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LETTER TO THE EDITOR

Determination of the Tb Γ_{4-} critical point energy from angle-resolved UV photoemission of Tb(0001)

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Abstract. We report an angle-resolved UV photoemission study of the clean (0001) surface of the rare-earth metal terbium. Normal emission spectra were recorded in the photon energy range 12–50 eV using synchrotron radiation. A number of well-defined features were observed which showed negligible dispersion with photon energy. Close similarity is found between these spectra and those from the (0001) surfaces of Y, Gd and Ho. The binding energy of the Γ_{4-} critical point is determined to be 1.5 (± 0.1) eV. We suggest that the apparent shift of the Tb Δ_1 band to higher binding energy reported by previous workers was a result of the significant Fe contamination of their sample.

In a recent paper Wu *et al* [1] reported an angle-resolved UV photoemission (ARUPS) study of the (0001) surface of the hexagonal close-packed (HCP) rare-earth metal Tb. Their results appeared to show a shift of the Δ_1 band to a binding energy 1.5 eV deeper than that predicted by their own bandstructure calculation, with the experimental Γ_{4-} critical point determined to be at a binding energy of 3.6 (± 0.15) eV. This result is inconsistent with other ARUPS studies of HCP rare-earth metals, in which the Γ_{4-} point has been observed at binding energies (± 0.1 eV) of 1.4 eV (Gd) [2], 1.7 eV (Y) [3] and 1.7 eV (Ho) [4]. Given the close similarity between the bandstructures of Gd [5], Y [6], Ho [4] and Tb [1,7], the value of 3.6 eV for Tb [1] seems rather high. Wu *et al* [1] have assumed that their results were characteristic of a clean surface, despite the fact that they observed 10–15% Fe contamination on their Tb sample. In order to determine whether the bandstructure was influenced by the presence of Fe, we have performed an ARUPS study of clean Tb(0001).

The Tb sample was spark machined from a high-quality single-crystal boule grown, using solid state electrotransport methods [8], by Dr D Fort of the School of Metallurgy and Materials, University of Birmingham, UK. *Ex situ* sample preparation was performed without electropolishing; the mechanically polished surface was not protected by a passivating chloride layer and so the sample was kept under rough vacuum ($\sim 10^{-2}$ mbar) prior to being inserted into the ultra-high-vacuum chamber.

The ARUPS experiments were performed on beamline 6.2 of the Synchrotron Radiation Source, SERC Daresbury Laboratory, UK. The spectrometer used was a Vacuum

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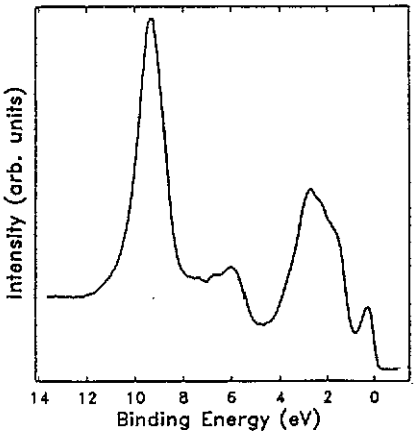

Figure 1. ARUPS spectra of clean Tb(0001). Photon energy 40 eV, incidence angle 30°, p-polarized radiation, normal emission.

Generators ADES 400 with overall energy and angular resolutions of 0.15 eV and 3° respectively. The base pressure of the chamber was $\sim 10^{-10}$ mbar. *In situ* sample cleaning was performed by means of repeated cycles of Ar^+ bombardment (beam energy $\simeq$3 kV, current density $\simeq 10\ \mu A\ cm^{-2}$) and annealing to $\simeq$650 °C. This cleaning method has been used for many rare-earth surfaces—Gd(0001) [9], Y(0001) [3,10,11], Y(11$\bar{2}$0) [12,13], Ho(0001) [4], Ho(11$\bar{2}$0) and Er(11$\bar{2}$0) [14], and Pr(0001) [15]—and is known to produce clean, well-ordered surfaces without any detectable transition metal contamination. Surface cleanliness and order were monitored principally using ARUPS; oxide- and hydride-induced features apear at $\simeq$6 eV binding energy [16,17] and the intensity of the surface-order-dependent state (SODS) at 9.6 eV binding energy is known to be extremely sensitive to the quality of the surface [3,12–15]. Approximately 30 cleaning cycles were required before the ARUPS spectra showed a low contamination level and an intense SODS (figure 1). We were unable to detect any Fe 3p emission in spectra taken over the binding energy range 40–60 eV, indicating an upper limit of 1% Fe on the surface. Low-energy electron diffraction (LEED) showed a sharp (1 × 1) pattern on a low-intensity background.

Normal-emission ARUPS spectra of the valence band region (0–5 eV binding energy) are shown in figure 2. The spectra show three main features (labelled a, b and c) at binding energies (±0.1 eV) of 0.3, 1.5 and 2.7 eV respectively. The 4f $^8S_{7/2}$ multiplet peak, at a binding energy of 2.3 (± 0.1) eV, can also be seen at photon energies above 40 eV. None of these features shows significant dispersion with photon energy; the short mean free path of electrons in rare-earth metals [2] causes momentum broadening which leads to spectra dominated by emission from points in the Brillouin zone with high density of states. These spectra are very similar to those from Y(0001) [3], Gd(0001) [2] and Ho(0001) [4], except for the presence of the 4f-derived peak. For these elements peak b was determined to be due to emission from the Γ_{4-} critical point and, by analogy, we suggest the same assignment applies to Tb(0001). Thus, we find the binding energy of the Tb Γ_{4-} critical point to be 1.5 (± 0.1) eV. As is found for Y [3], Gd [2] and Ho [4], this value is somewhat lower than that predicted theoretically. The calculation of Wu *et al* [1] shows that the Tb Γ_{4-} point at 2.3 eV and that of Jackson [7] shows it at 2.0 eV. This is marked contrast to the value of 3.6 eV determined experimentally for Tb by Wu *et al* [1], i.e., a shift of 1.5 eV to *higher* binding energy. We suggest that this shift was the result of the significant level of Fe contamination of their sample.

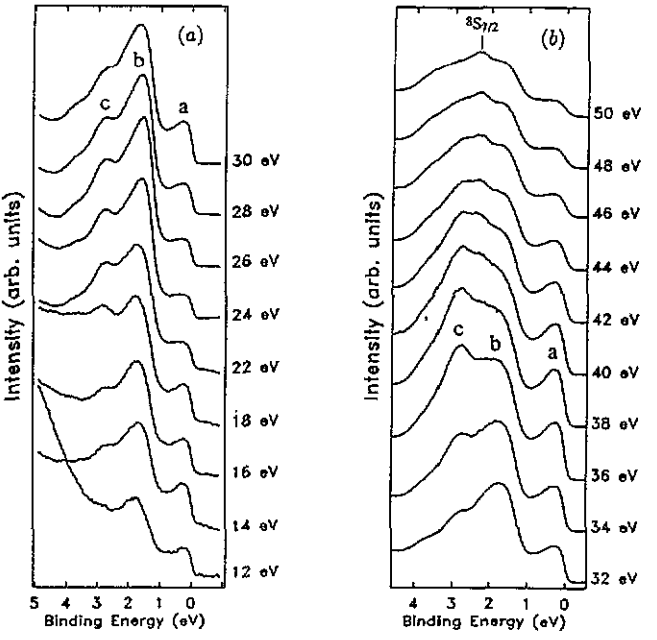

Figure 2. Normal-emission ARUPS spectra of the Tb(0001) valence band, normalized to the incident flux. (*a*) $h\nu$ = 12–30 eV, (*b*) $h\nu$ = 32–50 eV. Incidence angle 30°, p-polarized radiation.

Our value for the binding energy of the Tb Γ_{4-} critical point is consistent with those of other HCP rare-earth metals. The decrease in atomic radii across the lanthanide series (the lanthanide contraction) [18] leads to a corresponding increase in the occupied bandwidth [19]. It follows that the critical point binding energies for Tb (Z = 65) would be expected to lie between those of Gd (Z = 64) and Ho (Z = 67). Clearly, this is seen to be the case.

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References

[1] Wu S C, Li H, Tian D, Quinn J, Li Y S, Jona F, Sokolov J and Christensen N E 1990 *Phys. Rev.* B **41** 11912
[2] Himpsel F J and Reihl B 1983 *Phys. Rev.* B **28** 574
[3] Barrett S D and Jordan R G 1987 *Z. Phys.* B **66** 375
[4] Blyth R I R, Barrett S D, Dhesi S S, Cosso R, Heritage N, Begley A M and Jordan R G 1991 *Phys. Rev.* B at press
[5] Dimmock J O and Freeman A J 1964 *Phys. Rev. Lett.* **13** 750
[6] Blaha P, Schwarz K and Dederichs P H 1988 *Phys. Rev.* B **38** 9368
[7] Jackson C 1969 *Phys. Rev.* **178** 947
[8] Jordan R G 1974 *Contemp. Phys.* **15** 373

[9] Jordan R G 1986 *Phys. Scr.* T **13** 22
[10] Barrett S D, Begley A M, Durham P J and Jordan R G 1989 *Solid State Commun.* **71** 111
[11] Blyth R I R, Andrews P T and Barrett S D 1991 *J. Phys.: Condens. Matter* **3** 2827
[12] Barrett S D, Jordan R G and Begley A M 1987 *J. Phys. F: Met. Phys.* **17** L145
[13] Barrett S D, Blyth R I R, Dhesi S S and Newstead K 1991 *J. Phys.: Condens. Matter* **3** 1953
[14] Barrett S D, Blyth R I R, Begley A M, Dhesi S S and Jordan R G 1991 *Phys. Rev.* B **41** 4573
[15] Blyth R I R, Cosso R, Dhesi S S, Newstead K, Begley A M, Jordan R G and Barrett S D 1991 *Surf. Sci.* at press
[16] Netzer F P and Bertel E 1982 *Handbook on the Physics and Chemistry of Rare Earths* vol 5, eds K A Gschneidner and L Eyring (Amsterdam: North-Holland)
[17] Weaver J H, Peterson D T and Benbow R L 1979 *Phys. Rev.* B **20** 5301
[18] Beaudry B J and Gschneidner K A 1978 *Handbook on the Physics and Chemistry of Rare Earths* vol 1, eds K A Gschneider and L Eyring (Amsterdam: North-Holland)
[19] Skriver H L 1983 *Systematics and Properties of the Lanthanides* ed S P Sinha (Dordrecht: Reidel)