Pressure-induced $4f$ occupancy enhancement in the rare-earth metals

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Calculations of $4f$ excitation energies as functions of the Wigner-Seitz radius for Ce, Sm, Er, and Yb indicate that the occupancy of the $4f$ shell increases at elevated pressures in the rare-earth metals. For each metal investigated we find a $3+ \rightarrow 2+$ transition in the range of a few Mbar. The Yb results also feature a $2+ \rightarrow 3+$ valence change in accord with recent experiments, while for Ce there is *no* evidence for a trivalent $(4f^1) \rightarrow$ tetravalent $(4f^0)$ transition at any pressure.

Under compression the electronic structure of a solid is generally characterized by a proclivity for bands of lower angular momentum l to increase in energy relative to bands of higher l.[1] This tendency in the form of $4s \rightarrow 3d$ conversion is responsible for the 340-Mbar metal $\rightarrow$ insulator transition in nickel predicted[1] by McMahan and Albers. We have performed calculations for Ce, Sm, Er, and Yb which show that this general trend, extended to f levels, is operative in the rare-earth metals. We find that transitions from the ground metallic states to states of higher $4f$ occupancy first occur at pressures in the Mbar range, some of which may be experimentally accessible.

To investigate the relative stability of various $4f$ configurations we derive $4f$ excitation energies $\Delta_+(f^n \rightarrow f^{n+1})$ from total energy differences:

$$\begin{aligned}\Delta_+(f^n \rightarrow f^{n+1}) &\equiv E_{\text{metal}}[4f^{n+1}(5d,6s)^{m-1}] \\ &\quad - E_{\text{metal}}[4f^n(5d,6s)^m] \\ &\cong \xi_+ E^{\text{RHF}}_{\text{metal}}[4f^{n+1}(5d,6s)^{m-1}] \\ &\quad - E^{\text{RHF}}_{\text{metal}}[4f^n(5d,6s)^m] \ . \qquad (1)\end{aligned}$$

Our calculational technique[2,3] involves initial relativistic Hartree-Fock (RHF) computations for atomic configurations approximating those of the metal. Renormalized atom crystal potentials are then constructed, and band calculations for the $5d$ and $6s$ states are iterated until well-defined self-consistency criteria are met. Each $E^{\text{RHF}}_{\text{metal}}$ in Eq. (1) represents the total RHF energy of all the electrons in a Wigner-Seitz sphere (radius r_{WS}) of the metal having the specified electron configuration; m is the valence. Multiplet theory serves to place the $4f$ electrons into the Hund's rule terms.

Correlation effects attending a change in $4f$ occupancy can be significant, and Eq. (1) includes a term ξ_+ whose purpose is to approximately correct the solid-state excitation energies for such effects. Each ξ_+ is a *free-atom* correlation energy difference derived directly from available atomic spectral data and corresponding RHF total energies.[2,3] The corrections help bring the normal pressure Δ_+ values into good agreement with x-ray photoemission and bremsstrahlung isochromat spectroscopy measurements[4] of the $4f$ levels (both occupied and empty) in the metals.[2,3] The pressure dependence of ξ_+ can be neglected for the following reason. The factors by which the atomic $4f$ wave functions are scaled to normalize them to the WS sphere deviate from unity by at most a few percent, even at the lowest r_{WS} values of interest. The small change in $4f$ charge density argues for insensitivity of ξ_+ to pressure.

$\Delta_+(f^n \rightarrow f^{n+1})$ is calculated over a range of r_{WS} values and can be interpreted both as the energy difference of the $4f^n$ and $4f^{n+1}$ configurations, as well as the position of the $4f^{n+1}$ level relative to the Fermi energy ϵ_F if the $4f^n$ configuration is considered the nominal ground state. A sign change in Δ_+ signifies a $4f$ occupancy (or, valence) change, and we estimate the corresponding transition pressure by a Maxwell construction using $E^{\text{RHF}}_{\text{metal}}(4f^{n+1})$ and $[E^{\text{RHF}}_{\text{metal}}(4f^n) - \xi_+]$ expressed as functions of atomic volume.

Figure 1 displays results for two cerium $4f$ levels, $\Delta_+(f^0 \rightarrow f^1)$ and $\Delta_+(f^1 \rightarrow f^2)$, and we emphasize two points. First, over the entire r_{WS} range investigated $\Delta_+(f^0 \rightarrow f^1)$ is negative, implying [cf. Eq. (1)] that the trivalent $(4f^1)$ configuration is always stable with respect to the tetravalent $(4f^0)$ state. This result is consistent with

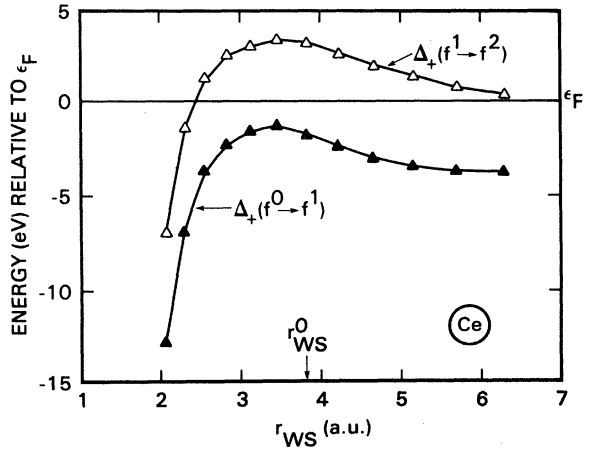

FIG. 1. Calculated $4f$ excitation energies $\Delta_+(f^0 \rightarrow f^1)$ and $\Delta_+(f^1 \rightarrow f^2)$ for cerium metal. The sign change of $\Delta_+(f^1 \rightarrow f^2)$ near $r_{\text{WS}} = 2.4$ a.u. indicates a $4f^1 \rightarrow 4f^2$ transition as the pressure P increases to approximately 6 Mbar; the percentage volume reduction is $\Delta V/V \sim 8\%$.

band structure work[5] and with photoemission,[6] Compton scattering,[7] muon spin rotation,[8] and positron annihilation[9] experiments which indicate little or no $4f$ population change through the $\gamma \rightarrow \alpha$ transition. Furthermore, the relative instability of the 4+ state indirectly supports the suggestion[10] of Bauchspiess *et al.* that no completely tetravalent Ce compounds exist. Second, $\Delta_+(f^1 \rightarrow f^2)$ changes sign for $r_{WS} \sim 2.4$ a.u., signaling a $4f^1 \rightarrow 4f^2$ transition which we estimate to occur at a pressure $P \sim 6$ Mbar. The $4f$ level width, determined by imposing WS-type boundary conditions on the $4f$ wave functions, is $W(4f) \sim 7$ eV at the transition [for comparison, $W(4f) \simeq 0.3$ eV at the equilibrium radius $r_{WS}^0 = 3.81$ a.u.]. This value is on the order of $U \equiv \Delta_+(f^1 \rightarrow f^2) - \Delta_+(f^0 \rightarrow f^1) \sim 5$ eV, the effective $4f$-$4f$ Coulomb interaction energy,[11] so that $4f$ band formation is likely involved and the transition may be more complex than a first-order change between integrally occupied $4f^1$ and $4f^2$ configurations. Regardless of the details, however, we expect the Ce $4f$ occupancy to *increase* at elevated pressures.

Our results for ytterbium and samarium, elements which, as does cerium, form fluctuating valence materials, are shown in Fig. 2. $\Delta_+(f^{13} \rightarrow f^{14})$ for Yb and $\Delta_+(f^5 \rightarrow f^6)$ for Sm are similar inasmuch as each curve crosses ϵ_F twice. In Yb [Fig. 2(a)] we find a 2+ → 3+ transition near $r_{WS} = 3.9$ a.u. corresponding to $P \sim 90$ kbar. Such a valence change was predicted[12] earlier by Johansson and Rosengren, who found $P \sim 140$ kbar, and recent measurements[13] of the L_3 absorption edge as a function of pressure by Syassen and co-workers have established that a transition indeed occurs, beginning near 40 kbar. We find in addition a reentrance to the divalent $(4f^{14})$ state for $r_{WS} \sim 2.5$ a.u., where $\Delta_+(f^{13} \rightarrow f^{14})$ again becomes negative. At this juncture $P \sim 3$ Mbar and the $4f$ level width has increased to only $\lesssim 3$ eV, so it is probable that the transition is between integrally occupied $4f^{13}$ and $4f^{14}$ states. For Sm [Fig. 2(b)] a 2+ → 3+ transition, which we examined[3] previously, first takes place as r_{WS} decreases from large values. This is followed by reentry to the divalent $(4f^6)$ state near $r_{WS} = 2.8$ a.u. with $P \sim 1$ Mbar. The f width at this point is ~ 2 eV, a value significantly smaller than $U \sim 5$ eV, suggesting that a genuine $4f$ band has not yet formed.

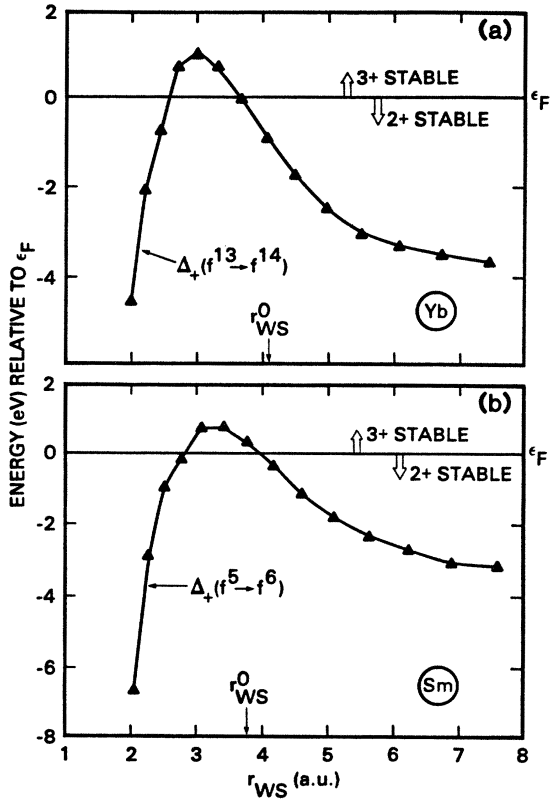

FIG. 2. (a) $\Delta_+(f^{13} \rightarrow f^{14})$ for ytterbium metal. The sign changes in the vicinity of $r_{WS} = 3.9$ and 2.5 a.u. correspond to $4f^{14} \rightarrow 4f^{13}$ ($P \sim 90$ kbar, $\Delta V/V \sim 25\%$) and $4f^{13} \rightarrow 4f^{14}$ ($P \sim 3$ Mbar, $\Delta V/V \sim 14\%$) transitions, respectively. (b) $\Delta_+(f^5 \rightarrow f^6)$ for metallic samarium. The zero crossing near $r_{WS} = 4.0$ a.u. corresponds to a $4f^6 \rightarrow 4f^5$ transition estimated in Ref. 3 to occur for a $\lesssim 8\%$ expansion of the equilibrium lattice, while that for $r_{WS} \sim 2.8$ a.u. indicates reentry to the $4f^6$ state for $P \sim 1$ Mbar, $\Delta V/V \sim 14\%$.

Our Ce, Yb, and Sm calculations thus support the contention that the $4f$ occupancy n in the rare-earth metals becomes progressively enhanced under high ($\gtrsim$ Mbar) pressures. In Ce and Sm we expect n to approach 4 and 8, respectively, with sufficient compression and, in general, $n \rightarrow Z - 54$ for any lanthanide metal of atomic number Z. From this point of view Er $(Z - 54 = 14)$ may provide the most intriguing manifestation of the overall tendency since filling of the f shell offers the possibility that Er undergoes a metal → insulator transition. Figure 3 displays our results for the three erbium f levels relevant to this possibility. With increasing pressure $\Delta_+(f^{11} \rightarrow f^{12})$, $\Delta_+(f^{12} \rightarrow f^{13})$, and $\Delta_+(f^{13} \rightarrow f^{14})$ become negative at successively smaller r_{WS} values, and these sign changes correspond to $f^{11} \rightarrow f^{12}$, $f^{12} \rightarrow f^{13}$, and $f^{13} \rightarrow f^{14}$ transitions for pressures ~ 6, ~ 40, and ~ 80 Mbar, respectively. We emphasize, however, the hybridization effects are not included in the calculations, making it uncertain as $n \rightarrow 14$ whether a gap will separate the $4f$ from higher-lying bands and lead to an insulating state.

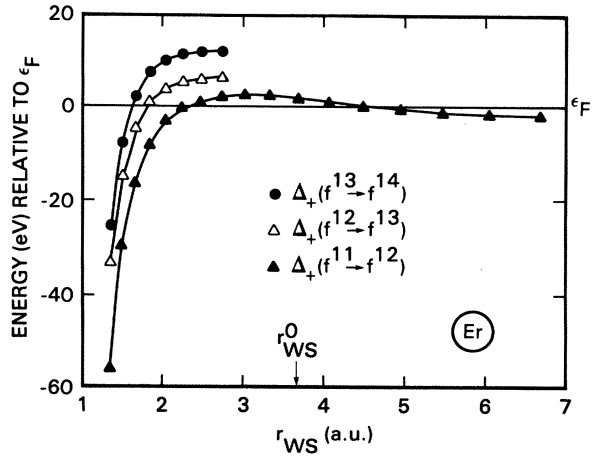

FIG. 3. $4f$ excitation energies in erbium metal. The sign changes in $\Delta_+(f^{11} \rightarrow f^{12})$, $\Delta_+(f^{12} \rightarrow f^{13})$, and $\Delta_+(f^{13} \rightarrow f^{14})$ for $r_{WS} < r_{WS}^0$ are, respectively, associated with $f^{11} \rightarrow f^{12}$ ($P \sim 6$ Mbar, $\Delta V/V \sim 12\%$), $f^{12} \rightarrow f^{13}$ ($P \sim 40$ Mbar, $\Delta V/V \sim 8\%$), and $f^{13} \rightarrow f^{14}$ ($P \sim 80$ Mbar, $\Delta V/V \sim 12\%$) transitions. The zero of $\Delta_+(f^{11} \rightarrow f^{12})$ for $r_{WS} \sim 4.6$ a.u. corresponds to a 2+ → 3+ valence change connected with formation of the trivalent $(4f^{11})$ equilibrium metal from divalent $(4f^{12})$ Er atoms.

The results presented here support the following general observations on the behavior of the lanthanide elements as r_{WS} decreases from infinity. Coalescence of the free atoms leads to overlap of the $5d$ and $6s$ wave functions and the formation of $5d$-$6s$ conduction bands. If the atoms are divalent (only La, Ce, Gd, and Lu are $3+$), the energy lowering accompanying this is sufficient in most cases to foster $4f \rightarrow 5d$ conversion and stabilization of the trivalent configuration for some WS radius r_{WS}^{3+} near the normal pressure value r_{WS}^{0}. For the elements whose atoms are trivalent, however, a $4+$ metallic state is not stabilized at any r_{WS}. (Our Ce calculations indicate this explicitly, and we expect the same statement to apply to La, Gd, and Lu.) As the pressure is increased further and r_{WS} is reduced below r_{WS}^{3+}, the $6s$ and then the $5d$ bands begin to rise in energy, favoring configurations having progressively fewer $6s$ and $5d$ electrons, lower valence, and enhanced $4f$ occupancy.

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[11]U is rather insensitive to volume in the regions of interest. In Ref. 3 we found $U=\Delta_+(f^5\rightarrow f^6)-\Delta_+(f^4\rightarrow f^5)\sim 5$–$6$ eV for Sm over a factor ~ 6 volume change. For Er (cf. Fig. 3) the U values relevant to the f^{12} and f^{13} configurations, $[\Delta_+(f^{12}\rightarrow f^{13})-\Delta_+(f^{11}\rightarrow f^{12})]$ and $[\Delta_+(f^{13}\rightarrow f^{14})-\Delta_+(f^{12}\rightarrow f^{13})]$, respectively, are each in the 5–7-eV interval over broad ranges of volumes centered around those of the $4f$ transitions.

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