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Yttrium and lanthanum hydride films with switchable optical properties

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Abstract

We discovered that yttrium-, lanthanum- and rare earth-hydride films exhibit remarkable optical properties near their metal–insulator transition: the dihydrides are metallic and shiny while the trihydrides are semiconducting and transparent. The transition between the shiny and transparent state is reversible and can simply be induced by changing the H_2 gas pressure or the voltage in an electrolytic cell. No deterioration of the films is detected if they are protected by a thin palladium caplayer. The optical switching is also observed in hydrides of alloys of Y and La. Several theoretical models leading to an insulating and transparent trihydride state are discussed.

Keywords: Switchable metal-hydride mirrors; Rare-earth trihydride films; Optical properties; Electric properties

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1. Introduction

During our quest for dirty atomic metallic hydrogen [1] we discovered that upon hydrogen uptake in a high pressure diamond anvil cell around 200 K, a 500 nm yttrium film changed from a shiny metallic mirror into a transparent yellowish sample. Although metal–insulator transitions had already been described in earlier work on rare-earth hydrides [2], no report whatsoever was made about such drastic changes in optical properties. Very much intrigued by the observed results we tried to induce the same transition at room temperature and low hydrogen gas pressure (typically 1 bar). It worked admirably well, provided the yttrium film was protected by a thin layer (5–20 nm) of palladium [3]. With this protective layer, which consists of typically 10 nm wide Pd islands, we could take the film, which was evaporated under ultra-high vacuum conditions, to air, without danger of oxidation of the otherwise highly reactive yttrium and carry out a whole series of experiments (temperature dependence of the resistivity, magnetoresistance, Hall effect, photoconductivity, pressure dependence of the semiconducting gap, optical transmission, etc. [1,3]). In the meantime, it was found by Ouwerkerk et al [4] that not only yttrium and lanthanum hydride films but also the hydrides of rare earth films exhibited a metal–insulator transition accompanied by drastic changes in their optical properties. These films are unique in the sense that they can continuously, reversibly and rapidly be switched between a low resistivity metallic state and a large gap semiconducting state.

The purpose of this article is to report on new measurements of the electric and optical properties of YH_x, LaH_x and $Y_{0.5}La_{0.5}H_x$ and to compare these properties to those of hydrogen intercalated blue bronzes [5].

2. Experimental details

Yttrium, lanthanum and yttrium–lanthanum films are evaporated under UHV conditions on various substrates (Al_2O_3, diamond, glass, etc.) by means of electron guns and Knudsen cells. The purity of the base materials is typically 99.9%. The film thicknesses are between 200 and 500 nm. For ex situ measurements a thin Pd caplayer is used for (i) its catalytic effect on H_2 dissociation, (ii) its increase of the hydrogen sticking coefficient and (iii) its protection of the yttrium film against oxidation, which would make hydrogenation totally impossible [6]. Details about the preparation of the films are given elsewhere [7].

For ex situ experiments the Pd covered Y films are removed from the UHV deposition chamber and transferred to the desired experimental setup in the ambient atmosphere. In this way it is possible to carry out a whole series of experiments [1]. It is remarkable that in all these experiments the films proved to be very robust and did not exhibit noticeable structural deterioration even under repeated hydrogen ab- and desorption cycles. The absorption kinetics can be remarkably fast and optical switching times as short as 100 ms have been observed. Although in most of the experiments carried out so far the films were loaded

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with hydrogen from the gas phase, Notten et al. [8] demonstrated that optical switching of YH_x can also be easily induced by electrolytic charging of a palladium protected yttrium film in a concentrated alkaline solution of 6 M KOH. The stability of the YH_x electrodes is found to be good as long as they are not exposed to light with photon energies higher than the semiconducting gap of $YH_{3-\delta}$ (i.e., $\hbar\omega$ not larger than approximately 2.3 eV).

3. Experimental results

3.1. Pressure-composition isotherm at room temperature

Until now the pressure-composition isotherms of YH_x have only been determined on bulk samples at relatively high temperatures. At low concentrations in the α-YH_x phase the enthalpy of solution is $\Delta H_\infty = -79$ kJ/mole H [9]. The enthalphy of formation of the dihydride phase is $\Delta H_{\alpha\to\beta} = -114$ kJ/mole H [10] and of the trihydride phase $\Delta H_{\beta\to\gamma} = -41.8$ kJ/mole H or -44.9 kJ/mole H determined by Flotow et al. [11] and Yannopoulos et al. [12], respectively. For our films we used an electrolytic method to determine the plateau pressure for the α→β coexisting phases [8] and a quartz-microbalance technique [1,7] for the isotherms at higher concentrations. The results obtained by means of these two methods are shown in Fig. 1. For a comparison with the values given above we estimate the enthalpies of formation from the isotherm in Fig. 1 by means of the relation [13]

$$\Delta H = \frac{RT}{2}\left[\ln P_{H_2} - \frac{S^0_{H_2}}{R}\right] \qquad (1)$$

where $S^0_{H_2} = 130.8$ J/kmole H_2 is the standard molar entropy of the hydrogen gas, R the gas constant and the hydrogen gas pressure p_{H2} is expressed in units of 10^5 Pa. For the α → β transformation we find from $p_{H2} \approx 10^{-28}$ Pa that $\Delta H_{\alpha\to\beta} = -114$ kJ/mole H which is in good agreement with the values mentioned above. For the β → γ transformation, with $p_{H2} = 9.2$ Pa in the plateau region we obtain $\Delta H_{\beta\to\gamma} = -31$ kJ/mole H, which is less negative than the bulk values obtained by Flotow et al. [11] and Yannopoulos et al. [12]. The difference is only partially due to the fact that Eq. (1) overestimates ΔH. For example, from the plateau pressure at 524 K in Fig. 1 one derives that $\Delta H_{\beta\to\gamma} = -36.6$ kJ/mole H instead of -44.9 kJ/mole H. Another reason for the less negative value $\Delta H_{\beta\to\gamma} = -31$ kJ/mole H is probably due to the clamping of the yttrium film by the substrate. It is interesting in this context to mention that both from ^{15}N-depth profiling measurements [1] and atomic-force-microscopy we concluded that the thickness of the sample increased by 11% during absorption from $YH_{\sim 2}$ to $YH_{2.86}$. This is remarkably close to the 10.4% increase calculated from X-ray data obtained on bulk (powdered) samples when x is increased from essentially 2 to 3 [14]. This implies that (i) most of the volume expansion takes place perpendicularly to the substrate and, consequently, that (ii) the c-axis of the hexagonal structure of YH_3 will be predominantly oriented perpendicular to the surface since the relative increase along the c-axis ($\Delta c/c = 14.6\%$) is much larger than in the basal plane ($\Delta a/a = 0.8\%$) during hydrogen absorption from Y to YH_3.

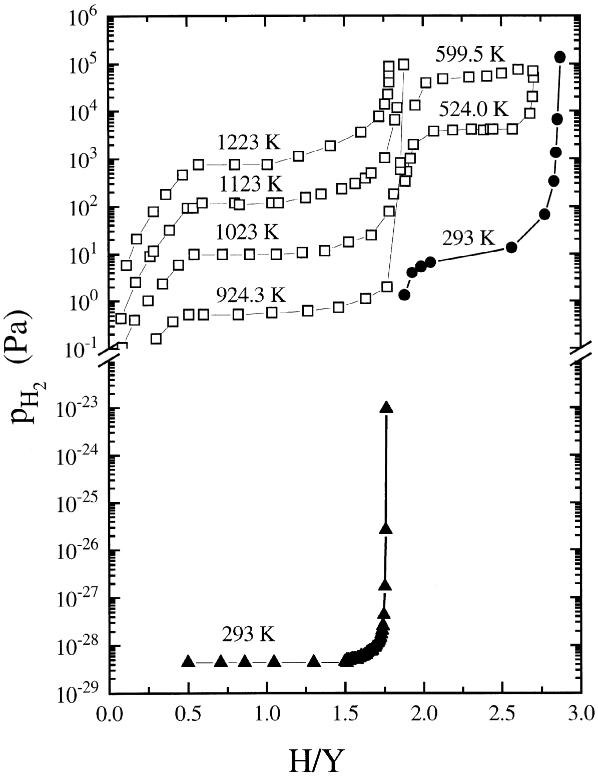

Fig. 1. Pressure composition isotherms of YH_x: (a) (———) for a 500 nm thick yttrium film protected by a 10 nm palladium caplayer determined from a combination of potentiostatic electrolytic (▲) and quartz microbalance (●) measurements. The highest concentration at $p_{H2} = 10^5$ Pa was confirmed by means of a ^{15}N nuclear method [1,7]. The plateau pressure for $2 < x < 3$ depends slightly on the deposition conditions of the film. (b) (☐) for bulk yttrium [12].

3.2. Optical switching and metal–insulator transition

Recently Huiberts et al. [3] reported on the remarkable changes in the optical transmission through a 500 nm yttrium film protected by a 20 nm Pd caplayer during hydrogen absorption at room temperature from gaseous H_2 at 10^5 Pa. As shown in Fig. 2 the electrical resistivity first increases as a result of electron scattering at the randomly distributed hydrogen in the yttrium metal lattice. As soon as the α-β mixed phase region is reached, ρ decreases since substoichiometric dihydride $YH_{2-\delta}$ has a much lower resistivity than pure Y [2]. On further hydrogen uptake the resistivity increases by several orders of magnitude and reaches values typically of the order of 10–50

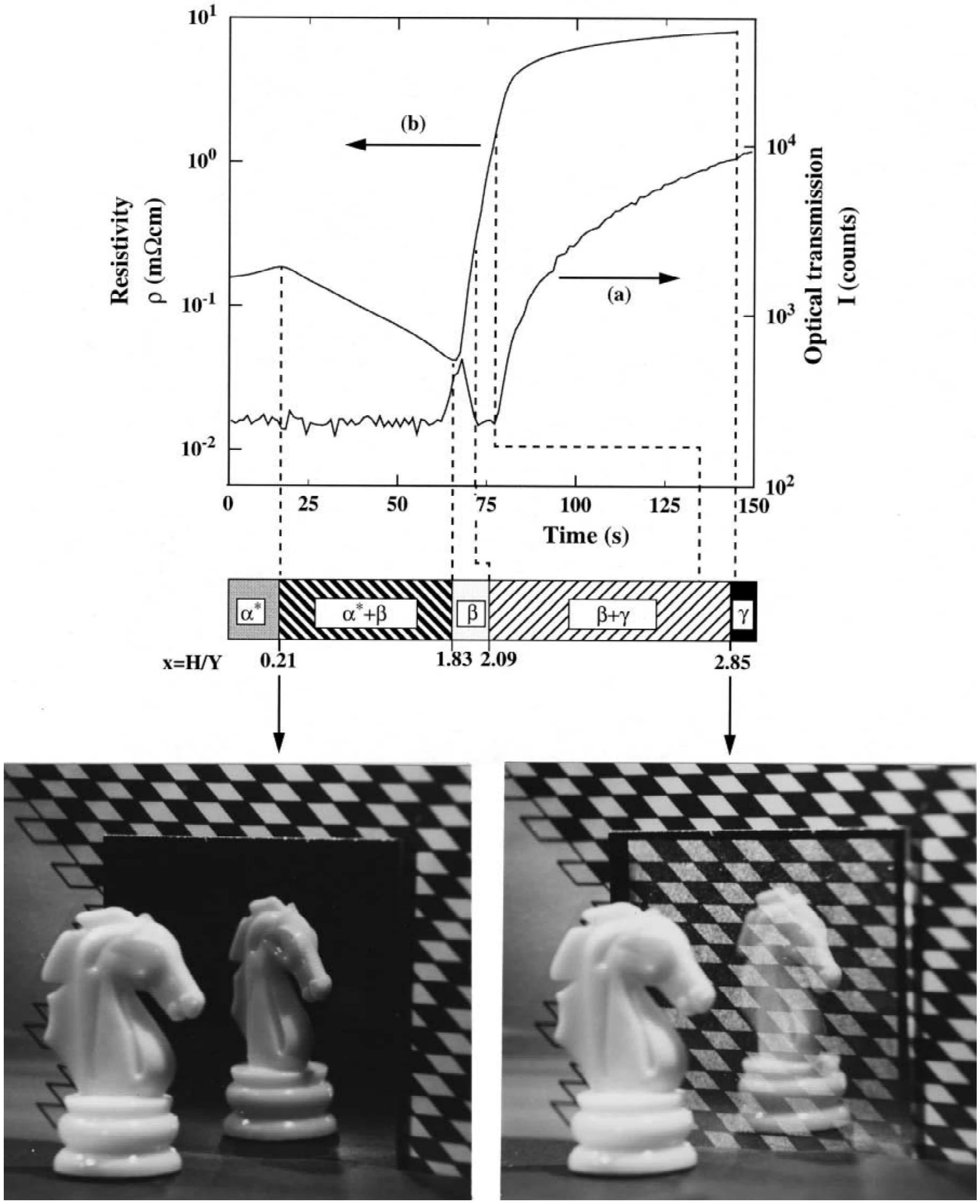

Fig. 2. Variation of the electrical resistivity and the optical transmission for photons with $\hbar\omega \approx 1.8$ eV (both on logarithmic scales) of a 500 nm $YH_x/20$ nm Pd heterostructure during hydrogen absorption at room temperature. At $t=0$ the hydrogen gas pressure is increased from 0 to 10^5 Pa and the film starts to absorb hydrogen. Near the β-dihydride phase the resistivity reaches a minimum while the optical transmission exhibits a transparency window near $t=67$ s. The dashed lines correlate characteristic features of the experimental curves with phase boundaries of the thermodynamic phase diagram. The α- and γ-phases are hexagonal while the β-phase is cubic. As an illustration of the drastic optical changes which take place during hydrogen loading, two photographs of the film are shown at the bottom of the figure. The appearance of the film in the visible part of the spectrum remains essentially unchanged as long as $x<2$. The knight which is placed in front of the film is perfectly reflected and the film is opaque for the light of a lamp placed behind the film and the transparent chess board pattern. However, as soon as the γ-trihydride phase is formed, the transparency of the film increases within a few seconds and the chess board pattern becomes visible throughout the photograph. At the same time the mirror picture of the knight is much weaker. The residual reflection originates mainly from the protective Pd caplayer. Note that the illumination is the same for both pictures (from [3]).

mΩcm near YH_3. Concomitant to these changes in electrical properties, one finds also a dramatic increase in the optical transmission. Up to $x\sim1.8$ the transmission of red light ($\hbar\omega = 1.8$ eV, $\lambda = 689$ nm) remains essentially zero. Near the dihydride phase there is a small transparency window followed by a minimum in transmission. Around x~2.7 the metal–insulator transition sets in and the transmission increases to reach ~20% after correction for the Pd-layer. (Note that for a 200 nm $YH_{3-\delta}$ film loaded under 10^5 Pa H_2 gas the transmission is as high as 52%).

The transition is fast and reversible and does not lead to a deterioration of the film.

The optical switching takes place not only at the particular photon energy of $\hbar\omega = 1.8$ eV chosen for the measurements in Fig. 2. This is clearly shown in Fig. 3 which is a three-dimensional representation of the photon energy and hydrogen concentration dependence of the optical transmission through a 500 nm Y film. This plot is generated from a large number of transmission spectra (for $1 \leq \hbar\omega \leq 2$ eV) measured as a function of hydrogen concentration. The full curve for $\hbar\omega = 1.8$ eV corresponds to the transmission curve in Fig. 2. From this representation it is evident that the transparency window near the dihydride β-YH_2 phase does not extend below $\hbar\omega = 1.5$ eV. This transmission window is responsible for the dark red appearance of YH_2 in transmission and the blue lustre of dihydrides. As mentioned below, the transparency window can be suppressed by alloying.

3.3. Switchable mirrors made of hydrides of alloys

As reported earlier [3] not only YH_x, but LaH_x and all trihydride forming rare earths [4] exhibit similar optical switching properties. It is, therefore, to be expected that alloys based on rare-earths will also be switchable mirrors. As an example we compare in Fig. 4 the optical transmission spectra of YH_x, LaH_x and $Y_{0.5}La_{0.5}H_x$ obtained after loading Y, La and the alloy $Y_{0.5}La_{0.5}$ films (500 nm thick and covered with 10 nm of Pd) under a pressure of 10^5 Pa at room temperature. In all three cases we expect $x \approx 2.9$ although the hydrogen concentration has not been determined explicitly. The transmittance edge of the alloy is found to be intermediate between that of $YH_{2.9}$ and $LaH_{2.9}$. Very interesting is the fact that no transparency window could be detected in $Y_{0.5}La_{0.5}H_x$ around $x=2$. This implies that a larger optical contrast can in principle be reached in alloys than in the hydrides of the constituents. More details on the optical and electric properties of alloy trihydrides will be published elsewhere [15].

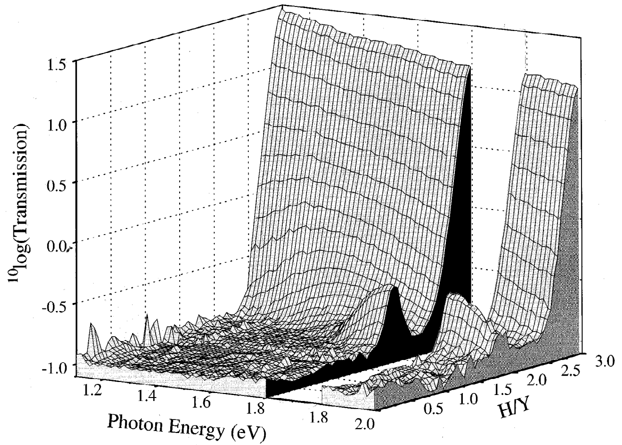

Fig. 3. Optical transmission spectra corrected for the Pd caplayer, for photon energies $1 \leq \hbar\omega \leq 2$ eV recorded during continuous electrolytic loading of a 500 nm Y/5 nm Pd film at room temperature. The concentration is determined from an integration of the constant loading current. The section at $\hbar\omega \approx 1.8$ eV is similar to curve (b) in Fig. 2 and shows that the transparency window is best developed for $\hbar\omega \approx 1.8$ eV.

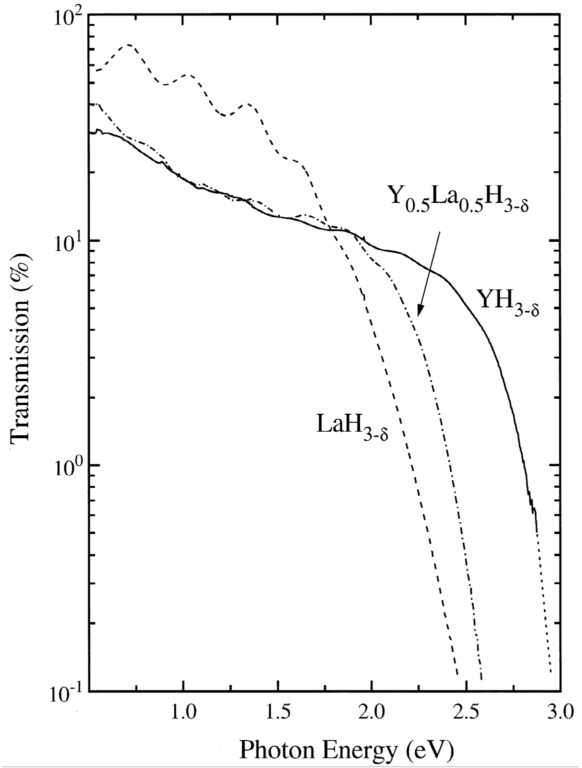

Fig. 4. Optical transmission spectra of YH_x, LaH_x and $Y_{0.5}La_{0.5}H_x$ films (with $x \approx 2.9$) 500 nm thickness protected by a 10 nm Pd caplayer, loaded at room temperature with hydrogen at 10^5 Pa pressure. The absorption edge of the alloy is intermediate between that of the constituting trihydrides. The oscillations in the transmittance for photon energies below 2 eV are due to interferences in the film.

4. Discussion

4.1. Origin of the metal–insulator transition

Although the occurrence of a metal–insulator transition could be expected on the basis of (i) the pioneering work of Libowitz and coworkers [16,17], (ii) the extensive work of Vajda and coworkers [2] and Shinar et al. [18,19] and (iii) the early band structure calculations of Switendick on Y, YH, YH_2 and YH_3 [20], the transparency of $YH_{3-\delta}$ discovered in our laboratory came as a great surprise, since recently Wang and Chou [21,22] and Dekker et al. [23] concluded from self-consistent band structure calculations, that YH_3 was a semi-metal. By minimizing the total energy, these authors found that the HoD_3-type structure was energetically more favourable than the cubic BiF_3-type structure originally assumed by Switendick [20]. By allowing for wavelike displacements of the hydrogen near the metal planes, they found that the total energy could be further lowered by an extra ~30 meV per YH_3. Finally, including rotational displacements of the tetrahedral hydrogen they obtained an electronic band structure with only two bands (an electron band and a hole band) crossing the Fermi energy E_F near the centre of the Brillouin zone (see Fig. 5). The total density of states at E_F is small and the hole and electron densities are approximately 5×10^{26} m^{-3}. This value is much larger than the value $<10^{24}$ m^{-3} expected for stoichiometric YH_3 on the basis of an extrapolation of our Hall effect measurements for $YH_{2.88}$ – $YH_{2.91}$ [1]. The predicted semi-metallic character is also not consistent with the existence of an optical gap of 2.3 eV (see Fig. 4).

It is presently not clear what is responsible for the insulating character of YH_3 observed in our experiments. As far as we know three possibilities have been considered: (i) Wang and Chou [21,22] proposed an excitonic insulating state resulting from the overlapping of the very similar electron and hole bands at the centre of the Brillouin zone. The estimated gap, 0.3 and 0.46 eV depending on the value assumed for the dielectric constant, is, however, far too small; (ii) Recent neutron powder diffraction measurements on YD_3 by Udovic et al. [24] demonstrate clearly that the D atoms occupy unusual interstitial positions of a slightly basal-plane-distorted, hexagonal close-packed metal lattice. It is conceivable that the electronic properties of YH_3 (and YD_3) are so sensitive to the exact position of all hydrogen atoms that even more accurate structural data will be required for a quantitative explanation. Alternatively, one can use this extreme sensitivity of the band structure of YH_3 to determine from first principles the hydrogen positions which lead to the lowest total energy. Very interesting results have been obtained by Kelly et al. [25] using the Car–Parrinello method to determine the ground state of YH_3. They found a structure with a direct gap of 0.8 eV. As calculations based on the local-density-approximation systematically underestimate semiconducting energy gaps by about 1 eV [26], the value of 0.8 eV obtained by Kelly et al. with such a method can be considered as being consistent with our experimental data. (iii) Finally, another possibility has been recently suggested by Sawatzky and Eder [27]. They expect that because H has only one electron, self-interaction effects are especially large. Furthermore, because the radius of the 1s orbital is about four times larger for the negative H^- ion than for the neutral H atom, the large electron correlation effects expected for yttrium, lanthanum and rare earth trihydrides cannot be described by a standard Hubbard model in which overlap integrals are assumed to be independent of the electronic configuration [28]. Preliminary results by Sawatzky and Eder do indeed confirm the existence of a large gap in YH_3.

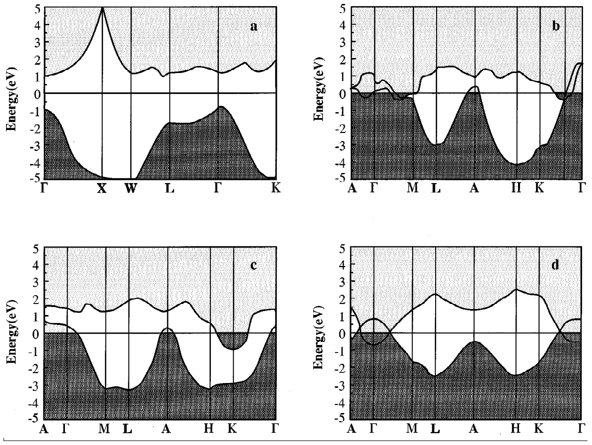

Fig. 5. Four band structure calculations of YH_3 for various crystal structures, obtained by means of a localized-spherical-wave method based on the local density functional approximation (for details see [23]). For simplicity only the border lines of the occupied (■) and unoccupied (□) bands are indicated. The Fermi energy is taken as the zero of energy. (a) YH_3 in the cubic BiF_3 structure as chosen by Switendick [20]. This calculation is not self-consistent, in contrast to the following three for (b) a perfect *hcp* structure with hydrogen atoms at all tetrahedral and octahedral sites, (c) a *hcp* LaF_3 structure in which the tetrahedral atoms are horizontally displaced in the *ab*-plane [23], (d) a HoD_3 structure in which both in plane rotational displacements of the tetrahedral hydrogen and vertical displacements of the other hydrogen atoms towards the yttrium plane are incorporated [22,23]. The three self-consistent calculations (b, c and d) all predict a semi-metallic ground state.

4.2. *Comparison with hydrogen intercalated tungsten oxide films*

At first sight the large change in optical transmission found in YH_x seems comparable to that observed in other electrochromic materials such as hydrogen- or lithium intercalated transition metal oxide films. For a very recent review the reader is referred to the excellent book of Granqvist [5]. Since H_zWO_3 is a typical electrochromic material [29] which has reached essentially industrial maturity, we compare here our switchable metal-hydride films to this intercalated tungstenate. Upon absorption of hydrogen H_zWO_3 changes from a transparent insulator at $x\approx0$ to a dark blue (still transparent) moderately conducting material for $x>0.32$. At maximum doping ($x<0.5$) the electrical resistivity has dropped to ~20 mΩ cm compared to 10^6 Ωcm at $x\approx0$ (see Fig. 6).

In sharp contrast, our YH_x -films are good metals in the dihydride β-YH_2 phase ($\rho\approx20$ μΩcm) while $\rho\cong$ 30 mΩcm at $YH_{2.86}$. Furthermore, they switch from a reflecting metal to a transparent semiconductor with an optical gap of 2.3 eV. The intercalated H_zWO_3 films and YH_x-films are thus systems with completely different optical and resistive properties.

The reason why the resistivity of $YH_{2.9}$ is lower than that of a typical semiconductor with a gap of 2.3 eV is probably due to two facts: (i) with $x=2.9$ there is a large fraction of still unoccupied octahedral sites which may act as donors and form an impurity band and (ii) even at stoichiometry YH_3 contains probably a sufficiently high density of impurities (the starting material is of 3N purity)

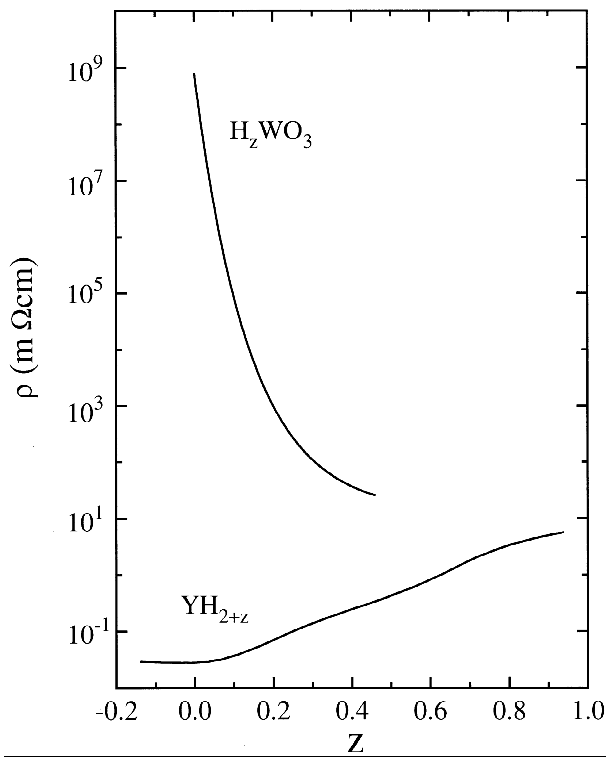

Fig. 6. Hydrogen concentration dependence of the electrical resistivity at room temperature of a switchable metal hydride YH_{2+z} film and the intercalated tungstenate H_zWO_3. The data for YH_{2+z} are similar to those in Fig. 2 (curve a). The data for H_zWO_3 are from Crandall and Faughnan [29]. Up to $z \approx 0.24$ the resistivity of H_zWO_3 varies as $\exp[-(T_o/T)^{1/4}]$ as expected for variable-range-hopping [5,29] below room temperature. In YH_{2+z} on the other hand, a remarkable logarithmic temperature dependence $1/\rho \propto \ln(T/T_o)$ has been observed [1].

to provide a relatively high level of doping. This high doping level is consistent with our Hall effect measurements which lead to 1.3×10^{25} m^{-3} in a $YH_{2.91}$ film at room temperature [1].

5. Conclusions

The possibility to load yttrium, lanthanum and rare earths films with hydrogen (from the gas phase or electrolytically) up to compositions close to the trihydride without deleterious effects makes it possible to investigate the physical properties of these hydrides in great detail.

The remarkable changes observed by Huiberts et al. [3] in the optical transmission of red light ($\hbar\omega = 1.8$ eV) through YH_x and LaH_x films have been found to occur over a wide range of photon energies. In the β-dihydride phase there is also a transparency window for photon energies higher than 1.5 eV. This transparency window can be quenched by alloying Y with La. This is technologically relevant as it makes it possible to enhance the contrast between the metallic dihydride phase and the semiconducting transparent trihydride phase. In addition to being transparent (albeit with a colour: $YH_{3-\delta}$ is yellowish and $LaH_{3-\delta}$ is reddish in transmission), the trihydrides of Y, La and $Y_{0.5}La_{0.5}$ have also relatively large electrical resistivities. It is presently not clear why these trihydrides are semiconducting since all band structure calculations published so far predict them to be semi-metals with a relatively large band overlap. Three possibilities are discussed: (i) the formation of an excitonic insulator; (ii) a complicated crystal structure and (iii) strong electron correlation effects. Much more work will be required to unravel the many remarkable properties of these hydrides which are very interesting from a fundamental as well as from a technological point of view.

6. Note added in proof

In a preprint of their manuscript entitled ‘‘Electronic structure of Lanthanum hydrides with switchable optical properties’’, which was submitted to *Phys. Rev. Lett.* in September 1996, Ng, Zhang, Animisov and Rice come also to the conclusion that electron correlation is important in H^--centers and in explaining the transparent insulating behaviour of LaH_3. The metal-insulator transition at $LaH_{2.8}$ takes place in a band of strongly localized states centered on H-vacancies of $LaH_{3-\delta}$. These results are similar to those of Sawatzky and Eder mentioned in text.

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