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Calculations of surface core-level shifts for the lanthanides

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We report self-consistent surface electronic-structure calculations for metals across the lanthanide series. We have used the self-consistent-field linear muffin-tin orbital method with the atomic-sphere approximation in a "supercell" geometry. The calculations provide values of the surface core-level shifts (SCLS) on the (0001) face for all the hcp lanthanides, which compare well with experimental results. We have confirmed that the trend of the increasing SCLS across the series can be explained by a monotonic decrease in the valence-d-electron count.

INTRODUCTION

Ever since 1978, when it was first shown[1] that surface core-level shifts (SCLS's) could be detected experimentally, there have been considerable developments in both theoretical calculations and experimental techniques. However, most of the experimental work has concentrated on the $4f$ elements due to the difficulties inherent in observing SCLS's from nonlocalized core states, whereas the theoretical effort has been applied throughout the Periodic Table. (For a review of the experimental work, see Refs. 2 and 3, and for the theory, see Refs. 3–5.) Thus, there is a paucity of data for elements other than the $5d$ transition metals and the lanthanides that has left the corresponding theoretical models largely untested.

The majority of previous calculations are based on non-self-consistent models, derived from free-atom to bulk-atom differences in core-level binding energies. In this way, SCLS's have been calculated[3,6] for all three transition-metal (TM) series from thermodynamical quantities alone. The trends of the SCLS across each TM series are based on the d-electron count in the valence band, due to the localization of the charge density of the surface atom and the underlying predominance of the d-character bonding. Accordingly, the trends and also some single-crystal values have been calculated by a tight-binding approach[7] involving the displacement of the d bands at the surface. When extensions to the thermodynamical model were made,[8,9] which used simple bond-breaking arguments, the SCLS's were calculated[9] for the different surfaces of most of the $3d$, $4d$, and $5d$ metals.

However, the calculations mentioned above are all non-self-consistent (NSC), and also do not take into account the "final-state" contribution from core-hole screening. They are clearly less reliable than the more sophisticated self-consistent (SC) type, even though the latter are also based purely on "initial-state" effects. The development in the last twenty years of SC surface electronic-structure calculations[10] has provided a more accurate test of the experimental data. They are based predominantly on an unsupported "slab" geometry and have been performed on a wide range of systems (clean and chemisorbed surfaces) by various different methods, e.g., pseudopotential,[11] Gaussian expansion local orbital,[12] and linearized augmented-plane-wave (LAPW) (Ref. 13) (see Refs. 3 and 5 for detailed references). The primary objective has been to calculate the densities of states for different layers of the crystal and, thus, determine the changes in electronic structure caused by the presence of the surface.

On the experimental side, there are abundant data for the $5d$ metals from nearly all of the crystal faces, which enables comparisons to be made with the theory (see Fig. 4 in Ref. 3). For the $3d$ and $4d$ metals, however, the SCLS's have been found for only five elements. Four of these samples were in polycrystalline form (Cu,Fe,Ag,Ru) and only one (Y) was a single crystal.[14] A review of the available experimental and theoretical data (NSC and SC) for the TM series is given in Ref. 3. From all the existing SC calculations the accompanying SCLS has been found for only the surfaces of Cu(100),[15–17] Cu(111),[18] Ag(100),[16] Ni(100),[16,19,20] Ti(0001),[21] Sc(0001),[21,22] Pt(001),[23] Ta(001),[24] Al(001),[25] Ru(0001),[26] Rh(111),[26,27] Rh(001),[16] Pd(001),[16] and W(001).[28] (See Refs. 3 and 5 for more detailed references.) Of those for which experimental values do exist [polycrystalline Ag, Cu(100), W(001), Ni(100), Pt(001), Ta(001)] the general agreement is inconsistent. It is generally thought that the discrepancy occurring in most cases is due to the final-state screening of the core hole, which should be less effective at the surface due to the coordination number being smaller. The net result is that the SCLS is more *positive* (where a positive SCLS means that the surface atoms are more tightly bound than their bulk counterparts). The magnitude of the final-state contribution has been calculated approximately in the case of Cu(100) (Ref. 29) and the result does verify the screening model. Although final-state screening will explain the discrepancies for certain elements to an extent, i.e., when the calculated SCLS is smaller than the experimental value, it is unlikely that it will provide an explanation when the reverse occurs, as in Ta(100), W(100), etc.

The overlap between accurate SC calculations and experimental data across an *entire* series of elements is, thus, nonexistent. Detailed comparisons, which are made possible by results of this kind, are necessary in order to test fully not only the validity of the theories, but also the precision of the experimental results. In the case of the lanthanides ($_{57}$La$-_{71}$Lu), a comprehensive experimental study of polycrystalline samples using ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) does exist,[30] but no SC calculations have been attempted. The valency remains constant across the series (all are trivalent except for Yb and Eu, which are divalent) while the localized $4f$ levels fill. Thus, the models based upon thermodynamical quantities suggest a constant SCLS across the series (neglecting Yb and Eu). However, the experimental study[30] has revealed a monotonic increase in the SCLS across the series from 0.4-0.8 eV; these authors suggested that this is not inconsistent with the theory if allowance is made for the slight variation in the d-electron count of the valence bands. Indeed, they quote bulk energy-band calculations which give a d band occupation number (n_d) of 2.0 for $_{57}$La and 1.4 for $_{71}$Lu. The trend in n_d across the entire series has been calculated for the bulk metals by Skriver,[31] and does prove to be monotonically decreasing. If this behavior is consistent for surface atoms as well as bulk atoms, then it would provide a reasonable explanation for the observed SCLS results.

CALCULATIONS

We have performed *ab initio* self-consistent surface electronic-structure calculations for the lanthanide series in order to test the experimental SCLS results. This is the first study by a self-consistent method of trends in the SCLS and the layer-decomposed d-band occupation number for elements across a series. We have used the self-consistent-field linear muffin-tin orbitals method with the atomic-sphere approximation (SCF-LMTO-ASA), which has been described extensively elsewhere.[32] In these calculations we utilize a "supercell" geometry, involving a ten-layer unit cell comprising five layers of lanthanide atoms and five of "empty" spheres in their normal hcp *ABABA* stacking sequence. This extension of the regular unit cell is then repeated over all real space to produce five-layer "slabs" of metal sandwiched between empty space. In this way the surface-vacuum interface of the single-crystal (0001) plane is modeled self-consistently (see Fig. 1). There are six inequivalent atom types, where the "surface," "subsurface," and "bulk" layers are represented by layer numbers, 1, 2, and 3, respectively. This supercell geometry allows us to calculate the relevant electronic properties for each of these six atom types, and thus make comparisons between the various layers.[33] The calculations were performed on the Floating Point Systems FPS-264 processor at the SERC Daresbury Laboratory. The charge densities were calculated using the von Barth–Hedin approximation for the exchange-correlation potential. The electronic structure was computed at 96 inequivalent $k_{\parallel}$ points in the irreducible wedge of the bulk Brillouin zone. The "core" consisted of all the atomic levels up to and including the $5p$'s, i.e., the xenon configuration, plus the $4f$ levels. The valence band was the typical $(5d6s)^3$. The $4f$ electrons were treated as corelike due to their extreme localization—an assumption which means that they play no effective part in the SCLS mechanism. All the core energy levels were iterated to self-consistency in the all-electron calculation in which the core-level eigenvalues for each layer were found by an atomic scheme. The difference between the eigenvalues for a particular core level of the "surface" (layer 1) and "bulk" (layer 3) atoms is taken to be the SCLS. All of the individual core levels in a particular metal produce the same value of the SCLS to within an error of 0.01 eV.

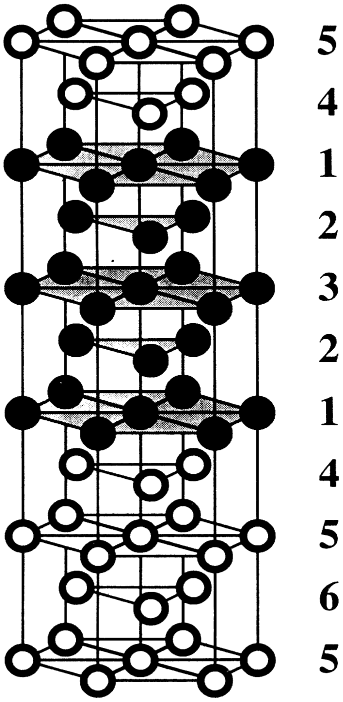

FIG. 1. Schematic diagram of the 10-layer hcp unit cell used in the "supercell" geometry. The dark spheres represent the lanthanide atoms, whereas the light spheres represent the "vacuum" atoms. The six inequivalent layers are labeled 1–6, where layers 1, 2, and 3 are composed of the "surface," "subsurface," and "bulk" atoms, respectively.

Calculations were attempted for all the lanthanides with the exception of (rhombohedral) samarium. The regular room-temperature crystal structures were used in each case, except for the dhcp elements (Pr,Nd,Pm), which were treated as hcp for simplicity. The experimentally determined lattice parameters were used throughout. Each calculation took approximately 100 iterations to converge fully, taking approximately 4 h of CPU time. We found that calculations on the non-close-packed surfaces of Ce,Yb (fcc), and Eu (bcc) did not converge properly due, presumably, to the breakdown of the atomic-sphere approximation, giving rise to too large sphere overlaps. The results from these three metals are thus omitted.

RESULTS AND DISCUSSION

The values of the SCLS on the $4f$ levels for the (0001) face of the hcp lanthanide metals are shown in Fig. 2. They can be compared directly with the $4f$ polycrystalline experimental resuts of Gerken *et al.*[30] Considering the relative simplicity of the calculation and the experimental difficulty in measuring such small peak shifts, reflected in the error bars, the agreement is excellent. If final-state screening always increases the shift, as is expected, then our theoretical results are even closer to the experimental values. It should also be noted that the experimental value for Lu is an upper limit due to oxidation problems with the sample. The significance of the polycrystalline nature of the samples on the magnitude of the SCLS has yet to be evaluated and may account for any further discrepancy between experiment and theory. We are currently carrying out an experimental investigation using UPS of the SCLS for single-crystal samples of Gd, Ho, and Er, which should help clarify this situation. It may be interesting to note that the SCLS's for the second ("subsurface") layer, i.e., the difference in eigenvalues between layers 1 and 2, are opposite in sign to the bulk SCLS values shown in Fig. 2.

Figure 3 shows the valence-d-band occupancy n_d across the series for the surface (layer 1), subsurface (layer 2), and bulk (layer 3) atoms as calculated in the supercell geometry. The figure shows clearly that the decrease in n_d with atomic number is monotonic, and very similar for the bulk and surface atoms. The values of n_d obtained by the supercell LMTO method are in excellent agreement with the previous bulk electronic-structure calculations,[31] which also employed the LMTO-ASA method but in the more normal "infinite-crystal" geometry.

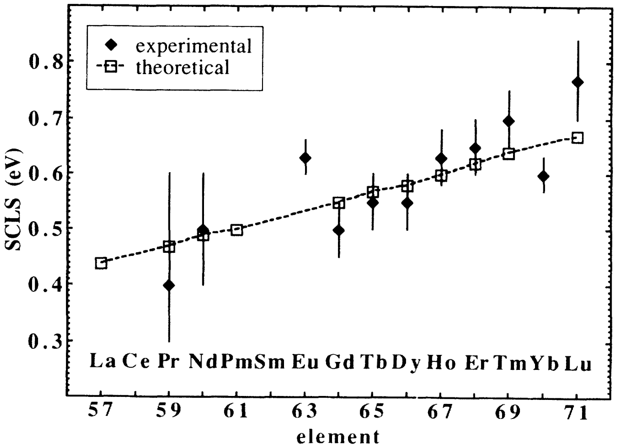

FIG. 2. Comparison of the experimental (Ref. 30) and our calculated values for the SCLS from the $4f$ levels of the lanthanides. The experimental samples were polycrysalline, whereas the LMTO calculations were performed on the (0001) face.

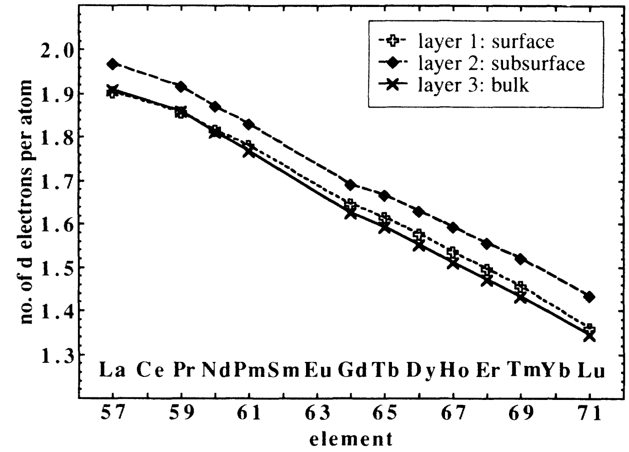

FIG. 3. The calculated valence-d-band occupation number for atoms in each of the first three layers. All of the lanthanides are nominally trivalent ($5d^26s^1$) except for Eu and Yb, which are divalent.

The limitations of this simplified approach—and of the ASA in particular—are recognized, especially when compared with the far more precise unsupported slab or thin-film approach used by the other SC methods. However, the values of n_d calculated correspond very well to previous theoretical results. Nevertheless, in order to justify our model further, we have carried out LMTO calculations for the rare-earth metal yttrium using both the supercell and the infinite-crystal geometry.[34] The LDOS of the "bulk" layer (i.e., layer 3) from the former calculation compares well with the total DOS of the latter. So, although we do not have the accuracy to calculate the work functions and the surface energetics in general, we feel that the method is appropriate for calculating the energy eigenvalues and the differences relevant to the SCLS.

CONCLUSION

We have calculated the $4f$ SCLS for the (0001) face of the metals across the lanthanide series. The results compare very favorably with the only experimental study, especially if final-state effects and the polycrystalline nature of the samples are considered. The trend of the SCLS across the trivalent lanthanide series was tentatively explained[30] by changes in the valence—d-band occupancy. Our study of surface effects across a series has closely reproduced this trend and verified the subsequent interpretation. The monotonic rise in the SCLS derives solely from the monotonic decrease in the number of valence d electrons.

Because of the versatility and speed of the SCF-LMTO-ASA method, the use of the supercell geometry should enable surface modeling for all kinds of systems. Although we experienced difficulties with the more "open" crystal structures, we hope to be able to extend this technique to fcc and bcc surfaces and, in particular, to the three transition-metal series. This work would then test with a self-consistent model all of the experimentally observed SCLS's and it would enable detailed comparisons to be made with other non-self-consistent models. Moreover, the results would also be a starting point for an *ab initio* study of the effects of core-hole relaxation on the calculated "ground-state" binding energies.

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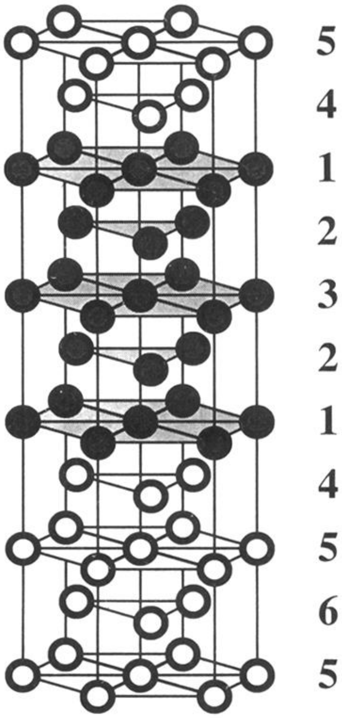

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