

Chemistry and Biochemistry Faculty Publications

Chemistry and Biochemistry

7-2002

# In-situ X-ray-absorption Spectroscopy Study of Hydrogen Absorption by Nickel-Magnesium Thin Films

B. Farangis *Lawrence Berkeley National Laboratory* 

Ponnusamy Nachimuthu University of Nevada, Las Vegas

T. J. Richardson

Lawrence Berkeley National Laboratory

J. L. Slack

Lawrence Berkeley National Laboratory

Rupert C. Perera Follow this and additional works at: https://digitalscholarship.unlv.edu/chem\_fac\_articles Lawrence Berkeley National Laboratory, rcperera@euvl.com

🍑 Part of the Analytical Chemistry Commons, Atomic, Molecular and Optical Physics Commons,

Biological and Chemical Physics Commons, Elementary Particles and Fields and String Theory Commons, See next page for additional authors and the Physical Chemistry Commons

#### **Repository Citation**

Farangis, B., Nachimuthu, P., Richardson, T. J., Slack, J. L., Perera, R. C., Gullikson, E. M., Lindle, D. W., Rubin, M. (2002). In-situ X-ray-absorption Spectroscopy Study of Hydrogen Absorption by Nickel-Magnesium Thin Films. *Physical Review B, 67*(085106), 29.

https://digitalscholarship.unlv.edu/chem\_fac\_articles/56

This Article is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this Article in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Article has been accepted for inclusion in Chemistry and Biochemistry Faculty Publications by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

Authors B. Farangis, Ponnusamy Nachimuthu, T. J. Richardson, J. L. Slack, Rupert C. Perera, Eric M. Gullikson, Dennis W. Lindle, and M. Rubin					

# In situ x-ray absorption spectroscopy study of hydrogen absorption by nickel-magnesium thin films

B. Farangis, P. Nachimuthu, T. J. Richardson, L. Slack, R. C. C. Perera, E. M. Gullikson, D. W. Lindle, and M. Rubin

<sup>1</sup> Environmental Energy Technologies Division <sup>2</sup> Center for X-ray Optics, Materials Sciences Division Lawrence Berkeley National Laboratory 1 Cyclotron Road, Berkeley, CA 94720

> <sup>3</sup> Department of Chemistry University of Nevada, Las Vegas, NV 89154

> > July 2002

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, Building Technologies Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Advanced Light Source is operated by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at LBNL. Financial support from the National Science Foundation under contract Nevada-NSF-EPSCoR is gratefully acknowledged.

*In situ* x-ray absorption spectroscopy study of hydrogen absorption by

nickel-magnesium thin films

B. Farangis, \*P. Nachimuthu, T. J. Richardson, J. L. Slack, R. C. C. Perera,

E. M. Gullikson, M. Rubin

Lawrence Berkeley National Laboratory

D. W. Lindle

\*University of Nevada

Structural and electronic properties of co-sputtered Ni-Mg thin films with varying

Ni to Mg ratio were studied by *in-situ* x-ray absorption spectroscopy in the Ni L-edge and

Mg K-edge regions. Co-deposition of the metals led to increased disorder and decreased

coordination around Ni and Mg compared to pure metal films. Exposure of the metallic

films to hydrogen resulted in formation of hydrides and increased disorder. The presence

of hydrogen as a near neighbor around Mg caused a drastic reduction in the intensities of

multiple scattering resonances at higher energies. The optical switching behavior and

changes in the x-ray spectra varied with Ni to Mg atomic ratio. Pure Mg films with Pd

overlayers were converted to MgH<sub>2</sub>: the H atoms occupy regular sites as in bulk MgH<sub>2</sub>.

Although optical switching was slow in the absence of Ni, the amount of H<sub>2</sub> absorption

was large. Incorporation of Ni in Mg films led to an increase in the speed of optical

switching but decreased maximum transparency. Significant shifts in the Ni L<sub>3</sub> and L<sub>2</sub>

peaks are consistent with strong interaction with hydrogen in the mixed films.

\*tjrichardson@lbl.gov

PACS: 61.10.Ht, 78.20.-e, 78.66.-w, 82.30.-b

1

#### I. INTRODUCTION

Switchable mirrors exhibiting variable optical, mechanical and electrical properties due to uptake and removal of hydrogen were discovered by Huiberts *et al.*<sup>1</sup> They have significant potential for applications in light and heat regulation, display devices, and optical communication systems. The first generation of switchable mirrors was based on rare earth metals which undergo a reversible metal-insulator transition when thin films coated with palladium are exposed to H<sub>2</sub>.<sup>2</sup> Van der Sluis *et al.*<sup>3</sup> reported that incorporation of magnesium increased the transparency of lanthanide hydride films. The larger optical band gap (3.4 eV) for Gd<sub>0.5</sub>Mg<sub>0.5</sub>H<sub>2.5</sub> makes this switchable mirror colorless in contrast to reddish GdH<sub>3</sub>. Recently Richardson *et al.*<sup>4,5</sup> reported switchable mirror effects in thin films of Mg and 3d transition metals (Ni, Mn, Fe, and Co). These are potentially more cost effective since they do not require the expensive and reactive rare earth metals.

A recent report<sup>6</sup> on the hydrogenation of 200 nm thick Mg films with Pd overlayers by H<sub>2</sub> gas at 0.1 MPa and 100° C showed that magnesium hydride is formed, with H<sub>2</sub> loading ranging from 2.9 to 6.6 wt.%. After 24 h, transparent magnesium hydride was obtained.<sup>7</sup> The temperature required for dehydrogenation decreased with decreasing degree of crystallization. Heating the hydride film led to the formation of nano-structured magnesium. H<sub>2</sub> absorption leads to lattice expansion and structural rearrangements, which modify the electronic properties of the films.

Near-edge x-ray absorption fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS) are powerful tools for understanding the electronic and structural properties of thin films.<sup>8-10</sup> These techniques are element-specific and capable of probing the short to medium range structure around an absorbing atom. Among the experimental techniques employed in determining the valence states of atoms in solids, NEXAFS plays a crucial role due to its simplicity and universal applicability. EXAFS is sensitive to the local structure around an atom, and is especially useful in studying amorphous materials.

X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are used to study the electronic and magnetic properties of 3d elements. Theoretical and experimental studies have shown that the band structure of bulk Ni is

different from that of Ni thin films grown on Cu and Co.<sup>11-14</sup> This results in different electronic and magnetic properties. The line shapes of XAS and XMCD spectra can change dramatically for varying film thickness due to electron transfer and hybridization at the interface or due to 3*d* electron correlation effects.<sup>15</sup> Srivastava *et al.*<sup>16</sup> have shown that the thickness dependent density of 3*d* holes for Ni thin films grown on Cu (001) gives rise to a modified XAS line shape. Therefore a detailed analysis of Ni L<sub>2,3</sub> edges (which is a direct measure of unoccupied d states) and Mg K-edge are a useful approach to study the electronic structure of our samples in the metallic and hydride state.

Here we report an investigation of the structural and electronic properties of Ni-Mg thin films with varying Ni to Mg atomic ratio using in-situ x-ray absorption spectroscopy. The mirror-like metallic Ni-Mg thin films become optically transparent due to  $H_2$  absorption. We followed the hydrogenation processes by recording x-ray absorption spectra at both the Mg K and Ni L-edges.

## **Experimental Procedure**

#### Sample preparation

Ni-Mg films for the present study were prepared by dc magnetron co-sputtering from 50 mm Ni and Mg (99.98%) targets inclined 22.5° from normal onto silicon nitride membrane substrates (Silson Ltd., Northampton, UK), which were mounted sequentially on a glass plate to obtain different Ni to Mg atomic ratios. The base pressure was 1.4x10<sup>-7</sup> Torr, process pressure 2 mTorr, Ni power 24 W, Mg power 47 W, target-to-substrate distance 7.5 cm. Deposition rates ranged from 0.33 to 0.55 nm/s, depending on location of the substrate. Palladium was deposited over all Ni-Mg films to protect them from air oxidation and to promote absorption of hydrogen. The Pd over-layer was applied at 10 mTorr, Pd power 12.4 W, with deposition rate 0.16 nm/s. Film thicknesses and compositions were measured by stylus profilometry and Rutherford back scattering (RBS). Mg<sub>2</sub>Ni (containing 20% excess Mg) was purchased from Ergenics, Inc., (Ringwood, NJ) and MgH<sub>2</sub> (nominal purity 90 %, remainder Mg) from Aldrich Chemical Co, (Milwaukee, WI). Powder x-ray diffraction patterns (xrd) for these compounds confirmed their bulk compositions and purity.

#### *X-ray absorption measurements*

The x-ray absorption spectra were measured at beamlines 6.3.1 and 6.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory.<sup>17</sup> During the measurements, the synchrotron was typically operated at 1.9 GeV between 200 and 400 mA. The spectra were recorded at the Mg K and Ni L absorption edges in the bulk-sensitive transmission detection mode, in an atmosphere of He using a 4.6x4.6 mm photodiode detector (Hamamatsu, G1127-02). Hydrogenation of the films was achieved by purging with 4 % H<sub>2</sub> in He. The spectra for reference materials Mg<sub>2</sub>Ni and MgH<sub>2</sub> were measured by total fluorescence yield (TFY) using a 28x28 mm windowless detector (Hamamatsu, S3584-06). The resolution at the Mg K and Ni L-edges was better than 1.5 and 1.0 eV, respectively. The photon energy was calibrated to the first inflection point of the Ni L<sub>3</sub> edge at 852.7 eV and Mg K edge at 1303.0 eV.<sup>18</sup> After calibration, the spectra were normalized to the absorption edge jumps.<sup>8</sup> All measurements were performed at room temperature.

#### **Results and Discussion**

Previous work<sup>3</sup> on Ni-Mg thin films showed that the Ni to Mg atomic ratio and the film thickness are factors in determining the speed at which switching takes place between the metallic state and the transparent hydride state. The freshly sputtered films were amorphous by xrd, showing only weak reflections due to Pd. Co-deposition from offset sources yielded films with position-dependent Ni–Mg atomic ratio and thickness (Table I). They absorbed hydrogen rapidly and reached maximum transparency within a few minutes. When samples were annealed at 125 °C in dry nitrogen, xrd reflections due to Mg<sub>2</sub>Ni, Mg, and Mg<sub>6</sub>Pd developed. The annealed films did not take up H<sub>2</sub> readily.

#### *Ni L*<sub>3,2</sub>-edge *NEXAFS*

Ni  $L_{3,2}$ -edge x-ray absorption spectra measured in transmission mode in He and in 4 %  $H_2$  (balance He) for a pure Ni film and two Ni-Mg films are shown in Fig. 1. The spectrum for  $Mg_2Ni$  powder measured by total fluorescence yield is included for comparison. The transitions denoted as  $L_3$  and  $L_2$ , at ~853.5 eV and ~870.8 eV, are from Ni  $2p_{3/2}$  and  $2p_{1/2}$  to 3d final states, respectively. Satellites at ~3 eV and ~6 eV above the  $L_3$ -edge are seen in all the spectra. The intensity of 6 eV satellite for Ni-Mg

films and Mg<sub>2</sub>Ni are reduced by a factor of five compared to pure Ni film. Recently Dhesi *et al.*<sup>19,20</sup> assigned these satellites to transitions to triplet (3 eV) and singlet (6 eV) states of the final 2p<sup>5</sup>3d<sup>9</sup> configuration, split by the core-valence exchange interaction (multiplet effects). The singlet state can be reached from the triplet 3d<sup>8</sup> initial state by spin-flip transitions due to the 2p spin-orbit interaction. More recently, Nesvizhskii *et al.*<sup>21</sup> based on one-electron multiple scattering and atomic multiplet calculations claimed that the effect of spin-flip transition is negligible and hence the 6 eV satellite is predominantly due to multiple scattering effect, but that the multiplet explanation of Dhesi *et al.*<sup>19,20</sup> is applicable for the 3 eV satellite. The reduced intensity for the 6 eV satellite observed for Ni-Mg films in the present study is therefore attributed to a decreased multiple scattering due to the presence of Mg and the amorphous character of the films.

Spectra were recorded at both Mg K and Ni L-edges during hydrogen loading of films. Ni L<sub>3,2</sub> spectra of Ni<sub>0.24</sub>Mg<sub>0.76</sub>H<sub>x</sub> at different exposure times are presented in Figure 2. The spectrum denoted as 'end of hydrogenation' was recorded after exposure to hydrogen for 24 h. Further exposure produced no changes in the spectrum. H<sub>2</sub> absorption led to a shift towards higher energy and an enhancement in intensity. The extent of both effects depended upon exposure time and Ni:Mg ratio. The time required to reach saturation, corresponding to the optical switching from mirror state to maximum transparency, also depended on the film thickness. Figure 3 shows Ni L<sub>3,2</sub> spectra for a Ni<sub>0.24</sub>Mg<sub>0.76</sub> film as-deposited, fully hydrogenated and dehydrogenated by exposure to air for 24 h. The hydrogen is apparently not completely removed under these conditions.

The full width at half maximum (FWHM) and integrated area for each band was obtained by fitting the Ni L-edge spectra with Gaussian functions. To exclude the edge jump, asymmetric double sigmoidal functions were also included in the fits. The results, along with branching ratios  $\beta_R = A_3/(A_3+A_2)$ , total integrated intensity  $(A_3+A_2)$ , and intensity ratio  $(A_3/A_2)$ , are given in Table II. It has been shown that, due to changes in the final state energies, Ni L<sub>3,2</sub> transitions shift towards higher energy by about 1 eV for each unit increase in oxidation state. <sup>22-25</sup> Since the integrated intensity  $(A_3+A_2)$  is a ground state property, it is a quantitative and a direct measure of 3d shell vacancies  $(n_h)$ . <sup>16,19,22,24</sup> Further, the initial state 3d spin-orbit coupling and the overlap of 2p and 3d wave

functions, the so called multiplet effects, are said to affect the branching ratio  $(\beta_R)^{26,27}$ . Another report, however, maintains that multiplet effects dominate all other interactions. Recent reports demonstrate that one can distinguish the nature of spin states, viz., low spin and high spin for a given oxidation state of Ni, based on the branching ratios  $(\beta_R)$  of  $L_{3,2}$ -edges.  $^{23-25}$ 

In the present study, the energy separation ( $E_3$ - $E_2$ ) between the  $L_3$  and  $L_2$ -edges, which is due to 2p spin-orbital splitting, for all the samples is found to be ~17.3 eV in accordance with earlier reports. <sup>15,16,19</sup> The transition energies (E) for both  $L_{3,2}$ -edges of a Ni film and Ni-Mg films in the metallic state show a small trend towards higher energy from pure Ni film to very Mg-rich (Ni<sub>0.13</sub>Mg<sub>0.87</sub>). The spectral profile and branching ratio for pure Ni film are in good agreement with the pervious reports on bulk Ni metal and for Ni films grown on Cu(001) and Co/Cu(001). <sup>16,19</sup> The Ni film was therefore utilized as a reference for Ni-Mg films. The total integrated intensity ( $A_3$ + $A_2$ ) is smaller and, the  $\beta_R$  and  $A_3/A_2$  are larger for Ni-Mg than for Ni (Table II). These results suggest that the addition of Mg produces structural changes and modification of Ni electronic states. Similar results were reported for Ni film on Cu(001) and Co/Cu(001) due to charge transfer to Ni. <sup>16,19</sup>

Hydrogen uptake by Ni-Mg films caused the transition energies for both  $L_{3,2}$ -edges to shift significantly towards higher energy, by ~2.3 eV for Ni<sub>0.33</sub>Mg<sub>0.67</sub> and ~2.6 eV for Ni<sub>0.13</sub>Mg<sub>0.87</sub>. The total integrated intensity and FWHM also increase. The values for  $\beta_R$  and  $A_3/A_2$  are comparable to those for the Ni film. In general, the effective charge transfer from metal to hydrogen is reported to be less for metal hydrides than for halides, oxides, etc. where the charge transfer is much greater. <sup>29,30</sup> This is supported by the values of  $\beta_R$  and  $A_3/A_2$  for Ni-Mg films in the hydride state, which are comparable to those for the Ni film, indicating that although Ni is in a higher oxidation state, the effective charge transfer in the hydride is less than in the metal. The values of  $\beta_R$  suggest that Ni in hydrided Ni-Mg films is in a high-spin state. <sup>23-25</sup> Hydriding also leads to the creation of non-equivalent Ni sites, which result in larger FWHMs.

#### Mg K-edge NEXAFS

Mg K near-edge transmission mode spectra of a pure Mg film (270 nm) and two extreme compositions of Ni-Mg films in He and in 4 % H<sub>2</sub> are shown in Fig. 4. The Mg K-edge is shifted to lower energy for Ni-Mg films in the metallic state (1302.2 eV) compared to pure Mg film (1303.0 eV). The intensity of the spectral profile at 1304.5 eV decreases for Ni rich Ni<sub>0.33</sub>Mg<sub>0.67</sub> film when compared to Mg rich Ni<sub>0.33</sub>Mg<sub>0.67</sub> and pure Mg films. Spectra reported for magnesium halides, magnesium oxide, and Mg in minerals and disordered systems show not only a sharp near-edge peak at ~1310 eV due to the 1s to 3p transition whose intensity depends on the degeneracy of the 3p states but also this feature shifts towards higher energy with increasing coordination around Mg.<sup>31-35</sup> In the present study, the transition at 1304.5 eV in pure Mg and Ni-Mg films is assigned to Mg 1s to 3p. The edge shift towards lower energy and reduction in the intensity of the peak with increasing nickel content suggest that the coordination around Mg decreases, resulting in lowering of 3p degeneracy.

The NEXAFS total fluorescence yield (TFY) spectra for the pure Mg film (270 nm), for Mg<sub>2</sub>Ni and MgH<sub>2</sub> powder samples, and a transmission mode spectrum of a thin Mg film (45 nm) in the presence of He and 4 % H<sub>2</sub> are shown in Figure 5. The similarity in the spectral profiles and edge positions for Mg<sub>2</sub>Ni and the Ni<sub>0.33</sub>Mg<sub>0.67</sub> film are consistent with Mg-Ni bonding in the film. The Mg K-edge TFY spectrum for the pure Mg film (270 nm) differs from the transmission mode spectrum (Figs. 4 and 5). Transmission measurements are bulk-sensitive, while TFY probes only to ca. 100 nm in depth. The TFY spectrum for the Mg film reflects both pure Mg and the Mg-Pd interface region. Comparison with the transmission spectrum of a thinner (45 nm) Mg film confirms the presence of different surface and bulk compositions.

The Mg K-edge spectra shifted towards higher energy by ~2.2 and ~2.9 eV for  $Ni_{0.33}Mg_{0.67}$  and  $Ni_{0.13}Mg_{0.87}$ , respectively, when hydrogen is introduced. In addition, the transitions at higher energies due to multiple scattering resonances were significantly reduced by the presence of hydrogen, which scatters weakly due to its low mass.<sup>36,37</sup> The spectrum of the thick Mg film showed no significant changes on exposure to  $H_2$  for 2 h, consistent with previous observations of very slow diffusion of hydrogen in relatively thick Mg films.<sup>29</sup> The thin Mg film, however exhibited a 3.5 eV shift following overnight

soaking in 4 %  $H_2$  at room temperature. This is consistent with optical properties of Mg film with Pd overlayer, which show that an increase in Mg thickness decreases the optical response to hydrogen exposure.<sup>38</sup> The Mg K-edge TFY spectrum for bulk MgH<sub>2</sub> also shows a shift of ~2.3 eV towards higher energy compared to the Mg film, consistent with the presence of divalent Mg.

#### **Magnesium K-Edge EXAFS**

EXAFS data were analyzed using a background-subtraction method<sup>39-43</sup> with optimization of the low *r* portion of the EXAFS, followed by Fourier transformation to *r* space. The normalized spectra of the 270 nm Mg film and two Ni-Mg films are shown in Figure 6. The magnitude of the oscillations decreased with increasing nickel concentration in as-deposited Ni-Mg films due to disruption of the Mg structure. In the hydride state only very weak EXAFS oscillations were observed irrespective of Ni content. Comparison of EXAFS for Ni-Mg films in the hydride and metallic states with bulk MgH<sub>2</sub> and Mg<sub>2</sub>Ni (Fig. 7) suggests that more of the magnesium in the Ni<sub>0.13</sub>Mg<sub>0.87</sub> film is hydrided than in the Ni<sub>0.33</sub>Mg<sub>0.67</sub> film, where unreacted Mg<sub>2</sub>Ni remains. To get more insight into the structural properties of Ni-Mg thin films, detailed analyses of the experimental EXAFS spectra were conducted by theoretical fits.

Scattering amplitudes and phase shift functions of the Mg-Mg, Mg-Ni, and Mg-O pairs in Mg, Mg<sub>2</sub>Ni and MgO were calculated using the program FEFF (7.02).<sup>40,41</sup> The FEFFIT (2.5*d*),<sup>42</sup> which is based on a nonlinear least squares technique was used to fit the experimental *r* space EXAFS data. Phase-corrected Fourier transforms of  $\chi(k)$  to *r* space with a  $k^2$  weighting factor and a Hanning window function (Dk1 and Dk2=0.1) were performed using values of K<sub>min</sub>, K<sub>max</sub>, r<sub>min</sub>, and r<sub>min</sub> of 1.8 Å<sup>-1</sup>, 5.6 Å<sup>-1</sup>, 2.1 Å and 5.1 Å, respectively. The value of the passive electron reduction factor ( $S_0^2$ )<sup>43</sup> was deduced from the spectrum of MgO and used for fitting Ni-Mg film spectra.

The Fourier transformed  $k^2$ -weighted Mg K-edge EXAFS intensities for Ni-Mg films in their metallic states are presented in Figure 8 along with theoretical fits. Figure 9 shows the fitting results in k space. The resultant structural parameters, coordination number (N), bond distance (R) and Debye-Waller factor ( $\sigma^2$ ) for Mg, Ni<sub>0.13</sub>Mg<sub>0.87</sub> and Ni<sub>0.33</sub>Mg<sub>0.67</sub> are given in Table III. Attempts were made to fit the data using Mg-Mg (first

and second shell), Mg-Ni and Mg-O interactions. No significant contributions from Mg-Ni and Mg-O were found. There is a decrease in amplitude of the Fourier-transformed intensity on the addition of nickel. The nearest neighbor and next nearest neighbor Mg-Mg shells experience a decrease in mean square relative displacement (MSRD) with increasing nickel concentration. Although the Ni-Mg films are amorphous by XRD, there is microscopic ordering up to the second shell (~4.5 Å), despite decreased coordination numbers and increases disorder with increasing Ni concentration.

Attempts to fit the EXAFS data for Ni-Mg films in the hydride states failed due to high signal to noise ratios and weak EXAFS oscillations due to the presence of hydrogen as nearest neighbor. The weak EXAFS oscillations in k space for Ni-Mg films in hydride state were therefore compared with reference materials MgH<sub>2</sub> and Mg<sub>2</sub>Ni (Fig. 10).

The hydrided 45 nm Mg film shows the features similar to those in bulk MgH<sub>2</sub>.<sup>6,7</sup> Hydrided Ni-Mg films, however, do not resemble bulk MgH<sub>2</sub>. Instead, Ni<sub>0.13</sub>Mg<sub>0.87</sub> and Ni<sub>0.33</sub>Mg<sub>0.67</sub> in both metallic and hydrides state look more like Mg<sub>2</sub>Ni. This suggests that the Ni-Mg films contain some Mg<sub>2</sub>Ni, which dominates the Mg EXAFS spectrum and that this phase persists even when the free magnesium is converted to its hydride. These results are also consistent with the lower transparency of films with higher Ni content. A relatively small amount of Ni (~10 mol %) is sufficient to facilitate absorption of H<sub>2</sub>.

#### **Conclusions**

The co-sputtered Ni–Mg films were amorphous. The presence of nickel led to increased disorder and decreased coordination around both Ni and Mg compared to pure metal films. Introducing H<sub>2</sub> into Ni-Mg films resulted in the formation of Mg-Ni and Mg hydrides, with significant positive edge shifts. The presence of hydrogen as a near neighbor around Mg produced a drastic reduction in the intensities of multiple scattering resonances at higher energies. The extent of hydriding depended on the Ni-Mg ratio. A thin pure Mg film also was converted to MgH<sub>2</sub>. Although the absorption was much slower without nickel, the extent of hydriding was greater. Addition of Ni led to an increase in optical switching speed, a decrease in maximum optical transparency, and a decrease in Mg utilization, probably due to the presence of unreacted Mg<sub>2</sub>Ni. Opimization of switching speed and desired transmittance and reflectance ranges requires adjustment both of the Ni-Mg ratio and film thickness.

### Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, Building Technologies Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Advanced Light Source is operated by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at LBNL. Financial support from the National Science Foundation under contract Nevada-NSF-EPSCoR is gratefully acknowledged.

# References

- <sup>1</sup>J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London) **380**, 231 (1996).
- <sup>2</sup>R. Griessen, Europhysics News **32**, 40 (2001).
- <sup>3</sup>P. van der Sluis, M. Ouwerkerk, and P. A. Duine, Appl. Phys. Lett. **70**, 3356 (1997).
- <sup>4</sup>T. J. Richardson, J. L. Slack, R. D. Armitage, R. Kostecki, B. Farangis, and M. D. Rubin, Appl. Phys. Lett. **78**, 3047 (2001).
- <sup>5</sup>T. J. Richardson, J. L. Slack, B. Farangis, and M. D. Rubin, Appl. Phys. Lett. **80**, 1349 (2002).
- <sup>6</sup>K. Higuchi, H. Kajioka, K. Toiyama, H. Fujii, S. Orimo, and Y. Kikuchi, J. Alloys and Compds. **293–5**, 484 (1999).
- <sup>7</sup>K. Yamamoto, K. Higuchi, H. Kajioka, H. Sumida, S. Orimo, and H. Fujii, J. Alloys and Compds. **330–2**, 352 (2002).
- <sup>8</sup>J. Stöhr, *NEXAFS Spectroscopy*, (Springer, New York, 1992),
- <sup>9</sup>J. G. Chen, Surf. Sci. Rep. **30**, 1 (1997).
- <sup>10</sup>F. M. F. de Groot, Chem. Rev. **101**, 1779 (2001).
- <sup>11</sup>D. Wang, A. J. Freeman, and H. Krakauer, Phys. Rev. B **26**, 1340 (1982).
- <sup>12</sup>J. Tersoff and L. M. Falicov, Phys. Rev. B **26**, 6186 (1982).
- <sup>13</sup>O. Eriksson, A. M. Boring, R. C. Albers, G. W. Fernando, and B. R. Copper, Phys. Rev. B 45, 2868 (1992).
- <sup>14</sup>O. Hjortstam, J. Trygg, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **53**, 9204 (1996).
- <sup>15</sup>S. S. Dhesi, E. Dudzik, H. A. Dürr, G. van der Lann, and N. B. Brookes, J. Appl. Phys. 87, 5466 (2000).
- <sup>16</sup>P. Srivastava, N. Haack, H. Wende, R. Chauvistré, and K. Baberschke, Phys. Rev. B 56, R4398 (1997).
- <sup>17</sup>J. H. Underwood and E. M. Gullikson, J. Eelctron Spectrosc. Relat. Phenom. **92**, 265 (1998).
- <sup>18</sup>X-ray Data Booklet, LBNL/PUB490 Rev. 2 (2001).

- <sup>19</sup>S. S. Dhesi, H. A. Dürr, G. van der Lann, E. Dudzik, and N. B. Brookes, Phys. Rev. B 60, 12852 (1999).
- <sup>20</sup>S. S. Dhesi, E. Dudzik, H. A. Dürr, N. B. Brookes, and G. van der Laan, Surf. Sci. 454-6, 930 (2000).
- <sup>21</sup>A. I. Nesvizhskii, A. L. Ankudinov, J. J. Rehr, and K. Baberschke Phys. Rev. B **62**, 15295 (2000).
- <sup>22</sup>H. Wang, P. Ge, C. G. Riordan, S. Brooker, C. G. Woomer, T. Collins, C. A. Melendres, O. Graudejus, N. Bartlett, and S. P. Cramer, J. Phys. Chem. B 102, 8343 (1998).
- <sup>23</sup>H. Wang, C. Y. Ralston, D. S. Patil, R. M. Jones, W. Gu, M. Verhagen, M. Adams, P. Ge, C. Riordan, C. A. Marganian, P. Mascharak, J. Kovacs, C. G. Miller, T. J. Collins, S. Brooker, P. D. Croucher, K. Wang, E. I. Stiefel, and S. P. Cramer, J. Am. Chem. Soc. 122, 10 544 (2000).
- <sup>24</sup>H. Wang, D. S. Patil, W. Gu, L. Jacquamet, S. Friedrich, T. Funk, and S. P. Cramer, J. Electron Spectrosc. Relat. Phenom. **114–6**, 855 (2001).
- <sup>25</sup>C. Y. Ralston, H. Wang, S. W. Ragsdale, M. Kumar, N. J. Spangler, P. W. Ludden, W. Gu, R. M. Jones, D. S. Patil, and S. P. Cramer, J. Am. Chem. Soc. **122**, 10553 (2000).
- <sup>26</sup>B. T. Thole and G. van der Lann, Phys. Rev. B **38**, 3158 (1988).
- <sup>27</sup>G. van der Lann and B. T. Thole, Phys. Rev. Lett. **60**, 1977 (1988).
- <sup>28</sup>F. M. F. de Groot, Physica B **208-9**, 15 (1995).
- <sup>29</sup>M. Gupta and L. Schlapbach, *Hydrogen in Intermetallic Compounds I*, edited by L. Schlapbach (Springer, Berlin, 1988), Chap. 6.
- <sup>30</sup>R. Yu and P. K. Lam, Phys. Rev. B **37**, 8730 (1988).
- <sup>31</sup>S. Naoé, T. Murata, and T. Matsukawa, Physica B **158**, 615 (1989).
- <sup>32</sup>T. Yoshida, T. Tanaka, H. Yoshida, T. Funabiki, and S. Yoshida, J. Phys. Chem. **100**, 2302 (1996).
- <sup>33</sup>H. Aritani, T. Tanaka, T. Funabiki, S. Yoshida, M. Kudo, and S. Hasegawa, J. Phys. Chem. **100**, 5440 (1996).
- <sup>34</sup>H. Aritani, H. Yamada, T. Nishio, T. Shiono, S. Imamura, M. Kudo, S. Hasegawa, T. Tanaka, and S. Yoshida, J. Phys. Chem. **104**, 10 133 (2000).

- <sup>35</sup>Ph. Ildefonse, G. Calas, A. M. Flank, and P. Lagarde, Nucl. Instr. and Meth. in Phys. Res. B **97**, 172 (1995).
- <sup>36</sup>R R. G. Agostino, G. Liberti, V. Formoso, E. Colavita, A. Züttel, C. Nützenadel, L. Schlapbach A. Santaniello, and C. Gauthier, Phys. Rev. B **61**, 13 647 (2000).
- <sup>37</sup>B. Lengeler, Phys. Rev. Lett. **53**, 74 (1984).
- <sup>38</sup>T. J. Richardson *et al.*, unpublished.
- <sup>39</sup>M. Newville, P. Livins, Y. Yacoby, J. J. Rehr, and E. A. Stern, Phys. Rev. B 47, 14126 (1993).
- <sup>40</sup>A. L. Ankudinov and J. J. Rehr, Phys. Rev. B **56**, R1712 (1997).
- <sup>41</sup>A. L. Ankudinov, Ph.D. thesis, University of Washington, 1996.
- <sup>42</sup>E. A. Stern, M. Newville, B. D. Ravel, Y. Yacoby, and D. Haskel, Physica B **208-9**, 117 (1995).
- <sup>43</sup>E. A. Stern and S. M. Heald, in *Handbook on Synchrotron Radiation*, edited by E. E. Koch (North-Holland, New York, 1983), Vol. 1.

**Table I.** Ni-Mg Film and Pd over-layer thicknesses and compositions.

Sample	Film thickness	Pd over-layer	Composition
	(nm)	thickness (nm)	
Ni128_1	100	20	Ni
NiMg130_2	154	11	$Ni_{0.33}Mg_{0.67}$
NiMg130_3	172	11	$Ni_{0.25}Mg_{0.75}$
NiMg130_4	218	11	$Ni_{0.17}Mg_{0.83}$
NiMg130_5	232	11	$Ni_{0.13}Mg_{0.87}$
NiMg129_3	262	22	$Ni_{0.24}Mg_{0.76}$
Mg131_5	270	10	Mg
Mg152_1	45	10	Mg

**Table II.** Transition energies (E), integrated areas (A), full width at half maximum (FWHM), branching ratios,  $\beta_R = A_3/(A_3+A_2)$ , total integrated intensities,  $(A_3+A_2)$  and intensity ratios  $(A_3/A_2)$  for Ni  $L_{3,2}$ -edge XRAS of (A) Ni (B & E) Ni<sub>0.33</sub>Mg<sub>0.67</sub> (C & F) Ni<sub>0.13</sub>Mg<sub>0.87</sub> and (D) Mg<sub>2</sub>Ni.

Sam	J	<u>_3</u>	]	$L_2$	FWHM	$\beta_R$	$A_3 + A_2$	$(A_3/A_2)$
ple	E <sub>3</sub> (eV)	A <sub>3</sub> (a.u.)	E <sub>2</sub> (eV)	A <sub>2</sub> (a.u.)	(eV)		(a.u.)	
$A^{\dagger}$	853.5	2.02	870.8	0.66	3.1	0.754	2.68	3.06
$\mathbf{B}^{\dagger}$	853.7	0.88	871.0	0.20	2.0	0.816	1.08	4.40
$\mathbf{C}^{\dagger}$	853.9	1.01	871.1	0.19	2.3	0.840	1.2	5.32
D‡	853.2	1.70	870.3	0.37	3.2	0.821	2.07	4.60
E*	856.0	2.55	873.4	0.81	3.9	0.758	3.36	3.15
F*	856.5	3.07	873.9	0.99	3.6	0.757	4.06	3.10

<sup>&</sup>lt;sup>†</sup> XAS measured in transmission mode in He atmosphere.

<sup>‡</sup> Total fluorescence yield (TFY) under vacuum.

<sup>\*</sup> XAS measured in transmission mode in 4 % H<sub>2</sub> in He atmosphere.

**Table III**. Coordination numbers  $(N_{Mg})$ , bond distances  $(R_{Mg-Mg})$ , and Debye–Waller factors  $(\sigma^2_{Mg-Mg})$  obtained from Mg K-edge EXAFS for thin films in metallic state.

	Mg-Mg (first shell)			Mg-Mg (second shell)		
Sample	N	R(Å)	$\sigma^2(10^{-2}\text{Å}^2)$	N	R(Å)	$\sigma^2(10^{-2}\text{Å}^2)$
Mg	12.00(66)	3.203(3)	2.21(19)	4.92(97)	4.568(24)	2.63(19)
$Ni_{0.13}Mg_{0.87}$	8.60(17)	3.098(1)	2.75(7)	2.92(25)	4.465(11)	3.27(7)
$Ni_{0.33}Mg_{0.67}$	3.33(39)	3.038(6)	1.65(35)	1.70(57)	4.472(35)	1.96(35)

#### **Figure Captions**

- **1.** Ni L<sub>3,2</sub>-edge transmission mode NEXAFS spectra of thin films measured in He: (a) pure Ni, (b) Ni<sub>0.33</sub>Mg<sub>0.67</sub> and (c) Ni<sub>0.13</sub>Mg<sub>0.87</sub>; in 4 % H<sub>2</sub> in He: (e) Ni<sub>0.33</sub>Mg<sub>0.67</sub> and (f) Ni<sub>0.13</sub>Mg<sub>0.87</sub>. Spectrum (d) Mg<sub>2</sub>Ni measured by total fluorescence yield in vacuum. The 6 eV satellite is indicated by arrow. All spectra were normalized to the background. Baselines were shifted for clarity of presentation.
- **2.** Transmission mode Ni  $L_{3,2}$ -edge NEXAS spectra of Ni<sub>0.24</sub>Mg<sub>0.76</sub> thin film measured in He (denoted as 'virgin') and in 4 % H<sub>2</sub> in He (all other curves) as a function of time. The curve denoted as 'end of hydrogenation' was recorded after 24h exposure.
- **3.** Transmission mode Ni  $L_{3,2}$ -edge NEXAS spectra of Ni<sub>0.24</sub>Mg<sub>0.76</sub> thin film in He (solid line), in 4 % H<sub>2</sub> after prolonged hydrogenation (dashed line), and in He after 1 day in air (dotted line).
- **4.** Transmission mode Mg K-edge NEXAFS spectra of thin films in He: (a) Mg, (b)  $Ni_{0.13}Mg_{0.87}$ , (c)  $Ni_{0.33}Mg_{0.67}$ ; in 4 % H<sub>2</sub> in He: (d)  $Ni_{0.13}Mg_{0.87}$  and (e)  $Ni_{0.33}Mg_{0.67}$ .
- **5.** Mg K-edge NEXAFS spectra of: (a) Mg 270 nm (TFY), (b) Mg 45 nm (transmission in He), (c) Mg<sub>2</sub>Ni (TFY), (d) MgH<sub>2</sub> (TFY), and (e) Mg 45 nm (transmission in 4 % H<sub>2</sub> in He).
- **6.** Mg K-edge EXAFS spectra of thin films measured by transmission in He: (a) Mg, (b)  $Ni_{0.13}Mg_{0.87}$ , (c)  $Ni_{0.33}Mg_{0.67}$ ; in 4 % H<sub>2</sub> in He: (d)  $Ni_{0.13}Mg_{0.87}$ , (e)  $Ni_{0.33}Mg_{0.67}$ .
- **7.** Mg K-edge EXAFS spectra of: (a) Mg 270 nm (transmission in He), (b) Mg 45 nm (transmission in He), (c) Mg<sub>2</sub>Ni (TFY), (d) MgH<sub>2</sub> (TFY), and (e) Mg 45 nm (transmission in 4 % H<sub>2</sub> in He).
- **8.** Phase corrected and Fourier transformed Mg K-edge EXAFS spectra of Mg,  $Ni_{0.13}Mg_{0.87}$ , and  $Ni_{0.33}Mg_{0.67}$  thin films in the metallic state.

- **9.** Fit results in k space for Mg K-edge EXAFS spectra of Mg,  $Ni_{0.13}Mg_{0.87}$  and  $Ni_{0.33}Mg_{0.67}$ , thin films in the metallic state.
- **10.** Mg K-edge EXAFS in k space for: (a) MgH<sub>2</sub>, (b) Mg (45 nm) thin film in hydride state, (c) Mg<sub>2</sub>Ni, (d) Ni<sub>0.13</sub>Mg<sub>0.87</sub> in hydride state, (e) Ni<sub>0.33</sub>Mg<sub>0.67</sub> in hydride, and (f) Ni<sub>0.33</sub>Mg<sub>0.67</sub> in metallic state.

Figure 1

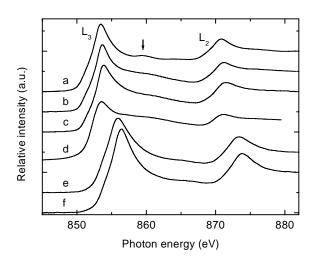


Figure 2

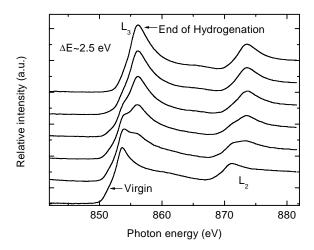


Figure 3

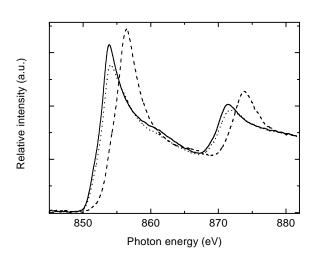


Figure 4

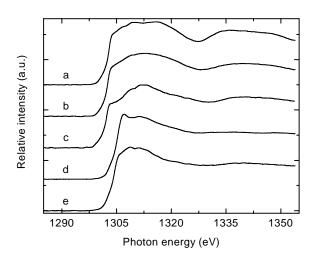


Figure 5

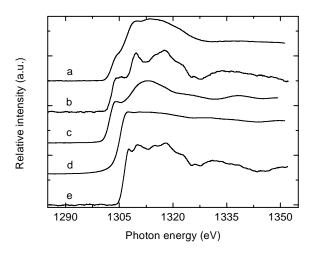


Figure 6

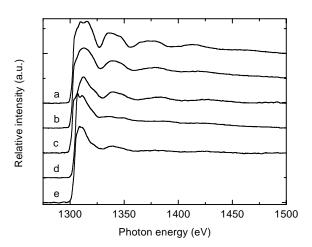


Figure 7

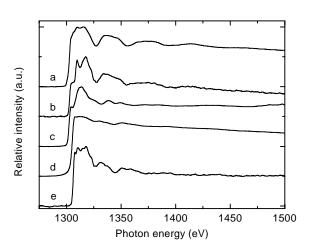


Figure 8

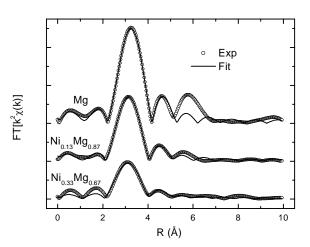


Figure 9

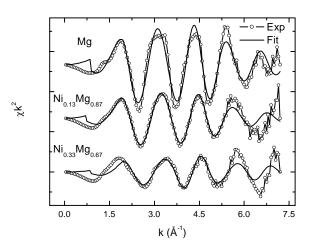


Figure 10

