Lattice-constant dependence of $4f$ levels in Sm metal: Evidence for a bulk valence transition

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We have calculated $4f$-level positions in samarium metal as functions of Wigner-Seitz radius r_{WS} and find that the $4f^6$ state, which is empty at normal pressure, becomes occupied at larger r_{WS}, signaling a trivalent-to-divalent transition. The valence change is estimated to occur for a volume expansion of approximately 8%. One-electron estimates of the $4f$ excitation energies fail to show this behavior. The Coulomb term U is confined to a narrow energy interval over the r_{WS} range considered.

I. INTRODUCTION

In previous publications we described relativistic calculations of both the occupied[1] and unoccupied[2] $4f$-level positions in the rare-earth metals. The computations were made for unit-cell volumes corresponding to the normal-pressure lattice constants, and the results are in excellent agreement with x-ray photoemission (XPS) and bremsstrahlung isochromat spectroscopy (BIS) measurements[3] of the level energies. Here we concentrate on samarium, one of the five lanthanide elements (Ce, Sm, Eu, Tm, and Yb) which form so-called fluctuating valence compounds. We investigate the lattice-constant variation of the $4f$ levels in Sm metal and find evidence for a trivalent-to-divalent transition (i.e., $4f^5$ state occupied $\rightarrow 4f^6$ state occupied) at increased lattice parameter. The signature of the transition is the sign change of $\Delta_+(4f^5 \rightarrow 4f^6)$, the unoccupied $4f$-level position relative to the Fermi energy ϵ_F; $\Delta_+(4f^5 \rightarrow 4f^6)$ is positive near the equilibrium atomic volume but turns negative at a larger volume.

Central to our study is the use of total band-energy differences, rather than one-electron eigenvalues, to estimate $4f$ excitation energies. Relativistic Hartree-Fock (RHF) computations for appropriate free-atom configurations are initially performed, and crystal potentials are constructed by means of

the renormalized atom method. Total band energies E_{band}^{RHF} emerge from relativistic band calculations for the $5d$ and $6s$ electrons; during the course of these computations, which are iterated to crude self-consistency, all other wave functions remain fixed. Further details can be found in Refs. 1 and 2.

Bulk samarium metal is normally trivalent with a complement of five $4f$ electrons, and $\Delta_+(4f^5 \rightarrow 4f^6)$ is given [2] by

$$
\begin{aligned}
\Delta_+(4f^5 \rightarrow 4f^6) &= E_{metal}(4f^6(5d,6s)^2) \\
&\quad - E_{metal}(4f^5(5d,6s)^3) \\
&\cong \xi_+ + E_{metal}^{RHF}(4f^6(5d,6s)^2) \\
&\quad - E_{metal}^{RHF}(4f^5(5d,6s)^3) \quad . \quad (1)
\end{aligned}
$$

Analogously, the position of the occupied $4f$ level with respect to ϵ_F is

$$
\begin{aligned}
\Delta_-(4f^5 \rightarrow 4f^4) &= E_{metal}(4f^4(5d,6s)^4) \\
&\quad - E_{metal}(4f^5(5d,6s)^3) \\
&\cong \xi_- + E_{metal}^{RHF}(4f^4(5d,6s)^4) \\
&\quad - E_{metal}^{RHF}(4f^5(5d,6s)^3) \quad . \quad (2)
\end{aligned}
$$

E_{metal} signifies the total energy per unit cell of the metal, and each E_{metal}^{RHF} term represents the total RHF energy of all the electrons in a Wigner-Seitz (WS) sphere of the solid having the indicated elec-

tron configuration. In accord with our assumption of complete screening,[4] which we believe best reflects the experimental situation, all configurations appearing in Eqs. (1) and (2) are electrically neutral. $\xi_{\pm}$ denote free-atom correlation energy differences which approximately account for correlation effects on $\Delta_{\pm}$; alternatively, they can be considered as insuring maintenance of the observed free-atom excitation energies. Hence, the role of the band calculations is to describe the transition from the atomic to the metallic state, and that transition in essence involves changing the boundary conditions satisfied by the $5d$ and $6s$ wave functions. All $4f$ states in Eqs. (1) and (2) are the Hund's-rule ground multiplets, so that our work is confined to *one* of the allowed transitions connected with a change in $4f$ occupation number; energies for excitation of different multiplets can be obtained in a straightforward fashion via atomic multiplet theory since the $4f$ wave functions in the solid remain atomiclike.

We have calculated $\Delta_{+}(4f^5 \to 4f^6)$ and $\Delta_{-}(4f^5 \to 4f^4)$ for thirteen WS radii r_{WS} specified by neighboring points on two different radial meshes, and Sec. II is devoted to the results. We find that one-electron energies are poor approximations to $\Delta_{\pm}$ and do not signal a valence change. Despite the significant variations of $\Delta_{\pm}$ over the range of r_{WS} values considered, the Coulomb term

$$U = \Delta_{+}(4f^5 \to 4f^6) + \Delta_{-}(4f^5 \to 4f^4) \ , \quad (3)$$

is confined to an energy interval only ~ 1 eV wide. Section III discusses aspects of the results, including connections with fluctuating valence behavior in compounds such as SmS; calculations of $\Delta_{+}(4f^6 \to 4f^7)$, the empty $4f$ level associated with an occupied $4f^6$ state, are also reported.

II. RESULTS

A. $\Delta_{-}(4f^5 \to 4f^4)$: Stability of the trivalent state with respect to the tetravalent

We find that Δ_{-} is an increasing function of r_{WS} over essentially the entire range investigated here; that is, the $4f^5$ level moves progressively further below ϵ_F as the unit cell expands. Figure 1 displays the results. At the equilibrium atomic volume (corresponding to $r_{WS} = 3.76$ a.u.) $\Delta_{-} \simeq 5.5$ eV, which compares quite favorably with the XPS value of $\simeq 5.1$ eV (Ref. 3).

The variation of Δ_{-} with r_{WS} stems from the changing atom $\to$ metal energy differences between the trivalent and tetravalent configurations entering

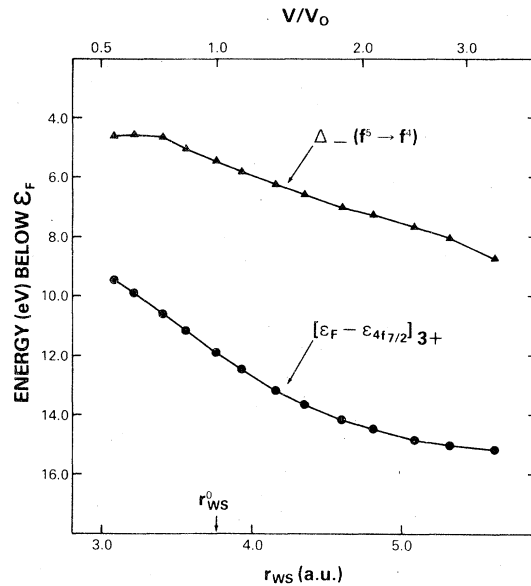

FIG. 1. $\Delta_{-}(4f^5 \to 4f^4)$ and its one-electron analog, $[\epsilon_F - \epsilon_{4f_{7/2}}]_{3+}$, as functions of r_{WS}. $r_{WS}^0 = 3.76$ a.u. is the equilibrium WS radius. The upper horizontal scale is for the ratio of the unit-cell volume V at a given r_{WS} to that for normal pressure, V_0.

Eq. (2). This can be seen through decomposition of Δ_{-} into its four principal constituents:

$$\Delta_{-}(4f^5 \to 4f^4) \equiv \xi_{-} + \delta E(\text{atom}) + \delta E(\text{Hund}) + \delta E(\text{atom} \to \text{metal}) \ . \quad (4)$$

The first three terms on the right side are independent of r_{WS}. The free-atom correlation energy difference ξ_{-} is ideally specified by

$$
\begin{aligned}
\xi_{-} &= E_{\text{corr}}(4f^4 5d^3 6s) - E_{\text{corr}}(4f^5 5d^2 6s) \\
&= [E(4f^4 5d^3 6s) - E(4f^5 5d^2 6s)]_{\text{expt}} \\
&\quad - [E(4f^4 5d^3 6s) - E(4f^5 5d^2 6s)]_{\text{gnd. atom}}^{\text{RHF}} \ ,
\end{aligned}
$$
$$ (5) $$

where all configurations denote the atomic ground states. Owing to the lack of atomic spectral data for the $4f^4 5d^3 6s$ configuration, however, we approximate ξ_{-} by the value for the $f^4 ds \to f^3 d^2 s$ transition in Nd for which atomic data[5] exist, $\xi_{-}(\text{Nd}) = 1.6$ eV. This introduces an uncertainty, perhaps as large as 0.5 eV, in ξ_{-} (the reliability of this approximation is discussed in connection with Fig. 3 of Ref. 2). $\delta E(\text{atom})$ is the total energy difference between the initial and final free-atom states; it is computed in the average of LS configura-

tion scheme[6] which involves averaging over the L, S, M_L, and M_S quantum numbers of the open shells:

$$\delta E(\text{atom}) = [E(4f^4 5d^3 6s) - E(4f^5 5d^2 6s)]_{LS\,\text{atom}}^{\text{RHF}}$$

$$= 4.9 \text{ eV} \ . \tag{6}$$

The calculated 4*f* shell electrostatic integrals together with the pertinent multiplet theory expressions yield the Hund's-rule correction (HRC) term, as discussed in the Appendix to Ref. 1:

$$\delta E(\text{Hund}) = [E(4f^4) - E(4f^5)]_{4f\,\text{HRC}} = 0.8 \text{ eV} \ . \tag{7}$$

The remaining component of Δ_- is

$$\delta E(\text{atom} \rightarrow \text{metal}) = [E_{\text{band}}^{\text{RHF}}(4f^4(5d,6s)^4)$$
$$- E_{LS\,\text{atom}}^{\text{RHF}}(4f^4 5d^3 6s)]$$
$$- [E_{\text{band}}^{\text{RHF}}(4f^5(5d,6s)^3)$$
$$- E_{LS\,\text{atom}}^{\text{RHF}}(4f^5 5d^2 6s)] \ . \tag{8}$$

It represents the difference in atom → metal energy lowering between the initial and final states and depends upon r_{WS}. Table I presents the values we have obtained. $\delta E(\text{atom} \rightarrow \text{metal})$ monotonically increases with r_{WS}, which means progressively more energy is gained in forming the trivalent state relative to that gained in forming the tetravalent state.

Although $\delta E(\text{atom} \rightarrow \text{metal}) < 0$ for $r_{\text{WS}} < 4.8$ a.u., the sum $[\xi_- + \delta E(\text{atom}) + \delta E(\text{Hund})] = 7.3$ eV prevents a sign change of Δ_-; the 3+ configuration is always stable relative to the 4+ over the r_{WS} range we consider. Table I also lists the 6*s* occupancies n_{6s}^{3+} and n_{6s}^{4+} resulting from the band calculations; the variation of $(n_{6s}^{3+} - n_{6s}^{4+})$ with r_{WS} correlates well with the behavior of $\delta E(\text{atom} \rightarrow \text{metal})$.

The one-electron analog of Δ_- is $[\epsilon_F - \epsilon_{4f_{7/2}}]_{3+}$, the $4f_{7/2}$ one-electron energy relative to ϵ_F in the trivalent configuration. This quantity is also displayed in Fig. 1. The $\epsilon_{4f_{7/2}}$ values emerging from the band work have been corrected to correspond to the Hund's-rule 4*f* state by the addition of $(2/n)\delta E$, where δE is the total energy correction required to place the 4*f* electrons (whose number $n = 5$ in this case) into the Hund's-rule multiplet. As Fig. 1 shows, $[\epsilon_F - \epsilon_{4f_{7/2}}]_{3+}$ greatly exceeds the total energy difference estimate Δ_- for the 4*f* promotion energy.

B. $\Delta_+(4f^5 \rightarrow 4f^6)$: Destabilization of the trivalent state with respect to the divalent as r_{WS} increases

In contrast to Δ_-, Δ_+ is smaller in magnitude and is a decreasing function of r_{WS} over most of the range studied here. Figure 2 summarizes the results. Δ_+ can be decomposed in the same

TABLE I. The $\delta E(\text{atom} \rightarrow \text{metal})$ component of $\Delta_-(4f^5 \rightarrow 4f^4)$ [see Eqs. (4) and (8)] and the 6*s* band occupancies n_{6s}^{3+} and n_{6s}^{4+} of the trivalent and tetravalent metallic states as functions of r_{WS}.

r_{WS} (a.u.)	$\delta E(\text{atom} \rightarrow \text{metal})$ (eV)	n_{6s}^{3+}	n_{6s}^{4+}
3.08	−2.6	0.3	0.5
3.22	−2.6	0.5	0.7
3.41	−2.6	0.7	0.8
3.56	−2.2	0.8	0.9
3.76	−1.8	0.9	0.9
3.93	−1.4	1.0	0.9
4.16	−1.0	1.1	1.0
4.35	−0.7	1.1	1.0
4.60	−0.3	1.2	0.9
4.81	+0.0	1.2	0.9
5.08	+0.4	1.2	0.9
5.32	+0.8	1.2	0.9
5.62	+1.5	1.2	0.8

manner as Δ_- :

$$\Delta_+(4f^5 \rightarrow 4f^6) \equiv \xi_+ + \delta E(\text{atom}) + \delta E(\text{Hund})$$
$$+ \delta E(\text{atom} \rightarrow \text{metal}) \quad . \quad (9)$$

The free-atom correlation energy difference is

$$\xi_+ = E_{\text{corr}}(4f^6 5d\, 6s) - E_{\text{corr}}(4f^5 5d^2 6s)$$

$$= [E(4f^6 5d\, 6s) - E(4f^5 5d^2 6s)]_{\text{expt}}$$

$$- [E(4f^6 5d\, 6s) - E(4f^5 5d^2 6s)]_{\text{gnd. atom}}^{\text{RHF}}$$

$$(10a)$$

$$\simeq -1.9 \text{ eV} \quad . \quad (10b)$$

The negative sign indicates that correlation is greater in the $4f^6$ state than in the $4f^5$ (just as the positive sign of ξ_- implies larger correlation in the $4f^5$ state than in the $4f^4$). The atomic spectral information[7] employed here (as well as in Ref. 2) to obtain the first bracketed term in Eq. (10a) is uncertain, perhaps as much as several tenths of an eV. The other constituents of Δ_+ are

$$\delta E(\text{atom}) = [E(4f^6 5d\, 6s) - E(4f^5 5d^2 6s)]_{LS\, \text{atom}}^{\text{RHF}}$$

$$= 0.7 \text{ eV} \quad , \quad (11)$$

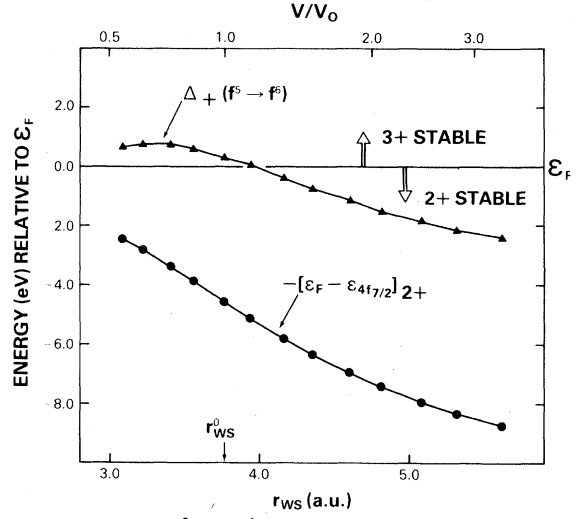$$\delta E(\text{Hund}) = [E(4f^6) - E(4f^5)]_{4f\, \text{HRC}} = -1.2 \text{ eV} \quad , \quad (12)$$

FIG. 2. $\Delta_+(4f^5 \rightarrow 4f^6)$ and its one-electron cognate, $-[\epsilon_F - \epsilon_{4f_{7/2}}]_{2+}$, as functions of r_{WS}. $\Delta_+ > 0$ means that the trivalent metallic state is stable, while $\Delta_+ < 0$ implies stability of the divalent state.

and $\delta E(\text{atom} \rightarrow \text{metal})$ is given by

$$\delta E(\text{atom} \rightarrow \text{metal}) = [E_{\text{band}}^{\text{RHF}}(4f^6(5d,6s)^2)$$

$$- E_{LS\, \text{atom}}^{\text{RHF}}(4f^6 5d\, 6s)]$$

$$- [E_{\text{band}}^{\text{RHF}}(4f^5(5d,6s)^3)$$

$$- E_{LS\, \text{atom}}^{\text{RHF}}(4f^5 5d^2 6s)] \quad . \quad (13)$$

TABLE II. The $\delta E(\text{atom} \rightarrow \text{metal})$ component of $\Delta_+(4f^5 \rightarrow 4f^6)$ [see Eqs. (9) and (13)] and the $6s$ band occupancies n_{6s}^{3+} and n_{6s}^{2+} of the trivalent and divalent metallic states as functions of r_{WS}.

r_{WS} (a.u.)	$\delta E(\text{atom} \rightarrow \text{metal})$ (eV)	n_{6s}^{3+}	n_{6s}^{2+}
3.08	3.1	0.3	0.1
3.22	3.2	0.5	0.3
3.41	3.2	0.7	0.5
3.56	3.0	0.8	0.7
3.76	2.7	0.9	0.7
3.93	2.5	0.9	0.9
4.16	2.0	1.0	1.0
4.35	1.7	1.1	1.1
4.60	1.2	1.1	1.2
4.81	0.9	1.2	1.3
5.08	0.5	1.2	1.4
5.32	0.3	1.2	1.5
5.62	-0.0	1.2	1.7

Values of δE(atom $\rightarrow$ metal) are given in Table II. For $r_{WS} > 3.2$ a.u. this quantity steadily decreases as r_{WS} grows larger, indicating that the stabilization of the trivalent metallic state relative to the divalent progressively diminishes. This trend is tracked by the occupation number difference $(n_{6s}^{3+} - n_{6s}^{2+})$, as Table II shows.

Returning to Fig. 2, we observe that $\Delta_+ \simeq 0.3$ eV at the normal pressure WS radius,[8] in reasonable accord with the BIS determination[3] of 0.65 ± 0.2 eV. The most remarkable feature of Fig. 2, however, is the sign change of Δ_+ near $r_{WS} = 4.0$ a.u. A negative value implies that the divalent state is stable relative to the trivalent [cf. Eq. (1)]. Consequently, bulk samarium metal is predicted to undergo a trivalent-to-divalent transition, involving the filling of the $4f^6$ level, at a cell volume larger than the equilibrium value. We note that a change in the sign of Δ_+ occurs even in the absence of the correlation term ξ_+, although it takes place at a different r_{WS}. $\Delta_+ - \xi_+$ is an RHF-only estimate of the excitation energy,

$$\Delta_+ - \xi_+ = \delta E(\text{atom}) + \delta E(\text{Hund})$$
$$+ \delta E(\text{atom} \rightarrow \text{metal}) , \qquad (14)$$

and this quantity becomes negative for $r_{WS} \simeq 5.3$ a.u. [cf. Eqs. (11), (12), and Table II)].

By simply rewriting Eq. (1) as

$$-\Delta_+ = E_{\text{metal}}(4f^5(5d,6s)^3) - E_{\text{metal}}(4f^6(5d,6s)^2) , \qquad (15)$$

it can be seen that $[\epsilon_F - \epsilon_{4f_{7/2}}]_{2+}$, the $4f_{7/2}$ one-electron energy relative to ϵ_F in the divalent state, can be interpreted as the single-particle cognate of $(-\Delta_+)$. As was done in the preceding section, the $4f$ eigenvalues have been corrected to correspond to the Hund's-rule $4f$ multiplet by incorporating $(2/n)\delta E$, where δE is the Hund's-rule total energy correction and $n = 6$ in this instance. Figure 2 displays values of $-[\epsilon_F - \epsilon_{4f_{7/2}}]_{2+}$, and it is clear that the one-electron energies offer no indication of a valence change over the r_{WS} range considered. In particular, they do not reproduce the *sign* of Δ_+ for $r_{WS} < 3.9$ a.u.

An accurate transition pressure P for the valence change cannot be extracted from the Δ_+ calculations in view of the errors inherent in our technique. There is an uncertainty of ≤ 0.2 eV in the δE(atom $\rightarrow$ metal) terms (which govern the shapes of the $\Delta_\pm$ curves in Figs. 1 and 2) arising from the self-consistent band convergence procedures. More importantly, an error possibly as great as 0.4 eV is

associated with the correlation contribution ξ_+ because of ambiguities in the spectral data. We can, however, estimate P by several means and, in doing so, assess the error in ξ_+.

First, we neglect ξ_+ entirely and consider the RHF-only quantities entering Δ_+. Figure 3 displays $E_{\text{metal}}^{\text{RHF}}$ for the $4f^5$ and $4f^6$ configurations versus atomic volume V ($E_{\text{metal}}^{\text{RHF}}$ differs from $E_{\text{band}}^{\text{RHF}}$ by the inclusion of the $4f$ Hund's-rule correction). From a numerical fit we find that the trivalent curve has a minimum corresponding to $r_{WS} \simeq 3.92$ a.u., 4% larger than the observed value of 3.76 a.u.; the calculated compressibility is $\simeq 2.7 \times 10^{-11}$ Pa^{-1}, which compares well with the low-temperature experimental value[9] of 2.63×10^{-11} Pa^{-1}. Consistent with expectation, both quantities are greater for the divalent state: $r_{WS} \simeq 4.61$ a.u. at the energy minimum, and the compressibility is $\simeq 8.1 \times 10^{-11}$ Pa^{-1}. The pressure P at which a first-order valence transition can be expected to occur is given by the slope of the common tangent to the curves (Maxwell construction). We obtain $P \simeq -3 \times 10^9$ Pa (-30 kbar), which corresponds to a volume expansion of $\sim 8\%$. [The common tangent extends from $V = 260$ a.u. ($r_{WS} = 4.0$ a.u.) on the trivalent curve to $V = 1440$ a.u. ($r_{WS} = 7.0$ a.u.) on the divalent curve; the latter was numerical-
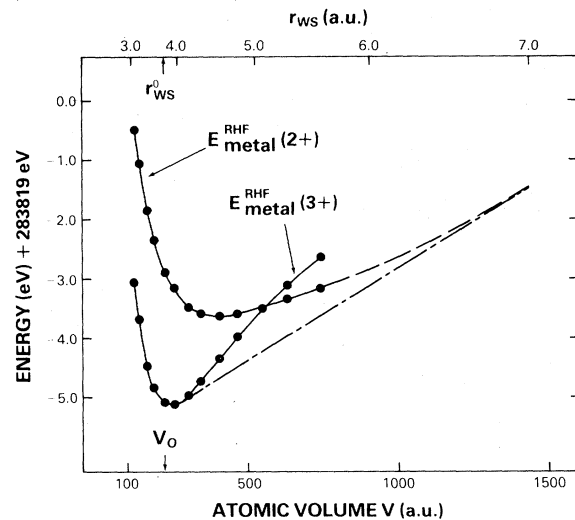

FIG. 3. $E_{\text{metal}}^{\text{RHF}}(4f^5(5d,6s)^3) \equiv E_{\text{metal}}^{\text{RHF}}(3+)$ and $E_{\text{metal}}^{\text{RHF}}(4f^6(5d,6s)^2) \equiv E_{\text{metal}}^{\text{RHF}}(2+)$ versus atomic volume. Filled circles denote the points at which calculations have been done. The dashed part of $E_{\text{metal}}^{\text{RHF}}(2+)$ was obtained by numerical extrapolation. The dot-dashed line is the common tangent needed for estimating the transition pressure.

ly extrapolated for the purpose, as shown in Fig. 3.] We emphasize that this procedure *overestimates* P since the $E_{\text{metal}}^{\text{RHF}}$ terms do *not* include correlation and ξ_+ is negative [cf. Eqs. (1) and (10)].

Second, we include ξ_+ by displacing the 3+ curve in Fig. 3 upward by $|\xi_+| = 1.9$ eV so that the separation between the curves at $r_{\text{WS}}^0 = 3.76$ a.u. is 0.3 eV, the *calculated* Δ_+ value at that radius. This raises the trivalent minimum *above* the divalent minimum. A Maxwell construction yields a *positive* transition pressure (of the same magnitude as before), a manifestly incorrect result.

Third, we exploit the BIS information and displace the curves of Fig. 3 so that their difference at r_{WS}^0 is 0.7 eV, the *observed* Δ_+ value. This procedure, which is tantamount to assuming $\xi_+ = -1.5$ eV, makes the energies at the minima essentially the same, implying $P \simeq 0$. These considerations suggest that (1) a $3+ \rightarrow 2+$ valence transition will occur in samarium metal for a volume expansion of no more than about 8% and (2) the value of ξ_+ used here is too negative by ~ 0.4 eV.

C. Coulomb term U

As specified by Eq. (3), U represents the separation of the two $4f$ levels based on the $4f^5$ configuration. It may also be interpreted as the Coulomb interaction energy required to transfer a $4f$ electron from one metallic cell to another while maintaining charge neutrality; in the process one $4f^4$ and one $4f^6$ site are created from two $4f^5$ sites. Values of U
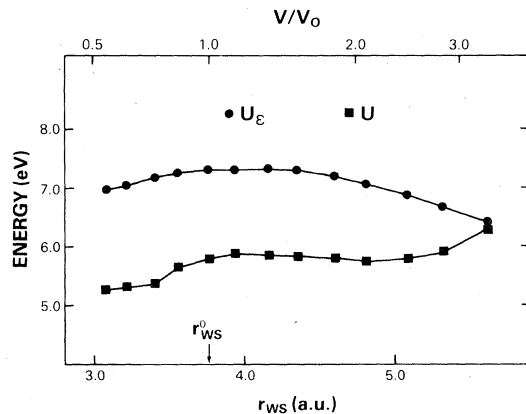
are given by the squares of Fig. 4. At normal pressure $U \simeq 5.8$ eV while combination of the XPS and BIS measurements[3] yields an experimental value of $\simeq 5.7$ eV. Figure 4 shows that U is confined to a rather narrow interval of ~ 1 eV over the r_{WS} range, while Δ_+ and especially Δ_- undergo larger excursions. By examining Eqs. (1), (4), and (9) and Tables I and II it can be seen that the relative insensitivity of U to WS radius stems from the near cancellation of the $\delta E(\text{atom} \rightarrow \text{metal})$ components of Δ_+ and Δ_-.

The simplest unscreened single-particle estimate of the Coulomb term is the $F^0(4f,4f)$ electrostatic integral, for which the RHF atomic calculations yield values in the $27-30$ eV range (see Table III). $F^0(4f,4f)$ is thus about a factor of 4 larger than the U results of Fig. 4 (squares). From Secs. II A and II B and Eqs. (2) and (15) it is clear that another one-electron estimate is afforded by the $4f$ eigenvalues computed for the solid:

$$U_\epsilon \equiv [\epsilon_F - \epsilon_{4f_{7/2}}]_{3+} - [\epsilon_F - \epsilon_{4f_{7/2}}]_{2+} \quad . \quad (16)$$

U_ϵ is given by the filled circles in Fig. 4 and differs from U by no more than 3 eV, the disparity decreasing for larger r_{WS}. Although screening and relaxation effects cause significant departure of either Δ_+ or Δ_- from its one-electron cognate (cf. Figs. 1 and 2), the *separation* between the two levels, which determines U, is much less sensitive to these influences.

D. $4f$ level widths

Imposition of WS conditions on a $4f$ wave function leads to a simple one-electron measure of the $4f$ level width, namely, the difference between the energies at which the large component of the wave function has zero value or zero derivative at r_{WS}:

FIG. 4. U and its one-electron analog U_ϵ [see Eqs. (3) and (16)] as functions of r_{WS}.

TABLE III. Values (in eV) of the $F^0(4f,4f)$ electrostatic integrals obtained from the RHF atomic calculations.

Sm configuration	$F^0(4f_{5/2},4f_{5/2})$	$F^0(4f_{7/2},4f_{7/2})$
$4f^65d\,6s$	26.86	26.51
$4f^55d^26s$	28.51	28.23
$4f^45d^36s$	29.95	29.70

$$W(4f) \equiv \epsilon_{4f}(\text{zero value}) - \epsilon_{4f}(\text{zero derivative}) \ .$$

$$(17)$$

Table IV lists values of this quantity for the $4f_{5/2}$ and $4f_{7/2}$ electrons in the divalent, trivalent, and tetravalent configurations as a function of r_{WS}. Although $W(4f)$ as specified by Eq. (17) can be determined to arbitrary precision, we emphasize that hybridization between the $4f$ and conduction states has *not* been included in the band calculations, so that the accuracy of these widths is difficult to assess. Nevertheless, $W(4f)$ provides at least a qualitative guide to the dependence of the level widths on valence (i.e., $4f$ occupation number) and lattice parameter. Table IV shows that $W(4f)$ decreases sharply with either increasing r_{WS} (as is to be expected in the atomic limit) or decreasing $4f$ occupancy. The statements made earlier concerning the inadequacy of the one-electron approximation to Δ_+ remain unaffected by these results.

III. DISCUSSION

Certainly the most striking result of our detailed microscopic calculations is the predicted valence change of Sm metal at an atomic volume greater than the equilibrium volume at normal pressure. The transition is linked to $4f \rightarrow 5d$ conversion of the sort occurring in the formation of most rare-earth metals from the atoms (the ground free-atom Sm configuration is $4f^6 6s^2$). Consideration of the

$4f$ level position $\Delta_+(4f^5 \rightarrow 4f^6)$, a purely electronic quantity, has thus led to an inference regarding a fundamental chemical attribute, the valence. We speculate that such an effect might be observable in Sm doped with a smaller metal ion to simulate reduced pressure. Observations[10] of a large divalent component at the surface of Sm metal as well as theoretical work[11] on the surface valence state of rare-earth metals provide at least some indication that a bulk valence transition may occur as well; this possibility is also encouraged by the fact that the Sm atomic ground state is divalent. The scheme employed here permits at most a change from one integral valence state to another; the fascinating possibility that bulk Sm metal can undergo a transition to a fluctuating valence regime (i.e., nonintegral average valence) is not excluded.

A new lowermost unfilled state, $4f^7$, will accompany the occupation of the $4f^6$ level, and for the sake of completeness we have also estimated its position:

$$\Delta_+(4f^6 \rightarrow 4f^7) = E_{\text{metal}}(4f^7 6s) - E_{\text{metal}}(4f^6(5d,6s)^2)$$

$$\cong \xi_+(f^6 \rightarrow f^7) + E_{\text{metal}}^{\text{RHF}}(4f^7 6s)$$

$$- E_{\text{metal}}^{\text{RHF}}(4f^6(5d,6s)^2) \ . \qquad (18)$$

Our calculations are based on the $4f^6 5d\,6s \rightarrow 4f^7 6s$ atomic transition, and the metallic final state is constrained to have a single $6s$ conduction electron. The free-atom correlation energy difference is

TABLE IV. $4f_{5/2}$ and $4f_{7/2}$ one-electron level widths for the divalent, trivalent, and tetravalent configurations as functions of r_{WS}. All values in eV.

r_{WS} (a.u.)	$4f^6(2+)$		$4f^5(3+)$		$4f^4(4+)$	
	$W(4f_{5/2})$	$W(4f_{7/2})$	$W(4f_{5/2})$	$W(4f_{7/2})$	$W(4f_{5/2})$	$W(4f_{7/2})$
3.08	1.4	1.5	0.71	0.76	0.35	0.38
3.22	1.0	1.1	0.49	0.53	0.23	0.24
3.41	0.70	0.77	0.29	0.32	0.12	0.14
3.56	0.50	0.56	0.19	0.21	0.078	0.085
3.76	0.32	0.36	0.11	0.12	0.042	0.046
3.93	0.22	0.25	0.071	0.080	0.026	0.028
4.16	0.14	0.15	0.040	0.044	0.014	0.015
4.35	0.091	0.10	0.025	0.028	0.008	0.009
4.60	0.054	0.063	0.013	0.015	0.004	0.005
4.81	0.035	0.041	0.008	0.010	0.002	0.003
5.08	0.020	0.024	0.005	0.005	0.001	0.001
5.32	0.013	0.015	0.003	0.003	0.001	0.001
5.62	0.007	0.008	0.002	0.002	<0.001	<0.001

$$\xi_+(f^6 \to f^7) = E_{corr}(4f^7 6s) - E_{corr}(4f^6 5d\, 6s)$$

$$= [E(4f^7 6s) - E(4f^6 5d\, 6s)]_{expt}$$

$$- [E(4f^7 6s) - E(4f^6 5d\, 6s)]^{RHF}_{gnd.\ atom}$$

$$= -3.1 \text{ eV} , \qquad (19)$$

and the atomic transition energy has been obtained from the data of Ref. 7. Results for $\Delta_+(4f^6 \to 4f^7)$, together with $\Delta_+(4f^5 \to 4f^6)$ and $\Delta_-(4f^5 \to 4f^4)$, are displayed in Fig. 5 with ϵ_F the energy zero. For $r_{WS} \geq 4.0$ a.u. the empty $4f^7$ state is approximately 3 eV above the Fermi level.

Finally, we note the qualitative similarity between our results and some experimental information on fluctuating valence Sm materials. SmS transforms from a divalent (pure $4f^6$) semiconductor to a fluctuating valence $(4f^5 \leftrightarrow 4f^6)$ metal at a pressure of 6.5 kbar. The binding energies of the $4f^6$ multiplet levels relative to ϵ_F decrease[12] with increasing x (i.e., decreasing lattice constant) in $Sm_{1-x}R_xS$ alloys with $R = $ Y, Gd, Th. Both sets of observations broadly correspond with the r_{WS} dependence of $\Delta_+(4f^5 \to 4f^6)$ examined here. On the other hand, calcium substitution in SmS also contracts the lattice but the $4f^6$ levels move further away from ϵ_F with increasing Ca concentration. Lattice contraction may be the principal driving mechanism for valence changes in the pure rare-earth metals, but the fluctuating valence behavior of the compounds likely depends on other factors as well.
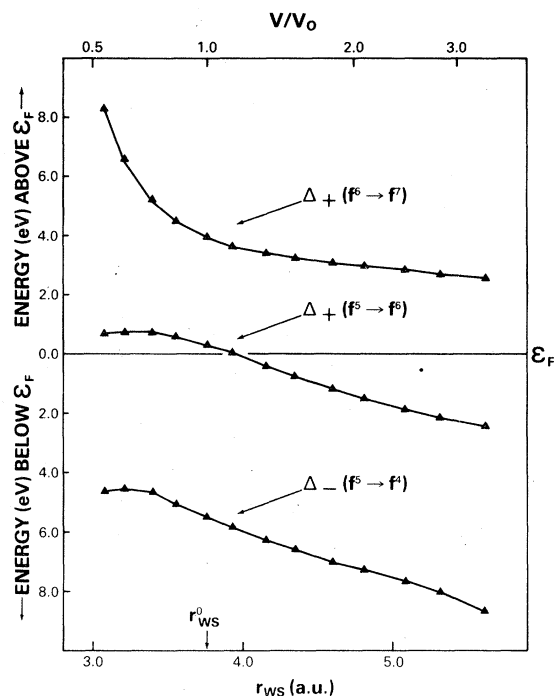

FIG. 5. $\Delta_+(4f^6 \to 4f^7)$, $\Delta_+(4f^5 \to 4f^6)$, and $\Delta_-(4f^5 \to 4f^4)$ as functions of r_{WS}.

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

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

[3]J. K. Lang, Y. Baer, and P. A. Cox, Phys. Rev. Lett. 42, 74 (1979); J. K. Lang and Y. Baer, J. Magn. Magn. Mater. 15, 1227 (1980).

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

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

[6]I. Lindgren and A. Rosén, Case Stud. At. Phys. 4, 93 (1974).

[7]L. Brewer, J. Opt. Soc. Am. 61, 1101 (1971).

[8]An improved convergence algorithm is used in the band calculations of the present work, and we find $\delta E(\text{atom} \to \text{metal}) = 2.7$ eV for $r_{WS} = 3.76$, compared

to the 2.6-eV value given in Table II of Ref. 2. This leads to $\Delta_+ \simeq 0.3$ eV at the equilibrium volume versus the 0.2-eV result of Ref. 2. Such differences are within the computational inaccuracies of the method.

[9]T. E. Scott, in Handbook on the Physics and Chemistry of Rare Earths, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 674.

[10]G. K. Wertheim and M. Campagna, Chem. Phys. Lett. 47, 182 (1977); G. K. Wertheim and G. Crecelius, Phys. Rev. Lett. 40, 813 (1978); J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagström, ibid. 41, 1499 (1978); G. K. Wertheim, J. Electron Spectrosc. Relat. Phenom. 15, 5 (1979); 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]G. K. Wertheim, I. Nowik, and M. Campagna, Z. Phys. B 29, 193 (1978).