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LETTER TO THE EDITOR

Probing the local electronic structure in the H induced metal–insulator transition of Y

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Abstract.   The occupied and unoccupied valence band states of yttrium (Y) metal, Y dihydride and Y trihydride were measured by soft x-ray emission and absorption spectroscopy. The experiments were complemented by first principles calculations. Both experiments and theory reveal the metallic character of Y and YH_2 whereas $YH_{3-\delta}$ exhibits a band gap, which was experimentally determined to be 2.5 eV. The results reveal strong hybridization between H and Y states, causing a breakdown of the rigid band model description.

The interest in the optical properties of Y and the lanthanide hydrides increased significantly with the discovery of hydrogen induced optical switching, causing metallic Y films to become transparent upon H loading [1]. Although this metal–insulator (M–I) transition is conceptually simple, the details of the changes in the electronic structure are not fully understood. The previous understanding of the transition was based on band structure calculations [2], where a band gap of ~ 1.5 eV was obtained. More recent band structure calculations failed, however, to reproduce these results [3, 4]. Furthermore, theoretical calculations focusing on the relation between the crystallographic and the electronic structure [5] are found to be inconsistent with the interpretation of recent experimental results [6, 7].

Recent transport measurements [8] provide the strongest evidence for the nature of the M–I transition. The electrical conductivity of the $YH_{3-\delta}$ films obeyed logarithmic temperature dependence, which was shown to be closely linked to the vacancy concentration in the trihydride phase. Concentrations between $YH_{2.85}$ and $YH_{2.99}$ were investigated and, hence, a substantial range in the vacancy density was addressed. The logarithmic temperature dependence may be linked to both Kondo scattering and weak 2D localization [8]. Both these mechanisms require the existence of metallic states, albeit with different dimensionality of the localization. The magneto-resistance results revealed three regions, which showed distinctly different behaviour. Magneto-resistance is negligible above 100 K whereas, below 100 K, $YH_{2.99}$ yielded strong negative magneto-resistance and finally, below 20 K, the magneto-resistance was positive. Thus additional support for localization was obtained. Consequently the optical transition could be based on localized s-electron states [9] and the electric conduction on hopping.

Here we will explore the density of states close to the Fermi level by soft x-ray emission and absorption spectroscopy, as well as by first principles calculations. The existence of a direct band gap for the trihydride state will be demonstrated, as well as the formation of a

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hydrogen induced sub-band below the Fermi level. All the experiments were performed on well characterized single crystal films.

The samples were grown using MBE techniques developed for single-crystal rare earth superlattices on sapphire substrates, described in detail elsewhere [10]. Niobium is used as a buffer to prevent reaction between the yttrium and the oxide substrate. The epitaxial relationships at the sapphire/niobium interface are (1120)S‖(110)Nb, [0001]S‖[111]Nb and at the niobium/yttrium interface (110)Nb‖(0001)Y, [001]Nb‖[1120]Y. Typical thicknesses of the Nb and Y layers were 5 and 200 nm respectively.

Ex situ x-ray diffraction analysis confirmed a good crystallinity of the Y layers. The out-of-plane lattice parameter, $c = 0.5739$ nm, was determined from this analysis. This value, when compared with the bulk value of 0.5732 nm, indicates that the Y layer has not relaxed completely and some of the epitaxial compressive strain is still present.

The hydrogen loading can introduce local strain fields which, in turn, can degrade the crystalline quality of the films. Recently, it was demonstrated that single crystalline Y films could be repeatedly loaded with hydrogen without significant loss of structural coherency, even at room temperature [11]. Here, the samples were heated to 330 °C in a UHV based H-reactor during the hydrogen loading. Thereafter the samples were slowly cooled to room temperature, to further reduce the strain induced defect formation. The samples were analysed by x-ray diffraction ($\theta - 2\theta$). A single Bragg peak corresponding to YH_2 was observed in the dihydride sample, with a measured atomic plane distance of 0.301 nm (cf bulk, 0.301 nm [12]). The trihydride sample exhibits a dominating $YH_{3-\delta}$ Bragg peak (hcp, $c = 0.663$ nm, cf bulk $c = 0.6659$ nm [12]) and an extremely weak YH_2 peak, observed in the low resolution mode. The ratio of the dihydride and the trihydride phases was estimated to be below 1/300. The trihydride sample appears green in transmission. The vacancy concentration (δ) is estimated to be below 0.05 in the trihydride phase from *in situ* conductivity measurements during loading.

Soft x-ray emission spectroscopy (SXES) allows direct probing of local partial density of occupied states distributions. Similarly, soft x-ray absorption spectroscopy (SXAS) probes the unoccupied part of the valence band. Combining these two techniques allows one to study the electronic structure near the Fermi level and to detect the appearance of a band gap in a metal–insulator transition. We have chosen to study the $M_{4,5}$ emission and absorption, since the 5p partial DOS of the valence band is known to be sensitive to H hybridization for transition elements (note that free yttrium atoms do not have 5p character; it appears as a result of the interaction with neighbouring atoms). The derived metal-p-spectral weight is usually well described within one-electron formalism, even in highly correlated electron systems. Furthermore, in the transitions from the valence d shell to a core p level, localization of d electrons may lead to excitonic effects. Thus, substantial change of the recombination probability [13] is expected, which complicates the DOS mapping near the Fermi level.

The soft x-ray emission and absorption experiments were performed at the 7.0 undulator beamline at the Advanced Light Source (ALS) in Berkeley [14]. In the present work, the Y $M_{4,5}$ soft x-ray emission was recorded by a grazing incidence spherical grating spectrometer, set at a resolution of 0.35 eV [15]. The monochromatized synchrotron radiation beam impinged at 60° from the sample surface normal, and the emission was recorded at a right angle with respect to the incoming beam, parallel to the polarization of the beam. The excitation energy bandpass was < 0.1 eV and the x-ray emission energy scale was calibrated and related to the excitation energy scale using the elastic (recombination) peaks. The emission spectra presented below are not corrected for self-absorption in the sample.

The theoretical work was done using a full potential linear muffin-tin orbital method [16]. The calculations were done without any geometrical restrictions on the electron density and effective potential, resulting in accurate energy bands. Convergence was investigated with

$4p \rightarrow 3d$
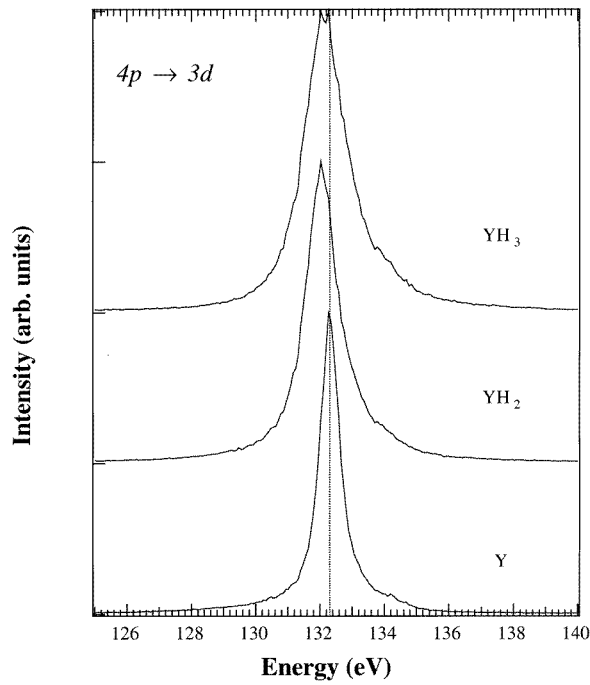
(a)
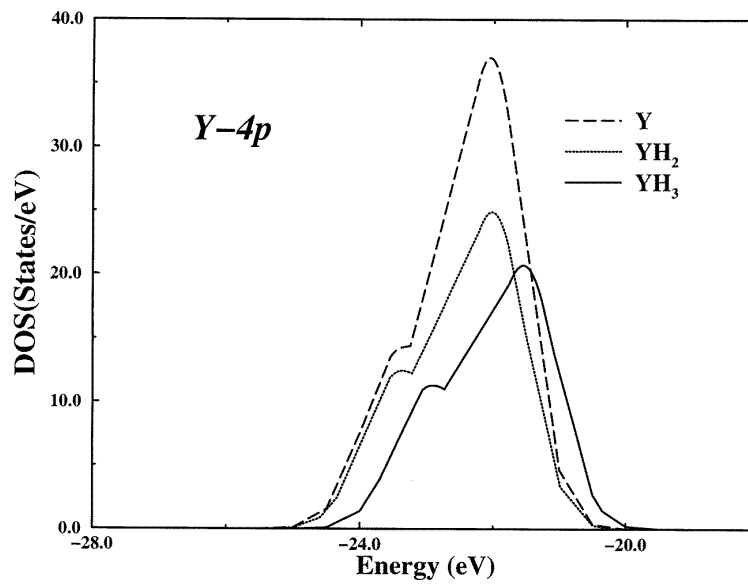
(b)

Figure 1. (a) Inner transitions (Y $3d_{5/2}$–$4p_{3/2}$) of the yttrium metal, yttrium dihydride and yttrium trihydride, respectively. (b) Theoretical results of 4p-DOS of Y, YH$_2$ and YH$_3$.
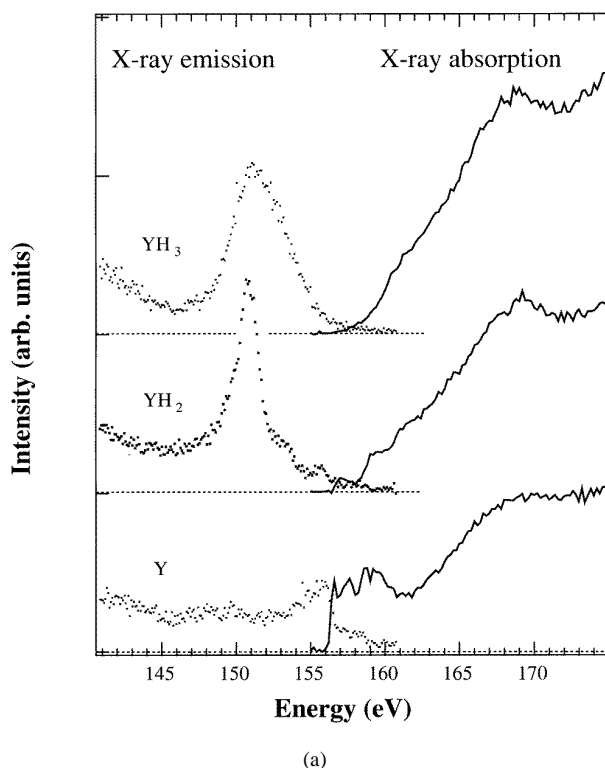
Figure 2. (a) Emission and absorption spectra which map occupied and unoccupied states close to the Fermi level, respectively. (b) Theoretical results of the 5-p DOS. For details, see text.

respect to k-point sampling, basis set truncation, and in the expansion of the density and potential.

Figure 1(a) depicts the Y $3d_{5/2}$–$4p_{3/2}$ emission spectra of the yttrium metal, yttrium dihydride and yttrium trihydride, respectively. The widths of the transitions are broader in the hydrides than in Y metal and shifted towards lower photon energies. The x-ray emission shift reflects a decreased energy separation between the involved levels. This can come about in two ways. Either the 4p level experiences a *larger* shift to *higher* binding than the 3d level or, alternatively, the 3d level is shifted to *lower* binding energy to a *larger* extent than the 4p level. In a simple one-electron picture the shift of a more localized electron orbital (the 3d orbital in this case) due to a screening charge is expected to be larger than that of a more delocalized orbital (the 4p orbital). Based on this argument†, the observations suggest that electron charge increases at the Y site, as a result of the hydride formation.

The first principles calculations of the electronic structure [18] reveal a somewhat more involved picture, in the sense that electron charge transfer is not prominent. Instead a strong hybridization between the H 1s states and the Y states is found, which causes shifts in the electron states similar to what one would expect from a charge transfer model. The calculated 4p DOS is displayed in figure 1(b) and, as seen in the figure, the binding energy of the 4p level is decreased in the hydride state, in agreement with experiment.

The current interpretation of the x-ray emission data is inconsistent with the previous

† Based on Coulomb interaction in the one-electron picture. See, for example, [17] p 9.
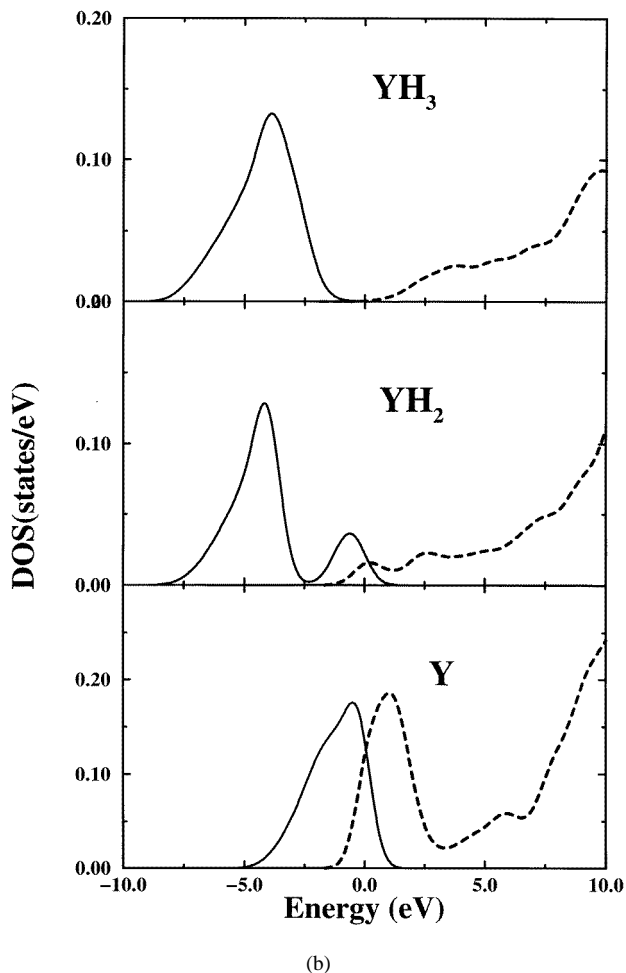
Figure 2. (Continued).

x-ray photoemission results [19]. The XPS measurements, made on dihydride and trihydride samples, revealed increased binding energy of the 3d and 3p levels. XPS is extremely surface sensitive, thus the discrepancy could be related to the different regions probed by these techniques.

Figure 2(a) shows the valence-core SXES spectra of the three samples along with the corresponding soft x-ray absorption spectra (SXAS) recorded in fluorescence yield mode. The emission spectra were all normalized with respect to the integrated intensity of the $3d_{5/2}$–$4p_{3/2}$ transitions (figure 1(a)). The $M_{4,5}$ emission reflects the p character partial DOS, as the core state is of d symmetry. Since yttrium metal should have weak 5p character, the intensity is expected to be low, which is consistent with the current observations. A sharp edge is observed at the top of the valence band in Y, a feature that is identified as the Fermi level (at 156 eV). The SXAS shows an onset at this energy, which implies an overlap between the top of the valence band and the bottom of the conduction band. Thus, the combined absorption-emission spectrum shows the unbroken density of states across the Fermi level, reflecting the metallic character of Y.

A substantial change is observed in the x-ray emission with increasing hydrogen content, as seen in figure 2(a). The total intensity (normalized to the 3d–4p inner-core transition) increases considerably and a strong feature appears at around 5 eV below the Fermi level, i.e. at 151 eV in figure 2(a). This observation is in agreement with a general behaviour of transition metal hydrides, in which the hydrogen and the host lattice form sub-bands below the Fermi level [20]. The trihydride spectrum displays a clear reduction of the DOS in the region corresponding to the Fermi level of the metal, resulting in a band gap with the estimated width of 2.5 eV.

The results of LDA calculations of the valence band are in overall agreement with the experimental results, as seen in figure 2(b). DOS theory predicts the Y and the YH_2 to be metallic and YH_3 to be insulating. The formation of a sub-band below the Fermi level is also reproduced, which originates from the Y_p-H_s hybridization. The unoccupied part of the 5p DOS is rather featureless in YH_2 and YH_3 whereas for Y, a peak at 2.0 eV and a dip at 4–6 eV are obtained. This is consistent with the XAS spectra (figure 2(a)). We point out here that one should not compare the relative intensities of the calculated 5p DOS, since the intensity depends to some extent on the choice of base geometry in the calculations (i.e. extension of the muffin-tin radius). However, the total DOS is insensitive to this choice.

Symmetry and anisotropy induced intensity enhancement is expected to cancel by the normalization to the 3d–4p transition. Thus, the $M_{4,5}$ x-ray emission results support the view of hydrogen as an electron donor, which is in line with the interpretation of the core-to-core spectra discussed above. These findings are in agreement with studies of the electronic structure of Y hydrides by positron annihilation [21, 22], which is also a bulk sensitive technique. However, a reversed charge transfer is inferred [23] in recent macroscopic transport measurements. This apparent contradiction could originate in an electronic structure, which is more complex than described by the donor-acceptor picture.

In summary, the results show a hydrogen induced band-gap in the trihydride phase of Y. The inferred DOS is in qualitative and semiquantitative agreement with calculations of the transition probabilities. A formation of a sub-band around 5 eV below the Fermi level is observed and, within the one-electron picture, the results strongly support the protonic-like type of bonding of H. However, the donor-acceptor description can be questioned, due to the strong hybridization of the constituents.

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