Hydrogen-assisted phase transition in a trihydride MgNi$_2$H$_3$ synthesized at high H$_2$ pressures: Thermodynamics, crystallographic and electronic structures

V.A. Yartys,$^a$, V.E. Antonov,$^b$ A.I. Beskrovnyy,$^c$ J.-C. Crivello,$^d$ R.V. Denys,$^a$ V.K. Fedotov,$^b$ M. Gupta,$^e$ V.I. Kulakov,$^b$ M.A. Kuzovnikov,$^{b,c}$ M. Latroche,$^d$ Yu.G. Morozov,$^f$ S.G. Sheverev$^e$ and B.P. Tarasov$^g$

$^a$Institute for Energy Technology, Kjeller, Norway
$^b$Institute of Solid State Physics RAS, Chernogolovka, Russia
$^c$Institute of Chemical Physics RAS, Chernogolovka, Russia
$^d$Institut de Chimie et des Matériaux Paris-Est, ICMPE, CNRS-UPEC, Thiais, France
$^e$Thermodynamique et Physico-Chimie d’Hydrures et Oxydes, Université Paris Sud, Orsay, France
$^f$Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia
$^g$Institute of Structural Macromodels and Materials Science RAS, Chernogolovka, Russia

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**Abstract**—MgNi$_2$ intermetallic was synthesized by powder metallurgy and crystallizes with a Laves-type C36 structure (space group $P6_3/mmc$ (No. 194); $a = 4.826; c = 15.832$ Å). At 300 °C during interaction with hydrogen (deuterium) gas compressed to 2.8–7.4 GPa, a trihydride Mg$_2$NiH$_3$D$_{1.2}$ was synthesized. The trihydride remained metastable at ambient conditions allowing its structure, stability and magnetic properties to be studied. The formation of Mg$_2$NiH$_3$ was associated with a complete rebuilding of the initial hexagonal structure into the orthorhombic distorted MoSi$_2$ lattice (space group $D1/a$). Neutron diffraction of the Mg$_2$NiH$_3$D$_{1.2}$ demonstrated that D atoms fill sites having octahedral Mg$_4$ (D$1/4b$) and planar Ni$_2$ (D$2/8f$) coordination. Within the framework of the density functional theory, density of states (DOS) calculations showed the formation of a structure around $-10$ to $-6$ eV caused by the chemical bonds of hydrogen and its 1s states mainly via interaction with the 3d states of Ni. Analysis of the electronic structure revealed a charge transfer from Mg to Ni, and to the H atoms. The calculated enthalpy of formation of Mg$_2$Ni$_2$H$_3$ is about $-30$ kJ/mol-H$_2$, which is consistent with the stability of the hydride at normal conditions. The initial sample contained a small amount of a secondary Mg$_2$Ni$_2$ intermetallic, which has been formed during the equilibrium interaction of magnesium and nickel at 800 °C. Thus this compound should be included in the phase diagram of the Mg–Ni system. Mg$_2$Ni$_2$ decomposes under high-temperature/high-pressure hydrogenation conditions and forms nickel monohydride.

**Keywords**: Metal hydrides; Crystal structure; High pressures; Neutron diffraction; DFT

1. Introduction

Magnesium-based alloys and composite materials containing magnesium dihydride (MgH$_2$) are important hydrogen and energy storage materials. Compared to the individual MgH$_2$ hydride, binary and ternary Ni-containing hydrogen storage alloys of magnesium demonstrate significantly improved rates of hydrogen charge and discharge that mean they can operate at lower temperatures while maintaining a high hydrogen storage capacity. The beneficial effect of nickel has been demonstrated for a variety of compositions and is caused by the following phenomena: (i) formation of Mg$_2$NiH$_2$ containing 3.6 wt.% H and having significantly lower working temperatures (0.1 MPa H$_2$ at 223 °C) for the reversible absorption and desorption of hydrogen as compared to MgH$_2$ [1]; (ii) nickel solubility in Mg-rich La–Mg alloys such as La$_2$Mg$_{17}$ takes place on both La and Mg sites to form La$_{1.80}$Ni$_{0.40}$Mg$_{16.73}$Ni$_{0.27}$ and, when the alloy is prepared in a nanostructured state, this results in the reversibility of H absorption–desorption and extremely fast kinetics of the processes of H exchange in the alloy [2]; (iii) substitution of La by Mg allows a fine tuning of the thermodynamic properties of the ternary La–Mg–Ni alloys and their hydrides, making them suitable for applications as anodes for advanced Ni-metal hydride batteries.

*Corresponding author. Address: Norwegian University of Science and Technology, Trondheim, Norway. Fax: +47 63 81 29 05; e-mail: volodymyr.yartys@ife.no

$^*$Present address: Institute of Physical Chemistry PAS, Warsaw, Poland.

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These include hydrides of the La$_{1.4}$Mg$_{0.6}$Ni$_{2.7}$ alloy formed on the basis of La$_2$Ni$_5$ [3] and La$_{1.4}$Mg$_{0.6}$Ni$_{2.7}$-based hydrides $(x = 0-2)$ with the hydrogen dissociation pressure increasing 1000-fold following an increase in the Mg concentration from $x = 0$ in LaNi$_3$ to $x = 2$ in LaMg$_2$Ni$_6$ [4]. The La$_2$Mg$_6$Ni$_4$ alloy corresponding to $x = 1$ has the best properties as battery anode material with the discharge capacity reaching 400 mAh g$^{-1}$ [5,6]. Hydrogen sublattic in La$_2$Mg$_6$Ni$_4$D$_{0.5}$ shows local ordering of H atoms around Mg and Ni and can be built from the MgH$_6$ octahedra and NiH$_4$ tetrahedra [7].

The alloy with the highest content of magnesium, LaMg$_2$Ni$_6$, has a structure composed of two building blocks with the stoichiometry LaNi$_5$ and MgNi$_2$. The corresponding deuteride LaMg$_2$Ni$_6$D$_{0.5}$ was synthesized at 950 bar $D_2$ [8] and showed hydrogenation properties dramatically different from those for LaNi$_3$. While LaNi$_3$ is prone to hydrogen-induced disproportionation, the Mg-containing intermetallic reversibly forms a hydride with $\Delta H_{\text{des}} = -24.0$ kJ/mol-H$_2$ and an equilibrium pressure of H$_2$ desorption of 18 bar at 20 °C. A pronounced hysteresis of H$_2$ absorption and desorption is evidenced by a high value of H$_2$ absorption pressure, ~100 bar higher than for desorption. The observed values of hydrogen capacities cannot be explained solely by hydrogen insertion into the LaNi$_3$ slabs, and require hydrogen incorporation into the MgNi$_2$ fragments of the structure to reach the experimentally observed H/M ratio. This clearly shows an influence of the LaNi$_3$ layer in the stacking structures on the hydrogenation of the MgNi$_2$ slabs, which for the individual MgNi$_2$ compound is achieved only at several kbar of H$_2$. Thus, LaNi$_3$-assisted hydrogenation of MgNi$_2$ in the LaMg$_2$Ni$_6$ hybrid structure takes place. Indeed, in the LaMg$_2$Ni$_6$D$_{0.5}$ ($a = 5.21-5.26$; $c = 25.81-25.85$ A), D atoms are accommodated in both Laves and CaCu$_5$-type slabs. In the LaNi$_5$ CaCu$_5$-type layer, D atoms fill three types of interstices: a deformed octahedron [La$_2$Ni$_5$], and [La(Mg)$_2$Ni$_5$] and [Ni$_4$] tetrahedra, to yield LaNi$_5$D$_{0.7}$ composition. The D distribution is very similar to that in the LaNi$_5$H$_{0.7}$ blocks with the stoichiometry LaNi$_5$D$_{0.5}$ as calculated in more detail elsewhere [14]. The experiment was carried out in a toroidal high-pressure chamber [13] using AlH$_3$ as an internal hydrogen source. The synthesized MgNi$_2$-H sample was then stored in liquid nitrogen to prevent hydrogen loss and oxidation by air.

A 1000 mg sample of the MgNi$_2$-D deuteride was prepared in a similar way by a 24 h exposure to a H$_2$ pressure of 7.4 GPa at 300 °C in a high-pressure cell. The synthesized sample was subsequently rapidly cooled to 100 K. The hydrogenation method is described in more detail elsewhere [14]. The experiment was carried out in a toroidal high-pressure chamber [13] using AlH$_3$ as an internal hydrogen source. The synthesized MgNi$_2$-H sample was then stored in liquid nitrogen to prevent hydrogen loss and oxidation by air. The starting MgNi$_2$ material was prepared from high-purity Mg (99.8 %; 44 mcm) and Ni (99.995 %; 150 mcm) powders mixed in a slightly overstoichiometric ratio 1:2, with an Mg excess of 2 wt.%, and compacted by pressing up to $1.47 \times 10^3$ MPa into pellets with a diameter of 15 mm. The obtained pellets were sintered in argon gas at 800 °C for 12 h and quenched into ice water after annealing.

To prepare the MgNi$_2$-H hydride, ~100 mg Mg$_2$Ni$_6$ were powdered in an agate mortar and loaded with hydrogen by a 24 h exposure to a H$_2$ pressure of 7.4 GPa at 300 °C in a high-pressure cell. The synthesized sample was subsequently rapidly cooled to 100 K. The hydrogenation method is described in more detail elsewhere [14]. The experiment was carried out in a toroidal high-pressure chamber [13] using AlH$_3$ as an internal hydrogen source. The synthesized MgNi$_2$-H sample was then stored in liquid nitrogen to prevent hydrogen loss and oxidation by air.

The thermal stability and the total hydrogen (deuteron) content of the samples were determined by hot extraction into a pre-evacuated calibrated volume, which involved heating the sample from ~186 to 660 °C at a rate of 20 °C min$^{-1}$. The mass of the analyzed probe was a few milligrams. The method is described in more detail in Ref. [16].

The virgin MgNi$_2$ powder was examined by X-ray diffraction (XRD) at room temperature with a Siemens D500 diffractometer using monochromated Cu $K_{\alpha1}$ radiation. The hydrogenated and deuterated samples were studied by XRD at 85 K with a Siemens D500 diffractometer using Cu $K_{\alpha1}$ radiation selected by a diffracted beam monochromator. The diffractometer was equipped with a home-designed nitrogen cryostat that permitted the powder samples to be loaded without any intermediate warming. The obtained diffraction patterns were analyzed using GSAS [17] and POWDERCELL2.4 software.
The neutron diffraction study of the MgNi$_2$-D sample was carried out with the time-of-flight (TOF) DN-2 diffractometer installed on the IBR-2M pulsed nuclear reactor at the Joint Institute for Nuclear Research in Dubna, Russia. The sample environment included a vanadium container and a closed-cycle helium refrigerator. The TOF patterns were recorded by a $^3$He gas-filled proportional detector positioned at the scattering angle $2\theta = 150^\circ$. The background from the sample environment was measured under the same conditions and subtracted from the TOF patterns. The patterns were normalized to the incoherent scattering spectrum of vanadium and the measuring time. Rietveld refinements of the neutron powder diffraction pattern were performed using VISUAL MRIA software [17].

The amount of magnetic impurities in the samples was additionally estimated by measuring their magnetization, $\sigma$, with a vibrating sample magnetometer (EG&G PARC M-4500). The $\sigma(H)$ curves were measured at two temperatures, 82 and 295 K, with the magnetic field, $H$, varying from +10 to −10 kOe and backward at a constant rate of 1.2 kOe min$^{-1}$.

3. Results and discussion

3.1. The starting MgNi$_2$ alloy

The XRD pattern of the powdered virgin MgNi$_2$ alloy is presented in Fig. 1. Profile analysis of this pattern showed that Laves-type MgNi$_2$ intermetallic compound constituted $>$90% of the sample. The sample contained also a few wt.% of three minor phases, Ni, MgNi$_3$ and MgO (see Table 1 for further details). The crystallographic parameters of the hexagonal crystal structure of the MgNi$_2$ compound (space group $P6_3/mmc$ (No. 194), $a = 4.82565(6)$, $c = 15.8323(3)$ Å) well agree with the reference data [10]. The lattice parameters of the impurities (Ni: face-centered cubic lattice; $a = 3.5301(3)$ Å and MgO: space group $Fm\bar{3}m$ (No. 225); $a = 4.212(1)$ Å) were also found to be very close to the literature data [18,19]. One unexpected minor constituent is the cubic MgNi$_3$ compound with a Cu$_3$Au-type structure (space group $Fm\bar{3}m$ (No. 225); $a = 3.7163(3)$ Å). This compound has not yet been presented on the phase diagram of the Mg–Ni system [9]. Recently, it was synthesized by ball milling of a mixture of Mg and Ni metals [20] and considered as a metastable phase. In the present work, the formation of MgNi$_3$ resulting from the sintering of Mg and Ni at $T = 800^\circ$C suggests that this compound should be an equilibrium phase at such a temperature.

3.2. Magnetic properties of the MgNi$_2$ alloy

The MgNi$_2$ compound is paramagnetic down to 4 K [21], whereas Ni metal is a ferromagnet with a rather high Curie temperature $T_C = 631$ K (358 °C) [22], and this allows a more accurate estimation of the Ni content in our samples by using magnetization measurements.

The magnetization measurements for the starting MgNi$_2$ alloy were performed at temperatures significantly lower than the Curie temperature of Ni. At these temperatures of 82 and 295 K, according to the measurements of Ref. [22], the magnetization of the bulk samples of Ni metal reaches saturation, $\sigma_S$, in fields below 4 kOe and it does not further change in fields up to 19 kOe. The noticeable increase in the magnetization of our sample at $H > 4$ kOe is a characteristic feature showing the presence of small ferromagnetic Ni particles. The magnetization of such particles should linearly depend on $1/H$ in the high magnetic fields approaching $\sigma_S$ at $1/H \rightarrow 0$ (e.g. [23]). As one can see from the inset in Fig. 2, the experimental $\sigma(1/H)$ dependences for the MgNi$_2$ alloy are approximately linear at $1/H < 0.25$ kOe$^{-1}$ (i.e. at $H > 4$ kOe). An extrapolation to $1/H = 0$ (dashed lines in the inset) gives $\sigma_S^{Ni}(82$ K)$ = 1.66$ emu g$^{-1}$ and $\sigma_S^{Ni}(295$ K)$ = 1.56$ emu g$^{-1}$. These values do not differ much from the corresponding values of the magnetization at $H = 10$ kOe, inspiring confidence in the adopted extrapolation procedure.

A comparison of the two obtained $\sigma_S^{exp}$ values with the values of $\sigma_S^{Ni}(82$ K)$ = 58.27$ emu g$^{-1}$ and $\sigma_S^{Ni}(295$ K)$ = 54.98$ emu g$^{-1}$ for bulk Ni metal determined in Ref. [22] gives converging results for the concentration $x_{Ni}$ of the Ni amount, i.e. $\sigma_S^{exp}(82$ K)$/\sigma_S^{Ni}(82$ K)$ = 2.84$ wt.% Ni and $\sigma_S^{exp}(295$ K)$/\sigma_S^{Ni}(295$ K)$ = 2.84$ wt.% Ni. This value agrees well with independent refinements of the XRD data where the Ni content was found to be 4.6(1) wt.% (see Fig. 1).

The good agreement of the ratio of $\sigma_S^{exp}(295$ K)$/\sigma_S^{exp}(82$ K)$ = 0.94(1)$ with the precise value of $\sigma_S^{Ni}(295$ K)$/\sigma_S^{Ni}(82$ K)$ = 0.944$ from Ref. [22] indicates that the Curie temperature of the Ni particles in the MgNi$_2$ alloy studied in the present work is close to that of bulk Ni metal. Together with the agreement between the estimates of the content of Ni metal resulting from the $\sigma_S^{exp}$ values and from XRD, this suggests that the magnetization of the starting alloy should solely be due to the Ni minor phase. Consequently, the MgNi$_2$ secondary phase (as well as the main MgNi$_3$ phase [21]) is not ferromagnetically ordered at $T > 82$ K.

The MgNi$_2$ compound is known to have a nearly stochiometric composition at room temperature and only shows a rather narrow interval of mutual solubility of the
Table 1. Crystallographic data for MgNi$_2$ from the profile refinements of the X-ray powder diffraction presented in Fig. 1. \( R_{wp} = 6.8\% \), \( R_p = 5.3\% \), \( \chi^2 = 2.6 \). MgNi$_2$ (content in the sample 90.1(1) wt.%): space group \( P6_m/mmc \); \( a = 4.8256(6) \AA; \ V = 319.290(6) \AA^3 \).

<table>
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<th>Atom</th>
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<th>( Y )</th>
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Components at higher temperatures, the limiting concentration of Ni reaching \( \sim 67.1\% \) at.\% at 800 °C [9]. As the studied MgNi$_2$ alloy was sintered from Mg and Ni taken in the atomic proportion slightly exceeding 1:2, the extra Ni found in this alloy could only be present as a result of evaporation of more volatile Mg in the course of sintering and further 12 h homogenization annealing at 800 °C. We could thus expect that the annealed MgNi$_2$ compound would contain \( \sim 67.1\% \) at.\% Ni, characteristic of its equilibrium with the Ni metal.

3.3. The MgNi$_2$-H Sample

High-pressure hydrogenation resulted in the formation of the trihydride MgNi$_2$H$_3$. The sample loaded with hydrogen at 7.4 GPa and 300 °C and quenched to liquid N$_2$ temperature had a metallic appearance.

Fig. 3 presents an XRD pattern of the “as-quenched” sample. A profile analysis of this pattern showed that the sample consisted of an orthorhombic phase very similar to the MgNi$_2$H$_3$ hydride described in Ref. [12] and a few per cent of the fcc nickel hydride. The data also show that the sample contained an unidentified hydride phase.

Let us consider the NiH phase first. Under the conditions of high-pressure synthesis, the nickel contained in the starting MgNi$_2$ alloy should have formed a monohydride NiH with a cubic NaCl-type structure (space group \( Fm\bar{3}m \); \( a = 3.740 \AA \)) [14]. The presence of such a phase with \( a = 3.734(2) \AA \) in the MgNi$_2$-H sample can easily be judged by the isolated (200) line at \( 2\theta \approx 48.7^\circ \) in the experimental diffraction pattern in Fig. 3.

Studies of the thermal desorption of hydrogen from the quenched MgNi$_2$-H sample showed that the NiH hydride rapidly decomposes at temperatures near \( T = 0 \) °C producing a step in the curve of hydrogen desorption (see Fig. 4). At room temperature, the decomposition of NiH is accomplished in just a few minutes. The remaining MgNi$_2$H$_3$ hydride is thermally stable at room temperature and shows no detectable loss of hydrogen over a period of days. X-ray examination of the sample exposed to room temperature for 3 h gave a diffraction pattern very similar to that presented in Fig. 3 except that the peaks of fcc Ni with \( a = 3.52(1) \AA \) replaced those of NiH.
As seen from Fig. 4, the MgNi₂Hₓ phase starts decomposing on heating at 100–120 °C. The decomposition of the tetragonal and orthorhombic hydrides MgNi₂Hₓ synthesized in Refs. [11,12] started at a considerably higher temperature of ~190 °C. A possible explanation of the higher thermal stability of the hydrides in Ref. [11,12] is that they were synthesized at much higher temperatures (700–800 °C) and their chemical reaction with the debris of the high-pressure cell could produce a surface layer, forming a barrier to hydrogen diffusion. The black color of the hydrides synthesized in Refs. [11,12] compared to the metallic appearance of our samples can serve as indirect evidence of the existence of such a layer.

A comparison of the desorption curves for the “as-quenched” MgNi₂-H sample and that with the NiH phase completely decomposed by a preliminary exposure of the sample to room temperature for 3 h shows that the exposure resulted in the release of ~0.15 wt.% H. At the same time, the NiH phase formed by 3 wt.% of the initial Ni phase could only evolve ~0.05 wt.% H, which is approximately 3 times less. To accurately determine the amount of NiH in the MgNi₂-H sample, we measured its magnetization in the “as-quenched” state and after the 3 h exposure to room temperature. The obtained σ(H) dependences are presented in Fig. 5.

The “as-quenched” sample was measured only at T = 82 K in order to avoid losses of hydrogen from the NiH phase at higher temperatures. The σ(H) dependence of this sample (curve 1 in Fig. 5) forms a hysteresis loop characteristic of a magnetically ordered material. Since NiH is neither ferromagnetic nor superconducting down to T = 0.3 K [24], the observed magnetization could be attributed to a certain amount of unreacted Ni (which is most likely), or to the MgNi₂Hₓ hydride (its magnetic properties have yet not been studied), or to the unidentified impurities. In any case, the magnetization is small and the extrapolated value of σ(H) = 0.2 emu g⁻¹ (see the inset in Fig. 5) corresponds to the presence of only ~0.3 wt.% Ni in the sample.

As seen from Fig. 5, the magnetization of the MgNi₂-H sample considerably increases after 3 h of annealing at room temperature because of the complete transformation of the NiH into Ni metal. Treating the experimental σ(H) dependences in the same way as in the case of the virgin MgNi₂ alloy gives σₓₓ(H = 82 K) = 3.97 emu g⁻¹ and σₓₓ(H = 295 K) = 3.70 emu g⁻¹ and, correspondingly, σₓₓ(H = 295 K)/σₓₓ(H = 82 K) = 0.93, which is close to σₓₓ(H = 295 K)/σₓₓ(H = 82 K) = 0.944 of bulk Ni measured in Ref. [22]. The concentration of the Ni determined as σₓₓ(H = 82 K)/σₓₓ(H = 295 K) reaches xNi = 6.8–7 wt.% (which is ~4 wt.% larger than xNi = 3 wt.% in the starting MgNi₂ alloy). A calculated profile of the contribution from 7 wt.% NiH to the XRD pattern of the “as-quenched” MgNi₂-H sample is shown in Fig. 3.

Nearly all peaks in the experimental diffraction pattern of the MgNi₂-H sample, present due to the contribution from 7 wt.% NiH, can be indexed in an orthorhombic unit cell with a = 4.55 Å, b = 4.69 Å and c = 8.80 Å. The measured values of the unit cell parameters agree with the results of Ref. [12]. However, in contrast with the data in Ref. [12], the actual symmetry of the orthorhombic unit cell of the trihydride MgNi₂Hₓ is face-centered orthorhombic and not a primitive one as proposed in Ref. [12]. The extinction symbol is found to be F̅mm̅m.

To derive the space group and the atomic structure of the orthorhombic phase, we started with the MoS₂-type structure (space group P4/mmm, No. 139) proposed for the tetragonal modification of the MgNi₂Hₓ hydride in Ref. [11]. An orthorhombic distortion of this structure along the (110) axis allowed a satisfactory description of the observed splitting of the diffraction peaks and their intensities. The relations between the orthorhombic and tetragonal cells are: a₁/orth. ≈ d₄tetrahedral/√2; b₁/orth. ≈ a₄tetrahedral/√2; c₁/orth. ≈ c₄tetrahedral. In Fig. 3, the orthorhombic splitting is clearly seen, for example, for the (200)₄tetrahedral and (020)₄orth. peaks, which appear at, respectively, 38.38° and 39.61° and stem from the (110)₄tetrahedral peak of the tetragonal unit cell.

Fig. 4. Vacuum thermal desorption spectroscopy of the decomposition of the MgNi₂-H sample (left scale) and MgNi₂-D sample (right scale), measured during their heating at a rate of 20 °C min⁻¹ in a pre-evacuated volume. The hydrogen content is expressed in the units of the mass ratio of the released hydrogen gas and the initial hydride sample.

Fig. 5. Magnetization, σ, as a function of the applied magnetic field, H, for a 20 mg sample of the MgNi₂-H sample in the “as-quenched” state (curve 1, T = 82 K) and after its 3 h exposure to room temperature resulting in the complete loss of hydrogen by the NiH phase (curve 2 measured at T = 82 K and curve 3 measured at T = 295 K). The field was varied from +10 to −10 kOe and backward at a constant rate of 1.2 kOe min⁻¹. The dashed lines in the inset show linear extrapolations of the experimental σ(1/H) plots to 1/H = 0.
Profile refinement of the XRD diffraction pattern suggested formation of the orthorhombic crystal structure of the MgNi$_2$H$_x$ hydride with space group $Pmmm$ (No. 69), giving the structural parameters presented in Table 2. Thus, the symmetry reduction to the space group $Pmmm$ (No. 47) suggested in Ref. [11] is not confirmed by the present refinement. Hydrogenation results in a volume expansion of 17.6% or 2.3 Å$^3$ per at.H.

As can be seen from the difference spectrum shown in Fig. 3, the unidentified phase in the MgNi$_2$ sample mostly manifests itself by significant differences in the calculated and experimental intensities of diffraction lines in the angular range $37 < 2\theta < 47^\circ$. Small unidentified peaks are also observed at $2\theta = 53.7$, 61.8, 69.7, 74.3 and 75.3$^\circ$. The secondary phase is different from those in the starting MgNi$_2$ alloy and its origin requires discussion.

Note in the first place that the MgNi$_3$ phase is absent in the hydrogenated sample; instead, this sample contains an additional 4 wt.% Ni compared to the starting alloy. The nickel concentration of 67.1 at.% in the MgNi$_2$ compound formed in the starting alloy lies well within the homogeneity region of $65 < X < 70$ at.% Ni of the MgNi$_2$H$_{x-3}$ hydrides synthesized in Ref. [11]. It is therefore unlikely that the extra Ni could precipitate from the nearly stoichiometric MgNi$_2$ compound in the course of its hydrogenation under a high hydrogen pressure. Most probably, the extra Ni resulted from the disproportionation of the MgNi$_3$ secondary phase present in the starting alloy and disappearing in the hydrogenated sample. Because of the thermodynamic instability of the intermetallic hydrides as related to the corresponding mixture of binary hydrides, disproportionation frequently occurs for many intermetallic compounds reacting with hydrogen gas, especially at high applied temperatures and hydrogen pressures.

Assuming a disproportionation reaction MgNi$_3$ + (5/2)H$_2$ = MgH$_2$ + 3NiH, the observed formation of the additional 4 wt.% Ni in the hydrogenated sample will require the presence of 4.5 wt.% MgNi$_3$ in the starting sample, which is consistent with its concentration of 2–4 wt.% MgNi$_3$ determined by XRD. The reaction will also produce about 0.6 wt.% MgH$_2$. However, its contribution to the XRD pattern should be very small because of the low content of MgH$_2$, small X-ray scattering length of Mg and because of the nearly amorphous structure of the MgH$_2$ precipitates usually formed in disproportionation reactions. The contribution from this MgH$_2$ to the total hydrogen content of the MgNi$_2$-H sample should mostly compensate for the presence of 1–2 wt.% MgO, which does not react with hydrogen under the chosen synthesis conditions (XRD and thermal desorption analysis revealed no traces of interaction of MgO with hydrogen in a quenched sample of MgO powder exposed to a hydrogen pressure of 7.4 GPa at $T = 300$ °C in an additional experiment).

Turning back to the unidentified phase in the MgNi$_2$-H sample, we think it most likely that it is actually the MgNi$_2$H$_x$ hydride with the same mean composition as the crystalline phase, but in the form of strongly deformed nanocrystalline grains containing many defects. Such a microstructure could result from the specific mechanism of the reconstructive transition of the MgNi$_2$ compound to the MgNi$_2$H$_x$ hydride. This suggestion can indirectly be supported by the observation that the reverse transformation from MgNi$_2$H$_x$ to MgNi$_2$ occurring on heating the hydrogenated sample in vacuum gives a sample with strongly broadened diffraction lines. A very strong broadening of diffraction lines of the MgNi$_2$ compound after decomposing a MgNi$_2$H$_{x-2}$ hydride by heating to 500 °C in a calorimeter was also observed in Ref. [11].

The assumption that the studied MgNi$_2$-H sample can be considered as only consisting of NiH and a homogeneous MgNi$_2$H$_{x-2}$ hydride is additionally confirmed by an analysis of the hydrogen balance. Decomposition of 7 wt.% of NiH after exposing the sample to room temperature should have decreased its hydrogen content by ~0.12 wt.% (hot extraction gave ~0.15 wt.% H, see Fig. 4). If the ~2.1 wt.% H remaining in the sample refers to 100–7 = 93 wt.% of the MgNi$_2$H$_{x-2}$ hydride, then this hydride contains ~2.26 wt.% H and this corresponds to the chemical formula MgNi$_2$H$_{x-2}$ in agreement with the results of Refs. [11,12].

3.4. The MgNi$_2$-D sample

The XRD pattern of the MgNi$_2$-D sample loaded with deuterium at 2.8 GPa and 300 °C and quenched to the liquid N$_2$ temperature was very similar to that of the MgNi$_2$-H sample synthesized at 7.4 GPa. The major phase was MgNi$_2$D$_x$ with the same orthorhombic $Fmmm$ structure and virtually the same parameters of the unit cell as the MgNi$_2$H$_{x-2}$ phase (see Table 1). The sample also contained a few per cent of fcc NiD with $a = 3.72(1)$ Å and of the order of 10 wt.% of an unidentified phase similar to the unidentified hydride phase found in the MgNi$_2$-H sample.

Thermal desorption analysis of ~5 mg of the MgNi$_2$-D sample demonstrated that the decomposition kinetics and the total content of the hydrogen isotope of the MgNi$_2$D$_x$ and NiD phases were similar to those of the MgNi$_2$H$_{x-2}$ and NiH phases in the MgNi$_2$-H sample (see Fig. 4). Measuring the magnetization of an ~20 mg portion of the MgNi$_2$-D sample with NiD completely decomposed to Ni metal by a 3 h exposure to room temperature gave $\sigma(H)$ dependences similar to those of the MgNi$_2$-H sample subjected to the same thermal treatment (see curves 2 and 3 in Fig. 5). The values of $\sigma_{20}^R$(82 K) and $\sigma_{20}^R$(295 K) corresponded to ~6.8–7 wt.% Ni in the partly outgassed MgNi$_2$-D sample and therefore ~7 wt.% NiD in the “as-quenched” sample. In view of the close similarity in the phase compositions of the MgNi$_2$-D and MgNi$_2$-H samples, a consideration analogous to that in the previous section leads to the conclusion that both MgNi$_2$D$_x$ phase and the unidentified phase have compositions close to MgNi$_2$D$_{x-2}$, the unidentified phase being a fine-grained and more inhomogeneous and distorted form of the crystalline MgNi$_2$D$_{x-2}$ deuteride. Fig. 6 presents a TOF neutron diffraction pattern of the “as-quenched” MgNi$_2$-D sample. The data are collected at $T = 100$ K. When loading and cooling the sample in the nitrogen cryostat of the DN-2 neutron diffractometer, it stayed near room temperature for a few minutes, and NiD partly decomposed to Ni. Under the constraint that the total concentration of the NiD and Ni phases was 7 wt.%, a profile analysis of the experimental diffraction pattern gave 4 wt.% NiD and 3 wt.% Ni. The profiles calculated for these phases are shown at the bottom of Fig. 6.

The best fit of the neutron diffraction pattern was achieved assuming that D atoms fully occupy two types of sites, the 4h and 8f sites, which gives the total composition MgNi$_2$D$_3$. The results of the refinements are presented in Table 2. The solid curve drawn through the experimental
The sum of the calculated contributions from the crystalline part of the MgNi\textsubscript{2}D\textsubscript{x} deuteride and the major secondary phases, NiD and Ni. In view of the large amount of the unidentified phase in the MgNi\textsubscript{2}-D sample, the profile fit of the experimental diffraction pattern is rather semiquantitative in character. Although no experimental peaks are left unindexed, the intensities of some peaks are not well reproduced. The largest and unresolvable difference between the calculation and experiment is observed near the interplanar distance $d = 1.46\ \text{Å}$ (marked by the vertical arrow in Fig. 6). Nevertheless, the quality of the refinement is sufficient to uniquely determine the positions of the D atoms in the crystal structure of MgNi\textsubscript{2}D\textsubscript{3} because these are the only interstitial sites in the metal lattice of the deuteride that match the constraints well established for the hydrides of intermetallic compounds such as the “rule of 2 Å” and Me–H distances of ($r_{\text{Me}} + 0.4$) Å [7,25].

The crystal structure of MgNi\textsubscript{2}D\textsubscript{3} is shown in Fig. 7. The position D1 of a deuterium atom is coordinated by an octahedron of Mg\textsubscript{4}Ni\textsubscript{2} (4 Mg–D1 = 2.275 Å; 2 Ni–D1 = 1.759 Å). In contrast, D2 atoms are not surrounded by Mg atoms and are centering buckled squares of Ni\textsubscript{4}, creating deformed planar networks located at $z = 1/4$ and $z = 3/4$ of the structure, with an Ni–D2 distance of 1.691 Å.

The closest interatomic metal–H distances in the structure agree well with the typical values observed in the Mg- and Ni-containing hydrides (1.97–2.33 Å for Mg–D and 1.52–1.73 for Ni–D in La\textsubscript{2}MgNi\textsubscript{9}D\textsubscript{13} [7]). The shortest D–D distance of 2.30 Å complies with the “rule of 2 Å” [25].

According to Refs. [11,12], the MgNi\textsubscript{2}H\textsubscript{3.2} hydride can exist in two modifications, the orthorhombic one studied in the present work as well as a related tetragonal modification (space group I\textsubscript{4}/mmm (No. 139), $a = 3.27(3)$ Å, $c = 8.78(9)$ Å) with a higher symmetry. Removing the orthorhombic distortion of the described Fmmm structure of the MgNi\textsubscript{2}D\textsubscript{3} deuteride, we can obtain the positions of H atoms in the unit cell of this tetragonal hydride. These will be two positions: H1 (2b) (00½) filling an Mg\textsubscript{4}Ni\textsubscript{2} octahedron, and H2 (4d) (0½1/2) located in the Ni net and having Ni\textsubscript{2} coordination.

3.5. Electronic structures of MgNi\textsubscript{2} and MgNi\textsubscript{2}H\textsubscript{3}

3.5.1. Methodology and crystal structures

The calculations reported in this work are based on the density functional theory (DFT). They have been performed using the projector augmented wave method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>Position</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>$B$ (Å\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgNi\textsubscript{2}H\textsubscript{3}</td>
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<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>8i</td>
<td>0</td>
<td>0</td>
<td>0.3189(8)</td>
<td>0.4</td>
</tr>
<tr>
<td>MgNi\textsubscript{2}D\textsubscript{3}</td>
<td>Mg</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
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<td>Ni</td>
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<td></td>
<td>D1</td>
<td>4b</td>
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<td>0</td>
<td>1/2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>8f</td>
<td>1/4</td>
<td>1/4</td>
<td>1/4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Table 2.** Results of profile analysis of the XRD patterns for the MgNi\textsubscript{2}H and MgNi\textsubscript{2}D samples ($T = 85$ K, Cu $K_a$ radiation) and a neutron diffraction pattern for the MgNi\textsubscript{2}D sample ($T = 100$ K, TOF spectrum). The calculations are carried out for stoichiometric MgNi\textsubscript{2}H\textsubscript{3} and MgNi\textsubscript{2}D\textsubscript{3} structures described by the space group Fmmm (No. 69).
(PAW) [26], implemented in the Vienna Ab initio Simulation Package (VASP) [27,28]. The exchange-correlation energy of electrons is described in the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof functional parametrization [29]. Semi-core $p$ electrons of Mg and Ni have been considered. After necessary tests to control the stability of the energy differences between phases, the energy cut-off for the PAWs was set to 800 eV. Charge transfers have been computed using Bader’s prescription [30,31]. As a first try, we have intentionally kept the $Fmmm$ space group whilst relaxing the crystal structure (volume and internal parameters). As a consequence, a spontaneous lowering of the symmetry was not possible. The introduction of 3-H in the metallic matrix leads to an increase of 20.75% of the host cell volume. Moreover, a calculation initiated with the experimental orthorhombic symmetry with an additional relaxation allowing the cell shape to be free has converged to a tetragonal symmetry with $a = b'$. Several orthorhombic crystal structures have been tested, such as the one reported by Okada’s group in $Pmmm$ [11]. Reducing the symmetry by adding a monoclinic tilt ($\beta$) leading to a $\beta$ angle of $\sim134^\circ$ allows the $C2/m$ space group. Tested crystal structures are represented on Fig. 8 and converged results are summarized in Table 3. The zero-point energy (ZPE) has been extracted from the phonon calculations, which have been done by the supercell approach (2 $\times$ 2 $\times$ 2) using the Phonopy code [32].

3.5.2. Analysis of the electronic structure

The total DOS of the MgNi$_2$ host compound plotted in Fig. 9 is mainly associated with Ni $d$-states hybridized with

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|}
\hline
Space group & $Fmmm$ (69) & $I4/mmm$ (139) & $Pmmm$ (47) & $C2/m$ (12) \\
\hline
\hline
$a$ (Å) & 4.7236 & 3.2970 & 3.3133 & 4.6562 \\
b (Å) & 4.5846 & – & 3.3034 & 8.3934 \\
c (Å) & 8.8590 & 8.8234 & 8.7700 & 7.4320 \\
\hline
Mg & & & & 116.27° \\
Ni & $4a$ & $2a$ & $1a, 1h$ & $2d$ \\
H1 & $8c; z = 0.3167$ & $4c; z = 0.3159$ & $2g; z = 0.3150, 2r; z = 0.1849$ & $4h; y = 0.1838$ \\
H2 & $4b$ & $2b$ & $1c, 1f$ & $2c$ \\
& $8f$ & $4d$ & $2r z = 0.2490, 2s z = 0.7490$ & $4g; y = 0.2402$ \\
\hline
$\Delta H$ (kJ/mol-H$_2$) & $-34.10$ & $-34.72$ & $-35.17$ & $-34.83$ \\
$\Delta H^{\text{corr}}$ (kJ/mol-H$_2$) & $-26.15$ & $-27.15$ & $-27.56$ & $-27.69$ \\
\hline
\end{tabular}
\caption{Relaxed crystal structure parameters and gross/ZPE-corrected heat of formation at 0 K of MgNi$_2$H$_3$ for several candidate structures.}
\end{table}

Fig. 8. The $I4/mmm$, $Pmmm$ and $C2/m$ symmetries are deduced from the $Fmmm$ symmetry.

Fig. 9. Total DOS of MgNi$_2$ ($C36$-type structure), left vertical scale, and number of electrons, right vertical scale. The Fermi energy, $E_F$, is chosen as the origin of energies.
Ni s- and p-states and Mg s- and p-states. An electronic charge transfer from Mg to Ni occurs, with respective final charges of $-1.51e^-$ and $+0.75e^-$, which explains the almost filled 3$d$-states of Ni. The compound is metallic and spin-polarized calculations lead to a paramagnetic state, in agreement with the magnetization measurements [20].

The total DOS of MgNi$_2$H$_3$ calculated in the $\bar{F}mmm$ space group and plotted in Fig. 10 shows three main structures that can be identified with the help of the partial wave analysis of the DOS (PDOS) presented in Figs. 10–13. The insertion of hydrogen leads to the low-energy structure of the DOS extending from around $-11$ to $-6$ eV, which is mainly due to Ni 3$d$, H s bonds, with smaller Ni s, p and Mg s, p contributions. Calculations of partial DOS for H1 and H2 show a slightly stronger interaction of Mg with H2 atoms as expected from the crystal structure. The bonding structure of PDOS of Fig. 13 is observed at slightly lower energy, around $-7$ eV, for H2 (at the center of the Ni$_4$ square) as compared to H1 (filling the Mg$_4$Ni$_2$ octahedron). The low-energy bonding structure is separated by an energy gap, located between $-5.5$ and $-3.5$ eV, from the main Ni 3$d$ structure. This structure is slightly, 0.5 eV, narrower for the hydride than for the intermetallic due to both lattice expansion and energy lowering of the Ni 3$d$-states involved in the Ni–H bonds. The hydride is found to be metallic with a DOS at the Fermi energy of 1.57 states/eV-f.u. lower than that of MgNi$_2$, 2.2 states/eV-f.u. associated with a further filling of the Ni 3$d$-states in the hydride. Above the Fermi level of the hydride, the structure extending up to 6 eV is associated with antibonding H-metal states. Bader’s calculation indicated a charge transfer from Mg ($-1.55e^-$) to Ni ($+0.18e^-$), H1 ($+0.6e^-$) and H2 ($+0.3e^-$).

Fig. 14 shows the electron localization function (ELF) plots in several planes. The more electron localized areas are around the H atoms, mainly because of the electronic charge transfer from the metallic elements. The hydride is clearly not a complex hydride as the Mg$_2$NiH$_4$ one, but rather an interstitial-type hydride. According to the crystallographic structure, the H1 atom is located at the center of the Mg$_4$Ni$_2$ octahedra, with a shorter distance between H–Ni than between H–Mg, as represented by the bond...
between H and Ni, whereas H2 is at the center of buckled squares Ni4.

3.5.3. Phase and lattice stabilities

In all cases, DFT and phonon calculations have been performed at 0 K for equilibrium relaxed structures. Phonon calculations of all products and reactants allowed their band phonon plot and the zero-point-energy correction at T = 0 K (ZPE) to be obtained. Table 3 presents the calculated heats of formation of compounds and the heat of the reaction: MgNi2 + 3/2 H2 → MgNi2H3.

Irrespective of the space group considered, the ZPE corrected enthalpy of formation of MgNi2H3 is about −30 kJ/mol-H2, which is consistent with the stability of the hydride at normal conditions and its decomposition above 100 °C. Whereas the orthorhombic Fmmm (69) description is the least stable structure at 0 K, and converges to the more stable tetragonal I4/mmm (139) one, the calculated orthorhombic Pmnm (47) or monoclinic C2/m (12) structures are both slightly lower in energy.

However, the phonon dispersion curves present negative frequencies for all structures (see Fig. 15a) except for the lowest-symmetry C2/m description (Fig. 15b). This means that all other structures are mechanically unstable at 0 K. We note that these structures may become stabilized by increasing the temperature. Since the Fmmm structure has been observed at 100 K, it is possible that a phase transition occurs leading to a lower-symmetry C2/m at low temperature. Some additional neutron measurements at 4 K may shed light on this hypothesis.

The partial phonon DOS for the C2/m structure are plotted in Fig. 15c. They show a dominant contribution of the heaviest Ni atom at the lowest frequencies coupled with Mg for some modes. The optical branches, at higher frequencies, are associated with the lighter H atom contribution (the modes of the two sites H1 and H2 are distinct and are not coupled).

4. Discussion and conclusions

Ti2PdH2 and Ti2PdH3 hydrides with MoSi2-related tetragonal structures have previously been studied experimentally and theoretically [33,34]. These studies showed that H atoms occupy tetrahedral Ti4 and octahedral Ti5Pd sites.

As mentioned above, the structure of MgNi2H3 is tetragonal with c/a ratios of 3.6–3.8. These studies showed that H atoms occupy tetrahedral Ti4 and octahedral Ti5Pd sites. This contrasts to the situation with the Ti2Pd-based hydrides, where the hydride-forming Ti fills the Si sites while Pd occupies the Mo sites. These major differences between the...
crystallographic aspects of the formation of MgNi$_2$H$_3$ and Ti$_2$PdH$_2$–3 hydrides and their chemistry result in the formation of different types of structures for MgNi$_2$H$_3$ as compared to Ti$_2$PdH$_2$ and Ti$_2$PdH$_3$.

MgNi$_2$ is found to form an orthorhombic hydride phase under high hydrogen pressures, 2.8–7.4 GPa, and a temperature of 300 °C. The crystallographic data for the studied hydride well agree with the reference data (where only the metrics of the unit cell was described). However, the present study is the first to report on the atomic structure of the trihydride MgNi$_2$D$_3$ and formation of an ordered type of the hydrogen sublattice. Interestingly, the arrangement of the D atoms within the unit cell is symmetric with respect to an $a$–$b$ axes exchange, and therefore does not explain the occurrence of the orthorhombic distortion.

In the present study, we have not observed the formation of the tetragonal phase MgNi$_2$H$_3$. Formation of orthorhombic or tetragonal structures has been experimentally confirmed to occur at various Mg/Ni ratios, in the area enriched by Mg (tetragonal hydride), or at stoichiometric MgNi$_2$ and overstoichiometric MgNi$_2$+$x$ compositions containing 67–70 at.% Ni.

Calculations of the electronic structure show that the total energies of the orthorhombic, tetragonal or monoclinic possible structures of the MgNi$_2$H$_3$ hydride are very close to each other. Although comparison of the heats of formation indicates that the monoclinic modification is slightly more stable, further work needs to be done to determine the stability ranges of these hydride phases, which are affected by the Mg/Ni ratios and applied $P$–$T$ synthesis and quenching conditions. The phonon calculation suggests that the monoclinic structure should be the only mechanically stable one at 0 K. Additional measurements at low temperature might confirm if any symmetry lowering occurs from the $Fmmm$ one when cooling down from 100 K.

Finally, electronic structure studies show that the bonding mechanism between the hydrogen atoms and metal atoms in MgNi$_2$H$_3$ is dominated by the formation of covalent bonds between Ni and H and a charge transfer from Mg to H, leading to a significant degree of ionic bonding between Mg (effective positive charge 1.55e$^-$) and H1 (effective negative charge $-0.6e^-$). Ni and H2 also receive electrons from Mg, but the effect is much lower as compared to the Mg$\rightarrow$H1 transfer.

Covalent Ni–H bonding has previously been found in CeNi$_3$H$_{2.7}$ and Ce$_2$Ni$_7$H$_{4.5}$ [35]. Both CeNi-based intermetallic hydrides contain spatial Ni–H–Ni–H nets covalently binding Ni and H atoms, which are similar to the one observed in the present study. Thus, covalent bonding between nickel and hydrogen should be considered as an important feature allowing formation of stable Ni-based intermetallic hydrides.

Acknowledgements

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