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<sup>22</sup>Recent angle-resolved measurements for CO on Ni(111) confirm the data shown in Figs. 2(a) and 3(a). The observed angular dependence is as expected from polarization selection rules for the  $2\pi^*$  orbital of a CO molecule bound normal to the surface [F. J. Himpsel and Th. Fauster, Phys. Rev. B **26**, 2679 (1982)].

## Atom-to-Solid Core-Level Shifts for the Lanthanides: $nl$ Dependence Introduced by Valence Changes

J. F. Herbst

Physics Department, General Motors Research Laboratories, Warren, Michigan 48090-9055

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Free-atom-to-metal shifts of the rare-earth  $2p$ ,  $3d$ ,  $4f$ , and  $5s$  core-level binding energies have been calculated. For Pr-Sm and Tb-Tm, elements which undergo a valence change on formation of the solid, the shifts are smaller and depend significantly on the  $nl$  core-state quantum numbers. Consequently, a unique shift characterizing all core levels of a given element cannot be assumed when a configuration change involving the  $4f$  states occurs on solid formation.

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Core-level binding energies determined by probes such as x-ray photoemission spectroscopy continue to provide valuable information regarding electronic structure. One focus of substantial effort is the binding-energy shift between the free-atom state and the metallic phase (see, e.g., Refs. 1-6). This paper reports the first direct calculations of such shifts for all the lanthanide elements; moreover, four different core states, the  $2p$ ,  $3d$ ,  $4f$ , and  $5s$ , are considered. The valence (or  $4f$  occupancy) change accompanying solid formation is found to produce significant quantitative differences among the shifts calculated for Pr-Sm and Tb-Tm. In particular, the

$5s$  shifts exceed those of the more spatially localized states by as much as 5 eV.

The atom-metal shift  $\delta E_B(nl)$  of a level having quantum numbers  $nl$  is here defined by

$$\delta E_B(nl) \equiv E_B^{\text{atom}}(nl) - \bar{\Delta}_-(nl), \quad (1)$$

where  $E_B^{\text{atom}}(nl)$  and  $\bar{\Delta}_-(nl)$  denote the free-atom and metal binding energies relative to the vacuum zero and the Fermi energy  $\epsilon_F$ , respectively. This definition is useful because binding energies are generally measured with respect to the same reference levels. Each  $E_B^{\text{atom}}(nl)$  is derived from a difference of relativistic Hartree-Fock (RHF) total energies:

$$E_B^{\text{atom}}(nl) \equiv E_{\text{ion}}^{\text{RHF}}((nl \text{ hole})4f^{k_a}(5d, 6s)^{q_a}) - E_{\text{atom}}^{\text{RHF}}(4f^{k_a}(5d, 6s)^{q_a}). \quad (2)$$

For Pr-Sm and Tb-Tm the atomic  $4f$  occupancy  $k_a$  and valence  $q_a$  differ from their metallic counterparts, as Table I indicates. Multiplet theory serves to place the  $4f$ ,  $5d$ , and  $6s$  electrons into the appropriate ground states for both initial and final configurations, while multiplet interactions between the  $nl$  hole ( $nl = 2p, 3d, 5s$ ) and the open  $4f$  and  $5d$  shells in the ionic final state are not included.

$\bar{\Delta}_-(nl)$  is also specified by a total-energy difference:

$$\bar{\Delta}_-(nl) \equiv E_{\text{metal}}^{\text{RHF}}((nl \text{ hole})4f^{k_m}(5d, 6s)^{q_m+1}) - E_{\text{metal}}^{\text{RHF}}(4f^{k_m}(5d, 6s)^{q_m}). \quad (3)$$

TABLE I. Atomic and metallic electron configurations of the lanthanide elements. For La, Ce, Eu, Gd, Yb, and Lu the atomic  $4f$  occupancy is maintained in the solid, while for Pr–Sm and Tb–Tm the  $4f$  number decreases by one on formation of the metal.

Element	Atomic configuration	Metallic configuration
La	$5d6s^2$	$(5d, 6s)^3$
Ce	$4f^1 5d 6s^2$	$4f(5d, 6s)^3$
Pr	$4f^3 6s^2$	$4f^2(5d, 6s)^3$
Nd	$4f^4 6s^2$	$4f^3(5d, 6s)^3$
Pm	$4f^5 6s^2$	$4f^4(5d, 6s)^3$
Sm	$4f^6 6s^2$	$4f^5(5d, 6s)^3$
Eu	$4f^7 6s^2$	$4f^7(5d, 6s)^2$
Gd	$4f^7 5d 6s^2$	$4f^7(5d, 6s)^3$
Tb	$4f^9 6s^2$	$4f^8(5d, 6s)^3$
Dy	$4f^{10} 6s^2$	$4f^9(5d, 6s)^3$
Ho	$4f^{11} 6s^2$	$4f^{10}(5d, 6s)^3$
Er	$4f^{12} 6s^2$	$4f^{11}(5d, 6s)^3$
Tm	$4f^{13} 6s^2$	$4f^{12}(5d, 6s)^3$
Yb	$4f^{14} 6s^2$	$4f^{14}(5d, 6s)^2$
Lu	$4f^{14} 5d 6s^2$	$4f^{14}(5d, 6s)^3$

RHF-Wigner-Seitz calculations of these quantities have been previously described.<sup>7-10</sup>  $E_{\text{metal}}^{\text{RHF}}$  represents the total RHF energy of *all* the electrons in a Wigner-Seitz sphere of the metal. The final state contains a hole in the  $nl$  shell as well as an additional  $5d$ - $6s$  conduction electron both to preserve charge neutrality and to describe screening effects approximately. The metallic valence is  $q_m$ , the  $4f$  electrons are placed into Hund's rule terms via multiplet theory, and  $nl$ - $4f$  multiplet splittings are neglected. For the  $2p$  and  $3d$  states  $E_B^{\text{atom}}$  and  $\bar{\Delta}_-$  are degeneracy-weighted average binding energies of the spin-orbit-split  $j=l \pm \frac{1}{2}$  levels.<sup>7,8</sup>

Values of  $\delta E_B(nl)$  are presented in Fig. 1. Two significant features are immediately evident. (1) The curves have a common qualitative aspect inasmuch as  $\delta E_B$  is larger for the elements whose  $4f$  occupancies in the atom and the metal are the same (La, Ce, Eu, Gd, Yb, and Lu; cf. Table I), and  $\delta E_B$  is smaller for the elements whose  $4f$  number decreases on solid formation (Pr–Sm and Tb–Tm). Exploiting thermochemical quantities

$$E_B^*(nl) \equiv E_{\text{ion}}^{\text{RHF}}((nl \text{ hole})4f^{k_m}5d^{q_m-1}6s) - E_{\text{atom}}^{\text{RHF}}(4f^{k_m}5d^{q_m-1}6s). \quad (5)$$

$E_B^*(nl)$  is the "metal atom" analog of  $E_B^{\text{atom}}(nl)$ . Each shift may now be written as

$$\delta E_B(nl) = \Delta E_B^{\text{config}}(nl) + \delta E_B^*(nl), \quad (6)$$

where

$$\Delta E_B^{\text{config}}(nl) \equiv E_B^{\text{atom}}(nl) - E_B^*(nl) \quad (7)$$

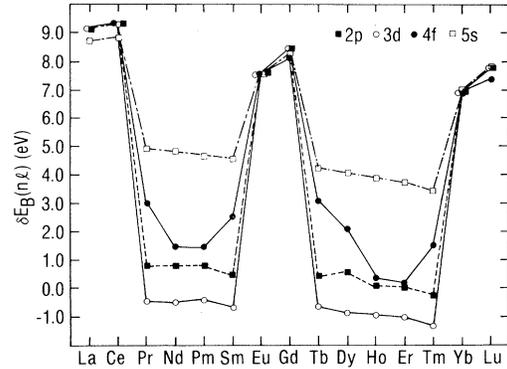


FIG. 1. Atom-to-metal shifts  $\delta E_B(nl)$  calculated for the  $2p$ ,  $3d$ ,  $4f$ , and  $5s$  levels of the lanthanide elements.

such as cohesive energies and ionization potentials, Johansson and Mårtensson have derived<sup>6</sup> a single,  $nl$ -independent shift for each element, and their results exhibit similar overall variation. (2) Differences among the shifts for Pr–Sm and Tb–Tm are apparent on a 1-eV scale. For each of those elements the hierarchical relation

$$\delta E_B(3d) < \delta E_B(2p) < \delta E_B(4f) < \delta E_B(5s) \quad (4)$$

is obeyed, with  $\delta E_B(5s)$  separated by as much as 5 eV from the other shifts.

The results displayed in Fig. 1 imply that a unique atom-to-solid shift characterizing all core states of an element *cannot* be assumed when a configuration change itself involving a core state (in this case the  $4f$ ) occurs on solid formation. A corollary implication is that a one-to-one correspondence between a macroscopic property, such as the cohesive energy or heat of formation, and  $\delta E_B$  does not exist in that circumstance. Since  $nl$ -dependent surface core-level shifts may also be expected, the important connection between those shifts and surface energies discussed<sup>11</sup> by Rosengren and Johansson may also require modification when the surface and atomic  $4f$  occupancies differ.

One way of analyzing the impact of the atom-metal configuration change is to introduce the  $nl$  binding energy in the  $4f^{k_m}5d^{q_m-1}6s$  excited atomic configuration:

is the correction to the atomic  $nl$  binding energy due to the configuration change, and

$$\delta E_B^*(nl) \equiv E_B^*(nl) - \bar{\Delta}_-(nl) \quad (8)$$

represents the effective atom-metal shift in the

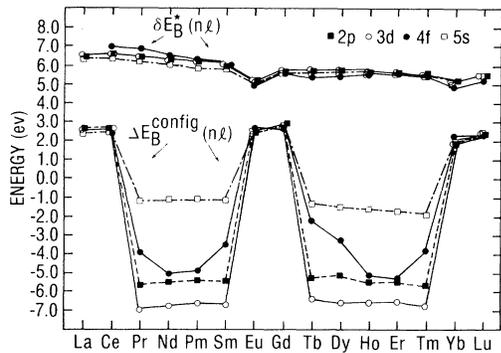


FIG. 2. Components of the atom-to-metal shifts.  $\delta E_B^*(nl)$  is the effective ("metal-atom"-to-metal) shift which corresponds to both atomic and metallic configurations having the  $4f$  occupancy of the solid.  $\Delta E_B^{\text{config}}(nl)$  represents the modification of the free-atom  $nl$  binding energy arising from the change to the metallike configuration.

absence of such a change. Figure 2 displays these two components.

It is apparent from Fig. 2 that  $\delta E_B^*(nl)$  is essentially independent of  $nl$ . The shifts are regularized when no configuration change occurs, showing only a slight decrease across the series which is associated with the lanthanide contraction (an effect also noted in Ref. 6). Comparison of Figs. 1 and 2 makes it evident that  $\Delta E_B^{\text{config}}$  is responsible both for the distinction between the  $\delta E_B$  results for Pr-Sm, Tb-Tm and the other elements, as well as for the differences among the shifts

for each member of the former group. The shifts for Pr-Sm and Tb-Tm are reduced because  $\Delta E_B^{\text{config}} < 0$  for those elements. This is a consequence of the fact that  $E_B^* > E_B^{\text{atom}}$  when the metallike configuration has one fewer  $4f$  electron and, hence, greater effective nuclear charge, than the ground atomic configuration.

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## Bound State between a Crystal-Field Excitation and a Phonon in $\text{CeAl}_2$

Peter Thalmeier and Peter Fulde

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

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The existence of a bound state between a crystal-field excitation and a low-lying phonon in  $\text{CeAl}_2$  is suggested. It can explain in a natural way the hitherto unexplained two-peak structure found in magnetic neutron-scattering experiments. Various checks are made to substantiate this suggestion. A similarity is pointed out to the exciton-phonon bound-state problem in semiconductors.

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The intermetallic cubic Laves-phase material  $\text{CeAl}_2$ , in which the Ce ions have a stable  $3^+$  configuration with  $J = \frac{5}{2}$ , has attracted considerable attention for various reasons. At low temperatures the system exhibits a Kondo effect ( $T_K \approx 6$  K) and antiferromagnetic order ( $T_N = 3.9$  K).<sup>1,2</sup> It

also shows a strong magnetoelastic coupling leading to pronounced low-temperature anomalies in the  $c_{44}$  elastic constant.<sup>3</sup> One striking observation<sup>4</sup> is the appearance of two inelastic lines in inelastic magnetic neutron-scattering experiments at energies  $\Delta_1 = 100$  K and  $\Delta_2 = 180$  K. This