Highly absorbing black Mg and rare-earth-Mg switchable mirrors

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Apart from a reflecting and a transparent state, rare-earth-Mg alloys (RE-Mg) exhibit also a highly absorbing, black state during loading with hydrogen. The occurrence of such a black state is due to the disproportionation into subwavelength size REH$_{3-x}$ and Mg grains during the first hydrogen loading. While the optical properties of REH$_x$ change continuously with a further increase in hydrogen concentration $x$, Mg changes abruptly from a good reflector to a transparent insulator (MgH$_2$). Thin pure Mg films also show this black state when (un)loaded carefully at elevated temperatures. By using the Bruggeman effective medium approximation in combination with the transfer matrix method it is shown that the coexistence of Mg and MgH$_2$ grains is the cause of this high absorption. Furthermore, we compare this phenomenon to the high absorption of light observed in metal-dielectric composites.

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I. INTRODUCTION

Since the discovery of switchable mirrors based on YH$_3$ and LaH$_3$ and rare-earth hydride (REH$_x$) films$^1$ a lot of research has been done on this type of materials. The special characteristic of these mirrors is that they can be continuously and reversibly switched between a metallic, reflecting state (REH$_{3-x}$) and an insulating, transparent state (REH$_{3-x}$) by the absorption (or desorption) of hydrogen. This can be done by gasochromic,$^1$ electrochromic,$^{2,3}$ or chemochromic$^4$ means. Furthermore, they display photochromic,$^5$ piezochromic,$^6$ and thermochromic$^7$ changes in their optical properties. Due to their optical changes, thin films of, e.g., Y can also be used as hydrogen indicators$^8,9$ in diffusion experiments. Another development is pixel switching, i.e., independent switching of small islands from reflecting to transparent, which can be observed in epitaxial REH$_x$ films.$^{10,11}$ This is a very important step for application as display. The most obvious application would be to use them as electrochromic smart windows.$^{12}$ The first prototype laboratory devices of switchable mirrors have been made already.$^{13}$ Since it is possible to dissolve large quantities of hydrogen in metallic and intermetallic compounds, these materials are also interesting for hydrogen storage applications.$^{14}$

In this paper, we focus on pure magnesium and magnesium containing RE metals. Switchable mirrors containing Mg are especially interesting since they can be tailored to be highly reflective in the unloaded state and transparent over the entire optical range$^{15–18}$ (i.e., colorless) in their transparent state. Technologically this is a significant improvement upon REH$_x$ that exhibits an optical transmission window in the red ($1.6 < h\omega \approx 2.1$ eV) at hydrogen concentrations $1.7 < x < 2.1$ in their reflective state and a transparent state (REH$_{3-x}$) with characteristic colors, e.g., yellow for YH$_{3-x}$ (absorption edge at 2.6 eV) and red for LaH$_{3-x}$ (absorption edge at 1.9 eV).$^{19}$

Apart from a reflecting and a transparent state, these RE-Mg alloys and thin Mg films exhibit also a highly absorbing, black state during loading with hydrogen. This black state has been observed in Gd$_{3-x}$MgH$_x$ with $z > 0.50$ (Refs. 3,15,20), in La$_{0.5}$Mg$_{0.5}$H$_5$ (Ref. 21) and in Y$_{1-z}$MgH$_z$ alloys. We believe that the black state is a fundamental property of all RE-Mg alloys with a considerable amount of Mg. It has, however, not been studied in detail. The purpose of this paper is to give a quantitative description of the mechanism responsible for the existence of the black state.

Nagengast et al.$^{22}$ have shown that thin films of RE-Mg alloys disproportionate as soon as they are exposed to hydrogen. During this disproportionation, which is also known for bulk RE-Mg,$^{23,24}$ Mg domains act as a microscopic optical shutter when changing from a shiny metal (Mg) to the large band gap insulator$^{25,26}$ (MgH$_2$) upon hydrogenation. The presence of a REH$_x$ (with $1.9 < x < 2.9$) matrix plays only a secondary role. This can be demonstrated by showing that a pure Mg film exhibits also a black state when appropriately loaded with H$_2$. Thus, the key ingredient is the coexistence of nanograins of Mg and MgH$_2$.

Furthermore, we show that this phenomenon is similar to the high absorption of light observed in metal-dielectric composites$^{27,28}$ such as Au-glass,$^{29–31}$ Ag-glass,$^{32}$ and Co-Al$_2$O$_3$.$^{33}$ Its origin is fundamentally different from that of other black materials such as microstructured Si$^{34}$ or Ni-P$^{35}$ for which a rough surface morphology is essential. The black state observed in Mg$_2$NiH$_3$ is also of different origin.$^{36}$ There a layered growth of the hydride plays an essential role.$^{37}$

II. EXPERIMENT

Polycrystalline LaMg, YMg, and Mg films are evaporated under ultrahigh vacuum conditions ($10^{-9}$ mbar) on quartz substrates and glassy carbon at room temperature and 100 or 300 °C (Mg and RE-Mg, respectively). Y and La are evaporated with an e-gun and Mg with a Knudsen effusion cell. To protect the La containing films against oxidation a 1.5 nm thick Al buffer layer is evaporated subsequently.$^{38}$ This thin layer is then oxidized to AlO$_x$ in $10^{-5}$ mbar of O$_2$ during 1000 s. To promote hydrogen dissociation and absorption a 2.5 to 10 nm thick Pd layer is deposited on top of the films. The evaporation rates and the total thickness are monitored.
However, when RE-Mg compounds form an intermetallic compound with the CsCl structure. Films 42 and 10 respectively limited angular range, usually with 2θ between 26° and 41° with a scan time of approximately 8 min per spectrum.

Optical transmission and reflection spectra at near-normal incidence are recorded in a Bruker IFS 66/S Fourier transform infrared spectrometer in the range 0.72 eV < hω < 3.5 eV (i.e., 1722–354 nm). Reflection spectra are measured from the backside of the samples through the substrate to circumvent the reflection of the metallic Pd cap layer.

The films are slowly hydrogenated (pressures lower than 1 bar of H₂) at room temperature or 50 to 100 °C for Mg in order to follow the optical changes in situ in detail. The resistivity is monitored in situ as well. For this, the sample is contacted with four 30 µm thick Al wires by means of an ultrasonic bonding machine and connected to a Keithley 2000 multimeter. We use Van der Pauw’s method 39 to determine the resistivity.

III. RESULTS

A. Structure

1. RE-Mg films

From x-ray diffraction (XRD) measurements on YMe-Hₓ and LaMe-Hₓ films 21 at room temperature we arrive at the following scenario for the hydrogenation of RE-Mg alloys. RE-Mg alloys (except Yb-Mg) deposited in a 1 to 1 ratio form an intermetallic compound with the CsCl structure. However, when RE-Mg compounds (both in bulk 23,24 and in thin film form 21,22,40,41) such as LaMg, CeMg, YMe, and GdMg are exposed to hydrogen they disproportionate. This is due to the great hydrogen affinity of RE metals that form dihydrides already at very low pressures (10⁻²⁵ bar for Y films 42 and 10⁻³³ bar for Gd films 40 at room temperature). Thus, the CsCl intermetallic compound of RE-Mg, when exposed to hydrogen, immediately disproportionates into REHₓ⁺e and Mg, which are both reflecting. In the fully hydrogenated state REHₓ⁻δ and MgH₂ coexist. Both are transparent. In between these two extreme states both REHₓ⁺e and Mg change from reflecting (metallic) to transparent (insulating). However, they do this in a different way. For example YHₓ does not undergo a structural phase transition between the dihydride and trihydride phases if more than 10 at. % Mg is added as was shown already by Van der Molen et al. 16 Thus, both YHₓ and LaHₓ stay fcc between x = 2 and x = 3 and their optical properties change gradually with hydrogen concentration. 19 Magnesium however, is hcp in the metallic phase and tetragonal (rutile) 43,44 or orthorhombic 44,45 in the insulating MgH₂ phase. Thus, magnesium forms MgH₂ grains (with a structural phase transition), whose volume fraction increases with increasing H uptake. The switching of REHₓ⁺e to REHₓ⁻δ and Mg to MgH₂ occurs at essentially the same hydrogen pressure as was shown by Di Vece et al. 40 for GdMg alloys and by Giebels et al. 18 for Y/Mg multilayers. Thus, the enthalpy of formation of REH₃ is very close to that of MgH₂. Furthermore, there are indications that MgH₂ is in the orthorhombic γ-phase when Mg is embedded in a matrix of YHₓ (Ref. 22) and rutile (α-phase) in a matrix of LaHₓ. 21

2. Mg films

Recently, we have succeeded to load thin films of Mg to MgH₂ at elevated temperatures and pressures. 25 This is not straightforward since palladium capped Mg films exhibit unusual kinetics due to the formation of a blocking MgH₂ layer at the interface between Pd and Mg. 46,47 The MgH₂ layer prevents H to diffuse to the metallic Mg that is still present underneath. The formation of this blocking layer can be circumvented by hydrogenation at a temperature of 50–100 °C. In Fig. 1 the evolution of the x-ray spectra during loading with hydrogen is given together with the resistivity and transmission of a 188 nm thick Mg film covered with 10 nm Pd. The sample is hydrogenated at 100 °C. At 39.95 ° the (111) peak of fcc Pd is observed. The (002) peak of hcp Mg is seen at 34.4 °. Two peaks corresponding to rutile MgH₂ appear at 53.7 ° (101) and 27.9 ° (110). However, only 90% of the Mg can be switched to MgH₂ at 100 °C and a pressure of 1 bar H₂. With a pressure of 100 bars the film can be fully loaded to MgH₂. 25 Using the Debye-Scherrer formula we can determine the x-ray coherence length which is an esti-
mate for the grain size. For a Mg sample deposited at room temperature the grain size is 27 nm, after hydrogenation the grain size decreases to about 23 nm.

### B. Optical behavior

Figures 2(a) and 2(b) show the reflection and transmission of a 200 nm thick YMg film on quartz covered with 10 nm Pd during loading at 10 mbar H₂. This low hydrogen pressure is chosen for a slow hydrogenation of the sample. From the measured reflection, R, and transmission, T, we calculate the absorption, A, with $A = 1 - R - T$ [see Fig. 2(c)]. Apart from a reflecting and a transparent state it is clear that there exists a highly absorbing, black state as well. This black state is not only observed during hydrogen absorption but also during desorption and is independent of the rate of hydrogen loading. The black state, which corresponds to the hill in A, occurs when the reflection is low and the film is just becoming transparent. Over the entire visible part of the spectrum the absorption is 85–90%. In Fig. 3 spectra around this highly absorbing state are shown. One should note that the large absorption in the fully hydrogenated sample ($t = 2.2$ h in Fig. 2) is due to the metallic Pd cap layer that limits the transmission and is thus not an intrinsic property of YMg-Hₓ.

After correction for the Pd cap layer and the quartz substrate there is still 70–80% absorption left in the visible part of the optical spectrum. This is exceptionally high since we are looking (through the transparent substrate) at the smooth interface between the substrate and the film (and not at a rough surface such as in microstructured Si34 or Ni-P black35). Moreover, it is not a narrow absorption line but it spans a wide energy range from the UV to the near-infrared. The same is observed in LaMg films on quartz covered with a 1.5 nm AlOₓ/2.5 nm Pd protecting stack.21 As this high absorption was also reported for GdMg alloys,3,15 we believe that it is a general feature of RE-Mg alloys with Mg playing a major role. Furthermore, this high optical absorption is also present in Mg/Y and Mg/Ni multilayers.48

This triggered us to investigate thin pure Mg films in detail. When hydrogenated carefully at temperatures between 50 and 100 °C thin films of Mg can indeed have a highly absorbing, black state as well. At room temperature and when the films are too thick Mg shows a layered hydrogenation from the top to the bottom. In that case the optical properties are very different. Thus, in order to observe the black state it is very important that the film is loading or unloading homogeneously, i.e., MgH2 (or Mg) nucleates everywhere in the sample. In Fig. 4 the reflection, transmission and absorption of a 100 nm thick Mg film covered with 10 nm Pd is given during unloading at 100 °C in air. Spectra around this highly absorbing state are shown in Fig. 5. We observe the same features as in YMg and LaMg. The total absorption (without correction) is 75–90% from the near-infrared to the ultraviolet.
C. Resistivity

The resistivity is monitored simultaneously both during XRD and optical measurements. As deposited LaMg and YMg have a resistivity of about 0.1 m\( \Omega \) cm (including Pd) typical for La and Y. Mg has a resistivity of only 6.5 \( \mu \Omega \) cm. The Pd top layer stays metallic during hydrogen loading. Therefore, it is shunting the resistivity of the underlying REMg\(_x\)H or MgH\(_x\) layer. The maximum resistivity obtained for the total stack in LaMg (with 1.5 nm AlO\(_x\)/2.5 nm Pd) is 1.02 m\( \Omega \) cm (see Fig. 6) and for Mg (with 10 nm Pd) only 0.39 m\( \Omega \) cm (see Fig. 7). At the black state the structural data indicate that Mg is transforming to MgH\(_2\) both in RE-Mg films\(^{21}\) and in Mg (see Fig. 1). The resistivity data are almost featureless in contrast to RE films without Mg.\(^{19}\) When the resistivity suddenly increases around \( t = 750 \) s (i.e., when the material goes from metallic to insulating), the reflection drops rapidly and the black state develops. This points to percolation phenomena in our films.

IV. MODELING

A. Effective medium theory

Since RE-Mg intermetallic compounds disproportionate upon hydrogen loading into small nanosized grains, our material is a heterogeneous mixture of REH\(_x\), Mg, and MgH\(_2\). To model the optical properties of such a mixture we use the Bruggeman effective medium approximation\(^{49}\) (BA). This (self-consistent) approximation is able to model absorption over a large wavelength range and gives good results near the percolation threshold.\(^{32,27,31}\) In this model...
respectively, and where \( m \) is a geometrical factor which depends on the particle shape. The underlying assumptions are (i) ellipsoidal inclusions, and (ii) dipole polarization only, near-field effects are neglected. Furthermore,

\[
f_m + f_d = 1.
\]

There are several solutions of which only one is physical since \( \langle \varepsilon \rangle \) must always be larger than zero.

In this paper we assume that the inclusions are spheroids with a rotation axis perpendicular to the film plane. This is adequate since our films exhibit out-of-plane texture. The depolarization factors are related to the semiaxis \( a, b, c \) via the eccentricity \( e \). For prolate (cigar-shaped) spheroids \( c \geq a = b \) and for oblate (pancake-shaped) spheroids \( c \leq a = b \). As in our experiments the optical properties are measured at perpendicular incidence of the light (i.e., electric-field in-plane) the relevant depolarization factor \( L \) is for the electric field perpendicular to the rotation axis of the ellipsoid. For prolate spheroids,

\[
L = \frac{1}{2e^2} - \frac{1}{4e^3} \ln \left( \frac{1 + e}{1 - e} \right),
\]

where \( \langle \varepsilon \rangle, \varepsilon_m, \varepsilon_d \) are the complex dielectric functions \( [\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)] \) of the effective medium, and inclusions of types \( m \) (metallic) and \( d \) (dielectric), in the host, respectively, and where \( f_m, f_d \) represent volume fractions of materials of types \( m, d \) in the total volume. \( L \) is a geometrical factor which depends on the particle shape. The underlying assumptions are (i) ellipsoidal inclusions, and (ii) dipole polarization only, near-field effects are neglected. Furthermore,

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\]
MgH₂ and REH₉. Mg and REH₂ are metallic, while MgH₂ and REH₂.₉ are semiconducting. The question is then which metal-semiconductor composite is most absorbing and resembles the measurements. First, the combinations of Mg with LaH₂.₉ or YH₂.₉, and the combinations of MgH₂ with LaH₂.₁ or YH₂.₁ are considered—see Fig. 9 for YMgHₓ.

However, none of these combinations gives a black state as observed experimentally—see Fig. 3! If Mg and REH₂.₉ coexist the transmission is zero and the reflection is too high, when MgH₂ and REH₂ coexist a transmission window around 1.₈ eV appears that is not observed in our experiments.

Since there are clear indications that the coexistence of Mg with MgH₂ is crucial for the observed highly absorbing state both in REMg-Hₓ and in MgH₉ (see Secs. III A and III C), the combination of Mg with MgH₂ without the RE material is now considered. The results for a 50 nm thick Mg-MgH₂ composite in vacuum with L = ¹/₅ are shown in Fig. 10 where the data are plotted as a function of the volume fraction of MgH₂ and the photon energy. This time a highly absorbing state is indeed observed with an absorption up to about 8₀% at high photon energies. Since Mg is a very good reflector, the absorption is very low at 1₀₀ vol % Mg (fₚ = ₀). When 0 vol % Mg is reached (i.e., 1₀₀ vol % MgH₂, fₚ = ₁) the film is highly transparent and thus the absorption is low again. Note that the calculation is without Pd. As we expect the black state to be related to a percolation phenomenon (see Sec. IV C) we calculated the dielectric function (ε) of a Mg-MgH₂ composite for fₚ values close to ¹/₅ for spherical inclusions (see Fig. 11). When the metallic fraction fₚ < ₀.₃₅, the metallic character of the film cannot be seen any longer optically since ε > ₀ for all photon energies. If we assume that our film is homogeneous and calculate from the transmission and reflection spectra how the dielectric function looks like in the black state it turns out that it is positive over the entire wavelength range. Thus, we conclude experimentally that fₚ must be smaller than ₀.₃₅ in the black state—see Secs. III A and III C.

When the quartz substrate and the Pd cap layer are taken into account—see Fig. 12—the calculated absorption reproduces nicely the experimental data for YMgHₓ [see Fig. 2(c)] as well as LaMgHₓ, especially in the fully loaded state. Now, there is considerable absorption in the end state (fₚ = ₁, 1₀₀ vol % MgH₂) due to the Pd cap layer. In the original state (fₚ = ₀, 1₀₀ vol % Mg) the absorption is still low since we look at the sample from the substrate side. In the experiment, however, the RE material is present as well. This material (Y or La) is not as reflecting as Mg. Therefore, the overall reflection decreases and the absorption increases especially in the unloaded state.

The results obtained for pure Mg films can be reproduced if we assume that ₁₀ at. % of the Mg is not switched to MgH₂ which is in agreement with the XRD data (see Sec. III A). We assume that a thin layer of ₁₀ nm Mg is present below the Pd cap layer of ₁₀ nm. Isidorsson et al. have shown that even when no Mg peak is observed in XRD any-
more there is still a top layer of about 20 nm thickness that is a mixture between Pd and Mg.25

In the Bruggeman approximation we can also explore the effect of the shape of the inclusions on the optical properties. In Fig. 13 the contour plots of the absorption for a Mg-MgH$_2$ composite is shown for $L = 0.2$, 0.3, and 0.5 which corresponds to oblate ellipsoidal, spherical and cylindrical shaped grains. The scale varies between 0 and 80% absorption in 12 steps. The dashed lines are guides to the eye. They indicate the maximum absorption.

FIG. 11. (a) Real and (b) imaginary parts of the dielectric function of a Mg-MgH$_2$ composite when the metallic fraction (i.e., volume fraction of Mg) is close to its percolation value $f_m = \frac{1}{3}$. All curves are calculated for spherical grains ($L = \frac{1}{3}$) with the Bruggeman approximation.

C. Percolation

So far we have focussed on the optical properties of the Mg-MgH$_2$ composite. As Mg is a metal and MgH$_2$ an insulator we expect also large changes in the electrical resistivity. A marked change occurs near the percolation limit $p_c$. For $f_m < p_c$ there is no longer an electrically conducting path of metallic grains in the material. The same relation as for the dielectric function [Eq. (1)] holds as well for the electrical conductivity $\sigma$ since this is the real part of the dielectric function at zero frequency. Intuitively one expects that the percolation threshold depends on the particle shape. This is indeed true for the Bruggeman approximation.53 The electrical percolation threshold $p_c$ occurs when

FIG. 12. (Color online) Calculated absorption of a 200 nm thick Mg-MgH$_2$ composite on quartz and covered with 10 nm Pd in the Bruggeman approximation. As in our experiments (see Fig. 2) the photon energy is chosen between 1 and 3.5 eV.

FIG. 13. (Color online) Contour plots of the absorption of a 50 nm thick Mg-MgH$_2$ composite for $L = 0.2$ (a), $\frac{1}{3}$ (b), and 0.5 (c) which corresponds to oblate ellipsoidal, spherical and cylindrical shaped grains. The scale varies between 0 and 80% absorption in 12 steps. The dashed lines are guides to the eye. They indicate the maximum absorption.
when the grain size is much smaller than the wavelength of light. In RE-Mg alloys this is indeed the case. Van der Molen et al.\textsuperscript{16} determined the x-ray coherence length $l_{coh}$ of YH$_3$ grains in Y$_{1-x}$Mg$_x$ alloys. It decreases with increasing Mg content from $l_{coh}=18$ nm when $z=0$ to $l_{coh}=4$ nm when $z=0.3$. Unfortunately MgH$_2$ is hardly visible with x-ray diffraction when Y or La is present. Probably the MgH$_2$ grains are comparable in size to the YH$_3$ grains. In (annealed) La$_{0.4}$Mg$_{0.6}$ alloys the coherence length is about 17 nm for LaH$_3$ and 13 nm for MgH$_2$.\textsuperscript{21} Di Vecce et al.\textsuperscript{11} conclude that in Gd$_{0.4}$Mg$_{0.6}$ loaded with hydrogen Gd hydride forms nanometer sized clusters. Thus, for both YMg, LaMg, and GdMg alloys the grain size is much smaller than the wavelength of light. As we have seen in Sec. III A the grain size in pure Mg films is 27 nm for Mg and 23 nm for MgH$_2$ which is also much smaller than the wavelength of light.

In the literature many examples of metal-dielectric composites can be found. For several cermets both the optical properties and resistivity have been studied extensively as a function of the volume percentage metal in an insulator. For systems such as Pt-Al$_2$O$_3$ (Ref. 27), Au on glass,\textsuperscript{29,30} and Co-Al$_2$O$_3$ (Ref. 33) large absorption has been reported in the transition regime around the percolation threshold. The shape and magnitude of the effective dielectric functions found for Pt-Al$_2$O$_3$ (Ref. 27) and Co-Al$_2$O$_3$ (Ref. 33) cermets are quite similar to what we find for YMg hydride or Mg-MgH$_2$. However, the dielectric properties for Au-MgO (Ref. 27) and Ag-SiO$_2$ composites are somewhat different since resonances can clearly be seen in the visible part of the optical spectrum.\textsuperscript{55,32} This gives rise to a dip in $\epsilon_1$ and a bump in $\epsilon_2$.

The unique feature of our system is that it can switch from a metallic, reflecting system via the black, highly absorbing state at the percolation threshold to a transparent and insulating material by simply changing the hydrogen concentration in our samples. In all other cermets a new sample is needed for each volume percentage of metal in the dielectric.

A. The origin of the large absorption

It is interesting to study in composites the role of the dielectric material and of the metal in their optically highly absorbing state. To investigate the effect of the dielectric material, the optical absorption of a Mg-ideal glass composite is calculated using the Bruggeman approximation and the transfer matrix method (see Sec. IV A) and compared to Mg-MgH$_2$. For Mg the dielectric function given by Palik\textsuperscript{52} is again used, for ideal glass we take $\epsilon_1=2.2$ and $\epsilon_2=0$ over the whole energy range (0.1–20 eV). In the case of MgH$_2$ we use the calculated dielectric function by Alford and Chou\textsuperscript{26} since it covers a wider energy range than the one we measured. The only difference with the measured dielectric function is a shift of 0.5 eV to higher energies so that the calculated gap is 6.1 eV instead of 5.6 eV.\textsuperscript{25} In Fig. 15 the contour plots of the absorption as a function of the volume fraction dielectric material $f_d$ is plotted both for (a) Mg-MgH$_2$ and (b) Mg-ideal glass. The major difference is observed at energies larger than 6.1 eV where MgH$_2$ has its direct band gap in GW calculations.\textsuperscript{26} Above this energy photons can be absorbed in MgH$_2$, thereby exciting electrons from the valence to the conduction band. As a consequence the optical con-
For comparison the absorption of a Ag-ideal glass composite which is studied extensively in literature is shown in Fig. 15(c). The dielectric function for Ag is taken from the handbook of Palik. The maximum absorption reached in this system is about 55% whereas in Mg-ideal glass an absorption up to 85% is observed. Using Eq. (6) we can estimate the photon energy of the surface plasmon resonance to be 3.0 eV. The bulk plasmon resonance is 3.8 eV. However, \( \varepsilon_2 = 0.75 \) and this is not so small compared to \( \varepsilon_1 \). This is due to the fact that Ag is not a free-electron metal like Mg. Silver has a relatively flat \( d \)-band from which a lot of interband transitions are possible. Therefore, the corresponding features are observed at lower energies than estimated.

At the percolation threshold, the light induced oscillating dipoles (surface plasmons) of different particles interact with each other forming collective optical excitations in the whole system. Because of the self-similarity of percolating clusters, every size of resonating clusters is present in a sample, and then every interaction length is active, giving rise to a wide plasmon spectrum near the percolation threshold. This is the cause of the absorption at \( \rho_c \) from the IR to the (bulk) plasmon energy (often in the UV) in metal-dielectric composites near percolation (see Fig. 15 at \( f_p = 0.66 \)).

Strong disorder in these metal-dielectric composites gives rise to strong localization of the surface plasmons in nanometer-sized regions around the percolation threshold. These resonances induce strong fluctuations of the local electric and magnetic fields that significantly exceed the applied fields. The fluctuations can lead as well to a corresponding enhancement of various nonlinear effects. For example surface plasmons in silver aggregates give rise to strong surface enhanced Raman scattering. Shalaev and Sarychev developed a theory to calculate the local electromagnetic fields in metal-dielectric films and are able to reconstruct the large absorption in these composites around the percolation threshold. However, they can model absorptions up to 50% only. Furthermore, they investigated various nonlinear optical properties of these kind of films. So called “hot spots,” spikes in electric (and magnetic) fields are indeed observed recently in gold-on-glass films using scanning optical near-field microscopy. These films also show strongly enhanced second-harmonic generation. It can be expected that these phenomena also exist in our Mg films and RE-Mg alloys.

VI. CONCLUSIONS

A rare-earth-Mg alloy with a considerable amount of Mg exhibits the three fundamental optical states of matter, i.e., reflecting, absorbing, and transparent as a function of hydrogen loading. In thin Mg films this can also be observed when the sample is carefully hydrogenated at elevated temperatures. Important is that MgH₂ starts to nucleate everywhere in the sample instead of the usually observed layered hydrogenation. The optical properties are continuously and reversibly tunable by simply changing the surrounding hydrogen gas pressure. This is a great advantage above conventional metal-dielectric films. The highly absorbing, black state in RE-Mg films is shown to be closely related to the coexist-
ence of Mg and MgH$_2$ nanograins. The high absorption occurs when the changes in the resistivity are large. By using Bruggeman’s effective medium approximation in combination with the transfer-matrix method it is shown that a combination of Mg and MgH$_2$ grains gives indeed rise to a high optical absorption. The role of the RE material is to disproportionate the film into small grains of REH$_2$ and Mg during the first hydrogen loading. These small grains can switch independently and do not suffer from kinetic limitations as in Mg films. The bulk plasmon frequency of the metal determines at what photon energy the absorption due to cluster resonances vanishes. It is expected that our Mg films and RE-Mg alloys exhibit various nonlinear optical effects just as other metal-dielectric compounds.

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43F.H. Ellinger, C.E. Holley, Jr., B.B. McInteen, D. Pavone, R.M.


56 C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).


