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Spectroscopic evidence for reversible hydrogen storage in unordered Mg₅Ni₁ thin films

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Abstract

Thin magnesium–nickel films grown on Mo(110) under ultra-high vacuum conditions were hydrogenated with atomic H and studied by high-resolution core-level photoelectron spectroscopy (PES) and thermal desorption spectroscopy (TDS). We show spectroscopic evidence for reversible hydrogen storage and clear evidence that no Mg segregation or desorption occurs when hydrogen is desorbed from the film. During the heat-up of the hydrogenated Mg₅Ni₁ film (0.7 K s⁻¹) TDS shows that hydrogen desorption starts at 350 K and reaches its maximum at 420 K. Mg desorption starts at 450 K. The stability of the storage can be enhanced by cooling.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen-absorbing materials are of great interest for potential applications as hydrogen storage in moving vehicles (for a review see e.g. [1]). One of them is Mg (MgH₂), which has a good weight to absorption capacity ratio. Photoemission studies of the hydrogenation of Mg single crystals have been done by Sprunger and Plummer [2, 3]. Hydrogen absorption and desorption have been further studied on thin Mg films by Ostefeld *et al* [4], as they are experimentally easier to handle and more relevant for applications. However, the bonds between Mg and H are too strong in pure Mg. For reaching the parameter space needed for mobile hydrogen storage regarding compressibility, desorption temperature and reusability [1], Mg compounds have been preferred to pure Mg, primarily Mg–Ni alloys. The hydrogen is stored in a hydride phase; in this case the hydrogen atoms are chemically bonded to Mg. Theoretical studies [5] show that Mg–Ni has relatively low hydride formation energy. Nevertheless, hydrogen absorption in Mg–Ni alloys has only rarely been studied by means of photoelectron spectroscopy (PES).

Our previous comparative study [6] of the hydrogenation of both Mg and Mg–Ni films revealed different mechanisms of hydride formation, and we found that Mg–Ni is more desirable for applications than Mg. For the Mg film a layer of hydride was found to form

at the Mg/Mo interface (due to the catalytic properties of Mo) and a sub-monolayer of hydride at the surface, while the intermediate region remained non-hydrogenated. For the Mg–Ni film a thick layer of surface hydride was detected, showing that Ni enhances the formation of Mg-hydride at the surface. Ni was thus found to act as a catalyst for the Mg-hydride formation and to influence both the magnitude of hydrogenation and its distribution within the Mg film. Under the influence of Ni a thick surface hydride layer was formed, which furthermore could be desorbed from the film.

In this paper we present a study based on PES and thermal desorption spectroscopy (TDS) of hydrogen absorption and desorption in thin Mg–Ni films grown on Mo(110). We focus on the reversibility of hydrogenation, i.e. the possibility to hydrogenize and dehydrogenize a Mg–Ni film, without altering the host material. This capability is crucial for hydrogen storage, and in this paper we show spectroscopic evidence for it.

2. Experimental details

The photoelectron spectra were measured at beamline I311 at the MAX-lab synchrotron radiation facility in Lund, Sweden. This beamline has a modified SX-700 plane grating monochromator and a Scienta SES-200 electron energy analyser and is therefore well suited for high-resolution electron spectroscopy at high photon energies (up to $h\nu = 1500$ eV). The base pressure in the vacuum chamber was in the low 10^{-10} mbar range. The experimental energy resolution was 600 meV for spectra measured with $h\nu = 810$ eV, 200 meV for spectra measured with $h\nu = 350$ eV, and 50 meV for spectra measured with $h\nu = 150$ eV. The FitXPS2 software [7] was used for core-level fits.

The Mo(110) crystal was cleaned by Ar-ion sputtering (3 keV) followed by annealing at 1300 K. Surface cleanliness was checked by PES and surface ordering by low-energy electron diffraction (LEED), which showed a sharp 1×1 pattern. Mg was evaporated from a Ta boat heated by a tungsten filament, and Ni was evaporated from a Ni wire which was wound around a tungsten filament. A 17 Å thick unordered Mg–Ni film was evaporated in 40 min at a rate of ~ 0.4 Å min^{-1} . The Ni to Mg ratio in the film was 1:5. After the evaporation the LEED pattern disappeared and $\sim 2\%$ of oxygen contamination was detected by PES.

The Mg–Ni film was hydrogenized using atomic H, which was disassociated on a hot tungsten filament ~ 5 cm from the sample. The sample was actually exposed to a mixture of H and H₂, but it is the H exposure which is relevant for the experiment because H₂ will not be absorbed [6]. By using a tungsten filament to disassociate H₂ we circumvented the use of an additional surface layer (e.g. Pd to disassociate H₂ [8]). This is a big experimental advantage, because PES is a surface-sensitive technique. Hydrogen was dosed for 5 min at the preparation chamber pressure of 1×10^{-5} mbar at room temperature.

The Mg–Ni film was both charged and discharged with hydrogen. The hydrogen charging is described above and the discharge was done by heating. The sample was heated up by running a constant current through the tungsten wire holding the Mo(110) crystal (substrate) while the hydrogenated Mg–Ni film was pointed towards a mass spectrometer (MKS, MicroVision Plus) to monitor the hydrogen ($m/e = 2$) and magnesium ($m/e = 24$) signals (i.e. no linear programming). The sample was ~ 15 cm from the mass spectrometer. The temperature was measured with a K-type (Cr/Al) thermocouple.

3. Results and discussion

The thicknesses of the Mg and Mg–Ni films were estimated from the attenuation of the Mo 3d (substrate) signal according to the following equation (see [9]):

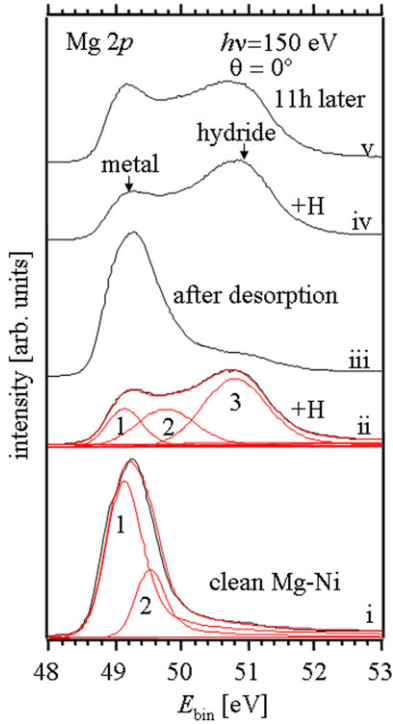


Figure 1. Mg 2p spectra from a clean Mg–Ni film (i), after H deposition (ii), after H₂ desorption (iii), after H redeposition (iv) and 11 h later (v). The spectra were measured at normal emission with a photon energy of 150 eV.

$$\frac{I_{\text{after}}}{I_{\text{before}}} = e^{-t/\lambda}, \quad (1)$$

where I is intensity of Mo 3d peaks before and after evaporation of the Mg–Ni film, λ is the inelastic mean free path and t is the thickness of the film. Mean free path values from the universal curve were used. The thickness of the film was found to be 17 Å (the estimated error is less than 20%). All beamline and analyser parameters were identical for the measurements used for this evaluation, and changes in the radiation flux have been taken into account.

The proportions of Mg and Ni in the Mg–Ni film were found by comparing Mg 2p and Ni 3p core-level spectra and taking photoemission cross-sections [10] into account, as formulated in the following equation:

$$\frac{\text{Ni}_{\text{conc.}}}{\text{Mg}_{\text{conc.}}} = \frac{I_{\text{Ni 3p}}/\sigma_{\text{Ni 3p}}}{I_{\text{Mg 2p}}/\sigma_{\text{Mg 2p}}}, \quad (2)$$

where I is intensity in core-level peaks and σ is the photoemission cross-section. Because of the similar kinetic energy of photoelectrons from Mg 2p and Ni 3p, the mean free paths, λ , were approximately the same and did not have to be included in equation (2). The Ni to Mg ratio in the film was found to be 1:5 (estimated error $\sim 10\%$). To check the Ni to Mg ratio in the whole film we measured spectra at different settings (810 eV at normal emission, 350 eV at normal emission and at a polar emission angle $\theta = 60^\circ$) and used equation (2). The same Ni to Mg ratio was obtained through the whole film (1:5).

All beamline and analyser parameters were identical for all compared peaks, and changes in the radiation flux have been taken into account (the Mg 2p peak and the Ni 3p peak were measured in the same spectrum).

Figure 1 shows the Mg 2p spectrum during two cycles of hydrogen being stored in and emptied from a Mg–Ni film. The clean Mg 2p spectrum (spectrum (i) in figure 1) changes

Table 1. Results from fit of the Mg 2p core-level spectra from figure 1. The spectra were measured with a photon energy of 150 eV at normal emission. The table shows the intensities of the Mg–Ni (peak 1), Mg (peak 2) and hydride peak (peak 3), as a percentage of the total emission.

Spectra	(i)	(ii)	(iii)	(iv)	(v)
$I_{\text{Mg-Ni}}$ (peak 1)	73%	17%	70%	14%	19%
I_{Mg} (peak 2)	27%	28%	21%	25%	29%
I_{Hydride} (peak 3)	—	55%	14%	62%	52%

when the film becomes hydrogenated in such a way that metallic emission decreases, while the hydride peak at the higher binding energy increases (spectrum (ii) in figure 1), in accordance with [6]. When the hydrogenated film was warmed up, H_2 left the sample and the hydride peak decreased. During the absorption/desorption cycles the heating was stopped at 420 K. Furthermore, it was possible to refill the sample again with hydrogen (see spectrum (iv) in figure 1). This is spectroscopic evidence for reusable hydrogen storage in Mg–Ni films. At these conditions (ultra-high vacuum (UHV) and room temperature) a slow dehydrogenation of the hydrogenated Mg–Ni film was detected. This is clear from spectrum (v) in figure 1 measured 11 h after spectrum (iv).

The Mg 2p spectra in figure 1 were analysed with a peak-fitting software [7]. The Mg 2p level from the Mg–Ni film was broad and the inclusion of a spin–orbit split in the fitting procedure was not obvious. We showed that it is possible to fit the Mg 2p level with three peaks [6]. These peaks are a Mg–Ni peak at 49.1 eV with a full width at half maximum (FWHM) of 0.65 eV (marked 1 in figure 1), a Mg peak at 49.6 eV with a FWHM of 1.0 eV (marked 2 in figure 1) and a hydride peak at ~ 50.8 eV with a FWHM of 1.2 (marked 3 in figure 1). Peak 1 originates from Mg bonded to Ni, peak 2 originates from Mg which is not bonded to Ni, and peak 3 originates from Mg bonded to hydrogen atoms. The deconvolution is shown for spectra (i) and (ii) in figure 1. Peak 1 and peak 2 were already present in the Mg 2p spectrum of the clean Mg–Ni film (spectra (i) and (iii) in figure 1), while peak 3 is significant only on hydrogenated surfaces (spectra (ii), (iv) and (v) in figure 1). For the clean or dehydrogenated surface (spectra (i) and (iii) in figure 1), peak 2 was at 49.5 eV and less wide. This is caused by a different surrounding i.e. metal and not hydride. The intensities of peaks 1, 2 and 3 were obtained by core-level fitting of all five spectra presented in figure 1 and are summarized in table 1.

By comparing the intensities of fitted core-level peaks corresponding to metal (peak 1 in figure 1) and hydride (peak 3 in figure 1), the thickness of the hydride layer was found to be ~ 8 Å (peak 2 should not be included while calculating the thickness of the hydride layer; this is further explained in [6]). In the photoelectron spectrum measured at a polar angle of 60° , (not shown) the hydride peak is stronger; this confirmed that the hydride was on top of the metal. During the absorption/desorption cycles the heating was stopped at 420 K. At this temperature, most of the hydrogen had desorbed from the film, but Mg segregation and desorption had not yet started, in accordance with [6]. The Mg 2p core-level spectrum after hydrogen desorption (spectrum (iii) in figure 1) is very similar to the one of the clean surface (spectrum (i) in figure 1). But core-level fits revealed emission from the hydride peak (compare spectra (i) and (iii) in table 1). But this hydride peak (peak 3 in spectrum (iii) in figure 1) is not surface sensitive, and therefore the remnant of the hydride seemed to be homogeneously distributed in the film. It is possible that with a slower temperature rise the dehydrogenation would be more complete. In the case of oxidation, peak 3 in spectrum (iii) could be a core-level shift from MgO. However, this can be excluded, because we had about the same amount of oxygen impurities (~ 2 – 3%) on the surface as on the clean film, and the clean film showed no MgO emission (spectrum (i) in figure 1). Also this peak (peak 3 in spectrum (iii)) was not surface

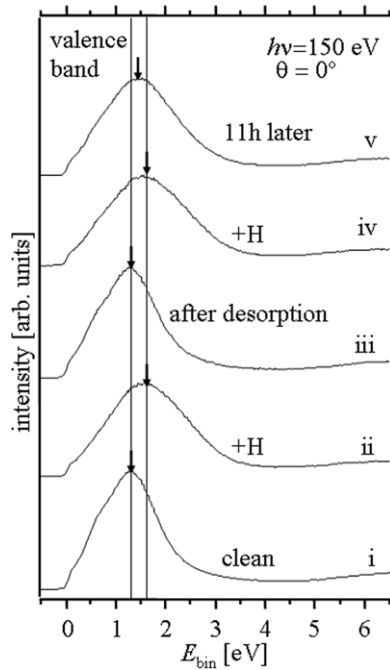


Figure 2. Valence band spectra from a clean Mg–Ni film (i), after H deposition (ii), after H₂ desorption (iii), after H redeposition (iv) and 11 h later (v). The spectra were measured at normal emission with a photon energy of 150 eV.

Table 2. Peak position and FWHM of the peak in the valence band (figure 2).

Spectra	(i)	(ii)	(iii)	(iv)	(v)
Peak position (eV)	1.31	1.59	1.28	1.56	1.47
FWHM (eV)	1.42	1.93	1.40	1.97	1.82

sensitive, which one would have expected for oxygen impurities. In spectrum (iv) in figure 1 the hydride peak is larger than in spectrum (ii) of the same figure. This is because the film was already partly hydrogenated when the H deposition started. Table 1 can also help to quantify hydride losses from the hydrogenated film over time. Spectrum (v) in figure 1 was measured 11 h after spectrum (iv) in the same figure, and according to table 1 the hydride peak had lost 10% of its intensity. This desorption at room temperature is related to UHV conditions, because a vacuum environment pulls out hydrogen from the film, while the surrounding of H₂ stabilizes the hydride. Therefore, this would not be an issue in future applications with a surrounding pressure of 1–10 bar [1].

Figure 2 shows the valence band spectra during the same two cycles of hydrogenation of the Mg–Ni film shown in figure 1. The spectra are dominated by a (mainly Ni 3d) peak centred at ~ 1.5 eV below the Fermi energy. This peak shifts towards higher binding energy and increases in width when the film is hydrogenated. The peak positions and the values of full width half maxima (FWHMs) are compiled in table 2. Spectrum (i) in figure 2 (clean) is very similar to spectrum (iii) in the same figure (after H desorption). And spectrum (ii) in figure 2 (after the first H deposition) is very similar to spectrum (iv) in the same figure (after the second deposition). After 11 h (spectrum (v) in figure 2) the peak had shifted to an intermediate position, due to a slow dehydrogenation of the hydrogenated Mg–Ni film. This confirms that valence band changes are in agreement with the observations of the core levels. The peak in the valence band shifted towards higher binding energies because of new states in the hydrogenated parts of the film. In the hydrogenated film (spectrum (ii) and spectrum (iv) in figure 2) the

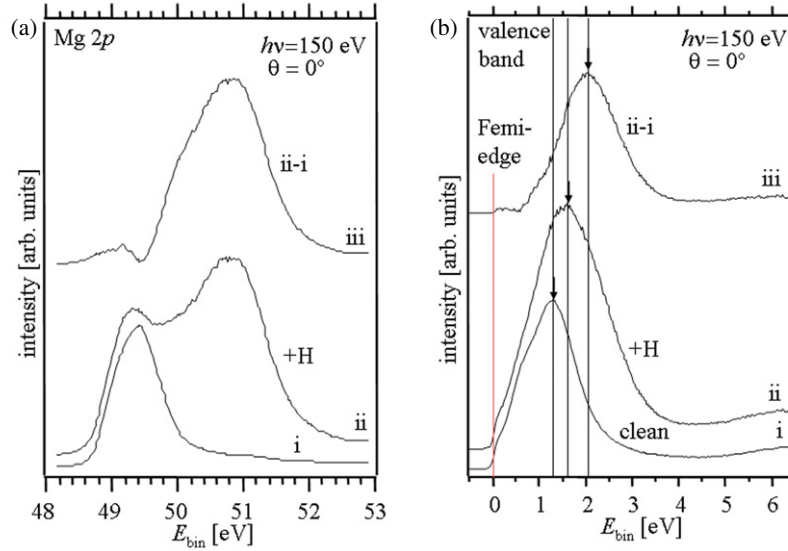


Figure 3. (a) Mg 2p spectra from a clean Mg–Ni film (i), after H deposition (ii) and the Mg 2p level from a completely hydrided Mg–Ni film (iii), constructed from a linear combination (subtraction) of (i) and (ii). (b) Valence band spectra from a clean Mg–Ni film (i), after H deposition (ii) and the valence band from a completely hydrided Mg–Ni film (iii), constructed from a linear combination (subtraction) of (i) and (ii).

valence band peak becomes broader. This is because the film is not completely hydrogenated and the peak is a superposition of contributions from both hydrogenated and metallic parts of the film.

We constructed a hypothetical spectrum from a fully hydrogenated Mg–Ni film by a linear combination. In figure 3(a) the Mg 2p spectra before (i) and after (ii) hydrogenation (same as in figure 1) are combined to construct a Mg 2p spectrum from a completely hydrogenated Mg–Ni film (spectrum (iii) in figure 3). Spectrum (iii) is found by taking $(iii) = (ii) - (i)$, where (i) is the flux normalized spectrum of the clean Mg–Ni film multiplied by 0.30 and (ii) is the flux normalized spectrum after the hydrogenation. The same procedure was used for the valence bands in figure 3(b), i.e. the spectrum before hydrogenation was multiplied by the same factor (0.30) before a hypothetical valence band spectrum of a completely hydrogenated Mg–Ni film (spectrum (iii) in figure 3(b)) was constructed by subtraction $((iii) = (ii) - (i))$. For the Mg 2p spectrum the factor 0.30 was found by eliminating the metallic peak (peak 1). For the valence band, the factor 0.30 was found by having very low emission close to the Fermi edge in the valence band spectrum.

When the Mg–Ni film was hydrogenated the environment changed also for Mg atoms which were not directly bonded to hydrogen; therefore the metal peak before (see spectrum (i) in figure 3(a)) and after (see spectrum (ii) in figure 3(a)) hydrogenation are a bit different and cannot be completely subtracted from each other. This is why spectrum (iii) in figure 3(a) shows some irregularities in the lineshape. The hydride peak has a shoulder on the low binding energy side which originates from Mg atoms not bonded to Ni atoms (peak 2 in figure 1 and table 1).

The peak in the valence band of the completely hydrogenated Mg–Ni film (spectrum (iii) in figure 3(b)) is shifted further towards higher binding energies. The binding energy of the peak is 2.0 eV and the FWHM becomes 1.4 eV. The emission at the Fermi level disappeared and a

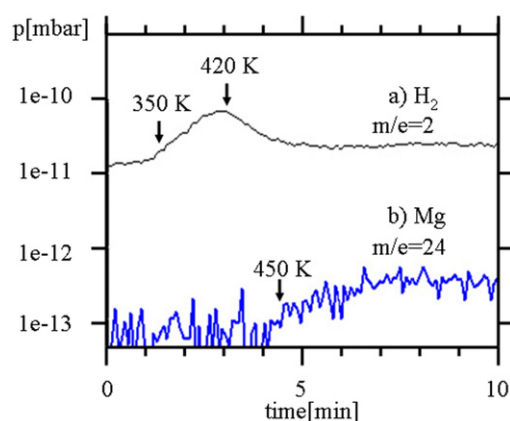


Figure 4. TDS spectra of (a) H_2 ($m/e = 2$) and (b) Mg ($m/e = 24$). The temperature of the sample was raised by a constant current of 7.5 A through the tungsten wire which held it.

gap of 0.7 eV opened up. This peak is more narrow than the peak in the spectrum from the hydrogenated film (figure 3(b) (ii) FWHM = 1.9 eV) which consisted of contributions from two (unresolved) peaks (metal and hydride). The previously reported optical band gap for a hydrogenated alloy with this Ni to Mg ratio (1:5) is 3.2 eV [8]. But the optical band gap is between the valence band maximum (lowest binding energy) and the lowest unoccupied states, while the gap we observed (0.7 eV) is between the valence band maximum and the Fermi level.

Figure 4 shows TDS spectra from (a) H_2 ($m/e = 2$) and (b) Mg ($m/e = 24$) during the final heat-up. We were probing $m/e = 2$ and not $m/e = 1$ because, despite the fact that hydrogen is stored as atomic H, it desorbs in its molecular form. Figure 4(a) shows that at 350 K the H_2 signal started to increase, and it reached its maximum signal at 420 K after 3 min. When desorbing hydrogen (from spectrum (ii) to spectrum (iii) in figures 1 and 2) we stopped there. Up to this point the temperature rise was almost linear (0.7 K s^{-1}). Figure 4(b) shows that at 450 K the Mg signal starts to rise, which indicates that Mg desorption has started.

When heating up a Mg–Ni film, Mg segregation could occur. This is a known problem with Mg–Ni alloys [11], and we have therefore performed a detailed comparison of spectra from the clean film and spectra from the film after hydrogen desorption. We have measured Mg 2p and Ni 3p spectra at different photon energies and angles before and after the first cycle of hydrogen absorption–desorption. The Ni to Mg intensity ratio from core levels remained unchanged for all spectra ($h\nu = 810 \text{ eV}$ at normal emission, $h\nu = 350 \text{ eV}$ at normal emission and $h\nu = 350 \text{ eV}$ at 60°), which showed that no segregation occurred. This means that it is possible to desorb hydrogen while leaving the film intact, because the hydrogen desorbs from the Mg–Ni film well before segregation sets in or before the film is irreversibly changed by desorption. This is why Mg–Ni films are better candidates for hydrogen storage than Mg films, in which hydrogen desorbs simultaneously with Mg [4].

Figure 5 presents live spectra (time-resolved) from a film with a Ni to Mg ratio of 1:4 at room temperature (figure 5(a)) and at LN_2 -temperature (figure 5(b)). Each contour plot comes from 12 spectra measured over 3 min for 15 s each. The spectral intensity is shown by a yellow hot (grey) colour scale. The difference between figures 5(a) and (b) became very clear. While the film underwent a fast dehydrogenation at room temperature, it was totally stable at liquid-nitrogen temperature.

The stability of the hydrogenated film was not only dependent on the environment, but also on the Ni to Mg ratio in the film. By increasing the Ni content in the film from 1:5 to 1:4 one gets a much faster spontaneous dehydrogenation at room temperature, as shown in figure 5(a). The low binding energy metallic peak is recovered, while the hydride peak disappeared already

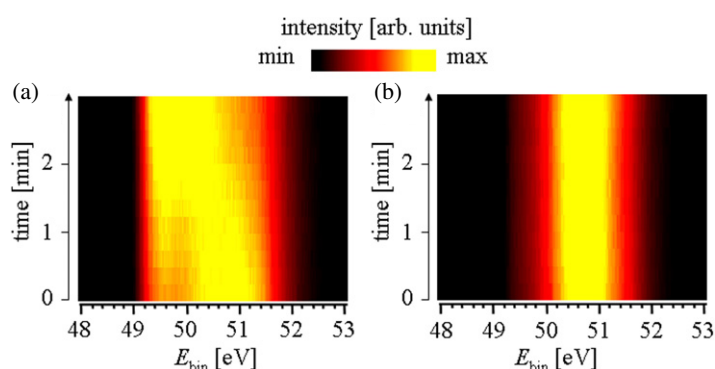


Figure 5. Mg 2p spectra from a more Ni-rich hydrogenated Mg–Ni film measured with 150 eV photon energy at (a) room temperature or (b) liquid-nitrogen temperature. The spectra are represented by a contour plot with high intensity in yellow and low intensity in black. The yellow hot colour scale is changed to greyscale in the printed version.

after a couple of minutes under the beam. However, spontaneous desorption or instability under the beam can be stopped by cooling the sample to liquid-nitrogen temperature, as shown in figure 5(b). While this experiment was performed at liquid-nitrogen temperature, which was the only one lower than room temperature which could be achieved under stable conditions at our beamline, some preliminary investigations showed that significantly higher temperatures would suffice to stabilize the hydrogenated film, presumably around 0 °C.

4. Conclusion

In this paper we have presented a high-resolution photoemission and thermal desorption study of the reversible hydrogenation of Mg–Ni films. We showed spectroscopic evidence for reversible hydrogen storage in a Mg₅Ni₁ film. We also showed that stored hydrogen can be desorbed from the Mg–Ni film without Mg segregation or desorption. Hydrogen desorption was found to start at 350 K, and it reached its maximum at 420 K at 0.7 K s^{−1} heating rate. And by following the Mg signal from the mass spectrometer we found that Mg desorption started at 450 K for this film. Spontaneous hydrogen desorption at room temperature was shown to depend on the Mg:Ni ratio in the film, and could be stopped by cooling.

Acknowledgments

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