Strucutral, electrical, and optical properties of \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) switchable mirrors

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Thin \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) films, in the composition range \( 0<z<1 \) and \( 0<x<3 \), are studied using x-ray diffraction, dc resistivity measurements, reflectance-transmittance measurements, and ellipsometry in the visible and near-infrared spectral range. For \( x=0 \) the structural phase diagram is similar to that of the bulk system. Upon hydrogen absorption and desorption, the \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) films do not disproportionate. All dihydrides have a fcc structure with a continuous shift of the lattice parameter, whereas the trihydrides undergo a transition from a fcc lattice structure for \( 0<z<0.67 \) to ahexagonal lattice structure for \( 0.81<z<1 \). No significant thin-film effects occur in the structural, electrical, and optical properties, whereas disorder effects are observed in the x-ray coherence length, the electron relaxation time at both zero and optical frequencies, and in the optical properties of the trihydrides. In \( \text{LaH}_3 \) a similar dihydride transmission window is observed as in \( \text{YH}_3 \). The suppression of this window upon alloying is a disorder effect. As in the case of their parent materials, all \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) alloys (both cubic and hexagonal) exhibit a metal-insulator transition for \( 2<x<3 \), which is a clear demonstration of the robustness of the metal-insulator transition in switchable mirrors. The optical band-gap shifts from \( 1.87 \pm 0.03 \) eV for \( \text{LaH}_3 \) to \( 2.63 \pm 0.03 \) eV for \( \text{YH}_3 \). The optical properties suggest that the fundamental band gap is \( 1.8 \) eV lower.

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I. INTRODUCTION

Switchable metal hydrides have received much attention since 1996, when Huiberts et al.\textsuperscript{1} discovered that the optical properties of thin films of \( \text{Y} \) and \( \text{La} \) exhibit drastic changes under exposure of hydrogen. In these films the hydrogen concentration \( x \) can be changed from 0 to 3 at room temperature by applying \( \text{H}_2 \) gas at moderate pressures (\( \approx 10^5 \) Pa). When \( x \) increases from 2 to 3 the material changes from a reflective metal into a transparent insulator. Shortly afterwards it was shown that not only \( \text{Y} \) and \( \text{La} \) but most rare-earth (RE) metals exhibit such a metal-insulator transition.\textsuperscript{2} In addition, by using RE-based alloys the optical properties can be tuned.\textsuperscript{2–4} This, together with the fact that \( \text{H} \) loading and unloading of these films is reversible and can also be done electrochemically,\textsuperscript{5,6} make these metal-hydride systems technologically interesting. However the \( \text{Y} \) and \( \text{La} \) hydride systems are also very interesting from a fundamental point of view. Before 1997 state-of-the-art band-structure calculations on \( \text{YH}_3 \) and \( \text{LaH}_3 \) predicted a metallic ground state of these materials. Since 1997 several theoretical calculations came up with explanations of why ordinary band-structure calculations failed.\textsuperscript{7–11} Although progress has been made, the physical mechanism underlying the metal-insulator (MI) transition is still under debate.

In this work we present a systematic study of \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) thin films. Yttrium and lanthanum are chemically very similar, both having a \( d^3 \) \( s^2 \) valence configuration. This similarity is reflected in the simplicity of the (bulk) phase diagram of the \( \text{La}_{1-z} \text{Y}_z \) system. The two metals form a solid solution over almost the whole composition range. For \( z<0.4 \) the alloys have a La double hexagonal close packed (dhcp) structure, and for \( z>0.6 \) a Y (hcp) structure.\textsuperscript{14} However, \( \text{YH}_3 \) and \( \text{LaH}_3 \) behave quite differently for \( x \) between 2 and 3: \( \text{YH}_3 \) changes from a fcc structure to a hexagonal lattice structure with a large increase in atomic volume, whereas \( \text{LaH}_3 \) stays fcc with a small decrease of atomic volume upon hydrogenation.

We show that \( \text{La-Y} \) alloys do not disproportionate upon hydrogenation, as is the case, for example, in the \( \text{Y-Mg} \) system,\textsuperscript{4} which makes the \( \text{La-Y} \) system particularly suitable for studying the influence of lattice structure, lattice parameters, and microscopic disorder on various physical quantities. We also show that a MI-transition occurs in all alloys regardless of their crystal structure (cubic or hexagonal).

After Sec. II, a short explanation of the MI transition in the \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) system is given. We then focus on the lattice structure of \( \text{La}_{1-z} \text{Y}_z \text{H}_x \) thin films. This information is used in the interpretation of later results that are mainly concerned with electrical and optical properties of \( \text{La}_{1-z} \text{Y}_z \text{H}_x \).

II. EXPERIMENT

A. Samples

\( \text{La}_{1-z} \text{Y}_z \) films of 300-nm thickness are made at room temperature and under ultrahigh-vacuum conditions (\( \approx 10^{-8} \) Pa) by e-gun codeposition of the parent metals (99.9% purity). The films are evaporated on quartz glass substrates (Suprasil\textsuperscript{TM} plaquettes and Heraasil\textsuperscript{TM} prisms, Heraeus), and are covered by a thin cap layer to protect the highly reactive La-Y layer against oxidation and to catalyze the dissociation of \( \text{H}_2 \) molecules. For \( z>0.5 \) this cap layer consists of 15-nm Pd. For \( z<0.5 \) we use a composite \( \text{AlO}_x / \text{Pd} \) cap
layer, consisting of 1.5-nm AlO_x subsequently covered with 15-nm Pd. As shown by van Gogh et al.,\textsuperscript{15} simply covering La-rich films with 15-nm Pd does not prevent them from oxidation, because of the strong Pd diffusion into the underlying La layer. However, a 1.5-nm layer of AlO_x effectively prevents this process. The Pd layer remains necessary because AlO_x does not act as a catalyst for H_2 dissociation. In every evaporation run three identical samples are made: one is used for simultaneous x-ray diffraction (XRD) and resistivity measurements. The second sample is used for simultaneous optical and resistivity measurements. A third sample is used for composition and thickness measurements using Rutherford backscattering (RBS) and profilometry, respectively. These measurements have shown that z values have an accuracy of 2 at.%. Film thicknesses are accurate to 2%, and values obtained from RBS and profilometry agree within experimental accuracy. We found oxygen contaminations of a few at. %.

B. X-ray diffraction

X-ray diffraction on a series of La-Y alloys is done using a RIGAKU diffractometer. The sample is mounted in a gas cell with Be windows to enable \textit{in situ} hydrogenation. Data are collected every 0.04° over a 2θ angular range of 20°–70°, with integration times varying between 10 and 20 s. The incident angle θ is kept fixed at 10° to optimize the probed volume. In this way many Bragg reflections are measured, optimizing the structural information. For each sample we measure the as-deposited film, after which we apply 10^5 Pa of H_2 gas. Subsequently, a trihydride spectrum is measured. The film is then taken out of the system and is put in an oven for 1 h at 100°C to ensure desorption back to the dihydride state. The sample is mounted back in the gas cell and a dihydride spectrum is measured. To check reproducibility the film is again loaded to the trihydride phase, and a second trihydride spectrum is measured.

C. Optical properties and dc resistivity

The optical properties for the as-deposited metal films and the (metallic) dihydride are determined by ellipsometry and reflectance-transmittance (R-T) measurements. For ellipsometry, we use a rotating analyzer ellipsometer (VASE, J. A. Woollam Co., Inc.) that measures the ratio of the complex Fresnel reflection coefficients

\[ \frac{R_p}{R_s} = \tan \Psi \exp i\Delta \]  

in terms of the ellipsometric quantities Ψ(ω) and Δ(ω) in the spectral range 0.75≤hω≤4.5 eV. The subscripts refer to polarizations parallel (p) and perpendicular (s) to the plane of incidence. As the Pd cap layer is strongly absorbing, we measure the optical properties through the substrate. With flat substrates there are difficulties in inverting the measured data into the (complex) dielectric function ε(ω). The reason for this is that substrates are macroscopically thick (≈1 mm), so that the reflected light from the air/quartz interface is spatially separated at the detector position from the reflected light coming from the quartz/La_{1-x}Y_xH_z interface. To circumvent this problem we have used, as substrates, quartz glass prisms with a top angle of 40° (see Fig. 1). The angle of incidence is set at 70°, and the light from the air/quartz interface is no longer reflected directly in the direction of the detector. Another advantage is that because of the perpendicular angle of incidence at the air/quartz interfaces no polarization changes occur at these interfaces. In the numerical inversion of Ψ and Δ the substrate therefore acts as an ambient, and not as part of the multilayer stack. Both advantages make the method very accurate (≈5%) when the La_{1-x}Y_xH_z layer is metallic. A disadvantage is that Ψ and Δ cannot be measured under different angles. This makes the prism method less accurate for transparent samples.

As there are more than two interfaces, no analytical functions exist between Ψ(ω) and Δ(ω) and the unknown dielectric function ε(ω) of the La_{1-x}Y_xH_z layer. To obtain ε(ω) numerically we use the program WVASE (J. A. Woollam Co., Inc.), which takes as input the measured Ψ(ω) and Δ(ω), the thicknesses of the various layers of the stack and the dielectric functions of the substrate, the Pd layer, and the AlO_x layer. For optically thick films, e.g., 300-nm metallic
La$_{1-x}$Y$_x$H$_x$ films, ellipsometry is easier and more accurate than $R$-$T$ measurements. However, when the films become optically thin, e.g., 300-nm La$_{1-x}$Y$_x$H$_x$ films in their transparent state, the numerical inversion of $\Psi$ and $\Delta$ becomes less accurate and not unique. This is one of the reasons for performing $R$-$T$ measurements.

The prism is mounted in a teflon electrochemical cell consisting of a reservoir filled with 1-M KOH electrolyte solution, a Hg/HgO reference electrode (RfE), and a Pt counter electrode (CE) as sketched in Fig. 1(c). The La$_{1-x}$Y$_x$ film acts as a working electrode (WE), and is connected to the potentiostat via the four stripes indicated in Fig. 1(a). During electrochemical loading, the four wires are inter-connected for optimal homogeneous loading. The hydrogen concentration $x$ is varied potentiostatically using a Wenking POS 73 potentiostat. At time $t_1$ a current $i(t)$ is forced to flow between the WE and CE such that the potential $\Delta V$ between the RfE and the WE reaches a certain value. At the working electrode the following reaction takes place:

$$\text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- ,$$  \hspace{1cm} (2)

and subsequently the adsorbed hydrogen atom $\text{H}_\text{ad}$ is absorbed by the switchable mirror. The equivalent hydrogen pressure $p_{\text{H}_2}$ is related to $\Delta V$ by the Nernst equation

$$\ln p_{\text{H}_2} = -\frac{2F}{RT}(\Delta V + 0.926 \text{ V}) ,$$  \hspace{1cm} (3)

in which $R$ is the molar gas constant, $F$ the Faraday constant ($= 96485.309 \text{ C mol}^{-1}$), and $T$ is the temperature. Hence determining $\Delta V(x)$ is equivalent to measuring the pressure-composition ($p$-$x$) isotherm. After the system reaches diffusive equilibrium, typically after $\Delta t = 1800 \text{ s}$, the hydrogen concentration $x$ can be determined using

$$\Delta x = -\frac{V_m}{AdF} \int_{t}^{t_1} [i(t') - i_{\text{leak}}] dt' ,$$  \hspace{1cm} (4)

in which $V_m$ is the molar volume of the La-Y material under consideration, $A$ is the sample area, $d$ the film thickness, and $i_{\text{leak}}$ is the leak current.

Electrochemical loading is done while the cell is mounted on the ellipsometer. After the sample reaches equilibrium, a spectrum is measured. Subsequently the four contacts [see Fig. 1(a)] are re-connected to a resistivity $\rho$ measuring circuit. We use a Keithley 2000 multimeter equipped with a 2000-scan scanner card, with which the four wires can be connected quickly. Accurate $\rho$ values are obtained by using the van der Pauw method.\textsuperscript{16} The hydrogen loss during a resistivity measurement, which takes $\sim 1 \text{ s}$, is negligible. By repeating this procedure we obtain the optical constant $\rho$ as a function of $x$ and the pressure-composition ($p$-$x$) isotherm.

It turns out that the first loading is inhomogeneous, whereas subsequent loadings are homogeneous and reproducible. Therefore the fresh sample is always switched to a trihydride and back to a dihydride before actual measurements are done. Note that at room temperature the sample cannot be desorbed further than the dihydride.

For reflectance transmittance measurements we use flat substrates ($7.5 \times 10^3 \times 1 \text{ mm}^3$). After deposition electrical contacts are made using ultrasonic bonding of 30-$\mu$m-thick aluminum wires. Subsequently the film is mounted in a gas loading cell placed into a Bruker IFS 66/S Fourier-transform infrared spectrometer equipped with a reflection/transmission accessory. During H$_2$ gas loading at $\sim 10^3 \text{ Pa}$, transmittance and (near-normal-incidence) reflectance spectra are measured alternately ($0.72 \text{ eV} < h\omega < 3.5 \text{ eV}$), and at the same time the resistivity $\rho$ of the film is measured continuously using the van der Pauw method. The H$_2$ gas pressure is chosen low enough to ensure that the film is in quasiequilibrium during one $R$-$T$ measurement cycle, which takes about 30 s. After stabilization of the optical reflectance, transmittance and resistivity, the pressure is increased stepwise toward $10^5 \text{ Pa}$.

III. RESULTS AND DISCUSSION

\textbf{A. Metal-insulator transition in La$_{1-x}$Y$_x$H$_x$}

In Fig. 2 the evolution of the dc resistivity and the optical transmittance is shown after a hydrogen pressure of $\sim 10^4 \text{ Pa}$.
is applied at a time $t = 0$. Results are shown for LaH$_x$, YH$_x$ and La$_{0.52}$Y$_{0.48}$H$_x$. Note that a comparison of the $\rho(t)$ curve with $\rho(x)$, as measured by Kooij \textit{et al.},\textsuperscript{6} shows that $x$ increases roughly linearly with time.

The qualitative behavior of the three materials shown in Fig. 2 (and of all other alloys) is the same. In order to compare the curves, they are scaled to the switching time $\tau_i$ for the $i$th loading, defined as the time between the minimum resistivity $\rho_{\text{min}}$ near $x = 2$, and $\rho = \rho_{\text{min}} + 1/2(\rho_{\text{final}} - \rho_{\text{min}})$, with $\rho_{\text{final}}$ the saturation value. The switching times for the first loading are of the order of 100 s, and are discussed later. Initially $\rho$ rises because of impurity scattering by the added H atoms. This initial rise is observed for all alloys, although the rise in $\rho$ becomes smaller for smaller $z$. This is due to the fact that the $\alpha$-$\beta$ phase boundary occurs at lower $x$ for LaH$_x$ than for YH$_x$ (at $x = 0.01$ and 0.24, respectively).\textsuperscript{17} After a certain time a low-resistivity $\beta$-phase dihydride precipitates into the $\alpha$-phase matrix. This causes a continuous lowering of $\rho$.

When $x$ approaches 2, the resistivity is minimal. In a simple picture at $x = 2$ all tetrahedral positions (two per metal atom) are filled and all octahedral positions (one per metal atom) are empty. A minimum in resistivity is then expected, because of minimal disorder. However, in practice premature octahedral filling (i.e., filling of the octahedral positions for $x < 2$) can occur. In bulk LaH$_x$, it is observed\textsuperscript{18} to happen at $x = 1.95$. Weaver \textit{et al.}\textsuperscript{19} concluded from optical measurements and band-structure calculations that premature octahedral filling occurs in bulk YH$_x$ between $x = 1.7$ and 1.9. Inelastic neutron scattering,\textsuperscript{20} neutron powder diffraction,\textsuperscript{21} and nuclear magnetic resonance\textsuperscript{22} yielded octahedral fillings of 8–16% for bulk YH$_{2.0}$. These results are consistent with the minimum in resistivity at $x = 1.8$, observed by Kooij \textit{et al.}\textsuperscript{6} for polycrystalline YH$_x$ films.

The premature filling of the octahedral positions decreases gradually for lower $z$. The dihydride resistivities are 2–6 times smaller than the resistivity of the as-deposited films.

After the material has fully transformed into the $\beta$ phase, the resistivity increases steeply. In this region the transmittance of the film also increases strongly. Between $x = 2$ and 3 the film changes from a low-resistivity metal into a transparent insulator. As will be shown later, for $z > 0.81$ another structural phase transition takes place in this region, resulting in the $\gamma$ phase precipitating within the $\beta$-phase matrix. However, for $z < 0.67$ the same steep increase of $\rho$ and $T$ is observed, clearly indicating that the MI transition is not driven by a structural phase transition. We thus find that a similar MI transition occurs for all La$_{1-x}$Y$_x$ alloys, showing the robustness of the MI transition and its electronic (i.e., non-structural) origin.

In the following sections we report on a systematic study of the structural, optical, and electrical properties for $x = 0$, 2, and 3. Note that these integer values for $x$ are only used to indicate the as-deposited alloy films of La$_{1-x}$Y$_x$, and their dihydrides and trihydrides. In fact, we know from independent investigations that the as-deposited films contain $x$\textsuperscript{=0.16} hydrogen. The dihydrides have $x \approx 1.9$. The hydrides have a composition close to 2.9 under $10^5$ Pa of H$_2$ gas at room temperature.

\section{B. Structure of La$_{1-x}$Y$_x$H$_x$}

\subsection{1. Structure of as-deposited films}

Figure 3 shows XRD spectra for $x = 0$, 2, and 3 for three La$_{1-x}$Y$_x$H$_x$ alloys. Similar results were obtained for all other alloys.

The structure and the lattice parameters for the as-deposited films are listed in Table I, and shown in Fig. 4. To compare the $c$ axes we used reduced values for the dhcp and the Sm structured films: $c = c_{\text{dhcp}}/2$ and $c = 2c_{\text{Sm}}/9$.

The narrow peaks at 27°, 45°, 53°, and 56° for the La spectrum ($z = 0$) in Fig. 3(a) are precipitations of LaH$_2$. The broad peak at 33.6° corresponds to fcc-La, that is known\textsuperscript{21} to form at a rather low temperature of 583 K. It might be formed during deposition due to sample heating by radiation from the metal sources.

Figure 3(a) shows five peaks between 25° and 35° for the La$_{0.48}$Y$_{0.52}$ alloy, which is characteristic of the Sm structure (hcp and dhcp give three and four peaks, respectively). However, the peak at 54.23° is characteristic of hcp material. We
TABLE I. Structural properties of La$_{1-z}$Y$_z$. Values for the c axis are reduced values, i.e., for hcp $c = c_{hcp}$, for dhcp $c = c_{dhcp}/2$, and for Sm $c = 2c_{Sm}$. The molar volume $V_m$ is per mole of metal atoms.

<table>
<thead>
<tr>
<th>$z$</th>
<th>Structure</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V_m$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>dhcp</td>
<td>3.769</td>
<td>6.102</td>
<td>22.60</td>
</tr>
<tr>
<td>0.15</td>
<td>dhcp</td>
<td>3.714</td>
<td>6.068</td>
<td>21.82</td>
</tr>
<tr>
<td>0.21</td>
<td>dhcp</td>
<td>3.697</td>
<td>6.059</td>
<td>21.59</td>
</tr>
<tr>
<td>0.30</td>
<td>dhcp</td>
<td>3.698</td>
<td>5.992</td>
<td>21.37</td>
</tr>
<tr>
<td>0.46</td>
<td>Sm</td>
<td>3.686</td>
<td>5.911</td>
<td>20.94</td>
</tr>
<tr>
<td>0.52</td>
<td>hcp+Sm</td>
<td>3.690</td>
<td>5.933</td>
<td>20.70</td>
</tr>
<tr>
<td>0.67</td>
<td>hcp</td>
<td>3.689</td>
<td>5.850</td>
<td>20.76</td>
</tr>
<tr>
<td>0.86</td>
<td>hcp</td>
<td>3.678</td>
<td>5.793</td>
<td>20.44</td>
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<tr>
<td>1</td>
<td>hcp</td>
<td>3.648</td>
<td>5.732</td>
<td>19.89</td>
</tr>
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</table>

thus conclude that the La$_{0.48}$Y$_{0.52}$ alloy is in a Sm-hcp mixed phase.

The values given in Table I have been corrected for H incorporation during evaporation, caused by rest H$_2$ gas in the molecular-beam-epitaxy system partly coming from the release of H$_2$ due to heating of the Y and La targets during film deposition. By making a linear fit to literature values of $a$ and $c$ for $\alpha$-$YH_x$, with $x$ between 0 and 0.22, we find $a(x) = 3.6482 + 2$ for $x < 0.073$, and $a(x) = 5.7318 + 2$ for $x > 0.073$. Using these factors the experimental La values also correspond to the literature values, justifies the correction method.

Note that the experimental values for Y are within 2% of those obtained from total energy calculations for hcp-Y: $a = 3.58$ Å and $c = 5.73$ Å. To our knowledge values for La were never calculated, one reason being the complexity of including f electrons in the calculations.

As far as the lattice parameters are concerned, the as-deposited thin films behave like their bulk counterparts. However, the phase boundaries (see Fig. 4) of the Sm-phase have shifted 0.065 to lower $z$ values compared to the boundaries proposed by Gschneidner et al. Such differences are also found among bulk data sets and are therefore probably not significant.

In RE metals and RE binary alloys a strong correlation exists between the $c/a$ ratio and the observed lattice structure. $c/a < 1.6$ for dhcp, and $1.6 < c/a < 1.606$ for Sm, and $1.606 < c/a < 1.633$ for dhcp. It turns out that for $z > 0.46$ the experimental lattice structures for the as-deposited films correspond well with those expected from the measured $c/a$ ratios. Although the ratio is large for the $z = 0.52$ alloy, it falls within the scatter of the bulk values. The dhcp alloys ($0.15 < z < 0.30$) have $c/a$ ratios that are significantly larger than their bulk counterparts, with a maximum value of 1.639 for $z = 0.21$. Figure 4 shows that the large $c/a$ ratio is mainly due to compressed $a$ axes, and to a lesser extent to expanded $c$ axes for $0.15 < z < 0.30$. This points to a clamping effect. All films show a preferred orientation with their $c$ axes perpendicular to the substrate. Tensile strains within the hexagonal planes, due to substrate clamping, result in a decrease of $a$ and consequently in an increase of $c$.

2. Structure of dihydride films

Table II shows that all dihydrides have the fcc lattice structure. The fcc structure differs from the hexagonal structures dhcp, dhcp and Sm only in the stacking of hexagonal planes: $ABCABC \ldots$ for fcc, $ABABA \ldots$ for dhcp, $ABACA \ldots$ for dhcp, and $ABABCBACA \ldots$ for Sm. Therefore, we can compare the lattice parameters for the dihydride films with those for $x = 0$ and $x = 3$, by defining $a = a_{fcc}/\sqrt{2}$ and $c = 2a_{fcc}/\sqrt{3}$. Figure 4 shows that, for $x = 2$, the alloys fulfill Vegard’s law, that is, the lattice parameters shift linearly between the LaH$_3$ and YH$_2$ values. The volume expansion is about 23% for $z = 0$ and 7% for $z = 1$ (see Fig. 5). Note that the measured lattice parameters for YH$_2$ agree with theoretical values better than for Y, probably because the electrons that are present in Y, give relatively large exchange correlation effects that are not properly included in local-
TABLE II. Structural properties of La$_{1-x}$YH$_2$. To compare the fcc lattice parameters with those for the hexagonal structures, we defined $a = a_{\text{hhc}}/\sqrt{2}$ and $c = 2a_{\text{hhc}}/\sqrt{3}$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Structure</th>
<th>$a_{\text{hhc}}$ (Å)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V_m$ (cm$^3$/mol)</th>
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<tr>
<td>0</td>
<td>fcc</td>
<td>5.694</td>
<td>4.026</td>
<td>6.575</td>
<td>27.79</td>
</tr>
<tr>
<td>0.15</td>
<td>fcc</td>
<td>5.648</td>
<td>3.994</td>
<td>6.522</td>
<td>27.13</td>
</tr>
<tr>
<td>0.21</td>
<td>fcc</td>
<td>5.614</td>
<td>3.970</td>
<td>6.482</td>
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</tr>
<tr>
<td>0.30</td>
<td>fcc</td>
<td>5.573</td>
<td>3.941</td>
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<td>26.06</td>
</tr>
<tr>
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<td>3.886</td>
<td>6.345</td>
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<tr>
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<td>3.868</td>
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</tr>
<tr>
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<td>3.804</td>
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<td>23.44</td>
</tr>
<tr>
<td>0.86</td>
<td>fcc</td>
<td>5.273</td>
<td>3.729</td>
<td>6.089</td>
<td>22.07</td>
</tr>
</tbody>
</table>

3. Structure of trihydride films

XRD results for $x \approx 3$ are summarized in Table III. Figure 4 shows that the trihydrides fulfill Vegard’s law within the fcc phase. For $x > 0.86$ we have too few points to conclude on this matter.

For $x > 0.86$ the films undergo a large uniaxial $c$-axis expansion of $9.7 \pm 0.2\%$ when $x$ changes from 2 to 3, which causes the extraordinary large $c/a$ ratio for $z \approx 0.86$ and $x = 3$. This strong uniaxial expansion causes large hysteresis effects in the optical, electrical, and structural properties between the dihydride and trihydride.

The large uniaxial expansion can be understood qualitatively as follows. In the ideal hcp structure, two H atoms per Y atom occupy the tetrahedral interstitial sites (H$_{\text{tet}}$) and one H atom the octahedral site (H$_{\text{oct}}$). However, neutron-diffraction experiments on powder samples 27 and thin epitaxial films 32 showed that YH$_3$ has a HoD$_3$ structure, in which the H$_{\text{oct}}$ atoms have shifted to positions in and close to the Y metal planes. Various total-energy calculations confirm that a shift of H$_{\text{oct}}$ indeed lowers the total energy significantly. 32–34 Dekker et al. calculated a strongly increased electronic charge density for the HoD$_3$ structure in the plane containing the Y and H atoms compared to hcp. 32 Wang and Chou found additionally that the energy lowering by the H$_{\text{oct}}$ displacement primarily comes from electron-ion interaction energy. 34 One thus can look at this as if the H$_{\text{oct}}$ atoms are bound to the metal plane Y atoms forming a covalent binding, which explains the small (0.9%) $a$-axis expansion going from YH$_2$ to YH$_3$ (see Tables II and III). A strong repulsive interaction between nearest-neighbor H$_{\text{oct}}$ pairs exists. In (hypothetical) hcp-YH$_3$ this repulsion is partially compensated for by the H atoms at the ideal octahedral positions, but in the HoD$_3$ structure this does not occur and there is a large $c$-axis expansion. 34

For $0.38 < z < 0.67$ the volume expansion is smaller than 4%, and for $z < 0.38$ the lattice even contracts. This lattice contraction is caused by the interaction in the fcc structure between the RE metal $d$ electron and the $s$ electron of the octahedral H atom. 24 The measured lattice parameters for YH$_3$ agree within 1% with theoretical values 34 $a = 3.678$ Å and $c = 6.549$ Å.

Using the Scherrer equation 35 we determined the x-ray coherence length $l_{\text{coh}}$ from the peak widths. We found $l_{\text{coh}} \approx 10$ nm, and that subsequent switching improves $l_{\text{coh}}$.

Although the Pd layer is only 15 nm thick, we observe in Fig. 3 the Pd (111) and (200) reflections at 20 = 40.12° and 46.66°, respectively [see Figs. 3(a) and 3(b)]. We determine for fcc Pd $a = 3.893 \pm 0.004$ Å , in agreement with the literature value $33, 34$ $a = 3.890$ Å . The Pd peaks have shifted to 38.55° and 44.81° in Fig. 3(c), because of H absorption by the Pd, and we find $a = 4.045 \pm 0.004$ Å . Comparing this with bulk

FIG. 5. Molar volume of La$_{1-x}$Y$_x$ as a function of $z$. The as-deposited films show no significant deviations from values obtained for bulk material. Solid vertical lines indicate the phase boundaries for the different structural phases. Dashed vertical lines indicate mixed-phase regions. Open symbols indicate literature values (Refs. 14, 27, 28).

TABLE III. Structural properties for La$_{1-x}$Y$_x$H$_2$. For the definitions of $a_{\text{fcc}}$, $a$, $c$, and $V_m$ see Tables I and II.

<table>
<thead>
<tr>
<th>$z$</th>
<th>Structure</th>
<th>$a_{\text{fcc}}$ (Å)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V_m$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>fcc</td>
<td>5.616</td>
<td>3.971</td>
<td>6.485</td>
<td>26.67</td>
</tr>
<tr>
<td>0.15</td>
<td>fcc</td>
<td>5.593</td>
<td>3.955</td>
<td>6.458</td>
<td>26.34</td>
</tr>
<tr>
<td>0.21</td>
<td>fcc</td>
<td>5.578</td>
<td>3.944</td>
<td>6.441</td>
<td>26.13</td>
</tr>
<tr>
<td>0.30</td>
<td>fcc</td>
<td>5.552</td>
<td>3.926</td>
<td>6.411</td>
<td>25.77</td>
</tr>
<tr>
<td>0.46</td>
<td>fcc</td>
<td>5.506</td>
<td>3.894</td>
<td>6.358</td>
<td>25.13</td>
</tr>
<tr>
<td>0.52</td>
<td>fcc</td>
<td>5.485</td>
<td>3.878</td>
<td>6.334</td>
<td>24.84</td>
</tr>
<tr>
<td>0.67</td>
<td>fcc</td>
<td>5.441</td>
<td>3.847</td>
<td>6.283</td>
<td>24.25</td>
</tr>
<tr>
<td>0.86</td>
<td>hex</td>
<td>3.760</td>
<td>6.670</td>
<td>24.59</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>hex</td>
<td>3.713</td>
<td>6.612</td>
<td>23.77</td>
<td></td>
</tr>
</tbody>
</table>
values for the PdH system gives \( x = 0.7 \), as expected for a hydrogen pressure of \( 10^5 \) Pa at room temperature.

By combining our results combined with those from literature we construct the schematic phase diagram for the \( \text{La}_{1-z} \text{Y}_z \) system, as shown in Fig. 6. From XRD we conclude that the fcc-hcp phase boundary for \( x = 3 \) lies at \( z \approx 0.86 \). However, the \( z \) dependence of the optical gap (see Sec. III E) suggests that this phase boundary is at \( z \approx 0.81 \).

In conclusion, thin polycrystalline \( \text{La}_{1-z} \text{Y}_z \) alloys on quartz are \( c \)-axis oriented, and behave as the corresponding bulk alloys for \( x = 0 \). No disproportionation takes place in the \( \text{La}_{1-z} \text{Y}_z \) system upon loading with hydrogen, and the preferential orientation is enhanced after the first loading. The latter two conclusions were confirmed by the dc resistivity measurements and the optical properties that are discussed below. Whereas all dihydrides are fcc, the trihydrides show a phase transition: for \( z < 0.67 \) the films are fcc and for \( z > 0.81 \) the films are hexagonal. The hexagonal trihydrides have an anomalously large \( c/a \) ratio, indicating another structure than hcp.

C. Pressure-composition isotherms

The pressure-composition \((p-x)\) isotherms as obtained from electrochemical H loading [see Eq. (4)] are shown in Fig. 7 for three alloys. Both \( \text{La} \) and \( \text{La}_{0.45} \text{Y}_{0.55} \) are essentially hysteresis free, in agreement with optical measurements. The \( \text{YH}_x \) isotherm exhibits large hysteresis, as discussed extensively by Kooij et al. The latter isotherm shows a coexistence region during desorption, whereas the \( \text{La} \)-rich alloys exhibit no plateau, in agreement with XRD measurements. The shape of their isotherms indicates that these alloys remain fcc at all concentrations above \( x = 2 \). There is no subplateau, related to the tetragonal phase that exists in bulk \( \text{LaH}_x \) at low temperatures.

In Eq. (5) the hydrogen pressure \( p \) is in bar, \( x_u-x_1 \) is the number of interstitial sites per metal atom, \( E_b \) is the \( \text{H}_2 \) binding energy \((-4.46 \text{ eV})\), \( E_0 \) is the hydrogen energy, and \( E_{\text{HH}} \) is the H-H interaction energy. The term \( c(T) = \frac{1}{2} \ln T - 7.051 \) is material independent, and is equal to 12.85 for \( T = 295 \) K. The results from the fits are given in Table IV.

The desorption \( \Delta H \) values for \( \text{LaH}_x \) and \( \text{YH}_x \) agree within experimental accuracy with those for bulk material. The small \( E_{\text{HH}} \) values obtained for \( \text{YH}_x \) and \( \text{LaH}_x \) are consistent with the small lattice expansion during hydrogenation between \( x = 2 \) and 3. The relatively large and positive \( E_{\text{HH}} \)
TABLE IV. Results of the fits of the isotherms in Fig. 7 to Lacher’s equation [Eq. (5)] and the partial molar heat of solution calculated from Eq. (6).

<table>
<thead>
<tr>
<th>z</th>
<th>$x_1$</th>
<th>$x_u$</th>
<th>$E_0$ (eV)</th>
<th>$E_{\text{HH}}$ (eV)</th>
<th>$\Delta H$</th>
<th>$\Delta H_{\text{liq}}$ (Ref. 38) (kJ/mole H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.10</td>
<td>2.79</td>
<td>-2.64</td>
<td>0.05</td>
<td>-37.1</td>
<td>-42.0</td>
</tr>
<tr>
<td></td>
<td>0.46</td>
<td>1.98</td>
<td>2.90</td>
<td>-2.75</td>
<td>0.25</td>
<td>-38.1</td>
</tr>
<tr>
<td>1 (des)</td>
<td>1.97</td>
<td>2.71</td>
<td>-2.61</td>
<td>-0.10</td>
<td>-41.5</td>
<td>-44.9</td>
</tr>
<tr>
<td>1 (abs)</td>
<td>1.96</td>
<td>2.70</td>
<td>-2.54</td>
<td>-0.04</td>
<td>-31.8</td>
<td></td>
</tr>
</tbody>
</table>

for the alloy is, however, a clear indication of the existence of a wide distribution of site energies.39,40

D. Resistivity

1. dc resistivity for $x = 0$ and 2

The $z$ dependence of the dc resistivity $\rho$ is given in Fig. 8 for the as-deposited La$_{1-x}$Y$_z$ films and the dihydrides La$_{1-x}$Y$_z$H$_z$. Open symbols are calculated from optical data (see below).

For both $x = 0$ and 2 we observe a clear nonlinear behavior, which is well described by

$$\rho(z) = [\rho_{\text{La}} + (\rho_Y - \rho_{\text{La}})z] + 4\rho_{\text{do}}x(z - 1),$$

(7)

with $\rho_Y$ and $\rho_{\text{La}}$ fixed. The constant $\rho_{\text{do}}$ represents the effect of disorder scattering and is of the same order of magnitude

![FIG. 8. Composition dependence of the dc resistivity of La$_{1-x}$Y$_z$H$_z$ (solid symbols). Small circles denote dc values of bulk La and Y (Ref. 23), and small squares of bulk LaH$_z$ and YH$_z$ (Ref. 17). Values calculated from optical measurements and Eq. (8) are indicated by open symbols. Solid lines are least-squares fits using Eq. (7). The large resistivity for as-deposited La$_{0.48}$Y$_{0.52}$ alloy is consistent with the fact that this film is in a Sm-hcp coexistence region (see Table I).](image)

TABLE V. Drude Lorentz parameters for the as-deposited La$_{1-x}$Y$_z$ films. All parameters are in eV except $\varepsilon_{\text{m}}$ and $\chi^2$, which are dimensionless. In this work $\chi^2$ is defined as the least-squares sum divided by two times the degrees of freedom.

<table>
<thead>
<tr>
<th>$z$</th>
<th>$\varepsilon_{\text{m}}$</th>
<th>$\omega_p$</th>
<th>$1/\tau$</th>
<th>$\sqrt{f_1}$</th>
<th>$\omega_{01}$</th>
<th>$\beta_1$</th>
<th>$\sqrt{f_2}$</th>
<th>$\omega_{02}$</th>
<th>$\beta_2$</th>
<th>$\sqrt{f_3}$</th>
<th>$\omega_{03}$</th>
<th>$\beta_3$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.461</td>
<td>5.588</td>
<td>0.284</td>
<td>8.065</td>
<td>2.476</td>
<td>3.450</td>
<td>6.299</td>
<td>0.908</td>
<td>1.315</td>
<td>3.675</td>
<td>4.554</td>
<td>2.052</td>
<td>0.057</td>
</tr>
<tr>
<td>0.25</td>
<td>0.117</td>
<td>5.693</td>
<td>0.467</td>
<td>11.216</td>
<td>1.756</td>
<td>4.383</td>
<td>2.193</td>
<td>0.925</td>
<td>0.872</td>
<td>2.784</td>
<td>4.623</td>
<td>1.594</td>
<td>0.050</td>
</tr>
<tr>
<td>0.46</td>
<td>0.46</td>
<td>4.770</td>
<td>0.397</td>
<td>6.334</td>
<td>2.518</td>
<td>3.563</td>
<td>6.559</td>
<td>0.990</td>
<td>1.352</td>
<td>3.441</td>
<td>4.920</td>
<td>1.813</td>
<td>0.049</td>
</tr>
<tr>
<td>0.60</td>
<td>0.151</td>
<td>4.412</td>
<td>0.347</td>
<td>1.294</td>
<td>1.747</td>
<td>1.157</td>
<td>9.836</td>
<td>1.325</td>
<td>1.431</td>
<td>5.016</td>
<td>5.307</td>
<td>3.161</td>
<td>0.033</td>
</tr>
<tr>
<td>0.81</td>
<td>0.243</td>
<td>3.720</td>
<td>0.246</td>
<td>3.259</td>
<td>1.817</td>
<td>1.520</td>
<td>8.477</td>
<td>1.431</td>
<td>1.342</td>
<td>6.471</td>
<td>5.099</td>
<td>3.320</td>
<td>0.053</td>
</tr>
<tr>
<td>1</td>
<td>0.182</td>
<td>3.430</td>
<td>0.142</td>
<td>4.090</td>
<td>1.876</td>
<td>1.556</td>
<td>7.248</td>
<td>1.342</td>
<td>1.365</td>
<td>7.389</td>
<td>5.658</td>
<td>3.869</td>
<td>0.065</td>
</tr>
</tbody>
</table>

as the resistivities of the parent metals (50±10 $\mu\Omega$ cm and 45±8 $\mu\Omega$ cm for $x = 0$ and 2, respectively), indicating that conduction-electron scattering by impurities dominates electron-electron scattering and electron-phonon scattering. Two other observations validate this conclusion: (i) optical analyses (see Tables V and VI) gave relaxation times $\tau \sim 10^{-14}$ s, which means that electrons are scattered by phonons and/or impurities, but that electron-electron scattering is not important. (ii) The temperature dependence of the free-electron optical response showed a 20–30% increase of $\tau$ upon cooling from 300 to 4.2 K, indicating that defect

TABLE VI. Drude Lorentz parameters for La$_{1-x}$Y$_z$H$_z$ with $x = 2$. All parameters are in eV except $\varepsilon_{\text{m}}$ and $\chi^2$, which are dimensionless.

<table>
<thead>
<tr>
<th>$z$</th>
<th>$\varepsilon_{\text{m}}$</th>
<th>$\omega_p$</th>
<th>$1/\tau$</th>
<th>$\sqrt{f_1}$</th>
<th>$\omega_{01}$</th>
<th>$\beta_1$</th>
<th>$\sqrt{f_2}$</th>
<th>$\omega_{02}$</th>
<th>$\beta_2$</th>
<th>$\sqrt{f_3}$</th>
<th>$\omega_{03}$</th>
<th>$\beta_3$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.460</td>
<td>3.883</td>
<td>0.179</td>
<td>1.497</td>
<td>2.037</td>
<td>0.544</td>
<td>3.641</td>
<td>2.037</td>
<td>0.544</td>
<td>7.335</td>
<td>5.072</td>
<td>2.193</td>
<td>0.129</td>
</tr>
<tr>
<td>0.25</td>
<td>0.575</td>
<td>4.097</td>
<td>0.247</td>
<td>1.765</td>
<td>2.074</td>
<td>0.641</td>
<td>3.946</td>
<td>2.074</td>
<td>0.641</td>
<td>9.341</td>
<td>5.158</td>
<td>2.312</td>
<td>0.130</td>
</tr>
<tr>
<td>0.46</td>
<td>0.802</td>
<td>4.180</td>
<td>0.271</td>
<td>1.831</td>
<td>2.129</td>
<td>0.629</td>
<td>3.914</td>
<td>2.129</td>
<td>0.629</td>
<td>9.283</td>
<td>5.196</td>
<td>2.261</td>
<td>0.145</td>
</tr>
<tr>
<td>0.60</td>
<td>0.735</td>
<td>4.260</td>
<td>0.223</td>
<td>1.873</td>
<td>2.195</td>
<td>0.602</td>
<td>4.011</td>
<td>2.195</td>
<td>0.602</td>
<td>9.383</td>
<td>5.265</td>
<td>2.243</td>
<td>0.170</td>
</tr>
<tr>
<td>0.81</td>
<td>1.407</td>
<td>4.275</td>
<td>0.203</td>
<td>1.935</td>
<td>2.313</td>
<td>0.566</td>
<td>4.011</td>
<td>2.313</td>
<td>0.566</td>
<td>7.864</td>
<td>5.116</td>
<td>2.052</td>
<td>0.238</td>
</tr>
<tr>
<td>1</td>
<td>2.198</td>
<td>4.454</td>
<td>0.142</td>
<td>2.001</td>
<td>2.410</td>
<td>0.558</td>
<td>4.039</td>
<td>2.410</td>
<td>0.558</td>
<td>7.633</td>
<td>5.272</td>
<td>2.514</td>
<td>0.242</td>
</tr>
</tbody>
</table>
scattering is comparable, though stronger than phonon scattering. The latter observation is consistent with the temperature dependence of \( \rho \) of 180 nm Y and YH\(_2\) measured by Curzon and Singh.\(^{41}\)

Note that the parabolic behavior is an indication of the high quality of our alloy films; oxidation, concentration inhomogeneities, and thickness variations readily blur disorder effects, causing much scatter in the measured values of \( \rho \).

To obtain the electron mean free path \( l_{\text{mfp}} = v_F \tau \), the Fermi velocity \( v_F \) is estimated using \( v_F = \sqrt{2m \nu_F} \) with \( \nu_F = 7.9 \times 10^3 \text{ms}^{-1} \). For Y we expect larger values because of broader conduction bands. From the band structure calculations for Y of Altmann \( et \) al., we find the largest Fermi velocity along [52x494]\( \nu_F \). From the band structure calculations for Y of Altmann \( et \) al., we find \( v_F = 9.9 \times 10^3 \text{ms}^{-1} \) along \( \Gamma \text{M} \). With \( \tau = 2.32 \times 10^{-15} \text{s} \) for La and \( \tau = 4.64 \times 10^{-15} \text{s} \) for Y (see Table V) we find \( l_{\text{mfp}} = 1.8 \text{nm} \) (= 4.9a) for La and \( l_{\text{mfp}} = 4.6 \text{nm} \) (= 13a) for Y.

For LaH\(_2\) the calculations of Ng \( et \) al.\(^7\) lead to \( v_F = 13.3 \times 10^3 \text{ms}^{-1} \) along \( \Gamma \text{X} \) (see also Fig. 22). From the calculations for YH\(_2\) of Peterson \( et \) al.\(^{44}\) \( v_F = 9.6 \times 10^5 \text{ms}^{-1} \) along \( \Gamma \text{X} \). With \( \tau = 3.68 \times 10^{-15} \text{s} \) for LaH\(_2\) and \( \tau = 4.64 \times 10^{-15} \text{s} \) for YH\(_2\) (see Table VI) we obtain \( l_{\text{mfp}} = 4.9 \text{nm} \) (= 8.6a\(_{\text{fcc}}\)) for LaH\(_2\) and \( l_{\text{mfp}} = 4.5 \text{nm} \) (= 8.6a\(_{\text{bcc}}\)) for YH\(_2\).

Thus, both for the as-deposited films and the dihydrides \( l_{\text{mfp}} \approx 10 \) lattice spacings. This, together with the earlier conclusion that \( \rho \) is dominated by impurity scattering, implies that disorder is present on atomic length scales, i.e., Y and La atoms are mixed on an atomic length scale. That this holds both for \( x = 0 \) and 2 is a further indication that the alloys are solid solutions and do not disproportionate upon hydrogenation.

The measured dc values for \( x = 0 \) are larger than the literature values (see Fig. 8). Because at room temperature \( l_{\text{mfp}} \ll d \), with \( d \) the film thickness, the discrepancy cannot be a thin-film effect. We also rule out the presence of oxides in the film as a possible cause, because then the discrepancy should be larger for La, which is much more sensitive to oxidation. However, we did not observe this.

The thickness dependence of \( \rho \) for Y was studied by Curzon and Singh\(^{41}\) for 20\(\leq d \leq 200 \) nm. They attributed the strong \( \rho \) increase for \( d < 90 \) nm to oxide contamination. For \( d > 90 \) nm oxide contamination no longer plays a role, as we already concluded above, and upon increasing \( d \) the resistivity decreases asymptotically to \( \rho \approx 120 \mu \Omega \text{cm} \). This value is comparable to 144.9 \( \mu \Omega \text{cm} \) found in this work. The fact that \( \rho \) does not decrease asymptotically to the bulk value means that surface effects are not important. Such effects are in general observed when \( l_{\text{mfp}} \ll d \), thus the measurements of Curzon and Singh imply that \( l_{\text{mfp}} \approx 90 \) nm that is consistent with \( l_{\text{mfp}} \approx 10 \) nm given above. Curzon and Singh attributed the discrepancy between bulk and thin films values above 90 nm to lattice defects; if films are well annealed, \( \rho \) turns out to decrease asymptotically to the bulk value.

A similar discrepancy exists between thin film and bulk values for the dihydride resistivities. Our value for YH\(_2\) agrees perfectly with the 23 \( \mu \Omega \text{cm} \) found by Curzon and Singh for a 180-nm YH\(_2\) film.\(^{41}\) We conclude that defect scattering accounts for the discrepancies for both \( x = 0 \) and 2.

So far we have only discussed data obtained from resistivity measurements. Values for \( \rho \) can also be derived from optical measurements (described in Sec. II E) by means of the Drude equation

\[
\rho_{\text{opt}} = \frac{1}{\varepsilon_0 \omega \tau},
\]

with \( \omega_0 \) the vacuum permittivity, \( \omega_0 \) the plasma frequency and \( \tau \) the electron relaxation time. Values for \( \rho_{\text{opt}} \) obtained from the parameters given in Tables V and VI are shown in Fig. 8. Although there is a difference in absolute values, \( \rho \) and \( \rho_{\text{opt}} \) exhibit the same trends, that is (i) the values for the dihydrides are smaller. For the La rich alloys this is not true for \( \rho_{\text{opt}} \), but, because the difference in resistivities for \( x = 0 \) and \( x = 2 \) are much smaller than for Y-rich alloys, we attribute this to the fact that \( \omega \tau \approx 1 \), which means that intrinsic differences between \( \rho \) and \( \rho_{\text{opt}} \) may occur.\(^{35}\) The low resistivities for YH\(_2\) and LaH\(_2\) are due to the larger \( v_F \) for \( x = 2 \) compared to \( x = 0 \). Tables V and VI show that it is a combined effect of larger values of \( \omega_0 \) and \( \tau \). (ii) The effect of disorder is reflected in both \( \rho_{\text{dc}} \) and \( \rho_{\text{opt}} \). For \( x = 0 \) we find \( \rho_{\text{dc}} = 52.5 \pm 7.5 \) and 50.0 \( \pm 1.0 \) \( \mu \Omega \text{cm} \) for \( \rho_{\text{opt}} \) and \( \rho_{\text{dc}} \), respectively. For \( x = 2 \) we find \( \rho_{\text{dc}} = 40.0 \pm 7.5 \) and 45.0 \( \pm 7.5 \) \( \mu \Omega \text{cm} \) for \( \rho_{\text{opt}} \) and \( \rho_{\text{dc}} \), respectively. The effect of disorder is thus the same both at \( \omega = 0 \) and optical frequencies \( \omega \approx 10^{16} \text{s}^{-1} \).

In summary, for both \( x = 0 \) and 2 the effect of disorder is of the same order of magnitude as the resistivity of the parent materials. Electron scattering is determined by defect scattering and \( l_{\text{mfp}} \approx 10 \) lattice spacings, which indicates microscopic mixing and no disproportionation. The scattering mechanisms are the same at optical frequencies as for the dc case.

2. dc resistivity for \( 2 < x < 3 \)

Figure 9 shows the concentration dependence of the resistivity together with its time derivative during the second hydrogenation from the dihydride to the trihydride. The behavior is representative for subsequent loading cycles. The final resistivities are of the order of 1 m\( \Omega \) cm. These low values are caused by shunting of the active layer by the metallic Pd cap layer when the resistivity of the La\(_{1-x}\)Y\(_x\)H\(_2\) becomes very large. One can correct for the Pd layer by treating the La\(_{1-x}\)Y\(_x\)H\(_2\) and Pd layer as two parallel resistors with resistance \( R \) and \( R_{\text{Pd}} \), respectively. The measured resistance is then \( R_{\text{tot}} = R_{\text{Pd}} R/(R_{\text{Pd}} + R) \) and the corrected resistivity

\[
\rho_{\text{cor}} = \frac{\rho_{\text{PdH}} d}{\rho_{\text{PdH}} d_{\text{tot}} - \rho d_{\text{PdH}}},
\]

with \( d_{\text{tot}} \) the sum of the thickness \( d_{\text{PdH}} \) of the cap layer and the thickness \( d \) of the active layer. With \( \rho_{\text{PdH}} = 0.1 \) m\( \Omega \) cm, we find for all alloys \( \rho \approx 100 \) m\( \Omega \) cm, which is three orders of magnitude larger than for \( x = 0 \).
We have used the above result to scale the switching times to values expected for 1000-mbar H\textsubscript{2}. In this way we are able to compare the switching times. No significant \(z\)-dependence of the switching times is observed. For the first loading we find \(\tau_1 = 20 \pm 13\) s. During the second loading the films switch roughly five times faster than for the first loading, and we find \(\tau_2 = 4.0 \pm 1.8\) s, in agreement with values of van der Molen \textit{et al.}\textsuperscript{47}. Subsequent loadings behave like the second loading. The ‘‘virgin’’ effects are likely to be caused by the irreversible \(\alpha\)-\(\beta\) transition that occurs for all films during the first loading, in which the films transform from an hexagonal structure (hcp, dhcp, or Sm) into an fcc structure.

Another virgin effect is caused by the Pd cap layer. During the first loading the wetting of the cap layer is improved by the large heat of formation of the (RH)\textsubscript{2} and the PdH\textsubscript{x}. A better wetting causes the film to be faster during subsequent loadings. This is consistent with our observation that the resistivity of the trihydride is significantly lower after the second loading for films covered with only 5 nm Pd. During the first loading the initial Pd islands transform into a closed layer that shunts efficiently the highly resistive trihydride.

From this section we conclude that switching times decrease with a factor 5 after the first loading. Intrinsic resistivities of trihydrides (i.e., corrected for the Pd cap layer) are \(\sim 100\) m\(\Omega\) cm. Hydrogenation in three stages is observed for LaH\textsubscript{x} for \(2<x<3\), whereas all other films exhibit a two-stage hydrogenation. The stages might be due to ordering of H vacancies.

### E. Optical properties

#### 1. Optical properties for \(x=0\)

Even more remarkable than the electric properties are the optical properties of switchable mirrors, since their MI transition is accompanied by dramatic changes in the reflectance and transmittance in the visible part of the spectrum. In this section we present what we believe is the first detailed investigation of the dielectric function \(\varepsilon(\omega)\) of La\textsubscript{1-x}Y\textsubscript{x}H\textsubscript{3}. The dielectric function \(\varepsilon(\omega)\) of the as-deposited La\textsubscript{1-x}Y\textsubscript{x} alloys, obtained from ellipsometry after correction for the substrate and the Pd layer, is shown in Fig. 10. Few data for either Y or La exist in the literature. One reason for this is their sensitivity to oxidation, which can severely affect the reflectivity. However, accurate measurements on single crystalline bulk samples of Y over a wide range of energy and temperature were done by Weaver and co-workers\textsuperscript{48,49} who measured reflectivity with the electric field vector perpendicular (\(\perp\)) and parallel (\(\parallel\)) to the \(c\) axis, and determined \(\varepsilon(\omega)\) by a Kramers-Kronig analysis. Below 4 eV a strong anisotropy is observed. For polycrystalline samples \(\varepsilon_{\text{polys}}(\omega) = \frac{1}{2}\varepsilon_{\parallel}(\omega) + \frac{1}{2}\varepsilon_{\perp}(\omega)\) would be expected. However, our \(\varepsilon(\omega)\) is similar to \(\varepsilon_{\perp}(\omega)\) of Weaver and co-workers. We do not see any contribution of \(\varepsilon_{\parallel}(\omega)\), which should be readily visible due to the large difference between \(\varepsilon_{\parallel}(\omega)\) and \(\varepsilon_{\perp}(\omega)\) for energies below 4.5 eV. We therefore conclude that, although polycrystalline, our films are preferentially oriented with the \(c\) axis perpendicular to the substrate. This is consistent with the XRD measurements (see Sec. III B).

---

**FIG. 9.** Time dependence of the resistivity of six La\textsubscript{1-x}Y\textsubscript{x}H\textsubscript{3} alloys during the second absorption from the dihydride to the trihydride. To compare the curves, the time was scaled by the switching time \(\tau_2\) as defined in Sec. III A. The time derivative clearly exhibits various loading stages. In (d) the hydrogen pressure was increased at \(t' = 1.6\) and 1.8, causing peaks in the time-derivative of \(\rho\).

The time derivatives in Fig. 9 indicate several reproducible stages during hydrogen absorption. All films, except LaH\textsubscript{x}, exhibit a two-stage absorption. After an initial steep increase of \(\rho\) a tendency to saturation occurs near \(t' \approx 0.5\), after which \(\rho\) increases faster again. LaH\textsubscript{x} shows even a three stage absorption. The increase of \(\rho\) in stages does not seem to be caused by a structural phase transition of the metal atoms; for \(0.30 \leq z \leq 0.67\) a similar behavior is observed as for \(z \geq 0.86\), whereas in the latter region the films exhibit an fcc-hex phase transition. However, the different stages might be caused by hydrogen ordering. For \(2<x<3\) phases are known to exist in which the randomly distributed hydrogen vacancies order in planes.\textsuperscript{17} Such transitions are likely to affect the resistivity.

We observed that the loading speed for \(\rho_{H_2} \leq 1\) bar is linearly proportional to the hydrogen pressure both in the \(\alpha\) phase as for \(x>2\). The linearity indicates that the switching kinetics are controlled either by H\textsubscript{2} transport in the gas phase or by H\textsubscript{2} dissociation.\textsuperscript{46} Note that this confirms our assumption that the loading pressures are low enough to ensure quasiequilibrium.
To analyze the data quantitatively, we model $\varepsilon(\omega)$ using a sum of one Drude oscillator and three Lorentz oscillators (LO’s):

$$
\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{j=1}^{3} f_j \frac{\omega_0^2 - \omega^2 + i\omega\beta_j}{\omega_0^2 - \omega^2 + i\omega\beta_j}.
$$

The constant $\varepsilon_\infty$ in Eq. (10) accounts for excitations far above 4.5 eV. The second term describes the free-carrier response and is of Drude form, characterized by the plasma frequency $\omega_p$ and the relaxation time $\tau$. The last three terms represent the effect of interband and/or impurity absorptions. Each LO is characterized by an oscillator strength $f_j$, a resonance frequency $\omega_0$ and a broadening parameter $\beta$. The choice for three LO’s is supported by fit results using two and four LO’s; it turns out that two LO’s clearly give worse fits than three LO’s, whereas fitting four LO’s leads to zero strength of the fourth LO. The excellent quality of the fits obtained by means of Eq. (10) is demonstrated for three materials in Fig. 11. Similarly, good fits are obtained for all alloys as can be seen from the $\chi^2$ values in Table V.

Modeling the optical properties with a Drude-Lorentz (DL) parametrization has several advantages: (i) It often gives a good description of both metals and insulators, and is therefore particularly suitable to study the MI transition in RE hydrides. (ii) Contrary to some other parametrization models, its parameters have a physical meaning. (iii) The model is intrinsically Kramers-Kronig consistent, and therefore implicitly checks the reliability of the experimental data. (iv) Often $\varepsilon_2(\omega)$ is calculated from the one-electron band structure by a calculation of the joint density of states (JDOS) and dipole transition matrix elements. Many-particle effects are not included, and therefore it is impossible to obtain the free-electron contribution to $\varepsilon_2(\omega)$ from such a calculation. For a good comparison with experiment and one-electron theory, one thus needs a way to separate the interband absorption contribution from the free-electron contribution, for which Eq. 10 is particularly useful.

The data in Table V show that large interband absorptions, centered at $\omega_{01}$ and $\omega_{02}$, occur below the plasma frequency $\omega_p$, which is typical for transition metals. The structures in $\varepsilon_2(\omega)$ are estimated at 1.1 and 1.7 eV from Fig. 10, and are comparable with the bulk values 1.15 and 1.75 eV.

The interpretation of the optical results is hindered by the fact that only few band-structure calculations exist for Y and La for the correct lattice structures. Calculations of the JDOS do not exist at all to our knowledge. However, the band structure and density-of-states (DOS) calculations of Altman and Bradley provided some information. Their DOS, which corresponds well to photoemission data, and their band structure suggest that the broad structure extending from $\sim 0.75$ to 2.5 eV originates from interband absorptions between $d$ bands along $\Sigma$ and $T'$. However, the width of the
experimental absorptions and the lack of calculations of theJDOS and dipole transitions matrix elements make it extremely difficult to identify the origin of interband absorptions unambiguously.

Figure 10 suggests that the electronic structure of La and Y differ very much. However, after a decomposition of $\varepsilon(\omega)$ into free- and bound-electron contributions, as shown in Figs. 12 and 13, it is clear that the interband absorption properties are actually very similar. The difference in their $\varepsilon(\omega)$ is only caused by the interplay of the Drude and contribution of the first LO. Both contributions are large and have opposite signs in $\varepsilon_1(\omega)$. Therefore relatively small differences in the DL parameters result in large differences in the resulting $\varepsilon(\omega)$.

The z dependences of the various DL parameters exhibit some clear trends. First, the plasma frequency decreases linearly with z, which is opposite to what one would naively expect from the larger volume of La, as $\omega_p$ is proportional to the free-electron density. However, the intrinsic free-electron properties, which in the simple Drude model are represented by $\omega_p$, depend strongly on the band structure near the Fermi energy, which is markedly different for La and y. Second, we see a clear nonlinear behavior of the relaxation time. This is due to disorder, and related to the nonlinear behavior of the resistivity shown in Fig. 8.

Third, the interband absorptions shift monotonically to the blue upon increasing z. This observation is not immediately clear for $\omega_{01}$ in Table V. The reason for this is that for decreasing z the widths of the two interband features at $\omega_{01}$ and $\omega_{02}$ increase, and their maxima tend to merge. As a result the parameters of the first two LO’s become strongly coupled, and clear trends for the parameters of the two separate LO’s disappear. For $z \leq 0.50$ it would have been more physical to use only one LO for the interband absorption feature around 1.5 eV. Hence, for a meaningful physical interpretation the first and second LO’s should be treated as one interband feature. This feature exhibits a clear red shift upon decreasing z, which points to a narrowing of the bands, caused by the 14% larger volume of La compared to Y. The volume effect is much stronger than the broadening effect due to larger radii of 4sp5d orbitals of La compared to the 3sp4d orbitals of Y. We will see the same effect in the dihydrides discussed below.

The measured optical properties indicate that the alloy is not a mesoscopic mixture of Y and La, in correspondence with the XRD results. We find for each alloy that $\varepsilon(\omega)$ is not enclosed over the whole spectral range by the corresponding Wiener bounds.\textsuperscript{51,52}

We conclude that the optical properties of La$_{1-z}$Y$_z$ alloys are well described by a DL model. All alloys show interband absorptions below the plasma frequency, and these interband absorptions shift to higher energies on increasing z. Clear disorder effects are observed in the optical properties.

2. Optical properties for $x=2$

The dielectric functions for the La$_{1-z}$Y$_z$H$_2$ (dihydride) films, obtained from ellipsometry after correction for the
substrate and the Pd layer, are given in Fig. 14. For all alloys interband absorptions exist below the plasma energy, which is typically 4 eV. At low energy a free-electron behavior is discerned and around 2.5 eV interband absorptions are visible. Around 4.0 eV there is an onset to another interband absorption band, that extends outside the measuring range. As in the $x^5$ case, typical features shift to higher energies on increasing $z$.

The optical properties of YH$_2$ are well understood, since the thorough studies of Weaver and co-workers$^{19,53}$ and Peterman and co-workers$^{44,54}$ Calculations of the electronic structure were shown to agree quantitatively with optics and photoelectron spectra. The structure in $\varepsilon_2$ around 2.5 eV (see Fig. 14) is caused by interband absorptions within the $d$-like complex of bands along $\bar{Q}$, $\bar{W}$-$\bar{K}$, and $\bar{S}$ in the first Brillouin zone of the fcc lattice$^{3}$ (see Sec. III E 4). The interband absorption onset increases along the sequence ScH$_2$(1.25 eV) $\rightarrow$ YH$_2$(1.6 eV) $\rightarrow$ LuH$_2$(1.9 eV) as a result of $d$-band dilation along $3d$-$4d$-$5d$.$^{53}$ In this light, the 1.3-eV onset for LaH$_2$ seems anomalous. However, the $d$ bands of LaH$_2$ are strongly narrowed due to its large atomic volume (31% larger than for YH$_2$ and 45% larger than LuH$_2$), which surpasses the $d$-band dilation.$^{54}$ From calculated band structures for YH$_2$ and LaH$_2$ we find for the onset for interband transitions 2.1 and 1.3 eV, i.e., a difference of 0.8 eV.$^{54}$ From Fig. 15 and our DL fits (see Table VI), we estimate 0.4 eV, which is a reasonable agreement. Narrowing of the $d$ bands also lowers the spectral width of the interband absorption feature in $\varepsilon$. From our measurements we estimate a difference of 0.3 eV.

Another indication that the interband absorptions arise from transitions between $d$ bands is that the difference in interband onset between LaH$_2$ and LuH$_2$ can be understood as a pure volume effect, because both materials have 5$d$ valence. For $d$ states the bandwidth scales as $a^{-5}$, with $a$ the lattice spacing.$^{55}$ The ratio of the interband onset energy $E_{\text{onset}}$ for LaH$_2$ and $E_{\text{onset}}$ for LuH$_2$ is thus given by

$$\frac{E_{\text{onset}}}{E_{\text{onset}}} = \left( \frac{a_{\text{LaH}_2}}{a_{\text{LuH}_2}} \right)^5. \quad (11)$$

With $E_{\text{onset}}^{\text{LaH}_2} = 1.9$ eV,$^{19}$ $E_{\text{onset}}^{\text{LaH}_2} = 1.2$ eV, $a_{\text{LaH}_2} = 5.033$ Å,$^{36}$ and $a_{\text{LaH}_2} = 5.694$ Å (see Table II), we find 0.63 and 0.54 for the left- and right-hand sides, respectively, which is a reasonable agreement.

Absorption above 3.5 eV arises from interband transitions mainly between the parallel bands along $\Sigma$, where the lower band is $d$-$s$ like and the upper band is $d$ like.$^{53}$ The sharp
structure in $e_2$ around 5 eV, from which in Fig. 14 only the onset is visible, is due to the flatness of the lower $d$-$p$ band near the K point.

Figure 15 shows that there is qualitative agreement between our results for YH$_2$ with those measured on polycrystalline bulk samples. Our maximum values of $e_1$ and $e_2$ are somewhat higher, and instead of three interband features between 2 and 3 eV we observe only two. We also do not observe the decrease of $e_1$ at 4.3 eV. However, the energies of different features in both YH$_2$ spectra are the same. The bulk values were obtained by a Kramers-Kronig (KK) analysis of absorption spectra. For such an analysis one needs to extrapolate the absorption both to zero and infinite energies, and it is well known that this can introduce inaccuracies in the final result for $\varepsilon(\omega)$. In our case, however, $\varepsilon(\omega)$ is obtained essentially directly. We believe that the differences of our results with those on bulk YH$_2$ are thus related to this KK transformation and are not a thin film effect.

There is a larger disagreement between our results for LaH$_2$ and the results obtained for bulk material, both in magnitude and in the energy positions of typical features. We have some indications that our measurements are more accurate than the bulk values: (i) The oxidation behavior of LaH$_4$ is notorious, and it is well known that a surface oxide can affect severely the reflectivity of a material. Our technique, where we measure through the substrate, seals well the LaH$_2$ from the ambient. (ii) The reflectance-transmittance spectra, calculated from our $\varepsilon(\omega)$, are in excellent agreement with direct reflectance measurements. This is not possible with the bulk dielectric function. In particular, the good agreement for the measured transmittance indicates that our $\varepsilon(\omega)$ is not affected by surface artifacts, since the transmittance probes the optical properties throughout the film and is rather insensitive to surface effects. (iii) In sharp contrast to our thin film data and the bulk YH$_2$ data, we cannot obtain a good DL fit of the bulk LaH$_2$ data. (iv) Our experimental interband absorption onset energy agrees very well with the theoretical value.

In addition to the XRD results, the optical properties of the dihydride films indicate that the alloys do not disproporionate upon hydrogenation. We find for each alloy that $\varepsilon(\omega)$ does not fall between its Wiener bounds$^{51}$ over the whole spectral range, which indicates that the alloys are not mesoscopic mixtures of YH$_2$ and LaH$_2$.

To analyze the optical properties of the dihydride alloys, we again use a DL parametrization for $\varepsilon(\omega)$. The results are listed in Table VI. Although the values of $\chi^2$ are somewhat larger than in the $x=0$ case, we still obtain good fits (see Fig. 16). The DL description of $\varepsilon(\omega)$ uses rather simple functional forms to model $\varepsilon(\omega)$ that is the result of a complicated electronic structure. Therefore, $\chi^2$ is expected to be larger when structures in $\varepsilon(\omega)$ are more pronounced. This is what is the case here: the larger $\chi^2$ for $x=2$ compared to the $x=0$ case is mainly due to the misfit for 1.25$\leq\hbar\omega\leq$2 eV. As for $x=0$, adding another LO does not improve the fit.

In summary, the DL model describes well the optical properties of the dihydrides. Interband features appear at higher energies for larger $x$, and effects of disorder are observed in the optical properties of the dihydrides.

3. Dihydride transmittance window

A peculiar optical property of YH$_2$ is that, although the material is a low-resistivity metal, it is slightly transparent in the red part of the optical spectrum. This window arises from a combination of small free-electron absorption, because the photon energies are close to the (screened) plasma energy, and low interband absorption. This results in a narrow region where the total absorption is small, and therefore the film is transparent even for rather thick films. Such transmission windows are present at higher energies in Au, Cu, and Ag. Based on the similar shape of $\varepsilon(\omega)$ for all La$_{1-z}$Y$_z$H$_2$ such a dihydride transmission window is expected to exist in all alloys. For this we measured directly the optical transmittance and reflectance of the dihydrides for different alloys. The transmittances are shown in Fig. 17.

Figure 18(a) shows that there is a monotonic shift of $\hbar\omega_{\text{max}}$ going from 1.52 eV for LaH$_2$ to 1.78 eV for YH$_2$. However, the amplitude is suppressed upon alloying in a very nonlinear fashion [see Fig. 18(b)]. The amplitude is minimal for $z=0.46$, and is one order of magnitude lower than for YH$_2$ or LaH$_2$. This suggests that the strong suppression is related to disorder. From a close analysis of the DL parameters in Table VI we find that disorder effects enter Eq. (10) via the DL parameters $\varepsilon_\infty$, the resonance frequencies $\omega_{0\delta}$, and the broadening parameters $\beta$ of the second and third LO, and $\tau$. 

![Figure 16](image-url) 

**FIG. 16.** Fits of the $\varepsilon(\omega)$ measured with ellipsometry for LaH$_2$, La$_{0.40}$Y$_{0.60}$H$_2$, and YH$_2$. For clarity, results are shown for only three alloys, and not all data points are plotted.
To explore the role of disorder, we calculated the transmittances of a 15-nm Pd/300-nm La\(_{1-x}\)Y\(_x\)H\(_x\)/Suprasil stack with a DL parametrization of \(\varepsilon(\omega)\), with all parameters linearized. Then we took the fitted values for one parameter and again calculated the dihydride windows, and so on. The dihydride window is 40% reduced by the nonlinearity of \(\varepsilon_\infty\), and 15% by the nonlinearity of each of the parameters \(\tau\), \(\omega_{bi}\), and \(\beta_1\). We conclude that the strong suppression of the dihydride window is caused by disorder, the largest contribution coming from optical absorptions at energies much larger than 4.5 eV.

4. Optical properties for 2\(<x<3\)

The variation of \(\varepsilon(\omega)\) upon hydrogenation from \(x=2\) for two alloys and YH\(_x\) is given in Figs. 19, 20, and 21. The qualitative behavior of all alloys is similar. The main trends indicated by arrows in these figures are (I) the disappearance of the free electron optical response with increasing \(x\), (II) a suppression of the interband absorptions around 2.5 eV, and (III) a shift to lower energies of the second interband absorption peak in \(\varepsilon_2\). We can immediately conclude that the systematic lowering in energy of the interband transitions is not caused by volume changes as LaH\(_x\) contracts for \(x=2\rightarrow3\), La\(_{0.54}\)Y\(_{0.46}\)H\(_x\) expands slightly, and YH\(_x\) expands a great deal. The origin of the trends can, however, be understood from the band structures for LaH\(_2\) and LaH\(_3\) calculated by Ng \textit{et al.}\(^7\) (see Fig. 22).

In their calculations, the insulating nature of LaH\(_3\) is due to electron correlations at the hydrogen sites, which narrows the valence band with strong hydrogen 1s character, and causes a gap to open. From a comparison of the band structures of LaH\(_2\) and LaH\(_3\) [Figs. 22(a) and 22(b), respectively] we see that LaH\(_3\) differs from LaH\(_2\) in a newly formed band below the Fermi energy. The rest of the band structure re-
mains essentially unaffected. Hybridization occurs along $D$, and pushes bands 1 and 2 away. Furthermore, small effects near $W$ and $K$ are observed. Along $L$ and $S$ a new band appears as a flat band above band 2. Near $x$ the new band has pushed band 3 upward above band 4. Along $Q$ and $S$, band 3 is also pushed upward above $E_F$.

We now discuss the three trends mentioned above. First, the decrease of the plasma frequency is consistent with the Kondo insulator picture of Ng et al. Above $x = 2$ every additional hydrogen binds an electron of the host metal into a sort of inert Zhang-Rice singlet. This leads to a linear depletion of the free-electron density. In a band picture this would correspond to a gradual shift of spectral weight from band 3 in LaH$_2$ to band 3 in LaH$_3$.

Second, we consider the weakening and shift downward in energy of the interband absorptions around 2.5 eV. We saw before that they arise from transitions between the $d$ bands 3 and 4 along $Q$, $W$-$K$, and $\Sigma$. By adding hydrogen, the states of band 3 hybridize to much lower energies, and as a result the optical interband transitions lose strength and finally disappear. Adding hydrogen causes more and more disorder. This can lead to band flattening, and consequently to a red shift of the interband absorptions.

The third effect is that interband absorptions present in the dihydride at high energies ($>3.5$ eV) also shift toward lower energy upon increasing $x$. Note that the onset of these transitions determine the final appearance of the thin-film transparent state: LaH$_3$ is orange and YH$_3$ is yellow. We saw earlier that high-energy absorption in the dihydride is caused by transitions between bands 2 and 3 along $\Sigma$. Figure 22 suggests that the energy shift is merely a combination of the disappearance of these initial transitions by hybridization of band 3 with the hydrogen 1$s$ states and the appearance of transitions between the newly formed $s$ band and band 4 near $\Gamma$ [see Fig. 22 (b)]. Although a neat calculation of $e_2$ should be made to conclude on this, Figs. 19 and 20 suggest that the increased strength of the high-energy interband transitions originates from the flatness of the new band near $\Gamma$. Note that the band-gap in Fig. 22(b) is 2 eV, in good agreement with the experimental value of 1.9 eV.

In conclusion, the qualitative behavior of the optical properties of La$_{1-z}$Y$_z$H$_x$ alloys between $x = 2$ and 3 is the same for all $z$. This again shows the robustness of the MI transition and its independence on the lattice structure. The MI transition in films that remain fcc indicates that the phase transition is not a discontinuous transition, but merely a continuous decrease of conduction electrons.

5. Optical properties for $x = 3 - \delta$

In Fig. 23 dielectric functions are shown for the alloys in their insulating trihydride state. The dielectric functions in
Fig. 23 are typical for insulators. When the energy approaches the band gap energy from below, $\varepsilon_2$ increases strongly because absorption starts. For $z = 0.81$ and $1$, an extra absorption above the optical gap exists near $4.2$ eV (see Fig. 23). Apparently this is characteristic for hexagonal trihydrides.

Figure 23 shows that $\varepsilon_2(\omega)$ is not completely zero below the optical gap. Depending on $z$, absorption below the optical gap exists to $1.8$ eV below the optical gap. This effect is also observed in the transmittances of the La$_{1-z}$Y$_z$H$_3$ films (see Fig. 24). The transmittance below the optical gap becomes significantly smaller when $z = 0.5$, which points to a disorder effect. The absorption below the optical gap might be due to lattice defects. It is also conceivable that because of disorder dipole forbidden transitions become allowed. This would be in agreement with $GW$ calculations of van Gelderen et al. $^{11}$ that predict a fundamental gap that is dipole forbidden. The inset of Fig. 24 shows that the maximum achievable transmittance lies between 65% for a La$_{0.85}$Y$_{0.15}$H$_3$ alloy and only 15% for a La$_{0.33}$Y$_{0.67}$H$_3$ alloy.

In addition to ellipsometric data we also analyzed transmittance spectra of the trihydride alloys shown in Fig. 24 to estimate the optical gap $E_g$. For this we first determined the frequency dependent absorption coefficient using the Lambert-Beer law

$$T(\omega) = T_0 \exp[-\alpha(\omega)d],$$

with $d$ the film thickness of the La$_{1-z}$Y$_z$ layer, and $T_0$ containing the absorptions of the other layers and the reflections at all interfaces. By assuming parabolic bands, the following forms for $\alpha(\omega)$ near the optical gap can be derived from time dependent perturbation theory: $^{57}$

$$\alpha(\omega) \propto \frac{(\hbar \omega - E_g)^{\nu}}{\hbar \omega},$$

in which for direct, allowed (forbidden) transitions $\nu = \frac{1}{2}$ ($\nu = \frac{3}{2}$) and for indirect, allowed (forbidden) transitions $\nu = 2$ ($\nu = 3$). Equation (12) is rewritten as

$$\ln T(\omega) = \ln T_0 - C \frac{(\hbar \omega - E_g)^{\nu}}{\hbar \omega},$$

and the constants $\ln T_0$, $C$, and $E_g$ are determined from a fit to the spectra near the transmission edge, where no interferences appear yet. In Table VII the obtained parameters are given.

We find that $\nu = 1/2$, i.e., an allowed, direct gap, cannot explain the measured data. Assuming an allowed, indirect gap ($\nu = 2$) gave good results for alloys with $z \approx 0.7$.

However, for $z = 0.86$ it is possible to fit the data equally well with $\nu = \frac{1}{2}$, 2, or 3, and with $2.3 < E_g < 2.7$ eV. This large spread is probably due to the fact that the data pertain to polycrystalline films with an hexagonal lattice structure.
FIG. 24. Measured transmittances (lines) and fitted transmission edges [symbols; see Eq. (14)] for the La$_{1-x}$Y$_x$H$_3$ alloys. The inset shows the transmittances of the La$_{1-x}$Y$_x$H$_3$ alloys 1 eV below the optical gap (see Fig. 25). The open squares are the measured values. Solid symbols are values corrected for the PdH$_{0.7}$ cap layer and the quartz substrate and represent the maximum achievable transmittance of the La$_{1-x}$Y$_x$H$_3$ films.

Their optical properties are anisotropic, and therefore the simple formula for $\alpha(\omega)$ is less accurate than for films with $z<0.7$, that are cubic thus optically isotropic. To check our assumption we carried out the same fits on transmittance spectra of polycrystalline YH$_3$. These films, evaporated on a CaF$_2$(111) substrate have their $c$ axis perpendicular to the surface, and the transmittance is thus measured along one optical axis. Again the best fits were clearly obtained with $\nu=2$ and $E_g=2.659$ eV. From ellipsometry we find for YH$_3$

TABLE VII. Fit parameters obtained by modeling the transmission edges of La$_{1-x}$Y$_x$H$_3$ with Eq. (12) with $\nu=2$. All parameters are dimensionless except $E_g$, which is in eV.

<table>
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<tr>
<th>$z$</th>
<th>$\ln T_0$</th>
<th>$C$</th>
<th>$E_g$</th>
<th>$\chi^2$</th>
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<td>38.26</td>
<td>2.551</td>
<td>0.0044</td>
</tr>
<tr>
<td>1 (epi)</td>
<td>-2.647</td>
<td>36.33</td>
<td>2.659</td>
<td>0.0007</td>
</tr>
<tr>
<td>1 (poly)</td>
<td>-2.374</td>
<td>21.73</td>
<td>2.424</td>
<td>0.0102</td>
</tr>
</tbody>
</table>

FIG. 25. Optical gap of La$_{1-x}$Y$_x$H$_3$ alloys determined by (i) by modeling the transmission edge using Eq. (14) (solid squares), and (ii) by taking the axis cutoff of $\varepsilon_z(\omega)$ in Fig. 23 (open circles). The solid/dashed line is a second-order polynomial fit of the data with $z<0.67$, and suggests an optical gap of 2.32 eV for fcc-YH$_3$.

$E_g=2.61$ eV (Fig. 23). These values are in good agreement with the calculations of van Gelderen et al. who predicted YH$_3$ to have an optical gap between 2.4 and 2.9 eV.

In Fig. 25 the optical gap as a function of $z$ is shown as determined in two different ways. The values are in excellent agreement with each other. The discontinuity between $z=0.67$ and 0.81 coincides with the structural phase transition (as a function of $z$) from fcc to hex (see Fig. 4). For the fcc trihydride region ($z<0.67$) the optical gap increases nonlinearly with increasing $z$, and reaches 2.33 eV for $z=0.67$. The shift of $E_g$ is probably a volume effect, because (i) within one phase $E_g$ increases monotonically with decreasing molar volume, and (ii) the discontinuity in $V_m(z)$ coincides with the discontinuity in $E_g(z)$.

6. Polycrystalline vs epitaxial YH$_{3-x}$

The trihydride $R$-$T$ spectra of polycrystalline YH$_3$, and of an epitaxial film are compared in Fig. 26. The epitaxial film was grown at high temperature on a CaF$_2$(111) substrate. Some differences from polycrystalline films are observed. The optical band gap seems slightly larger for the epitaxial film and the interferences in the reflectance have a larger amplitude. Moreover, the reflectance of the polycrystalline film exhibits a downward trend for lower energies, which is not observed for the epitaxial film.

To obtain the dielectric function from the data, the reflectance and transmittance of a multilayer is calculated using the transfer-matrix method. The optical properties of the substrate layer, Al$_2$O$_3$ layer, and Pd layer are taken from the literature, and the dielectric function of the YH$_3$ layer is parametrized using Eq. (10), with the Drude term set to zero, because of the insulating nature of the trihydrides. The result of the fit is shown in Fig. 26.

From the fitted $\varepsilon(\omega)$ we calculated the absorption coefficient via

$$\alpha(\omega) = \sqrt{\frac{\omega}{c}} \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}. $$
Figure 27 shows that the absorption edge is sharper for the epitaxial film. This effect is also seen in other materials, and is often explained by impurity absorptions and is known as the Urbach tail. The difference between the epitaxial and polycrystalline material can also be caused by the optical anisotropy of the hexagonal YH$_3$. Note that we only probe the optical properties along the $c$ axis in the epitaxial case, while we measure a mixture of properties along the $a$ axis and the $c$ axis in the polycrystalline case. A comparison between polycrystalline and epitaxial LaH$_x$, which is cubic and therefore isotropic, could give more information on this point.

Figure 27 also shows that the absorption below the optical gap is lower for the epitaxial film. This can also be due to the anisotropy of YH$_3$. It may also be caused by lattice defects that affect the lattice periodicity and in this way may give rise to optical transitions that are forbidden in the epitaxial case. This supports the results of $GW$ calculations on YH$_3^{11}$ of a 1-eV dipole forbidden fundamental gap.

**IV. CONCLUSIONS**

We have determined the structural phase diagram and the optical and electrical properties of the La$_{1-x}$Y$_x$H$_x$ system for $x=0, 2, \text{ and } 3$. We also studied the switching kinetics, thermodynamics, dc resistivity behavior, and optical properties in the regions $2 \leq x < 3$, the region where the MI transition takes place.

The structural and optical data reveal that La and Y atoms form a disordered solid solution, and that the alloys do not disproportionate upon hydrogenation. This makes the system a very useful system for studying the nature of the MI transition.

From dc resistivity measurements we observe that LaH$_x$ shows a three-stage hydrogenation for $2 < x < 3$, whereas all other films show a two-stage hydrogenation. The different stages might be due to hydrogen ordering.

La$_{1-x}$Y$_x$ films and their hydrides behave in many aspects like their bulk counterparts. The phase diagram for $x=0$, the heat of formation of the trihydride, and optical properties exhibit similar behavior to that of data known for bulk systems. This is what one expects for crystallite sizes of 10–100 nm. The higher resistivity of films compared to bulk values for $x=0$ and 2 are not thin-film effects, but due to the polycrystalline nature of the samples; the electronic mean free paths are of the order of 10 nm for metallic LaH$_x$ and YH$_x$ and therefore much smaller than the film thickness.

Disorder effects are observed throughout the work. They reduce the x-ray coherence length and the free-electron relaxation time, affecting both the dc resistivity as the optical free-electron response. The strong suppression of the dihydride transmission window is also an effect of disorder as well as the lowering of the transmittance of the alloy trihydrides.

La$_{1-x}$Y$_x$H$_x$ alloys show a similar MI transition for $x$ be-
between 2 and 3, indicating the robustness of the MI transition.
From this and the optical behavior of the various materials between \(x = 2\) and 3, we conclude that the MI transition is of electronic nature.

We have been able to determine accurately the optical band gap of \(\text{La}_{1-x}\text{Y}_x\text{H}_3\) trihydride alloys. The optical gap increases monotonically with \(z\) from 1.87\(\pm\)0.03 eV (orange) for \(\text{LaH}_3\) to 2.63\(\pm\)0.03 eV (yellow) for \(\text{YH}_3\), and is affected both by the molar volume as the lattice structure. There are indications that the fundamental gap is dipole forbidden and 1–1.8 eV lower than the optical gap. This is in agreement with recent \(GW\) calculations.

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35 P. Scherrer, Göt. Nachrichten 2, 98 (1918).
52 This conclusion is premature, because Wiener bounds are valid for materials that are optically isotropic. However, the conclusion turns out to be correct after analyzing the isotropic dihydrides.
55 W. A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980).
56 The mechanism is similar to that proposed by Peterman et al., based on optical measurements on bulk LaH$_x$ (Ref. 54).
58 Earlier we reported an optical gap for YH$_3$ of 2.8 eV (Ref. 13). This value was obtained from data on polycrystalline films, and is therefore less accurate than the value $2.63 \pm 0.03$ eV presented here.
62 Because hydrogen vacancies in the substochiometric trihydrides act as electron donors, a nonzero plasma frequency is expected. Indeed Lee and Shin (Ref. 63) observed a Drude-like free-electron contribution in the optical constants of YH$_{3-\delta}$, but with a plasma frequency of 0.16 eV, which is outside our measurement region.