Insulating fcc $YH_{3-\delta}$ stabilized by MgH_2

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We study the structural, optical, and electrical properties of Mg_zY_{1-z} switchable mirrors upon hydrogenation. It is found that the alloys disproportionate into essentially pure $YH_{3-\delta}$ and MgH_2 with the crystal structure of $YH_{3-\delta}$ dependent on the Mg concentration z. For $0<z<0.1$, both hcp and fcc $YH_{3-\delta}$ are observed, whereas for $z \geqslant 0.1$ only cubic $YH_{3-\delta}$ is present. Interestingly, cubic $YH_{3-\delta}$ is expanded compared to YH_2, in disagreement with theoretical predictions. From optical and electrical measurements we conclude that cubic $YH_{3-\delta}$ is a transparent insulator with properties similar to hexagonal $YH_{3-\delta}$. Our results are inconsistent with calculations predicting fcc $YH_{3-\delta}$ to be metallic, but they are in good agreement with recent *GW* calculations on both hcp and fcc YH_3. Finally, we find an increase in the effective band gap of the hydrided Mg_zY_{1-z} alloys with increasing z. Possibly this is due to quantum confinement effects in the small YH_3 clusters.

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I. INTRODUCTION

In 1996, Huiberts *et al.* reported that thin yttrium and lanthanum films exhibit spectacular changes in their optical properties upon hydrogenation.[1–4] The dihydrides are cubic metals that are reflective at energies lower than that of a characteristic transparency window (for YH_2 at 1.8 eV); the trihydrides (YH_3, hexagonal; LaH_3, cubic) are transparent, large-gap semiconductors. Reversible switching between these two states is possible at ambient temperatures, by changing the surrounding hydrogen gas pressure[1–4] or electrolytic cell potential.[5] Besides YH_x and LaH_x, all trivalent rare earth hydrides (RH_x) as well as their alloys with Mg exhibit similar switching properties,[6–8] hence the name ''switchable mirrors'' for the entire group. Switchable mirrors containing Mg are of special interest as they can be tailored to be reflective (i.e., the small transparency window is suppressed) and transparent over the entire optical range in the unloaded state and loaded state, respectively. Recently, it was shown that in these systems Mg acts as a microscopic, optical shutter[8] changing from the shiny metal Mg to the large-gap insulator[9,10] MgH_2 upon hydrogenation.

The insulating ground state of the rare earth trihydrides presented theorists with an interesting challenge. In the early 1990s, calculations on YH_3 were performed in the local density approximation (LDA), using a variety of structures. However, in all cases, including the lowest energy hexagonal HoD_3 structure, a metallic state was obtained.[11,12] The large discrepancy between experiment and LDA calculations stimulated other theorists to consider different approaches. Kelly *et al.*[13] demonstrate that small displacements of the hydrogen atoms, relative to the HoD_3 structure, can induce a gap.[14,15] Ng *et al.*[16] and Eder *et al.*[17] on the other hand claim that strong electron correlation effects are the key ingredient in explaining the insulating state.[18]

The importance of electron correlation effects was also taken into account in *ab initio* band structure calculations using the *GW* approximation. van Gelderen *et al.*[19] performed calculations on YH_3 in three hexagonal structures (LaF_3, HoD_3, and the broken symmetry structure proposed by Kelly *et al.*), whereas Miyake *et al.*[20] used the cubic BiF_3 and hexagonal LaF_3 structures. For the cubic as well as for the hexagonal cases, YH_3 is found to be an insulator. These results are in disagreement with the work by Ahuja *et al.*[21] who claim that a hcp to fcc transition in YH_3 is accompanied by an insulator to metal transition. Up to now, however, a comparison between cubic and hexagonal YH_3 was not possible experimentally.

In this article we show that (i) one can stabilize fcc YH_3 by alloying Y with Mg prior to hydrogenation; (ii) in contrast to LaH_x, YH_x expands when loaded from dihydride to trihydride; (iii) fcc $YH_{3-\delta}$ is a large-gap semiconductor similar to hcp $YH_{3-\delta}$; (iv) the electrical properties of the hydrogenated alloys depend nontrivially on the Mg content.

II. EXPERIMENT

A series of polycrystalline Mg_zY_{1-z} samples of 300 nm thickness are prepared by coevaporation of Y and Mg under UHV conditions (10^{-9} mbar) on an *R*-plane Al_2O_3 substrate using an electron gun and Knudsen cell, respectively. Two different geometries are used in this work. For the first, the complete Mg_zY_{1-z} alloy is covered *in situ* with a 15 nm Pd layer. These samples are initially transferred to a Rigaku x-ray diffractometer and then to a Bruker IFS 66/S Fourier transform infrared spectrometer to study structural properties and optical transmission, respectively. The x-ray measurements are performed in a Bragg-Brentano geometry by moving the detector (2Θ) from 10° to 75° with a fixed sample angle of 10°. In both setups, hydrogenation (up to $p_{H_2} = 1$ bar) is done slowly at room temperature, and checked by continuous recording of diffraction or optical transmission spectra. For the second set of samples, we use a geometry similar to the one introduced by den Broeder *et al.*[3] to study lateral H diffusion optically in switchable mirrors [see Fig. 4(a) below]. In this case, the Mg_zY_{1-z} layer is only partly covered by Pd (making use of a shadow mask) after which the uncovered part of the alloy is superficially oxidized in ambient air. Subsequently, the sample is transferred either to the x-ray setup, or to a chamber equipped with

optical windows, temperature control, and electrical leads. This chamber is placed onto the positioning table of an optical microscope (Olympus BX60F5) on top of which a three-charge-coupled device camera is mounted. When 1 bar of H_2 is introduced, the Pd covered part of the sample absorbs H immediately and switches to the fully hydrided state. However, hydrogen can enter the oxide covered Mg_zY_{1-z} layer only by diffusing laterally out of the Pd covered area, as H_2 dissociation is not possible at the oxide surface.[22] During the diffusion process, which can be followed optically, the hydride phases of the system are spatially separated. Phases with a high hydrogen concentration stay closest to the Pd strip.[3,23] A series of electrical contacts along the sample allows for resistivity measurements of the various areas. In this way, one circumvents electrical shortcut due to the Pd cap layer, which presents a problem for the first kind of sample. In this paper we mainly discuss the electric properties of the system. An extensive lateral diffusion study has also been performed but will not be reported on here.[24]

Sample composition (yielding the Mg content z) and homogeneity are checked using Rutherford backscattering spectroscopy (RBS). The presence of a well-separated Pd peak shows that there is little interdiffusion of Pd and Mg_zY_{1-z}. On one particular sample ($Mg_{0.37}Y_{0.63}$, second geometry), we performed scanning Auger microscopy (SAM) while the film was sputtered away. The resulting depth profile gives local chemical information.

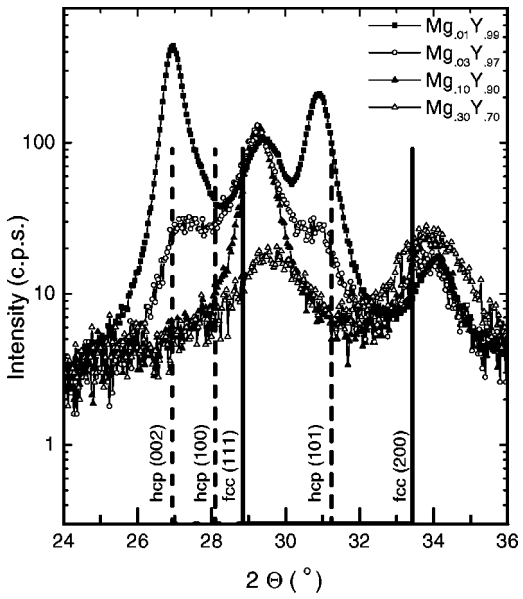

FIG. 1. X-ray diffraction measurements in Bragg-Brentano geometry ($\Theta = 10°$) of Mg_zY_{1-z} films after hydrogenation in 1 bar H_2 at room temperature. For clarity, only four results are shown ($z = 0.01, 0.03, 0.10$, and 0.30), in a limited 2Θ range. Furthermore, the diffraction lines of hcp YH_3 (dashed) and hypothetical fcc YH_3 (solid) are displayed, the latter lines having been calculated assuming $V^{fcc}_{YH_3} = V^{hcp}_{YH_3}$. Comparing our data with these lines, we conclude that a transition from hcp YH_3 (at $z=0$) to fcc YH_3 (at $z=0.10$) takes place with increasing z.

III. RESULTS AND DISCUSSION

A. Structure

First we focus on x-ray diffraction (XRD) analysis, starting with the virgin films. For $0.01 \leqslant z \leqslant 0.37$, XRD reveals the presence of two metallic phases, hcp α-Y and cubic γ-YMg, which are randomly oriented. For $z=0$ and $z=0.5$, we find only Y and YMg reflections, respectively. These results are in accordance with the Y-Mg phase diagram.[25] The absence of YMg_2 peaks for $z<0.5$ confirms that our films are homogeneous in composition.

As soon as we load our samples with hydrogen, γ-YMg disproportionates into YH_2 and Mg clusters,[8] an effect also found in other Mg alloys such as LaMg and CeMg.[26,27] Upon additional H uptake, small clusters of $YH_{3-\delta}$ and MgH_2 are formed. In Fig. 1, we show XRD spectra of a set of alloys in equilibrium with 1 bar H_2 at room temperature. Note that only the YH_x peaks are observed due to the low Mg concentration and the large difference between the atomic form factors of Y and Mg (ratio 12:1). For comparison, peak positions of randomly oriented hcp YH_3 and fcc YH_3 (*a priori* assuming its existence) are indicated as well. The hcp reflections are calculated using bulk YH_3 lattice constants[28] ($a_0 = 0.3673$ nm and $c_0 = 0.663$ nm). For an indication of the fcc peak positions, we initially assume that fcc and hcp YH_3 have equal volume per formula unit, implying a fcc lattice constant $a_{fcc} = 0.537$ nm. Inspecting Fig. 1 for Mg concentrations $z=0.01$ and $z=0.03$, we find that $YH_{3-\delta}$ is present in both cubic and hexagonal symmetry, with peak positions at 29° [fcc (111)] and 34° [fcc (200)], as well as at 27° [hcp (002)] and 31° [hcp (101)]. For Mg concentrations $z \geqslant 0.10$, however, only fcc $YH_{3-\delta}$ is observed.

Figure 2 shows the volume per $YH_{3-\delta}$ formula unit as a function of Mg concentration in the fully hydrided alloys.[29] In the fcc-hcp coexistence region ($z<0.10$), the unit cell volume of both structural phases is approximately independent of z. However, for $z \geqslant 0.10$, where hcp $YH_{3-\delta}$ is no longer present, the unit cell volume of fcc $YH_{3-\delta}$ decreases with increasing Mg content. Both these phenomena can be understood by considering the volume expansions of Y and Mg during hydrogenation.[30] Upon transforming to hcp $YH_{3-\delta}$, bulk Y expands by approximately 17%, mostly in the out-of-plane direction.[28] The transition from Mg to MgH_2, however, involves a volume increase of as much as 32%.[10,31] This enormous expansion causes large stresses in the film.[8,32] For $z<0.10$, the system is able to reduce the internal pressure by transforming hcp $YH_{3-\delta}$ to the smaller fcc $YH_{3-\delta}$. For $z \geqslant 0.10$, this is no longer possible and the fcc $YH_{3-\delta}$ is increasingly compressed with increasing Mg content.

A transition from hcp to fcc $YH_{3-\delta}$ was indeed predicted by Ahuja *et al.*[21,33] However, there is a large difference between the theoretically calculated and the experimentally observed volumes per formula unit. Whereas Ahuja *et al.* expect 36.4 Å^3 for hcp $YH_{3-\delta}$ and 32.3 Å^3 for fcc $YH_{3-\delta}$, we find $V_{hcp}(z<0.1) = 39.5$ Å^3 and $V_{fcc}(z<0.1) = 36.9$ Å^3.

Figure 2 also shows the volume of fcc YH_2 as determined after unloading the films. Once more, we observe a plateau for $z<0.10$ (where the dihydride volume has the bulk value[28]

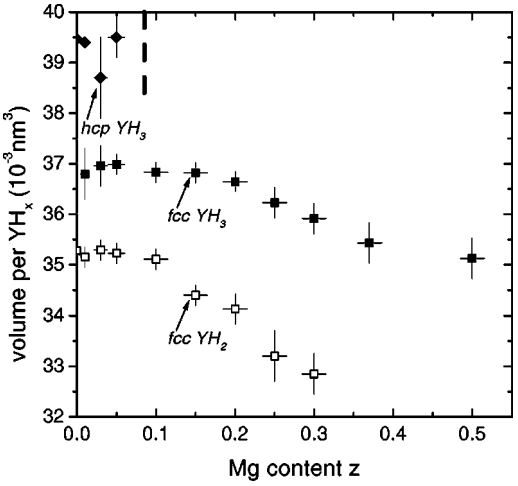

FIG. 2. Closed symbols: Volume of YH_3 (per formula unit) in fully hydrogenated Mg_zY_{1-z} alloys as a function of z ($p_{H_2}=1$ bar, room temperature). For $z\lesssim 0.1$, there is a two-phase region of hcp YH_3 (diamonds) and fcc YH_3 (solid squares). For $z\geqslant 0.1$ only fcc YH_3 is present. Open symbols: Volume of YH_2 (per formula unit) as measured after unloading the samples.

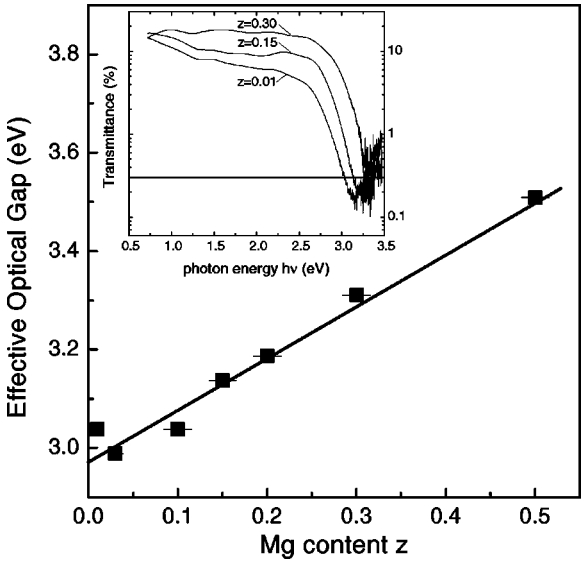

FIG. 3. Effective optical band gap E_{gap}^{opt} versus Mg content z. The inset shows the optical transmittance T_{opt} as a function of photon energy $h\nu$ for three hydrogenated films ($z=0.01$,0.15, and 0.30). The effective optical gap E_{gap}^{opt} is defined here as the energy at which T_{opt} drops below 0.3%. The line is a guide to the eye.

35.2 $Å^3$) and a decrease for $z>0.1$. Interestingly, the volume change upon loading from $YH_{2-\varepsilon}$ to $YH_{3-\delta}$ is positive for all z. At first glance, this is a rather surprising result. It is well known that fcc LaH_2 contracts upon loading to fcc LaH_3. Furthermore, calculations by Sun *et al.* predict that fcc YH_3 has a smaller volume than fcc YH_2 (34.5 $Å^3$ and 35.1 $Å^3$ per formula unit, respectively).[34] However, our results are consistent with the recent work by van Gogh *et al.*[35] who performed a study of the $La_{1-y}Y_yH_x$ system. In contrast to the films studied here, their samples show no segregation upon hydrogen loading, i.e., Y and La stay mixed on an atomic scale. van Gogh *et al.* find that (i) $La_{1-y}Y_yH_3$ is cubic for $y<0.67$ and (ii) $La_{1-y}Y_yH_x$ contracts for $y<0.38$, but expands for $y>0.38$, when x increases from 2 to 3. These results suggest strongly that if fcc YH_3 exists its volume should be larger than that of fcc YH_2. Extrapolating the volumes of the fcc trihydrides $La_{1-y}Y_yH_3$ to $y=1$ (i.e., to ''pure fcc YH_3'') one obtains a value of 38 $Å^3$. This is somewhat larger than the fcc YH_3 volumes in Fig. 2, a difference that may be attributed to the different way the Y is distributed in the two systems (mixing on an atomic scale versus segregation) as well as to the different stress states.

B. Optical transmission

In the inset of Fig. 3, the optical transmittance T_{opt} as a function of photon energy is shown for three alloys ($z=0.01$,0.15,0.30) in equilibrium with 1 bar H_2 at room temperature. Clearly, the addition of Mg makes these switchable mirrors more transparent and more color neutral in the loaded state. From the optical transmission curves we determine an effective optical gap E_{gap}^{opt} defined arbitrarily as the energy at which T_{opt} falls below 0.3%. The main frame of Fig. 3 shows this quantity as a function of z.

Let us first focus on the two-phase fcc-hcp YH_3 region ($z<0.1$). In this interval, the optical gap does not change significantly with z, although hcp YH_3 is increasingly substituted by fcc YH_3. Since MgH_2 is a large-gap insulator (a very recent measurement[9] yields an optical gap of approximately 6 eV), this is only possible if the optical properties of fcc YH_3 are comparable to those of hcp YH_3. Therefore, the optical measurements suggest strongly that fcc YH_3 is a large-gap semiconductor just like hcp YH_3. This conclusion is substantiated by the electrical resistivity data presented in Sec. III C.

Next, we focus on the region $z\geqslant 0.10$ where only fcc YH_3 and MgH_2 are present. Figure 3 shows that the optical band gap increases nearly linearly with z, i.e., when YH_3 is gradually replaced by MgH_2. To obtain an intuitive picture of this effect, we first consider the simplest possible model. The cluster size of YH_3 being much smaller than the film thickness (see below), a simple optical analogy is a double layer structure of YH_3 [with layer thickness $d_{YH_3}(z)$] and MgH_2. As the optical gap of MgH_2 is much larger than that of YH_3, (i.e., MgH_2 is basically transparent in the energy range of our measurements), T_{opt} is dominated by YH_3. For a double layer, we approximately have the Lambert-Beer relation $T_{opt}(h\nu)\approx T_0\exp[-\alpha_{YH_3}(h\nu)d_{YH_3}]$, where T_0 and $\alpha_{YH_3}(h\nu)$ denote the original light intensity and the energy dependent absorption coefficient of YH_3, respectively. Since $d_{YH_3}(z)\propto(1-z)$, this relation predicts an exponentially increasing transmission over the entire energy range with increasing z. As a consequence of its definition, this implies a higher effective optical gap. Figure 3 shows that both these effects do indeed occur in the alloys.

Interestingly though, the two-layer model fails to work on closer inspection. This is seen in the work by Giebels *et al.*[36] who compare the optical properties of hydrogenated Mg_zY_{1-z} alloys with those of multilayers with equal overall

composition. They find that the effective optical gap of an alloy shifts to higher energies than that of a multilayer. In other words, a quantitative description of the optics of loaded Mg_zY_{1-z} alloys is not possible just using a layered model. A reason for this may be that the MgH_2 clusters have an irregular distribution through the film (unfortunately the x-ray data do not allow for a MgH_2 cluster size determination for low z). Another, much more fundamental, cause could be a mutual influence of MgH_2 and YH_3 clusters, perhaps of electronic origin. This is discussed in Sec. III C.

Finally, we report on an interesting consequence of the suppression of the fcc YH_2 to hcp YH_3 structural phase transition: there is a large increase in the size of the thermochromic effect[24,37] for samples in which fcc YH_3 instead of hcp YH_3 is formed (i.e., for $z \geqslant 0.1$). Most likely, this is due to a difference between the fcc-YH_2/hcp-YH_3 isotherms and the fcc-YH_2/fcc-YH_3 isotherms, the latter probably being less steep near $x=3$. As a result, the equilibrium H concentration (and therefore the optical transmission) in 1 bar H_2 is much more temperature dependent for fcc $YH_{3-\delta}$ than for hcp $YH_{3-\delta}$.

C. Resistivity

To confirm the insulating nature of the hydrided samples, a series of resistivity measurements are performed. Unfortunately, it is difficult to accurately determine the resistivity of the transparent layer for the first kind of sample. This is due to the 15 nm Pd cap layer shunting the insulating layer. To circumvent this problem, we use samples of the second geometry [see Fig. 4(a)]. As explained above, a lateral diffusion process takes place in these samples,[3,23] as soon as they are in contact with 1 bar H_2. During the process, the transparent phase appears next to the Pd cap layer, slowly growing away from the Pd edges. To accelerate its migration, we apply a voltage to the sample. As a result, the transparent phase grows in the direction of the anode with constant velocity.[38] This implies that H in the insulating phase behaves as a negative particle, consistent with our recent work[18,38,39] on $YH_{3-\delta}$.

When the insulating phase has moved by more than 100 μm from the Pd edge [see Fig. 4(b)], we determine its resistance. Figure 4(c) shows the room temperature resistivity ρ of the insulating area in the diffusion samples as a function of Mg content z. A remarkable relation is observed: ρ grows almost exponentially with z, increasing by as much as four orders of magnitude from $z=0$ to $z=0.25$. The data point at $z=0.37$ deviates from the general trend. We note, however, that on this sample a dense pattern of hillocks appeared at the oxide surface [see inset Fig. 4(c)]. SAM depth profiles taken at and away from two hillocks yield a large variation in Mg content. Hillocks turn out to be Mg rich, whereas the rest of the film is Mg poor. Therefore, the data point initially at $z=0.37$ should probably be shifted toward the left in Fig. 4(c). The profiles taken away from the hillocks show a nearly constant Mg content as a function of depth, once more confirming the homogeneity of the as-deposited films.

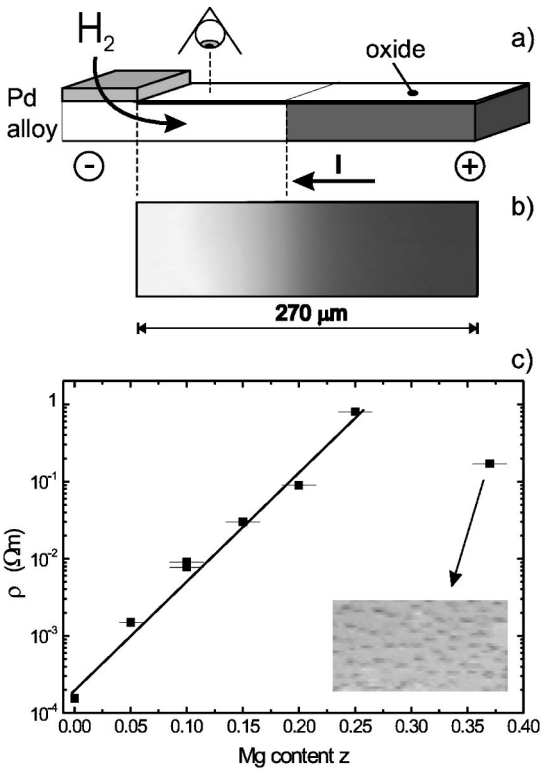

FIG. 4. (a) Geometry of a lateral diffusion sample. In 1 bar H_2, hydrogen enters the film via the Pd strip and migrates laterally underneath the superficial oxide layer. Upon applying a current through the sample, the transparent hydride phase is attracted by the (+) pole. (b) Micrograph in optical transmission of one of the $Mg_{0.10}Y_{0.90}$ samples after lateral H migration. For clarity, the Pd covered area is not shown. When the transparent area has grown large enough, its resistance is measured. (c) Resistivity ρ of the transparent area versus Mg content z. The line is a guide to the eye. Shown in the inset is a transmission picture [same scale as (b)] of the $Mg_{0.37}Y_{0.63}$ sample, on which a dense hillock pattern is observed.

The main message of Fig. 4(c) is that the resistivity of fcc $YH_{3-\delta}$ is equal to or larger than that of hcp $YH_{3-\delta}$. If this were not the case, the sample resistivity would drop from $z=0$ to $z=0.10$, i.e., when hcp YH_3 is substituted by fcc YH_3. We note that at such low MgH_2 content no serious percolation problems are expected (as argued below). From the combination of optical transmission and electrical transport data, we conclude that fcc $YH_{3-\delta}$ is an insulator with a gap comparable to (if not larger than) that of hcp $YH_{3-\delta}$. This result is in flagrant disagreement with the prediction by Ahuja *et al.*[21] that a transition from hcp to fcc YH_3 is accompanied by an insulator-metal transition. Moreover, it shows that the insulating nature of YH_3 is not very sensitive to its precise lattice structure at all; the dominant parameter determining the electronic state of YH_x seems to be the hydrogen concentration. This suggests that the band gap is primarily controlled by the electronic interactions in the system.[20] Interestingly, these conclusions are consistent with recent *GW* calculations, which show that YH_3 is insulating in four quite different structures.[19,20] Our results are also in agreement with the strong correlation theories proposed by Ng *et al.*

and Eder *et al.* as these are inherently of local character.[16,17] Unfortunately, we are not aware of calculations on various structures using either of the latter models.

Finally, it seems that the insensitivity of the insulating state to structural changes is not in agreement with the original calculations by Kelly *et al.*[13] In their view, subtle rearrangements of the (hydrogen) lattice are responsible for the insulating ground state. Without these, YH_3 would be metallic. We do note, though, that the recent calculations by van Gelderen *et al.*[19] do not show much difference between the HoD_3 and the broken symmetry structures: both have a comparable gap in the *GW* approximation. Thus, although the broken symmetry structure may exist,[40] its presence is not a prerequisite for an insulating ground state.

Figure 4(c) not only confirms the insulating nature of fcc YH_3, it also shows an almost exponential dependence of the film resistivity on Mg content. In the following, we discuss a number of explanations for this relation, starting with two trivial ones. A first possibility is that the films have oxidized heavily, resulting in a large increase of resistivity. This hypothesis is easily rejected, since both RBS and SAM depth profiles show that the lowest 60% of the films is oxygen-free (see also Ref. 22). Furthermore, we tested reversibility by unloading the films in air, pushing the insulating area back to the Pd by the use of a (positive) voltage.[3] After unloading, the resistivity of the oxide covered part of the films is approximately equal to that of the virgin films ($\sim 10^{-6}\Omega$ m), i.e., many orders of magnitude smaller than in the hydrided state. Since oxidation of switchable mirrors is irreversible, this experiment tells us that the results in Fig. 4(c) are entirely due to hydrogenation.

Next, we focus on the composition of the insulating area. As mentioned above, disproportionation leads to the formation of clusters of $YH_{3-\delta}$ (possibly doped with Mg), as well as clusters of MgH_2. The resistivity of pure $YH_{3-\delta}$ is known to be relatively low ($\sim 10^{-4}\Omega$ m in 1 bar H_2), despite its large optical band gap. This is due to the fact that H vacancies in $YH_{3-\delta}$ act as donors,[41,42] and thereby determine the conductivity, i.e., $\rho = 1/\sigma \propto 1/\delta$ in $YH_{3-\delta}$. On the other hand, MgH_2 is an insulator with a gap of approximately 6 eV and a resistivity much higher than $YH_{3-\delta}$. The large conductivity difference between the two cluster species suggests that Fig. 4(c) may well be the result of a classical percolation problem: with increasing number of MgH_2 clusters, fewer and fewer current paths through the $YH_{3-\delta}$ are available, resulting in a drastic resistivity increase near the percolation threshold (where no such path exists). Comparison with percolation theory, however,[43] immediately shows that this cannot be the main mechanism here. Percolation thresholds lie around 75 (50) vol % of low conductivity material for three (two) dimensions, whereas here we already see a large effect when only a few volume percent of MgH_2 is present. (Note that $z = 0.25$ corresponds to 23 vol % of MgH_2.) Furthermore, Fig. 4(c) does not exhibit power law behavior.[43] Having rejected oxidation and percolation as explanations, we conclude that the resistivity measured in our films is dominated by the $YH_{3-\delta}$ clusters, and not by MgH_2, or any oxide.

The rest of this section will therefore focus on the question of how the properties of the $YH_{3-\delta}$ clusters are influenced by the presence of Mg. Let us consider the possibility that $YH_{3-\delta}$ clusters themselves contain Mg impurities (i.e., on an atomic scale, apart from the clusters of MgH_2). Since Mg has only two valence electrons whereas Y has three, a Mg atom in an $YH_{3-\delta}$ matrix may act as an acceptor, compensating for the electrons donated by H vacancies. Consequently, the resistance of $YH_{3-\delta}$ clusters increases with increasing concentration of Mg impurities, i.e., with increasing z. This leads to the expectation $\rho(z) \propto [n(\delta, z=0) - N_{\mathrm{Mg}}(z)]^{-1}$, where $n(\delta, z=0)$ is the electron density in $YH_{3-\delta}$ and $N_{\mathrm{Mg}}(z)$ is the concentration of Mg impurities in the $YH_{3-\delta}$ grains. Although this effect goes in the right direction, it is clear that it cannot explain the exponential behavior of Fig. 4(c). Moreover, exponential resistivity behavior is in general expected only if there is a change in some energy parameter. Therefore, we consider the effects of a change in the YH_3 heat of formation ΔH as a function of z. For a metal-hydride system in equilibrium with H_2, the hydrogen concentration is directly related to ΔH: the more negative ΔH, the larger the concentration and, consequently, the lower the H vacancy concentration and the higher the resistivity. Suppose ΔH depends on z via $\Delta H(z) = \Delta H_0 - \alpha z$ where ΔH_0 is the enthalpy of formation of Mg-free $YH_{3-\delta}$. For an $YH_{3-\delta}$ sample in equilibrium with H_2 gas at chemical potential μ_{H_2}, the lattice gas model of Lacher[44] yields

$$\frac{1}{2}RT \ln\left(\frac{p_{H_2}}{p_0(T)}\right) = RT \ln\left(\frac{1-\delta(z)}{\delta(z)}\right) + \Delta H_0 - \alpha z, \qquad (1)$$

where $p_0(T) \propto T^{7/2}$ is a reference pressure and R is the gas constant. Solving for $\delta(z)$, we find

$$\delta(z) = \left[1 + \sqrt{\frac{p_{H_2}}{p_0(T)}} \exp\left(\frac{-\Delta H_0 + \alpha z}{RT}\right)\right]^{-1} \approx \sqrt{\frac{p_0(T)}{p_{H_2}}} \exp\left(\frac{\Delta H_0 - \alpha z}{RT}\right) \equiv \delta(z=0) \exp\left(\frac{-\alpha z}{RT}\right). \qquad (2)$$

Hence, since $\rho \propto 1/\delta$,

$$\rho(z) \approx \rho(z=0) \exp\left(\frac{\alpha z}{RT}\right), \qquad (3)$$

where $\rho(z=0)$ represents the resistivity of Mg-free $YH_{3-\delta}$. Clearly, this gives a form compatible with Fig. 4(c) if $\alpha > 0$, i.e., if ΔH decreases with increasing z. Electrochemical measurements, however, show that this is not at all the case:[36] ΔH increases (toward zero) with increasing z. This is confirmed by a crude estimation of the change $d\Delta H$ due to stress in the films. For this we make use of the relation $d\Delta H = -BV_H dV/V$ (see Ref. 8), where B is the YH_3 bulk modulus, V_H is the volume change upon addition of 1 mole of hydrogen, and dV is the volume change due to stress. From Fig. 2 we have $V_H > 0$ (the volume increases upon

hydrogen uptake) as well as $V(z) \leqslant V(z=0)$ and thus $dV \leqslant 0$ (the volume decreases upon Mg addition, as a result of stress). This yields $d\Delta H(z) > 0$. Consequently, the resistivity change in Fig. 4(c) is not due to a change in ΔH.

Since the foregoing mostly nonelectronic pictures fail, we finally discuss the possibility that the band structure of $YH_{3-\delta}$ is influenced by the presence of MgH_2. In fact, one way to interpret the optical data of Fig. 3 and the differences between alloys and multilayers is that the band gap of $YH_{3-\delta}$ increases with increasing z. Interestingly, such an effect could also explain the resistivity data. If we assume the simple relation $\rho(z) = \rho(z=0)\exp[E^{\rho}_{gap}(z)/2k_BT]$ and calculate E^{ρ}_{gap} as a function of z from Fig. 4(c), we find that $\Delta E^{\rho}_{gap}/\Delta z = 1.6$ eV. This is close to the change in the effective optical gap obtained from Fig. 3, $\Delta E^{opt}_{gap}/\Delta z = 1.1$ eV, indicating that the same physical phenomenon lies at the heart of both Figs. 3 and 4(c). We discuss two possible reasons for a shift of electron energy levels: band bending and quantum confinement. Both are related to the small size of the YH_3 clusters.

The first effect occurs when the bands of YH_3 bend in the contact region with MgH_2 (compare, e.g., GaAs-$Al_xGa_{1-x}As$ nanostructures). If the spatial extent of band bending is comparable to the YH_3 cluster size, the effective band gap of YH_3 increases, because the ''bulk'' gap value is not reached within the cluster. We note, however, that due to the low carrier concentration in MgH_2 one does not expect band bending to be of key importance.

Quantum confinement has been put forward to explain cluster size dependent luminescence in nanocrystalline or porous Si.[45,46] The smaller a cluster, the higher the energy levels, as in the textbook particle-in-a-box problem. A reasonable estimate is[45]

$$\Delta E^{QC}_{gap}(L) \approx \frac{2\pi^2\hbar^2}{L^2}\left(\frac{1}{m^*_e} + \frac{1}{m^*_h}\right), \tag{4}$$

where $m^*_{e(h)}$ denotes the electron (hole) effective mass and L is the diameter of the YH_3 clusters. To estimate L, we use the x-ray coherence length l_{coh}, which is determined from the width of the XRD peaks via the Debye-Scherrer formula. As seen in Fig. 5(a), l_{coh} decreases as a function of Mg content z, from $l_{coh} = 18$ nm for $z=0$ to $l_{coh} = 4$ nm for $z=0.3$. To calculate the energy shift due to quantum confinement, we need the effective masses m^*_e and m^*_h in YH_3. Since no experimental data are available, we use the GW band structure calculations by van Gelderen *et al.*[19] to obtain $m^*_e \approx 0.35m_e$ and $m^*_h \approx -0.74m_e$. In Fig. 5(b), we plot ΔE^{QC}_{gap} as a function of z, calculated using Eq. (4) and presuming that $L = l_{coh}$. As z increases, ΔE^{QC}_{gap} increases significantly, and we have approximately $\Delta E^{QC}_{gap}/\Delta z \approx 0.3$ eV$/0.3 = 1$ eV. This change is remarkably close to the increase observed in Figs. 3 and 4(c). Therefore, it is conceivable that quantum confinement effects play an important role in hydrided Mg_zY_{1-z} alloys.

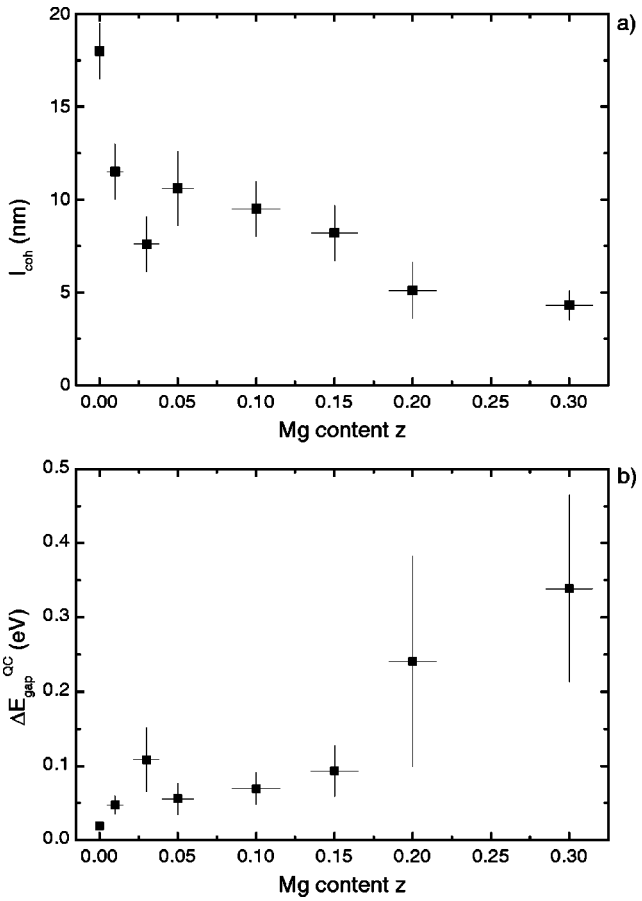

FIG. 5. (a) X-ray coherence length l_{coh} of the YH_3 clusters in fully hydrogenated Mg_zY_{1-z} alloys versus z. (b) Change in band gap $\Delta E^{QC}_{gap}(z)$ as a result of quantum confinement. To estimate ΔE^{QC}_{gap}, we use Eq. (4) and assume $L = l_{coh}$.

IV. CONCLUSIONS

We have synthesized fcc $YH_{3-\delta}$ making use of the disproportionation reaction and stresses in Mg_zY_{1-z} films upon hydrogen loading. In contrast to LaH_x as well as to theoretical predictions, fcc YH_3 has a larger unit cell volume than fcc YH_2. Furthermore, it is an insulator with a gap comparable to that of hcp $YH_{3-\delta}$, as concluded from optical transmittance and resistivity measurements. This result is in clear disagreement with the prediction by Ahuja *et al.* that fcc $YH_{3-\delta}$ should be metallic. The fact that the properties of $YH_{3-\delta}$ are not at all sensitive to the exact crystal structure is consistent with a series of recent GW calculations. Furthermore, it is compatible with the essentially local models proposed by Ng *et al.* and by Eder *et al.*

There is a rather large influence of the Mg content on the overall film properties. The effective optical gap, defined here as the energy at which the transmittance is 0.3%, increases linearly with z. Furthermore, the sample resistivity (as measured in a lateral diffusion geometry) increases exponentially with z. Although the optical data alone could have a trivial explanation (the cluster distribution is essential in optics), the combination of both data sets hints at a change in the $YH_{3-\delta}$ band structure as a function of z. Possibly, this is

a result of quantum confinement effects in the small YH_3 clusters.

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