

Valence Transition in Yb Hydrides*

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Yb exhibits an unstable 4f configuration in certain compounds. It has been shown experimentally and theoretically that 3d core-level spectra of some rare earth ions exhibit satellite features which can be quantitatively related to the 4f occupancy in the ground state. We present 3d photoelectron spectra of various Yb-hydrides, measured with Si K α radiation at 1740 eV photon energy. The results indicate divalent Yb in YbH_{1.8} and mixed valency in the trihydrides (YbH_{2.6}).

Introduction

At moderate pressure and temperature Yb forms a solid solution phase with hydrogen, a nonmetallic dihydride phase (YbH_{1.8}) and a metallic trihydride phase (YbH_{2.5}). The dihydride is orthorhombic and nonmagnetic, whereas the trihydride has been reported to be of fcc structure and magnetic [1]. Apparently the amount of hydrogen uptake is related to valence changes, which have not been studied previously.

Photoelectron spectroscopy has been shown to be a powerful tool for studying valence transitions in rare earth materials [2,3,4,5,6,7] including hydrides [8,9,10,11]. Photoemission spectra of valence band and core levels of some rare earth ions (La, Ce, Sm, Yb, Lu) show features which can be understood in a many-electron picture only.

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Model calculations /3,5,6/ based on the degenerate Anderson impurity hamiltonian describe spectroscopic data quite well. These models involve initial and final states of mixed 4f occupancy and as important interaction a hybridisation term between 4f and valence states. In the case of Yb the groundstate $|g\rangle$ is the superposition of two states with 13 and 14 4f electrons, respectively:

$$|g\rangle = \alpha_g |4f^{13}3d^{10}val^3\rangle + \beta_g |4f^{14}3d^{10}val^2\rangle \quad (1)$$

The first term corresponds to trivalent, the second to divalent Yb. Similarly, the final state $|f\rangle$ of the 3d photoemission process is written as :

$$|f\rangle = \alpha_f |4f^{13}3d^9val^3\rangle + \beta_f |4f^{14}3d^9val^2\rangle \quad (2)$$

For the sake of brevity we use the obvious abbreviations $4f^{13}$ and $4f^{14}$, respectively, for the two contributions to the final and the ground state.

A localized 4f electron screens a 3d hole much better than a continuum state. In the photoemission process the outgoing electron is much stronger coupled to a poorly screened ion than to one with a full 4f orbital. Therefore the kinetic energy of the former is lower and in the 3d photoemission experiment the $4f^{13}$ final state appears to be more strongly bound than the $4f^{14}$. In the case of the Yb hydrides the difference in binding energy is almost 10 eV, making it possible to separate the two components of the final state in the spectra. A comparison of experimental intensities of the $4f^{13}$ and $4f^{14}$ final states with model calculations allows the extraction of the parameters of the modified Anderson hamiltonian, in particular the 4f binding energy and the hybridisation strength. With these parameters one can calculate the ground state $|g\rangle$ and thus the 4f occupancy.

The relative intensities of the different $4f^n$ final states contributions in the photoemission spectra are a direct measure of the 4f occupancy in the ground state as Gunnarsson and Schönhammer /3/ have shown in the case of Ce, and Monnier et al. /6/ in the case of Yb /12/. In Yb the missing of a final state contribution implies the missing of the corresponding ground state. Therefore 3d photoemission is a strong tool for determining the Yb valency.

Experimental

The XPS spectra were taken in a VG Escalab 5 spectrometer at a base pressure $1 \cdot 10^{-10}$ mbar. Si K α radiation was used and the overall resolution was 1.6 eV FWHM

of the Au $4f_{7/2}$ peak at 84.0 eV. $K\alpha_{3,4}$ satellites were numerically corrected in the spectra. The nonmetallic $\text{YbH}_{2.0}$ showed a shift in binding energy due to charging effects. The energies were calibrated with a gold wire on the surface of the hydride.

Yb metal (99.9%, Research Chemicals) was cleaned in the preparation chamber of the spectrometer 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. The hydriding conditions are summarized in Table 1. Hydrogen was first cleaned by a LN_2 cooled trap and a getter station down to about 1ppm contamination level.

Table 1:

Hydride	pressure (bar)	temperature ($^\circ\text{C}$)	exposure time (hours)
$\text{YbH}_{1.8}$	50 \rightarrow 1	400	6
$\text{YbH}_{2.0}$	50	$400 \xrightarrow{10^\circ\text{C/h}} 375$	6
$\text{YbH}_{2.2}$	50	$400 \xrightarrow{10^\circ\text{C/h}} 350$	8
$\text{YbH}_{2.6}$	50	$400 \xrightarrow{25^\circ\text{C/h}} 250$	10
$\text{YbD}_{2.6}$	50	$400 \xrightarrow{25^\circ\text{C/h}} 250$	24 + 4

Hydriding conditions of several hydrides. In $\text{YbH}_{1.8}$ the pressure was 50 bars during 30 minutes. The hydrides were prepared in a high pressure cell inside the spectrometer, the deuteride in a separate reaction cell.

The samples were of cylindrical shape with about 1 cm of diameter. The hydride samples were of dark grey colour and brittle, but did not disintegrate into powder. To reduce oxygen diffusion to the surface the samples were cooled with liquid nitrogen to ≈ 100 K in the analyzing position. The hydrides were cleaned with a diamond file in situ immediately before taking the spectra. The contamination as determined from O1s, C1s, and Yb4p peaks measured with $\text{MgK}\alpha$ radiation was below 2%. Structure, composition and homogeneity of the samples were checked after photoemission measurements by X-ray diffraction and volumetric determination of the hydrogen liberated upon dissolution of parts of the samples in dilute acid.

The deuteride was prepared in two steps. After a first deuteration of the Yb metal, it was pulverized in an argon atmosphere and deuterated again. The powder was then filled in a copper coated vanadium vessel. Neutron measurements were performed at the multidetector powder diffractometer DMC at SAPHIR. The wavelength was 1.708 Å.

Results

Fig. 1 shows the Yb 3d_{5/2} XPS spectra of Yb metal, several Yb hydrides and Yb + 100L O₂ (1 L = 1 s at 10⁻⁶ Torr). The hydride spectra are characterized by two main features. The first is at about 1522 eV binding energy and corresponds to a $|4f^{14}3d^9val^2\rangle$ final state (4f¹⁴). It is a single line and is broadened only by lifetime and instrumental effects. The second is centered around 1530 eV and corresponds mainly to a $|4f^{13}3d^9val^3\rangle$ final state (4f¹³). The 3d and 4f holes produce a multiplet structure, which significantly broadens this contribution. This multiplet is most clearly seen as the strong peak in the Yb + 100 L O₂ spectrum, which is included in the figure as a reference. Yb₂O₃ is known to be trivalent having 4f¹³ configuration. The small 4f¹⁴ final state signal is due to remaining divalent Yb, resulting from poor oxidation kinetics at room temperatures.

The most interesting and clearest result is the increase of the weight of the 4f¹³ peak from about zero in the dihydrides to about 50 % in YbH_{2.6}. The intermediate compound YbH_{2.2}, which is a two phase mixture of YbH₂ and YbH_{2.5}, shows some scatter of the 4f¹³ final state relative intensity around a mean value of 30%.

The spectra of the two dihydrides, YbH_{1.8} and YbH_{2.0}, are dominated by the 4f¹⁴ final state. In the region of the 4f¹³ final state there is a very broad peak of low intensity. The center of this feature is at significantly higher binding energy than that of the 4f¹³ final state, suggesting a very low 4f¹³ final state intensity. This broad peak may be caused by band transition losses of the 4f¹⁴ final state. The backscattering electron energy loss spectra (EELS) of the dihydrides show broad losses starting 4.5 eV below the elastic line, with a maximum at 14 eV.

The divalent Yb metal exhibits a pronounced 4f¹⁴ final state peak. Between 1525 and 1535 eV electron losses from the 4f¹⁴ final state dominate the spectrum. A bulk and a surface plasmon 5.4 eV and 9.4 eV, respectively, below the 4f¹⁴ line, overlap with a broad peak caused by band transition losses. Again these losses have been seen in recent EELS experiments [13].

The experimental results clearly show a valence transition from divalent YbH₂ with 4f¹⁴ configuration to mixed valent YbH_{2.6} with 4f¹³/4f¹⁴ configuration. Our calculations of the 3d core level spectrum of YbH_{2.6} based on the Gunnarsson-Schönhammer formulation of the degenerate Anderson impurity model agrees qualitatively and quantitatively very well with a 50 % 4f¹³ / 4f¹⁴ mixed valent configuration [11].

Magnetic properties, specially the absence of magnetic ordering at low temperature and the reported cubic symmetry of YbH_{2.6} indicate homogeneous mixed valence.

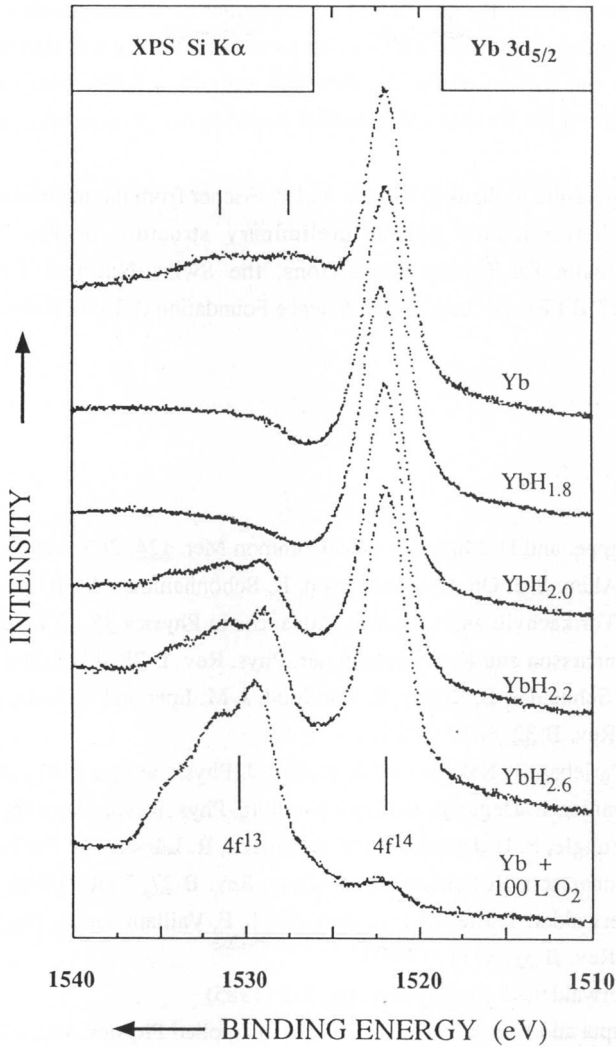


fig. 1: Yb 3d_{5/2} core level spectra of Yb metal, Yb hydrides and Yb+100 L O₂. A clear transition from divalent YbH₂ (4f¹⁴) to mixed valent YbH_{2.6} (4f¹³4f¹⁴) occurs. Si Kα_{3,4} satellite structures have been numerically subtracted. 4fⁿ indicates a 4fⁿ3d⁹val³ final state configuration. In the Yb spectrum a bulk and a surface plasmon are indicated.

In order to clarify the question of homogeneous or inhomogeneous mixed valence a structure refinement of neutron diffraction patterns of YbD_{2.6} was started. Some peaks in addition to the pattern of the fcc structure suggest a larger unit cell due to small displacements of the Yb ions and a possible smearing out of some octahedral D sites /14/.

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