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Bulk and surface 4f states of Gd

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Self-consistent spin-polarized electronic-structure calculations for a seven-layer slab are carried out to find the positions of the highly localized 4f surface and bulk bands of Gd. The 4f states are treated as valence states along with s, p, and d orbitals. Both the occupied and unoccupied 4f bands shift down in energy with respect to the bulk bands. The calculated shifts with different approximations are compared with the photoemission and inverse photoemission data. The results based on local-density $+U$ approximation are in very good agreement with the experimental shift of 0.4 eV for both the occupied and unoccupied states. [S0163-1829(97)07008-2]

The filling of the 4f shell in the rare earths gives them some very interesting properties such as the large magnetic anisotropy due to the highly localized f electrons. A large number of experimental and theoretical studies exists on the bulk and surface 4f states of rare earths. There has been a considerable interest in the magnetic ordering and relaxation at the Gd surface.[1] A closely related problem is the bulk to surface shift of the 4f bands of Gd. The various photoemission (PES) and inverse photoemission (IPES) studies show that the occupied and unoccupied 4f bands of Gd shift down in energy as one goes from the bulk to the surface with the shift being in the range of 0.3–0.5 eV.[2–4] Begley *et al.* used the linear-muffin-tin-orbital (LMTO) method to find a shift of about 0.5 eV for the 4f occupied band of Gd.[5] This is a self-consistent calculation in the local-density approximation (LDA) for a five-layer slab with the 4f electrons treated as corelike. Aldén *et al.* calculated these shifts for the rare earths as the surface segregation energy of a fully screened 4f ionized impurity in an otherwise unperturbed host.[6] The surface relaxation is neglected and the 4f electrons are unpolarized in these calculations. Since the 4f electrons are part of the frozen core, all the shift in these calculations comes from the differences in the screening charge in the bulk and at the surface. The downward shifts of 0.34 and 0.54 eV for the occupied and unoccupied f states, respectively, are in good agreement with the PES and IPES studies in Ref. 3.

The recent PES and IPES studies in Ref. 4 show that both the occupied and unoccupied Gd 4f states at the surface shift down in energy with respect to the bulk states by 0.4 eV. This result was a stimulus for the electronic structure calculations reported here. Unlike the calculations mentioned above, we include the 4f orbitals as valence states in our LDA and LDA+U calculations. Also we assume the ferromagnetic order[7] and the relaxation[8] at the surface as observed experimentally.

To simulate the bulk and (0001) surface states we consider a periodic structure of seven Gd and two empty-sphere layers. The self-consistent spin-polarized electronic-structure calculations are carried out in the scalar-relativistic approximation with s, p, d, and f orbitals as basis functions. We use the linear tetrahedron method with 798 k points in the irreducible wedge of the Brillouin zone to calculate the density of state (DOS).

Figure 1 shows the f-projected DOS based on LMTO (LDA) calculations. These calculations are in the atomic-sphere approximation (ASA) but include the combined correction (COR) term. The f-DOS for the bulk is the same as obtained by other calculations, i.e., a fully occupied majority band at about 4.2 eV below the Fermi energy and an almost unoccupied minority band around 0.5 eV above the Fermi energy.[9,10] The center of mass of the surface f bands are shifted down with respect to the bulk bands by 0.13–0.15 eV, a shift much smaller than the experimental value of 0.4 eV (Table I). However, the LDA results agree with the experimental data in that shifts for the occupied and unoccu-

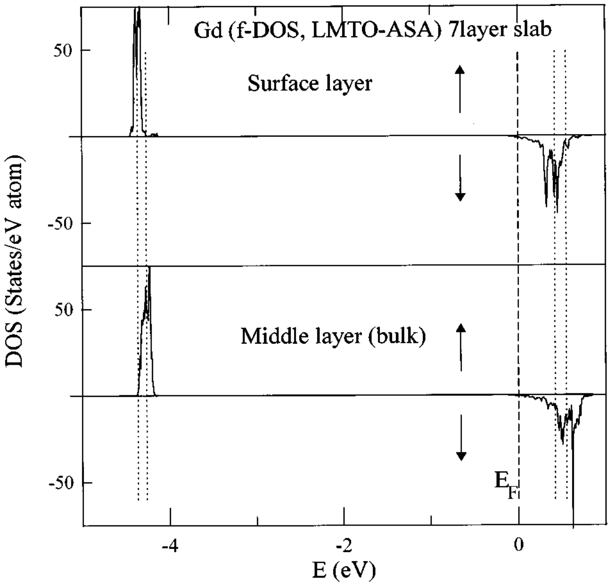

FIG. 1. Bulk and surface f-projected density of states of Gd(0001) by the LMTO-ASA(LDA) method. The centers of mass of the f bands are indicated by the vertical dashed lines.

TABLE I. Bulk to surface downward shifts in eV of the occupied and unoccupied $4f$ bands of Gd(0001).

	LMTO-ASA(LDA)	FP-LMTO-(LDA)	LMTO-ASA (LDA+U)	Expt.[a]
Occupied $4f$	0.13	0.23	0.43	0.4
Unoccupied $4f$	0.15	0.23	0.44	0.4

[a] Reference 4.

pied f states are about the same, implying no change in the exchange splitting between the bulk and surface states. The smaller shift is due to the fact that the unoccupied f band is pinned by the Fermi energy.

The calculations in the last paragraph are repeated with the full-potential (FP) LMTO (LDA) method and the f-projected DOS are shown in Fig. 2. The results are similar to that of LMTO-ASA. The unoccupied f band now is at a somewhat higher energy than the LMTO-ASA value which lowers its pinning by the Fermi energy. As a result, the bulk to surface shifts of the f bands are somewhat larger but still smaller than the experimental value (Table I).

The problem of pinning mentioned above is related to the well-known limitations of the LDA in describing the properties of the highly localized $4f$ electrons in the rare earths. The LDA calculations give the locations of the occupied and unoccupied $4f$ levels to be -4.2 and 0.5 eV with respect to E_f, respectively, whereas the corresponding values from PES and IPES data are -8.5 and 3.5 eV. The full-potential calculations described in the last paragraph produce minor changes in the location of the $4f$ peaks. Thus one must go beyond the LDA to understand the photoemission results. It has been shown in Refs. 11 and 12 that the standard electronic structure calculations combined with the transition-state analysis give results in very good agreement with PES and IPES data for the $4f$ states in Gd. This procedure can be simulated by LDA+U calculations as shown recently by Harmon *et al.* in their calculations for Gd.[13] Since the LDA $+U$ method predicts the PES and IPES $4f$ peak positions quite well and eliminates the pinning by the Fermi energy, we use it to study the bulk to surface shifts of the $4f$ bands in Gd.

Since the (FP) LMTO (LDA) method only effects the pinning slightly and pinning is no longer a problem in LDA+U, we use the LMTO-ASA (LDA+U) method in the following calculations. To estimate the effect of the surface on U we calculated $F°$, the $4f$ Coulomb integral, in the bulk and at the surface. The bulk and surface values of $F°$ are the same within 3 meV. On the basis of this result we expect U to be essentially the same throughout the slab. The same should hold for the exchange parameter J. This conclusion about U and J is supported by the experimental results in Ref. 4 that the downward shifts for the occupied and unoccupied $4f$ states are the same. The bulk U (6.7 eV) and J (0.7 eV) parameters found in Ref. 13 are used in these calculations. The results for f-projected DOS are shown in Fig. 3. The bulk results are similar to the FP-LMTO results in

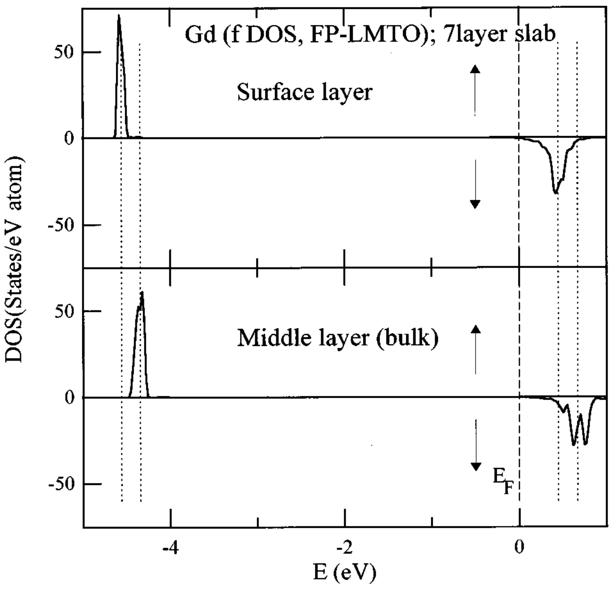

FIG. 2. Bulk and surface f-projected density of states of Gd(0001) by the FP-LMTO(LDA) method. The centers of mass of the f bands are indicated by the vertical dashed lines.

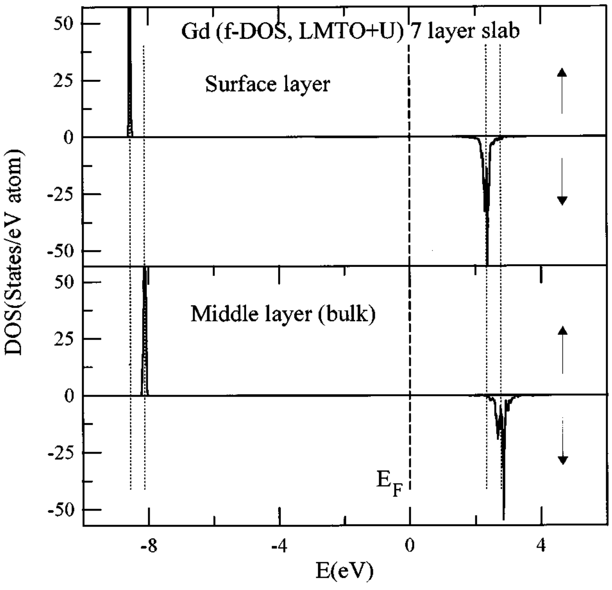

FIG. 3. Bulk and surface f-projected density of states of Gd(0001) by the LMTO-ASA(LDA+U) method. The centers of mass of the f bands are indicated by the vertical dashed lines.

Ref. 13. The unoccupied f band is no longer pinned by the Fermi energy. As a result the bulk to surface f band shift of 0.44 eV for both the occupied and unoccupied states is in very good agreement with the experimental data (Table I).

In conclusion, the exchange splitting for the highly localized $4f$ electrons of Gd is the same in the bulk and at the surface. Based on LDA+U method, the calculated bulk to surface downward shift of 0.44 eV for the occupied and unoccupied $4f$ bands of Gd is in very good agreement with the PES and IPES data of 0.4 eV.

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