RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 19 15 NOVEMBER 1993-I

Surface core-level shift of $4f$ states for Tb(0001)

E. Navas, K. Starke, C. Laubschat, E. Weschke, and G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

(Received 2 September 1993)

For Tb(0001), a surface core-level shift of the $4f^7$ photoemission multiplet of $\delta_s = 0.26 \pm 0.03$ eV is determined. This value is by more than a factor of 2 smaller than the result of a recent self-consistent SLAB calculation, but agrees with the prediction of a thermochemical model. It is demonstrated that the larger values of δ_s reported previously for polycrystalline samples originate from contributions of low-coordinated surface sites. Implications of the present findings for an improved understanding of the surface electronic structure of rare-earth metals are briefly discussed.

Surface-induced energy shifts of $4f$ states in rare-earth materials are well-known phenomena in photoemission[1-5] (PE) and recently also in inverse PE.[6] They are directly related to the different cohesive energies in the bulk and at the surface.[5] Apart from insight into the thermochemical and structural properties of the surface, a detailed knowledge of surface core-level shifts provides an understanding of surface valence transitions,[3,7] and hence of some essential aspects of the chemical, catalytic, and magnetic properties of these materials. For the elemental rare-earth metals, relatively large surface core-level shifts have been reported ranging from 0.48 eV for La (Ref. 2) to 0.77 eV for Lu metal.[1] The self-consistent results of recent SLAB calculations for close-packed surfaces of rare-earth metals seem to be in good agreement with these experimental results.[8] This is amazing in view of the fact that the experimental data were taken on polycrystalline samples, where the assumption of close-packed surfaces cannot be expected to be valid. Since surface core-level shifts are known to increase with decreasing coordination number of surface atoms,[4,9] a substantial fraction of surface atoms at low-coordinated sites will result in larger shifts than those representative for the atomically flat close-packed surface.

In the present paper we show that the surface core-level shift of Tb $4f$ states depends critically on the quality of the surface, amounting to only 0.26 ± 0.03 eV for a well-annealed close-packed Tb(0001) surface; this value is by more than a factor of 2 smaller than reported previously for a polycrystalline surface. The observed shift is in striking disagreement with the result of the recent SLAB calculation of Ref. 8, but can be quantitatively accounted for by a simple thermochemical model. The present finding reveals the stringent necessity to reanalyze the surface core-level shifts of essentially all rare-earth metals both experimentally and theoretically and sheds further light on some weaknesses of present *ab initio* calculations of surface properties of highly correlated materials.

The photoemission experiments were performed at the high-resolution U2 beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using an angle-integrating hemispherical electron-energy analyzer. The total-system resolution was set to 90 meV (full width at half maximum) at $h\nu = 48$ eV. Monocrystalline Tb(0001) films were grown on a W(110) substrate by thermal evaporation of Tb metal from a resistively heated Knudsen cell. The evaporation rate was $\cong 4$ Å/min as monitored by a quartz microbalance and calibrated by the intensities of PE lines from W and Tb. During Tb evaporation, the sample was kept at 250 K and the pressure rose to 1×10^{-10} mbar, returning readily to its base value of 3×10^{-11} mbar after the end of evaporation. Under these clean conditions, a layer-by-layer growth mode is achieved as known from analogous studies with Gd films.[10,11] The as-deposited 130 ± 10-Å-thick Tb film gave only a diffuse low-energy electron diffraction (LEED) pattern indicating a relatively rough sample surface. Subsequent annealing of the film for 2 min at 900 K led to sharp LEED spots. Oxygen contaminations were checked by monitoring the O 2p PE signal at a photon energy of 48 eV, and they were found to be negligible.

Figure 1 displays normal emission PE spectra of the $4f$ and valence-band region of Tb(0001) taken at a photon energy of 48 eV: (a) for the as-grown film and (b) after annealing at $T = 900$ K. The leading doublet at a binding energy (BE) of about 2.5 eV originates from emission to the $4f^7$-$^8S_{7/2}$ final state; it is split into a bulk component at a BE of $\cong$ 2.3 eV and a surface component shifted by the surface core-level shift to higher BE. A similar splitting into surface and bulk components is readily seen for the other prominent $4f$ component (^6I) at a BE of $\cong$ 7.5 eV. It is striking that the surface core-level shift changes by a factor of more than 2 upon annealing of the Tb(0001) film.

For the as-grown film, the surface core-level shifts amounts to $\cong 0.57$ eV; at the same time, the width of the surface component is much larger than that of the bulk component, and the valence-band emission close to E_F reveals a triangular shape characteristic for polycrystalline surfaces of rare-earth metals.[1] Upon annealing of this film, a sharp peak appears just below E_F,[12] which has also been observed previously for ordered (0001) surfaces of Gd metal[13,14] as well as of Ho, Tm, and Yb metal,[15] and has been assigned to a nonbonding surface state of d_{z^2}-orbital character in a band gap of the surface-projected bulk band structure at $\bar{\Gamma}$.[12,16] At the same

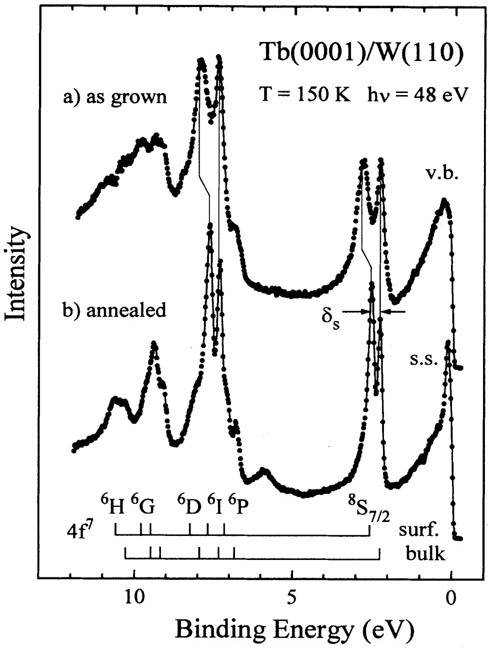

FIG. 1. PE spectra of a 130-Å-thick Tb(0001) film at $T=150$ K grown on W(110): (a) as-grown at $T=150$ K; (b) after annealing for 2 min at $T=900$ K. The solid lines through the data points serve as a guide to the eyes. The vertical-bar diagrams in (b) indicate the strongest components of the $4f^7$ final-state multiplets from bulk and surface. Note the surface state (s.s.) in the spectrum of the well-annealed film.

time, the surface core-level shift decreases to $\cong 0.26$ eV, and the width of the $4f$ surface component reduces to a value comparable with the one of the bulk component. The appearance of the surface state, the LEED pattern, and the small width of the $4f$ surface component for the annealed film can be taken as strong evidence for an atomically smooth, well-ordered Tb(0001) surface. Thus, we assign the small surface core-level shift to atoms at surface sites with coordination 9, while the larger shift observed for the as-grown film is explained by a substantial fraction of low-coordinated surface sites at steps and corners.

Within the framework of a simple tight-binding model, the electron bandwidth, the cohesive energy, and hence the $4f$ binding energy relative to the free-atom value are proportional to the square root of the coordination number.[4,9] Starting with a surface energy shift δ_N for coordination N, one obtains for the energy shift δ_Z for coordination Z the expression

$$\delta_Z=(1-\sqrt{Z/12})/(1-\sqrt{N/12})\delta_N \ , \qquad (1)$$

with 12 being the bulk coordination in the hcp lattice.

For a quantitative analysis of the data, the spectra were least-squares fitted employing Eq. (1) for relating the surface shifts of differently coordinated surface sites. Taking electron-hole-pair excitations into account, Doniach-Sunjic line shapes[17] were used to describe the individual components. Inelastic electron-electron scattering was simulated by adding an integral background to the bulk components, and contributions from valence-band emission were accounted for by superposition with a constant plus a triangle-shaped background. Finally, the model spectra were convoluted by a Gaussian to simulate finite experimental resolution. The results of this analysis for the leading $^8S_{7/2}$ multiplet component are shown in Fig. 2 by the solid curves through the data points; the subspectra, corresponding to contributions from the differently coordinated sites, are also given. While the as-grown film contains surface sites with coordinations 9 (shaded), as well as 8, 7, and 6 (short-dashed), the spectrum of the well-annealed Tb(0001) film can be described by only a single surface component in addition to the bulk component, resulting in a surface core-level shift of $\delta_s=0.26\pm0.03$ eV; this value corresponds to a smooth close-packed Tb(0001) surface. For the as-grown film, the best fit results in a shift for the coordination-9 component of $\delta_9=0.31\pm0.04$ eV; within the limits of experimental accuracy, this value agrees with δ_s for the well-annealed film.

Our result for δ_s is strikingly smaller than the value of 0.57 obtained in the recent SLAB calculation.[8] On the other hand, δ_s is in good agreement with the value derived from a thermochemical model based on the equivalent-cores approximation.[5] In this model, the $4f$ BE is calculated from a Born-Haber cycle consisting of the evaporation of a metal atom with valence Z, excitation of a $4f$ electron into an unoccupied $5d$ orbital in the

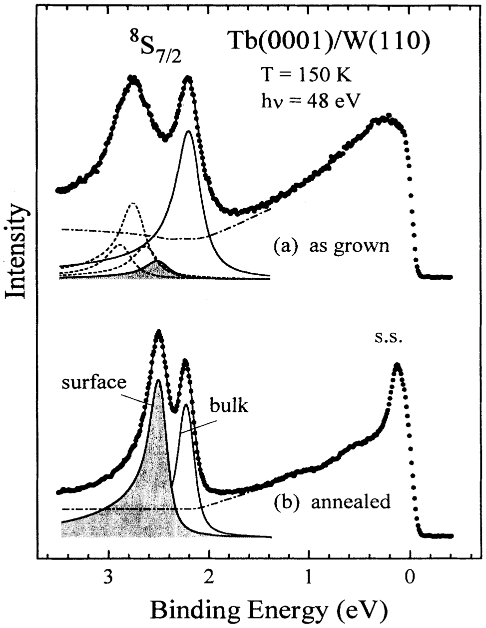

FIG. 2. Results of least-squares-fit analysis of the leading $^8S_{7/2}$ multiplet component in the PE spectra of (a) the as-grown Tb film and (b) the well-annealed Tb(0001) film. While spectrum (b) is well described by a doublet of Doniach-Sunjic lines from bulk (solid) and surface (shaded), spectrum (a) is decomposed into four components from surface atoms with coordination 9 (shaded), as well as 8, 7, and 6 (short-dashed). For details see text.

free atom, condensation of the excited free atom, and dissolution of this condensed phase with zero concentration in the *Z* metal. Summing up the different energies involved, the heat of formation of a $(Z+1)$ impurity atom in the *Z* metal is obtained, which is identical to the energy required for producing a PE final state (E_B). Thus we obtain for the BE, E_B:

$$E_B = E_{fd} + E_{\mathrm{coh}}^{Z} - E_{\mathrm{coh}}^{Z+1} + E_{\mathrm{imp}} \ , \tag{2}$$

where E_{fd} denotes the $f \rightarrow d$ excitation energy, E_{coh}^{Z} and E_{coh}^{Z+1} the respective cohesive energies for valence states *Z* and $(Z+1)$, and E_{imp} the heat of solution of a dilute $(Z+1)$ impurity in the matrix of the *Z* metal. In analogy to Eq. (1), we then obtain for the surface shift δ_N:

$$\delta_N = E_B^N - E_B^{\mathrm{bulk}} = (1 - \sqrt{N/12})(E_{\mathrm{coh}}^{Z+1} - E_{\mathrm{coh}}^{Z} - E_{\mathrm{imp}}) . \tag{3}$$

Taking as cohesive energy of a trivalent rare-earth metal the value for Gd metal, and as that of the corresponding tetravalent metal the value for Hf, and calculating E_{imp} in the framework of the semiempirical Miedema scheme,[18] one obtains for δ_9 a value of 0.26 eV, in good agreement with the observed shift.

The above discussion of the surface core-level shift is based on the assumption that the simple tight-binding approach is valid and the cohesive energies vary proportional to $\sqrt{N}$. This assumption can be questioned if a surface state, contributing to chemical bonding, is occupied, possibly altering the surface cohesive energy. If we assume, e.g., that the formation of the *d*-like surface state on the Tb(0001) surface causes an increase in the surface cohesive energy, the difference in cohesive energies between bulk and surface, and hence the resulting surface core-level shift would be smaller. The good agreement between the experimental result and the prediction of the thermochemical model, however, supports the view that the contribution of the surface state to bonding is relatively weak and the state is basically nonbonding in nature.[16]

A further point to be considered regards a possible influence of *fd* hybridization on δ_s. In a recent publication[19] it was shown that the surface shift of the $4f^1$ state in Ce metal is very small, since the effect of the reduced 4*f* hybridization at the surface cancels the surface shift of the bare, i.e., hypothetically unhybridized $4f^1$ state. An analogous hybridization effect could be responsible for the small δ_9 value of Tb(0001). In fact, the binding energy of the $^8S_{7/2}$ final state is almost identical to the one of the ^1S final state of Ce, however, the hybridization parameter is expected to be considerably smaller in the former case due to the large Coulomb potential and the smaller number N_f of unoccupied *f* states.[20] The recent observation of a 4*f* surface core-level shift of 0.29±0.03 eV for the Gd(0001) surface,[21] where hybridization effects can be essentially excluded due to the high stability of the $4f^7$ ground state, however, favors the view that hybridization effects on the surface core level shift of Tb(0001) are small.

The present results have some implications for the surface electronic structure of rare-earth metals: Since hybridization effects on δ_s seem to be negligible in the case of Tb(0001), similarly small surface shifts are also expected for the other heavy rare-earth metals, and the large values reported so far[1,2] have presumably been the results of poorly defined surfaces with substantial fractions of low-coordinated surface sites. The theoretical side requires also substantial improvements as demonstrated by the results of the self-consistent *ab initio* SLAB calculations of Ref. 8, which deviate by more than a factor of 2 from reality in the case of Tb(0001). Further experimental and theoretical work is required for a better understanding of the surface electronic structure of rare-earth materials.

This work was supported by the Sfb-6 of the Deutsche Forschungsgemeinschaft, TPA06, and the Bundesminister für Forschung und Technologie, Project No. 05-5KEAXI-3/TP01. Valuable assistance by the staff of BESSY is gratefully acknowledged.

---

[1] F. Gerken, A. S. Flodström, J. Barth, L. I. Johansson, and C. Kunz, Phys. Scr. **32**, 43 (1985).

[2] A. Nilsson, N. Mårtensson, J. Hedmann, B. Eriksson, R. Bergmann, and U. Gelius, Surf. Sci. **162**, 51 (1985).

[3] C. Laubschat, G. Kaindl, W.-D. Schneider, B. Reihl, and N. Mårtensson, Phys. Rev. B **33**, 6675 (1986).

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

[5] B. Johansson, Phys. Rev. B **20**, 1315 (1979).

[6] A. V. Fedorov, C. Laubschat, K. Starke, E. Weschke, K. U. Barholz, and G. Kaindl, Phys. Rev. Lett. **70**, 1719 (1993).

[7] B. Johansson, Phys. Rev. B **19**, 6615 (1979).

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

[9] R. P. Gupta, Phys. Rev. B **23**, 6265 (1981).

[10] J. Kolaczkiewicz and E. Bauer, Surf. Sci. **175**, 487 (1986); U. Stetter, M. Farle, K. Barberschke, and W. G. Clark, Phys. Rev. B **45**, 503 (1992).

[11] K. Starke, E. Navas, L. Baumgarten, and G. Kaindl, Phys. Rev. B **48**, 1329 (1993).

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

[13] D. Li, C. W. Hutchings, P. A. Dowbin, C. Hwang, R. T. Wu, M. Onellion, A. B. Andrews, and I. L. Erskine, J. Magn. Magn. Mater. **99**, 85 (1991).

[14] G. A. Mulhollan, K. Garrison, and J. L. Erskine, Phys. Rev. Lett. **69**, 3240 (1992).

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

[16] R. Wu, C. Li, A. J. Freeman, and C. L. Fu, Phys. Rev. B **44**, 9400 (1991).

[17] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[18] A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica **100B**, 1 (1980).

[19] E. Weschke, C. Laubschat, C. T. Simmons, M. Domke, O. Strebel, and G. Kaindl, Phys. Rev. B **44**, 8304 (1991).

[20] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4319 (1983).

[21] A. V. Fedorov, E. Arenholz, K. Starke, E. Navas, L. Baumgarten, C. Laubschat, and G. Kaindl (unpublished).

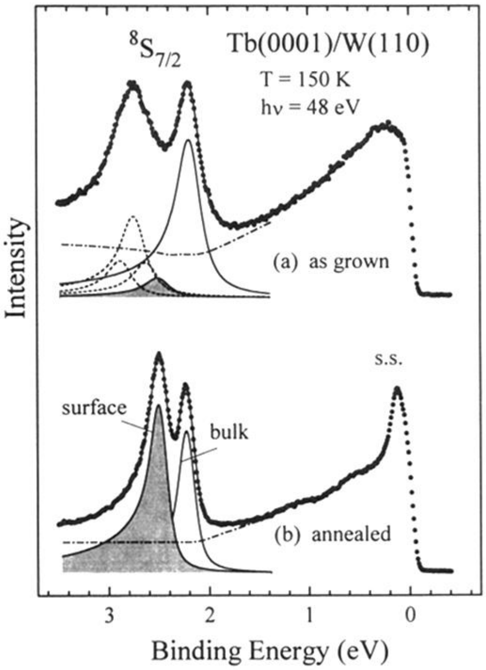

FIG. 2. Results of least-squares-fit analysis of the leading $^8S_{7/2}$ multiplet component in the PE spectra of (a) the as-grown Tb film and (b) the well-annealed Tb(0001) film. While spectrum (b) is well described by a doublet of Doniach-Sunjic lines from bulk (solid) and surface (shaded), spectrum (a) is decomposed into four components from surface atoms with coordination 9 (shaded), as well as 8, 7, and 6 (short-dashed). For details see text.