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3d PHOTOEMISSION FROM MIXED VALENT $\text{YbH}_{2.6}$

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Dans certains composés, l'ytterbium possède une configuration intermédiaire entre $4f^{13}$ et $4f^{14}$. Le même phénomène dans le cérium, cette fois pour les configurations $4f^0$ et $4f^1$, a fait l'objet de nombreuses études, en particulier en ce qui concerne les répercussions sur la photoémission des états de coeur 3d, qui est maintenant tout à fait comprise. Nous avons fabriqué une anode de silicium ($\text{SiK}\alpha = 1740$ eV) et présentons des spectres d'états de coeur 3d dans $\text{YbH}_{2.6}$, que nous comparons à des calculs théoriques, et qui démontrent la valence mixte de Yb dans ce composé.

In certain compounds Yb has an unstable $4f^{13}$ - $4f^{14}$ ground state configuration, comparable to the unstable $4f^0$ - $4f^1$ configuration of Ce, for which numerous studies of the 3d core levels converged to a high level of understanding of ground state and final state properties. We have manufactured a Si anode ($\text{SiK}\alpha = 1740$ eV) and present measured and calculated 3d photoelectron spectra of $\text{YbH}_{2.6}$ which clearly demonstrate mixed valent behaviour.

It has been shown experimentally [1] and theoretically [2] that 3d core-level spectra of light rare earth (La,Ce) compounds exhibit satellite features which can be quantitatively related to the 4f occupancy in the ground state. Analogous phenomena are expected [3] for heavy rare earth (Yb,Lu) compounds. Their 3d core-levels are, however, not accessible with standard Al or Mg radiation. We have recently manufactured a Si anode ($\text{SiK}\alpha = 1740$ eV), and measured and calculated the Yb 3d core-level spectra of a series of Yb pnictides [4,5] confirming the above expectations.

With hydrogen at moderate pressure Yb forms a solid solution phase, a nonmetallic nonmagnetic dihydride phase of orthorhombic structure and a metallic magnetic $\text{YbH}_{2.6}$ phase of cubic symmetry [6-9]. Apparently Yb is divalent ($4f^{14}$) in the dihydride and possibly mixed valent in $\text{YbH}_{2.6}$. At pressures in the 10 kbar range, trihydrides $\text{YbH}_{2.96}$ were synthesized [10]. According to magnetic susceptibility data, the trihydrides are trivalent ($4f^{13}$). Very recently the synthesis of cubic $\text{YbH}_{2.74}$ at moderate pressure was reported [11].

In this paper we present measured and calculated 3d photoelectron spectra of $\text{YbH}_{2.6}$. The XPS spectra were taken in a VG Escalab 5 spectrometer at base pressure $1 \cdot 10^{-10}$ mbar. The ordinary Mg/Al twin anode was replaced by a home made Mg/Si anode. The resolution was set to give 1.6 eV ($\text{SiK}\alpha$) FWHM of the Au $4f_{7.2}$ peak at 84.0 eV. Yb (99.9%, Research Chemicals) was cleaned in the preparation chamber by repetitive Ar^+ bombardement, filing and outgassing at 400°C at $p \approx 10^{-9}$ mbar.

Hydrogenation was performed in a specially designed high pressure cell inside the spectrometer at 50 bar hydrogen pressure between 400 and 250°C for several hours.

The hydride samples were of dark grey colour and brittle, but did not des-integrate into powder. To reduce oxygen diffusion to the surface the samples were cooled with liquid N₂ to ≈ 100 K in the analyzing position. They were cleaned with a diamond file in situ immediately before taking the spectra. The contamination as determined from O1s, C1s and Yb 4p peaks measured with MgKα radiation was below 2%. Structure, composition and homogeneity of the samples were checked by X-ray diffraction and volumetric determination of the hydrogen liberated upon dissolution of parts of the samples in dilute acid.

Fig. 1 shows the uncorrected Yb 3d_{5/2} and 3d_{3/2} spectra of YbH_{2.6}. They consist of a rather narrow peak at 1521.7 and 1569.3 eV, respectively and multiplet-split satellites at 7-12 eV higher binding energy. These satellites are completely absent in the spectra of divalent YbH₂. Accordingly the narrower peaks reflect the 4f¹⁴ configuration of the ground state and correspond to the 3d¹⁰ 4f¹⁴ → 3d⁹ 4f¹⁴ ionization process, while the satellites are due to the 4f¹³ ground state contribution and correspond to the 3d¹⁰ 4f¹³ → 3d⁹ 4f¹³ transition. Valence band analysis excludes divalent surface YbH₂.

The cubic crystal structure of YbH_{2.6} points to homogeneous mixed valency, though the compound is nonstoichiometric. This is supported by measurements of the magnetic susceptibility down to 1.7 K, which yield no ordering and a paramagnetic Curie temperature of - 75 K. A structure refinement has been started to clarify remaining doubts.

For comparison with the theoretical predictions (Fig. 2) the measured Yb 3d_{5/2} spectrum was numerically corrected for background and SiKα_{3/4} radiation following a procedure described earlier [4].

Our calculation of the 3d core level spectrum of YbH_{2.6} is based on the Gunnarsson-Schoenhammer (GS) [2] formulation of the degenerate Anderson impurity model. In this approach, the relative weight of the 4f¹³ and 4f¹⁴ configurations of the Yb ion in the ground state of the compound is determined by the energy dependent hybridization function V²(ε) between the localized 4f orbitals and the valence and conduction band Bloch functions. Since ytterbium dihydride is an insulator, with the Yb ion in a pure 4f¹⁴ configuration, we shall assume that all the mixing takes place with a band of conduction states derived from the extra 0.6 hydrogens in the system. We model V²(ε) by a semiellipse of total width 2B = 5 eV, i.e. of the same order of magnitude as that of the band due to the hydrogens at octahedral sites in the trihydrides of the light rare earths [12,13]. The experimental spectrum shows that roughly 0.5 electrons per ytterbium are transferred to that band, which is then slightly more than half filled. In the calculations we take V²(ε) to be symmetric around the Fermi level E_F, and set the parameter Δ ≡ π max V(ε)², which measures the degree of hybridization to 0.1 eV, a typical order of magnitude also found in Ce compounds [2].

While the GS method allows for an accurate determination of the weights of the 4f¹³ and 4f¹⁴ configurations in the ground state from a measurement of the inte-

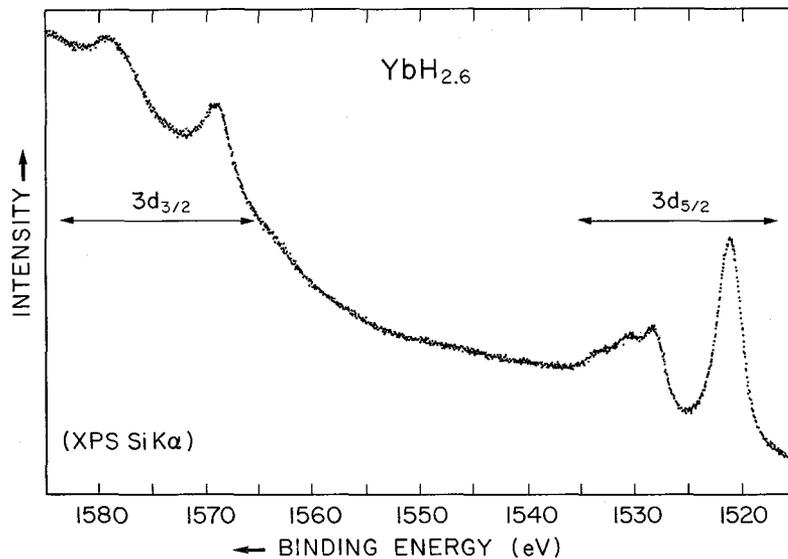
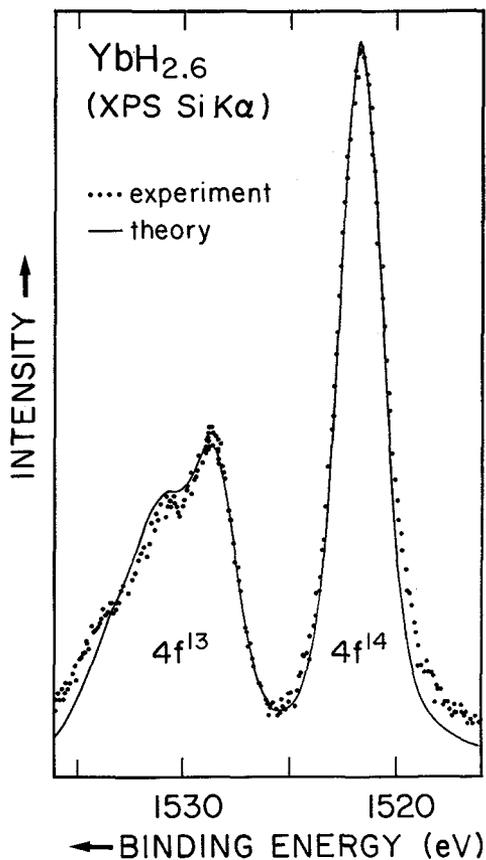


Fig. 1 - Yb 3d_{5/2,3/2} photoelectron spectra of YbH_{2.6} (raw data) each of them showing a narrow 4f¹⁴ peak and a multiplet-split satellite at higher binding energy due to 4f¹³ ground state configuration.

Fig. 2 - Experimental 3d_{5/2} photoelectron spectrum of YbH_{2.6}, corrected for background and SiKα_{3,4} satellite radiation, compared to calculated spectrum.



grated intensities of the corresponding peaks in the 3d photoemission spectra, it is too simple to account for the complex lineshape of the " f^{13} -peak". This is due to the multiplet splittings in the final state, with two open shells, and can be obtained from an atomic calculation. By distributing the total intensity for the $4f^{13}$ configurations among the different multiplets according to the rules given in our recent work on YbP [4] a close agreement with experiment is found in the present case also, confirming our observation that the mixing with the conduction and valence bands does not produce any interference between final state multiplets within a given 4f configuration. The calculations yield a ground state with 0.53 4f-hole per Yb ion, i.e. slightly less than would be expected from the stoichiometry on the basis of a purely anionic model for the hydrogen.

In conclusion, we have shown that the 3d-core level spectra of $\text{YbH}_{2.6}$ can be consistently interpreted in terms of a homogeneously mixed valent ground state for this system.

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