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LETTER TO THE EDITOR

The unoccupied states of a rare earth metal: Y(0001)

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Abstract. Normal incidence inverse photoemission spectra of Y(0001) have been measured in the photon energy range 12–32 eV. In the photon energy range 19–23 eV fluorescence from the radiative decay of a 4p core hole largely obscures the direct transitions. Outside this range a number of features were observed, which vary in intensity but show negligible dispersion with photon energy. Their positions are in good agreement with high density-of-states points along the ΓA direction of published bandstructure calculations. A feature is observed 0.5 (\pm 0.2) eV above the Fermi level, in the gap between the Γ_{4-} and Γ_{3+} critical points, which may be due to either a surface state or to the high overall density of states at the Fermi level.

Angle-resolved ultra-violet photoemission (ARUPS) [1] is now well established as the preferred technique for mapping the occupied electronic structure of crystalline solids. In recent years the corresponding technique of momentum (k)-resolved inverse photoemission (KRIPES) [2] has become increasingly used in the investigation of unoccupied states. Due to the short mean free path of electrons in solids both these spectroscopies are extremely surface sensitive, and thus the preparation of clean, ordered single-crystal surfaces is essential. The high reactivity of the rare earth metals (Sc, Y, La and the lanthanides) makes this preparation particularly difficult. Consequently the number of ARUPS studies of these materials [3–12] is relatively small and there have been no reported KRIPES studies prior to this work. Interest in the electronic structure of the lanthanide metals is due to the presence of the partially occupied, but highly localized, 4f levels. The treatment of these levels within bandstructure calculations is an area of some controversy [13], and it is important that experimental data be obtained to determine the validity of such calculations. Yttrium, which has the hexagonal close packed (HCP) crystal structure, with lattice parameters very similar to those of the heavy lanthanides, provides a suitable material for initial investigation, since its outer electronic configuration of $(4d5s)^3$ is analogous to that of the lanthanides' $(5d6s)^3$. The absence of f electrons, which in the lanthanides are often energetically degenerate with the valence band, simplifies both interpretation of experimental results and the calculation of energy bands; a full-potential linearized-augmented-plane-wave bandstructure calculation [14] has recently been published.

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The first ARUPS study of Y(0001) [7] showed a number of features, in particular an intense surface-order-dependent state (SODS) at 9.6 eV binding energy, which could not be explained in terms of one-electron states in bandstructure calculations. A recent paper [15] suggested that the SODS was due to hydrogen contamination, but it was subsequently shown [16] that the authors had misinterpreted both their own data and those of [7]. This feature appears to be common to all close-packed trivalent rare-earth surfaces since it has also been observed, at similar binding energies, on the (0001) surfaces of Gd [6, 12], Ho [11, 12] and Pr [12] and the reconstructed (11 $\bar{2}$ 0) surfaces of Y [8, 12, 17], Ho and Er [11, 12]. Its origin remains unclear—its presence on Y clearly precludes the involvement of f electrons—but it has been suggested, [7], that it may be derived from many-body excitations involving the presence of an unoccupied surface state in order to explain its surface sensitivity. However, no mechanism has been suggested by which such a surface state could give rise to a peak with the characteristics of the SODS. A band gap exists between the (occupied) Γ_{4-} and (unoccupied) Γ_{3+} critical points in the bandstructure of Y [14], which should be similar to those of the other HCP rare earths. This may be a suitable location for such a state.

The Y(0001) crystal was spark-machined from the same high-quality boule as the crystals used in previous low energy electron diffraction (LEED) and UV photoemission studies [7, 9, 12, 17]. This boule was grown by Dr D Fort (School of Metallurgy and Materials, University of Birmingham, UK) using solid state electrotransport methods [18] and had a residual resistance ratio greater than 500, indicating a low impurity concentration (<0.1 at.%). *Ex-situ* sample polishing was performed using standard metallographic techniques.

The KRIPES experiments were performed using the Liverpool grating spectrometer [19] which has been modified recently by the addition of an x-ray source and hemispherical electron energy analyser enabling the monitoring of sample cleanliness with x-ray photoemission (XPS). The overall energy resolution in KRIPES mode was 0.6 eV at a photon energy of 20 eV, rising to ~ 1 eV at a photon energy of 32 eV and the nominal momentum resolution was 0.1 \AA^{-1} . The base pressure in the chamber was $\sim 6 \times 10^{-11}$ mbar. *In-situ* sample cleaning was performed by repeated cycles of Ar⁺ bombardment (beam energy ~ 2 kV, current density $\sim 5 \mu\text{A cm}^{-2}$) for ~ 30 min, followed by annealing for ~ 30 min to ~ 1000 K. About 40 cycles were necessary before the KRIPES spectra were completely reproducible; XPS indicated an upper limit of 6% oxygen with no visible C 1s peak, and LEED showed a sharp 1×1 pattern on a relatively low background [12]. It is likely that a large fraction of the observed O signal was due to the Ta sample mount, as the area sampled by the analyser was $\sim 50\%$ bigger than the Y crystal.

Normal-incidence KRIPES spectra in the photon energy ranges 12–19 eV and 24–32 eV, corresponding to direct transitions along the ΓA direction of the Brillouin zone, are shown in figure 1. The spectra in the photon energy range 18–23 eV (figure 2) are all obscured to some degree by fluorescence from the decay of a 4p core hole. This occurs when the incident electron is energetic enough to ionize a 4p electron, and the photon energy being detected is in the range produced by the radiative decay of the resulting hole. This is analogous to the Auger features seen in ARUPS; the corresponding $N_{4,5}$ VV Auger peak can be seen in the ARUPS spectra of Y(0001) [7]. This phenomenon is to be expected when the material being studied by KRIPES has shallow core levels and has been reported for several other materials [20–22].

There are four features in the spectra of figure 1 at energies (± 0.2 eV) of 0.5 eV, 2.0 eV, 4.8 eV and 7.0 eV above the Fermi level, labelled a*, b*, c* and d*, respectively.

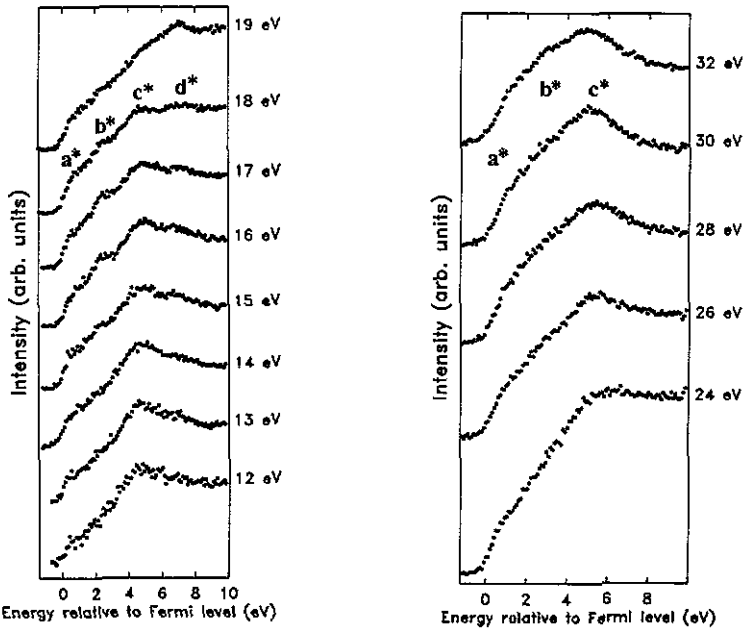


Figure 1. Normal incidence isochromat KRIPES spectra from Y(0001). (a) $h\nu = 12\text{--}19\text{ eV}$. The photon yield for each electron energy has been divided by the incident charge, and the spectra then normalized to the intensity of peak c^* . (b) $h\nu = 24\text{--}32\text{ eV}$, normalized to the incident charge.

We choose this notation to avoid confusion with that of the ARUPS peaks of [7]. None of these features displays significant dispersion with photon energy. Momentum broadening in the initial state, due to the short mean free path of electrons in rare earths, combined with the low crystal momenta in the ΓA direction, leads to spectra which are dominated by transitions to points with high densities of states. This has also been observed in ARUPS of Gd(0001) [3] and Y(0001) [7]. The apparent shift of a^* towards higher energy in figure 1(b) is attributed to the worsening energy resolution in the higher photon energy range. Peaks b^* and c^* are most likely due to transitions to high-density-of-states points along ΓA , since such points occur at 1.8 eV (A_3) and 4.9 eV (Γ_{5-}) in the calculated bandstructure of Blaha *et al* (figure 3) [14]. The calculated total density of states [14] shows peaks at these energies and these have been observed in inverse photoemission [23] and bremsstrahlung isochromat spectra [24] of polycrystalline Y films. Blaha *et al* do not show energies greater than 6.5 eV above the Fermi level so we cannot determine the origin of peak d^* from their bandstructure. However the calculation of Papaconstantopoulos [25] shows the unoccupied Γ_{4-} point at 6.9 eV and this may well be the origin of this peak. The feature labelled a^* lies in the gap between the Γ_{4-} and Γ_{3+} critical points and thus it is tempting to associate it with a surface state—and it is possible that peak a in the ARUPS spectra [7] is the occupied tail of this state. We were unable to determine whether the intensities of the two features have the same photon energy dependence, as the design of our instrument [18] does not permit us to take measurements in the same photon-energy range as the ARUPS spectra (25–60 eV) [7]. It is also possible that a^* is due to a failure of momentum conservation. Although the density of states along ΓA is calculated [14] to be very low at this point, the total density of states is peaked at the Fermi level, due to the flat bands along the LM and KH directions.

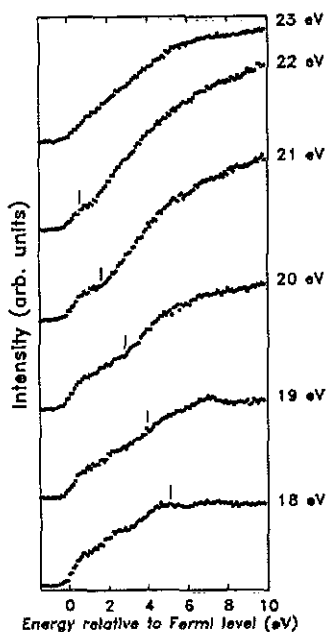


Figure 2. Normal incidence isochromat KRIPES spectra from Y(0001), normalized to the incident charge. The tick marks indicate the onset of fluorescence due to the decay of a 4p core hole.

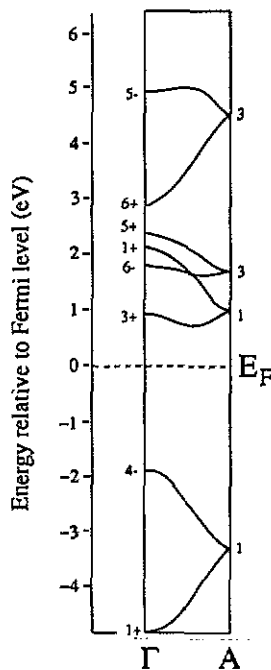


Figure 3. Energy bands of Y along the ΓA direction, as calculated by Blaha *et al.* Adapted from [14].

In conclusion, the features seen in our KRIPES spectra appear to be entirely explicable in terms of one-electron bands, in marked contrast to the ARUPS spectra of Barrett and Jordan [7]. We are unable to identify unambiguously the feature labelled a^* as a surface state, and it is difficult to see how such a weak feature could be responsible for an ARUPS peak as intense as the SODS. The results of Barrett and Jordan [7] have been reproduced [26] using the same crystal as was used in the present work so we believe our results to be characteristic of the same surface. We conclude that many-body effects are considerably less important in KRIPES spectra than in ARUPS spectra of Y, and probably throughout the HCP rare-earth metals in general, and that consequently KRIPES has an important role to play in the study of rare-earth electronic structure.

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