L. Vander Sluis and L. J. Nugent, Phys. Rev. A 6, 86 (1972).

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

[37] B. Johansson (unpublished).

[38] G. K. Wertheim, I. Nowik, and M. Campagna, Z. Phys. B 29, 193 (1978).

[39] E. Kaldis and P. Wachter, Solid State Commun. 11, 907 (1972).

[40] A. R. Miedema, J. Less-Common Metals 46, 167 (1976).

[41] A. Chatterjee, A. K. Singh, and A. Jayaraman, Phys. Rev. B 6, 2285 (1972).

[42] L. I. Johansson, J. W. Allen, T. Gustafsson, I. Lindau, and S. B. M. Hagström, Solid State Commun. (to be published).

[43] B. Johansson, Philos. Mag. 30, 469 (1974).