PHYSICAL REVIEW B VOLUME 51, NUMBER 12 15 MARCH 1995-II

Surface core-level shifts and surface states for the heavy lanthanide metals

G. Kaindl, A. Höhr, E. Weschke, S. Vandré, C. Schüßler-Langeheine, and C. Laubschat*
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

(Received 7 November 1994)

We report on a systematic study of surface core-level shifts of $4f$ photoemission lines for the close-packed surfaces of monocrystalline films of the heavy lanthanide metals and for the (110) surface of Eu metal. Data are presented for Eu, Dy, Ho, Er, and Lu metals. Surface states close to the Fermi level were observed for all close-packed surfaces studied so far. The magnitudes of the surface core-level shifts were found to be distinctively smaller than previously reported results.

Surface shifts of core-level photoemission (PE) lines had first been observed more than a decade ago for Au metal.[1] They are due to the reduced coordination of surface atoms and can be related to the difference in cohesive energies of the initial and final state.[2] In the case of lanthanide materials, particularly well-resolved surface shifts are observed for the $4f$ PE lines due to the relatively narrow intrinsic linewidths.[3] A few years ago, a self-consistent-field linear-muffin-tin-orbitals calculation with the atomic-sphere approximation,[4] considering only initial-state contributions to the surface core-level shifts, claimed very good agreement between theory and experiment.[3] The subject was therefore considered to be fairly closed until recently, when a high-resolution PE study of a well-ordered (0001) surface of a monocrystalline film of Tb metal, grown epitaxially on W(110), resulted in a surface core-level shift that was more than a factor of 2 smaller than the previously reported value.[5] Similarly, small surface core-level shifts were subsequently observed for close-packed surfaces of Gd metal,[6] as well as Tm and Yb metals,[7] suggesting a systematic reanalysis of surface core-level shifts for the entire series of lanthanide metals. Apart from these surface-related binding-energy shifts of core states, the appearance of valence-band-derived surface states has been observed for lanthanide metals. An occupied surface state was first theoretically calculated and experimentally observed for the (0001) face of Gd metal.[8,9] Subsequently, such surface states were also found for close-packed surfaces of Tb metal,[10,5] Tm and Yb metals,[7,11] as well as La metal.[12] From the variation of the PE cross section as a function of photon energy, these surface states were characterized as d like,[7,11] in agreement with the theoretical prediction.[8]

In the present paper, we report on a systematic PE study of surface core-level shifts for the close-packed surfaces of monocrystalline films of the heavy lanthanide metals and for the (110) surface of Eu metal, with the metal films grown epitaxially on W(110). Data are presented for Eu, Dy, Ho, Er, and Lu metals, with the magnitudes of the derived surface core-level shifts being distinctively smaller than the previously reported experimental and theoretical values. On the experimental side, the differences are explained as a consequence of the rough polycrystalline surfaces studied previously, while on the theoretical side, the discrepancy with the experimental results suggests the importance of final-state contributions to the surface core-level shifts. In addition, d-like surface states were observed for the close-packed surfaces of all lanthanide metals studied so far.

The PE experiments were performed with a high-resolution spectrometer equipped with a Leybold-Heraeus EA11 hemispherical electron analyzer employing either He II radiation from a resonance lamp or synchrotron radiation from the SX700/II monochromator operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). The total-system resolution varied between 25 and 50 meV (full width at half maximum). Most measurements were performed with the metal samples at room temperature; to reduce thermal broadening, a few spectra were taken with the samples cooled to temperatures as low as 20 K using a closed-cycle helium refrigerator. To this end, a special sample holder had to be constructed that allowed us to heat the W(110) single-crystal substrate up to $\simeq 2000$ K for cleaning and, on the other hand, to cool it down to $\cong 20$ K for the PE measurements. About 100-Å-thick films of the lanthanide metals were grown epitaxially on the clean W(110) substrate at typical growth rates of 5–10 Å/min by thermal evaporation of the high-purity metals from either resistively heated W coils or Ta crucibles heated by electron bombardment. Similar to the case of Gd(0001), the substrate was kept at room temperature during deposition in order to achieve layer-by-layer growth.[6,13,14] The base pressure in the experimental chamber was 3×10^{-11} mbar rising to $\cong 2\times10^{-10}$ bar during deposition. A quartz microbalance served for monitoring the thickness of the deposited films. Immediately after deposition, rather diffuse low-energy electron-diffraction (LEED) patterns were observed, which sharpened considerably upon subsequent annealing at elevated temperatures (between 400 and 700 K).

Figure 1 displays PE spectra of the close-packed (0001) surfaces of well-ordered monocrystalline films of Dy, Ho, Er, and Lu metals grown epitaxially on W(110). The spectra on the left side of the figure represent the $4f^{n-1}$ final-state PE multiplets; they were taken at the given photon energies. The spectra on the right side were recorded with 40-eV photons, and they all show the spectral signature of a narrow occupied surface state at the

0163-1829/95/51(12)/7920(4)/$06.00

Fermi level. We shall first turn to an analysis of the $4f^{n-1}$ PE multiplet spectra and discuss the d-like surface states further below.

The simplest $4f^{n-1}$ PE multiplet is observed for the Lu(0001) metal surface, with a $4f^{14}$ configuration in the ground state. It consists of two spin-orbit doublets, one from the bulk (solid subspectrum) and one from the topmost surface layer (dashed subspectrum), which are separated by a surface core-level shift of $\delta_s = -(0.53\pm0.02)$ eV. The negative sign means that the surface component is shifted to lower energy with respect to the bulk component, i.e., to higher binding energy; the chosen sign convention is in agreement with that of Ref. 6. The spin-orbit splitting turns out to be 1.48 ± 0.02 eV. Note the substantially larger widths of the components of the surface doublet, which are mainly caused by thermal broadening.[15] The $4f^{n-1}$ final-state PE multiplets of the spectra of Er(0001), Ho(0001), and Dy(0001) were least-squares fitted by assuming, in each case, identical multiplet spectra for the bulk and surface, however, allowing for broader lines of the surface multiplets. The relative positions of the $4f^{n-1}$ multiplet components were taken from the atomic calculation of Gerken,[16] while the agreement between the theoretical and experimental intensities of the individual multiplet components was found to be relatively poor; they were accordingly varied to obtain good fits of the spectra. Note that the multiplet splittings had to be stretched by a typical factor of 1.10 as compared to the values given in Ref. 16; this is a consequence of the increased core potential in the PE final state. In this way, the following surface core-level shifts were obtained: Dy(0001), $\delta_s = -(0.30\pm0.03)$ eV; Ho(0001), $\delta_s = -(0.43\pm0.05)$ eV; Er(0001), $\delta_s = -(0.39\pm0.07)$ eV. Note that the quoted value for Dy metal was derived from the high-resolution PE spectrum of the ^7F multiplet component shown in Fig. 1, which was measured with 100-eV photons and the sample cooled to 150 K.

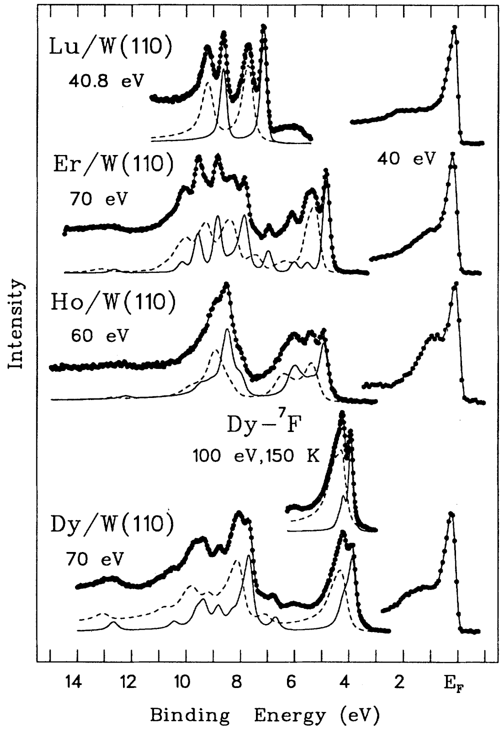

FIG. 1. Photoemission spectra taken from the (0001) faces of monocrystalline films of Dy, Ho, Er, and Lu metal grown epitaxially on W(110). The spectra were taken at the given photon energies, with the samples at room temperature; in the case of Dy metal, the shallowest $4f$-multiplet component was also measured with the sample cooled to 150 K. Note the intense PE peaks from surface states very close to the Fermi level observed in all cases. The results of least-squares-fit analyses are given by the solid lines through the data points as well as by the solid and dashed subspectra, respectively, representing the $4f$ multiplet signals from the bulk and from the topmost surface layer.

A high-resolution PE spectrum of the (110) face of a monocrystalline film of bcc Eu metal at a temperature of 20 K is displayed in Fig. 2; the formation of the (110) face was confirmed by LEED. Note the individual ^7F_J multiplet components in the bulk spectrum that could be resolved. The spectrum from the topmost surface layer (dashed subspectrum) is less well resolved and is again shifted to higher binding energies by the surface core-level shift; by least-squares fit, a surface core-level shift of $\delta_s = -(0.48\pm0.03)$ eV is derived.

The present results for the surface core-level shifts are summarized in Table I. This table also contains recently published δ_s values by our group for the close-packed surfaces of Gd,[6] Tb,[5] as well as Tm and Yb.[7] In this way, a complete sequence of surface core-level shifts for the heavy lanthanide metals becomes available, allowing a comparison with previously published experimental and theoretical results.

Figure 3 gives a graphical representation of the surface core-level shifts of $4f^{n-1}$ electron-removal states of the

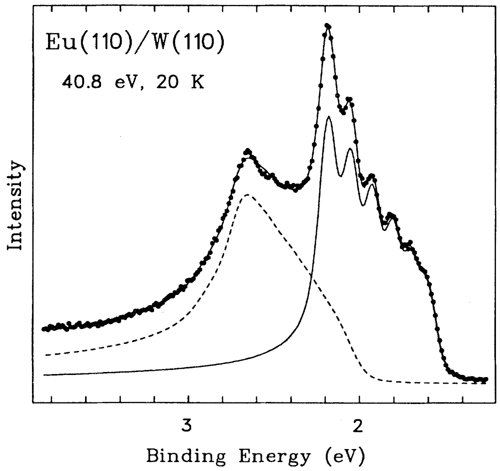

FIG. 2. High-resolution photoemission spectrum of the (110) surface of a monocrystalline film of bcc Eu metal at 20 K taken with He II radiation; the film was grown on W(110). Note that the individual components of the bulk subspectrum are resolved.

TABLE I. Summary of experimental results for the surface core-level shift δ_s of $4f$ PE lines for the given faces of the heavy lanthanide metals.

Lanthanide metal	Face	$-\delta_s$ (meV)	Ref.
Eu	(110)	480±30	Present work
Gd	(0001)	290±30	6
Tb	(0001)	260±30	5
Dy	(0001)	300±30	Present work
Ho	(0001)	430±50	Present work
Er	(0001)	390±70	Present work
Tm	(0001)	470±50	7
Yb	(111)	450±30	7
Lu	(0001)	530±20	Present work

heavy lanthanide metals from Eu to Lu. In addition to the present results and those of Refs. 5–7 for smooth surfaces of monocrystalline films (filled circles), previous experimental values obtained on polycrystalline films (open circles; Ref. 3) are also included. The open diamonds represent the results of an *ab initio* calculation for the (0001) faces of the lanthanide metals;[4] the open square represents the more recent theoretical value for Lu(0001) by Aldén, Skriver, and Johansson,[17] which is in good agreement with the experimental result. Note that the experimental δ_s results for close-packed surfaces of the lanthanide metals exhibit an overall increase in magnitude from Gd to Lu; they are, however, strikingly smaller than the previously published experimental results as well as the theoretical values of Begley *et al.*[4] For completeness, we refer to three other recent experimental results for epitaxial Gd(0001) films, which are less accurate than the present result and are not included in Fig. 3: $\delta_s = -0.4\pm0.1$ eV;[18] $\delta_s = -0.45$ eV;[19] $\delta_s = 0.3-0.4$ eV.[20] The δ_s value for the more open Eu(110) surface deviates from the observed systematics for the close-packed surfaces. This is in agreement with theoretical predictions[21] as well as experimental observations for other materials,[22] which show that the δ_s values are usually smaller in magnitude for close-packed surfaces than for more open ones.

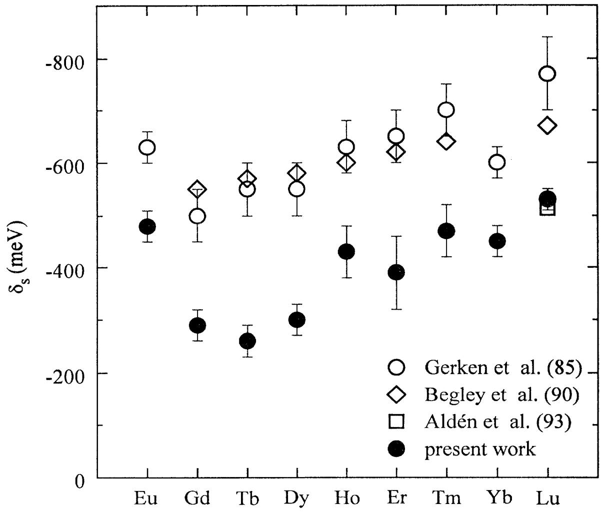

FIG. 3. Surface core-level shifts of $4f^{n-1}$ electron-removal states for the heavy lanthanide metals. In addition to the present results (filled circles), previous experimental values obtained on polycrystalline films by Gerken *et al.* (open circles, Ref. 3) are included. The open diamonds represent the results of an *ab initio* calculation for the (0001) faces of the lanthanide metals (Ref. 4); the open square gives the theoretical value of a more recent calculation of Aldén, Skriver, and Johansson (Ref. 17).

On the experimental side, the discrepancy between previously published δ_s values and the present results can be explained as a consequence of rough surfaces of the polycrystalline materials, while rather smooth surfaces were investigated in the present paper. As discussed recently in connection with Tb(0001),[3] the magnitude of δ_s increases with decreasing coordination number.[23] This means that on rough surfaces, with an abundance of low-coordinated sites, the surface signals are not representative for the topmost layer of an atomically smooth surface.

On the theoretical side, the striking discrepancy between the results of Begley *et al.*[4] and the present experimental δ_s values suggests the importance of final-state contribution to δ_s, since only initial-state effects were taken into account in those calculations. In this respect, we would like to refer to a very recent study of surface shifts of $4f^{n+1}$ electron-addition states (populated by inverse photoemission) and $4f^{n-1}$ electron-removal states (reached by photoemission) in Gd(0001),[6] where a separation of the observed surface core-level shifts into initial-state and final-state contributions was achieved. The observed sign of the final-state shift determined for Gd(0001) explains at least part of the discrepancy between the theoretical results of Ref. 4 and the present experimental results, since the final-state screening contribution causes a decrease in the magnitude of δ_s for the electron-removal state by $\cong 0.10$ eV.[6] A very recent theoretical study of surface core-level shifts of occupied and unoccupied $4f$ states in lanthanide metals, with full inclusion of final-state screening contributions,[24] has in fact achieved a much better agreement with the present experimental results; this holds also for the surface core-level shift calculated by the same group for Lu(0001).[17]

We finally comment on the surface states observed close to the Fermi level for the close-packed surfaces of Dy, Ho, Er, and Lu. As in the case of Gd,[6] Tb,[5,10] La,[12] as well as Tm and Yb metals,[7,11] the photon-energy dependence of the PE-signal intensity supports a $5d$-like character in all cases, in agreement with the theoretical prediction for Gd(0001). In the case of La(0001),[12] Gd(0001),[25,26] and Tb(0001),[26] the unoccupied part of the surface states has additionally been studied by inverse photoemission with a variable photon-energy spectrometer. In the latter two cases, the magnetic exchange splitting was also investigated as a function of temperature. It is now clear that such a d-like surface state exists directly at the Fermi level on the close-packed surfaces of all heavy lanthanide metals as well as on La(0001) (Ref. 12) and Nd(0001).[27] It is thus a common property of close-packed surfaces of lanthanide metals. Since this surface state is highly localized, it can influence the surface core-level shift[6] and is subject to strong magnetic exchange splitting in magnetically ordered materials such as Gd and Tb metals.[25,26] In this way, it may well be responsible for the enhanced magnetic surface properties observed for ferromagnetic lanthanide metals.[28] We hope that the present systematic results will stimulate further theoretical work on the surface electronic structure of lanthanide metals.

This work was supported by the Bundesminister für Forschung und Technologie, Project No. 05-5KEAXI-3/TP01, and the Sonerforschungsbereich-290, TPA06, of the Deutsche Forschungsgemeinschaft.

---

*Present address: Institut für Oberflächen- und Mikrostrukturphysik, Technische Universität, D-01062 Dresden, Germany.

[1] P. H. Critin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. **41**, 1425 (1978).

[2] B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980).

[3] F. Gerken, A. S. Flodström, J. Barth, L. I. Johansson, and C. Kunz, Phys. Scr. **32**, 43 (1985); R. Kammerer, J. Barth, F. Gerken, A. Flodström, and L. I. Johansson, Solid State Commun. **41**, 435 (1982).

[4] A. M. Begley, R. G. Jordan, W. M. Temmerman, and P. J. Durham, Phys. Rev. B **41**, 11 780 (1990).

[5] E. Navas, K. Starke, C. Laubschat, E. Weschke, and G. Kaindl, Phys. Rev. B **48**, 14 753 (1993).

[6] A. V. Fedorov, E. Arenholz, K. Starke, E. Navas, L. Baumgarten, C. Laubschat, and G. Kaindl, Phys. Rev. Lett. **73**, 601 (1994).

[7] M. Bodenbach, A. Höhr, C. Laubschat, G. Kaindl, and M. Methfessel, Phys. Rev. B **50**, 14 446 (1994).

[8] R. Wu, A. J. Freeman, and C. L. Fu, J. Magn. Magn. Mater. **99**, 81 (1991).

[9] D. Li, C. W. Hutchins, P. A. Dowben, C. H. Wang, R. T. Wu, M. Onellion, A. B. Andrews, and J. L. Erskine, J. Magn. Magn. Mater. **99**, 85 (1991).

[10] S. C. Wu, H. Li, Y. S. Li, D. Tian, J. Quinn, D. Jong, and D. Fort, Phys. Rev. B **44**, 13 720 (1991).

[11] M. Bodenbach, Doctoral thesis, Freie Universität Berlin, 1992.

[12] A. V. Fedorov, A. Höhr, E. Weschke, K. Starke, V. K. Adamchuk, and G. Kaindl, Phys. Rev. B **49**, 5117 (1994).

[13] J. Kolaczkiewitz and E. Bauer, Surf. Sci. **175**, 487 (1986).

[14] U. Stetter, M. Farle, K. Baberschke, and W. G. Clark, Phys. Rev. B **45**, 503 (1992).

[15] E. Weschke, S. Vandré, C. Schüßler-Langeheine, A. Höhr, F. Bødker, and G. Kaindl (unpublished).

[16] F. Gerken, J. Phys. F **13**, 703 (1993).

[17] M. Aldén, H. L. Skriver, and B. Johansson, Phys. Rev. Lett. **71**, 2457 (1993).

[18] J. E. Ortega, F. J. Himpsel, Dongqi Li, and P. A. Dowben, Solid State Commun. **91**, 807 (1994).

[19] E. Vescovo, C. Carbone, and O. Rader, Phys. Rev. B **48**, 7731 (1993).

[20] D. LaGraffe, P. A. Dowben, and M. Onellion, Phys. Rev. B **40**, 3348 (1989).

[21] D. Tomanek, V. Kumar, S. Holloway, and K. H. Bennemann, Solid State Commun. **41**, 273 (1982).

[22] See, e.g., R. Nyholm, J. N. Andersen, J. F. van Acker, and M. Quarford, Phys. Rev. B **44**, 10 987 (1991).

[23] W. D. Schneider, C. Laubschat, and B. Reihl, Phys. Rev. B **27**, 6538 (1983).

[24] M. Aldén, H. L. Skriver, I. A. Abrikosov, and B. Johansson (private communication).

[25] A. V. Fedorov, K. Starke, and G. Kaindl, Phys. Rev. B **50**, 2739 (1994).

[26] A. V. Fedorov, F. Hübner, C. Schüßler-Langeheine, E. Weschke, and G. Kaindl (unpublished).

[27] E. Weschke (private communication).

[28] H. Tang, D. Weller, T. G. Walker, J. C. Scott, C. Chappert, H. Hopster, A. W. Pang, D.S. Dessan, and D. P. Pappas, Phys. Rev. Lett. **71**, 444 (1993).