The Influence of Hydrogen on Structural and Magnetic Transformations in RMn$_2$H$_x$ Hydrides with Laves Phase C15 and C14 Structures—A Review

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Abstract: Laves phases crystallize in simple structures and are very common intermetallic phases that can form from combinations of elements throughout the periodic table, giving a huge number of known examples. A special feature of AB2 or AB5 phases is the ability to absorb hydrogen. This study attempts to collect, systematize and summarize the knowledge about RMn$_2$H$_x$ (R: Tb, Gd, Ho, Dy, Er, Sm, Nd and Y) hydrides available in the literature that is mainly related to structural and magnetic transformations. Due to the enormous wealth of data, the analysis focused on hydrides with $x < 4.5$ H/f.u., i.e., hydrides obtained at relatively low pressure (less than a few bars). The hydrides obtained in this way can be treated as potential hydrogen stores, which undoubtedly accounts for their current attractiveness.

Keywords: metal hydrides; Laves phases; hydrogen storage; X-ray diffraction; magnetic measurements

1. Introduction

1.1. Laves Phases

One of the most widespread and most studied groups of solids is the metallic phases. These phases are divided into simple phases (metallic elements), solid solutions and intermetallic phases. Solid solutions include substitution and interstitial solutions. Interstitial solutions are formed when relatively small atoms of a solute element do not occupy atomic positions, but positions in the interstitial voids of the solvent. A characteristic feature of solid solutions is that they retain the crystallographic structure of the solvent. Intermetallic phases assume crystal structures different from those of the individual components of the phase. In general, intermetallic phases are described by the formula A$_m$B$_n$ and are divided into the following types according to the adopted classification [1-3]:

- Phases with a dense filling of space (Laves phases), which are classified according to the size of atoms/ions;
- Electronic phases, which are classified according to the electron concentration, i.e., the ratio of the number of valence electrons to the number of atoms in the unit cell;
- Phases with mixed, metallic-ionic and metallic-covalent bonds.

The most important properties of the Laves phases include the following:

- They are metal alloys with the general stoichiometric formula AB$_2$;
- The main factor influencing their formation is the ratio of the radii of the component atoms, and $r_A/r_B$ is equal, theoretically, to 1.225. In fact, this ratio for the Laves phases is within the range of 1.05-1.68 Å. Here, Å refers to larger atoms (e.g., rare earths), and B refers to smaller atoms (e.g., Cu, Zn, Fe, Mn, Cr, etc.);
- They do not create secondary solutions;
• They exhibit an almost purely metallic type of bonding;
• They are phases with the densest space filling;
• They crystallize in one of three homothetic types, C14, C15 and C36, as determined by the value of the electron concentration [4].

The RMn$_2$ intermetallic compounds crystallize either in the hexagonal C14 type for $R$ = Pr, Nd, Sm, Ho, Er, Tm and Lu or in the cubic C15 type for $R$ = Y, Sm, Gd, Tb, Dy and Ho [5–14]. Other elements (A: La, Ce, Eu and Yb) do not form stable intermetallic compounds with Mn [15].

A more detailed description of the crystal structures of Laves C14 and C15 phases is presented in Supplementary Material.

1.2. Structural and Magnetic Properties of RMn$_2$ Compounds

The RMn$_2$ compounds have been widely studied because of their very interesting structural and magnetic properties. Changes of the unit cells for RMn$_2$ as a function of the temperature are presented in Figure 1a [16]. For the (Tb, Gd, Sm, Nd, Pr, Y)Mn$_2$ compounds, the first-order phase transition is observed, and temperature dilatometer and X-ray diffraction measurements revealed significant increases in the volume of unit cells of these alloys at temperatures below 105 K. The magnetic ordering was also observed below the temperatures of the structural changes [17–19]. The largest, an almost 5% change in volume, was recorded for YMn$_2$. This significant magneto-volume effect is related to the appearance of a well-localized magnetic moment in the Mn sublattice (~2.7µB) below the magnetic ordering temperature [20]. The (Er, Ho, Dy)Mn$_2$ compounds do not show changes in the volume cell; they undergo a second-order phase transition in the temperature range of 15–35 K [14,21].

![Figure 1](image)

**Figure 1.** (a) Changes of the unit cells for RMn$_2$ as a function of the temperature for RMn$_2$ [16]; (b) Relation between the $^{55}$Mn hyperfine field $H_{hf}$ and the lattice parameter of RMn$_2$ at 4.2 K. The transferred hyperfine fields from rare-earth moments are subtracted from the observed ones. The effective lattice parameter of C14 compounds (closed circles) is given by $a_{eff} = (3a\sqrt{3})^{1/3}$. The scale for the estimated Mn moment from $H_{hf}$ is given on the right-hand side [22].

The type of the phase transition can be related to the occurrence of a magnetic moment of Mn atoms or its absence. The measurements of the hyperfine field on the $^{55}$Mn nuclei in RMn$_2$ compounds carried out by Yoshimura (Figure 1b) indicate that below a
certain distance of ~2.66 Å between the nearest Mn atoms ($d_{\text{Mn-Mn}}$), the localized magnetic moment of the Mn atoms is not observed. This distance is called the critical distance and denoted as $d_c$. Based on the $d_{\text{Mn-Mn}}$ distance, RMn$_2$ compounds can be divided into three groups [23]:

- $d_{\text{Mn-Mn}} < d_c$, (LuMn$_2$, ErMn$_2$, TmMn$_2$), where the Mn subnet is non-magnetic, and the Er and Tm sublattices are ferromagnetic [24];
- $d_{\text{Mn-Mn}} > d_c$, (NdMn$_2$, PrMn$_2$), where the dominant Mn magnetic sublattice is stable and enforces antiferromagnetic ordering in the sublattice of R-atoms with the R-Mn type interaction [25];
- $d_{\text{Mn-Mn}} \sim d_c$, (GdMn$_2$, TbMn$_2$, DyMn$_2$, HoMn$_2$, YMn$_2$), where the Mn sublattice is on the verge of stability. Generally, non-collinear magnetic structures are observed in this group of compounds. In some cases (TbMn$_2$, DyMn$_2$, HoMn$_2$), only a part of the Mn atoms carries a magnetic moment [20,26–34].

The magnetism of the RMn$_2$ compounds is related to the electronic structure of Mn and R atoms. Mn has an unfilled outer 3d electron shell affecting the crystalline field from other ions. However, in the R atoms, the unfilled inner 4f electron shell is shielded by the 5p outer shell, which facilitates the behavior similar to that noted for the free ion.

In the RMn$_2$ compounds, three types of exchange interactions can be distinguished as follows:

- Between 3d–3d magnetic moments (Mn–Mn),
- Between 3d–4f moments (Mn–R),
- Between localized 4f–4f moments (R–R).

The strongest among the above is the 3d–3d exchange interaction, as evidenced by the high temperature of ordering of the magnetic relationship with non-magnetic rare earths (YMn$_2$, $T_N \approx 105$ K). The band model, which is applicable here, assumes that the difference in concentration between electrons with spins ↓ and ↑ is responsible for the formation of the magnetic moment.

The weakest is the 4f–4f interaction, as indicated by low temperatures of magnetic ordering of the ErMn$_2$ and TmMn$_2$ compounds with the non-magnetic Mn sublattice (Figure 1a,b). The R atoms having an unfilled 4f electron shell are characterized by well-localized magnetic moments; the wave functions that describe them have a short range in comparison to the distance between atoms (magnetic moments). The magnitude of the interaction of 4f–4f depends on the density of the polarized conduction electrons; their oscillating nature as a function of distance is described by the RKKY theory.

The magnetic interaction 3d–4f has an intermediate value between 3d–3d and 4f–4f. It occurs mainly through the polarization of electrons of 5d rare earth atoms [35].

1.3. Hydrogen in Metals

Rare earth (R) metals react with hydrogen forming stable di- and trihydrides. The RH$_2$ dihydrides are very stable, with reported formation enthalpies of about ~200 kJ/molH$_2$; thus, they decompose in a vacuum, releasing hydrogen and forming individual RE metals at very high temperatures only [36]. On the other hand, manganese, which is also the main building block of the discussed RMn$_2$H$_4$ structures, behaves differently under the influence of hydrogen in comparison to RH$_2$. At ambient pressure conditions and room temperature, the subhydride MnH is the only stable compound. With increasing pressure, MnH is stabilized, and then hydrogen-rich hydrides appear at higher pressure [37].

A simplified scheme of hydrogen penetration into the crystal structure of the metal (intermetallic compound) can be divided into three stages (Figure 2): (a) Physisorption: gaseous hydrogen molecules interact with electrons on the metal surface using weak attractive van der Waals forces; (b) Chemical adsorption: hydrogen molecules dissociate, overcoming the surface energy barrier, and form a metallic hydrogen bond; (c)
Absorption: in this step, the chemisorbed hydrogen atom can jump to the subsurface layer to finally diffuse through the crystalline structure of the metallic host [38].

After absorption, the hydrogen atoms/ions remain in the sites of the crystal structure until they are given a surplus of energy necessary to overcome the diffusion barrier as a result of thermal activation. Under these conditions, the diffusion coefficient satisfies the classical Arrhenius relationship: \( D = D_0 \exp \left( -\frac{E_a}{kT} \right) \), where \( D_0 \) is the diffusion constant. Assuming the simple activated diffusion, the typical diffusion constant for \( H \) in intermetallic compounds equals \( 1 \times 10^{-10} \text{ m}^2/\text{s} \) and \( E_a = 45 \text{ kJ/mol} \) at room temperature [39,40]. Researchers also point to the \( D_0 \) and the \( T \) on the structure on the structure of the metal. For example, for Pd (fcc structure), \( D_0 = 2.9 \times 10^{-3} \text{ cm}^2/\text{s} \) and \( E_a = 0.230 \text{ eV} \), while \( D_0 = 4.2 \times 10^{-4} \text{ cm}^2/\text{s} \) and \( E_a = 0.40 \text{ eV} \) for Fe (bcc structure) [41].

One of the first experiments indicating the dissociation of \( H_2 \) molecules in the process of its absorption by metals was the study of the \( p-c-T \) relationship (hydrogen pressure-concentration-temperature) [39]. In numerous metal hydrides, hydrogen atoms are characterized by high mobility already at room temperature, especially when the number of available positions is greater than the number of hydrogen atoms. Hydrogen atoms can jump from one position to another without creating a crystallographic ordered structure—the positioning is accidental. The frequency of hydrogen jumps is huge (e.g., in vanadium hydrides at room temperature, it is \( \sim 10^{10–10^{12}} \text{ Hz} \) [39]. With the lowering of the hydride temperature, the frequency decreases. Therefore, it may also happen that hydrogen atoms occupy selected positions in an orderly manner, and they create a superstructure. Skripov states that in many hydrides of the Laves phase, even two types of hydrogen jumping motions with different characteristic jump rates coexist. While the slower jump process is responsible for long-distance diffusion, the faster process corresponds to the localized movement of hydrogen over small groups of interstitial sites. In some of the Laves-phase compounds, the localized hydrogen motion is not ‘frozen out’ on the frequency scale of \( 10^7 \) to \( 10^8 \) Hz down to 20 K [42]. At low temperatures, there is also the possibility of non-activation, tunnel transitions of the hydrogen atom from one position to another [38,43,44].

Figure 3a shows the typical hydrogen absorption isotherms in metal. The isotherms form a phase diagram of the equilibrium pressure as a function of the hydrogen concentration \( P_{eq}(x) \), in which three essential areas can be distinguished: (i) the \( \alpha \) region is the “solid” solution of hydrogen in the parent metal, where the hydrogen pressure \( p \) increases with the hydrogen content \( x \) according to Sievert’s law \( p = (Kc)^2 \) (\( K \)—Sievert’s constant, \( c \)—hydrogen concentration), (ii) the two-phase region (\( \alpha + \beta \)) and (iii) the \( \beta \) region—metal hydride. As the temperature increases, the latter narrows and disappears at the critical temperature \( T_{c_{\alpha\beta}} \), which is characteristic for a given element. The isotherms in the middle region show a hydride characteristic plateau, corresponding to the equilibrium pressure as a function of the hydrogen concentration.
Figure 3. (a) Schematic plot of hydrogen absorption in metal ($p$-$c$-$T$ isotherms). $P_{eq}$—gas pressure, $c$—hydrogen concentration in the metal; (b) Construction of the Van’t Hoff relation. Based on [45,46].

The equilibrium pressure zone is ideally suited for the isothermal absorption and desorption of hydrogen from metal. The state of equilibrium can be described by a phase diagram analogous to the Van der Waals diagram of the non-ideal gas. $P_{eq}$ equilibrium pressure is associated with changes in enthalpy ($\Delta H$) and entropy ($\Delta S$) in the two-phase region via the empirical temperature of the Van’t Hoff relationship (Figure 3b) [45,46]. For a typical equilibrium pressure, e.g., for PdH$_x$—hydride at 423 K, it is 0.1 MPa, and it is 1.0 MPa at 518 K. The critical point of this hydride is $T_{crit} = 565$ K at $x = 0.25$ H/f.u. [39].

The two-phase region characteristic for hydrides is related to the spinodal decomposition, which is a consequence of the long-range, attractive H-H interaction. Two phases with hydrogen concentrations $x_1$ and $x_2$ co-exist when the equilibrium condition is realized:

$$\frac{1}{2} \mu^\theta = \mu^a(x_1) = \mu^a(x_2) = \frac{1}{x_2-x_1} \int_{x_1}^{x_2} \mu^a(x)dx$$  \hspace{1cm} (1)

where $\mu^\theta$ is the chemical potential of hydrogen gas per molecule, and $\mu^a$ is the chemical potential of hydrogen in solid solution per atom. Critical points ($T_{crit}$ and $x_{crit}$) determine the condition:

$$\frac{\partial \mu^a}{\partial x} = 0 = \frac{\partial^2 \mu^a}{\partial x^2}$$  \hspace{1cm} (2)

Spinodal decompositions can be related to anomalous changes in the physical properties of hydrides, such as, for example, reductions in diffusion rates, fluctuations of high amplitude density or anomalies in the specific heat [40].

Metal hydrides are hard and brittle (fragile); they are obtained primarily in powder form. Due to the considerable expansion of the unit cell of the metallic element (more than a dozen or so percent) during the hydrogenation process, it is practically impossible to obtain hydride monocrystals (the single crystal is destroyed because of decrepitation). In general, metal hydrides show quite high resistance to weather (atmospheric) conditions, and they are good conductors of electricity [47].

2. RMn:H$_x$ Hydrides

2.1. Localization of Hydrogen

The physical properties of rare earth hydrides with manganese RMn:H$_x$ largely coincide with the properties of metal hydrides (MH$_x$). Also, alloys of RMn$_2$: compounds absorb hydrogen very easily. At close to atmospheric hydrogen pressure and temperatures above 100 °C, it is possible to achieve a hydrogen concentration of ~4.5 H/f.u. [48]. As noted in metal hydrides, hydrogen occupies the interatomic sites of the elements that comprise the
RMn\textsubscript{2} unit cell. There are three types of tetrahedral sites in RMn\textsubscript{2} compounds: A2B2, AB3 and B4, where A and B represent atoms of R and Mn, respectively, surrounding the site (Figure 4). The largest and at the same time most willingly filled by hydrogen site (below \(x \approx 3.5\) H/f.u.) is the A2B2 type. For \(x \approx 3.5\) H/f.u., there is also a tendency to fill smaller sites, such as AB3 sites [49–52]. However, no B4 site filling was observed. The same types of sites occur in both C14 and C15 types of Laves phases. When filling the sites, hydrogen occupies crystallographic positions (Table 1).

![Figure 4. Three crystallographic positions accessible for hydrogen in C15 Laves phase: 96g (inside of A2B2 tetrahedra), 32e (inside of AB3 tetrahedra) and 8b (inside of B4 tetrahedra). The Fd\textbar{3}m space group. Some atoms were removed for clarity. Big, dark balls: R; small, bright balls: Mn. Based on [51].](image)

**Table 1.** Hydrogen positions in C14 and C15 phases.

<table>
<thead>
<tr>
<th>Laves Phase</th>
<th>Positions of Hydrogen</th>
<th>Number of Sites/f.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C14})</td>
<td>(24l, 12k, 6h_1, 6h_2)</td>
<td>(\text{A2B2} \quad 12)</td>
</tr>
<tr>
<td>(\text{C15})</td>
<td>(96g, 32e)</td>
<td>(\text{AB3} \quad 4)</td>
</tr>
</tbody>
</table>

Although the number of sites is significant, every site cannot be occupied by hydrogen. Two criteria are useful: (i) the Switendick criterion [53] states that the distance \(d_{\text{AB}}\) must be larger than \(-2.1\) Å and (ii) the Westlake criterion indicates that the radius of the sphere available for hydrogen cannot be less than \(-0.37\) Å. [54] As an effect, criteria preclude occupancy of A2B2 tetrahedrons that have a common wall, and the B4 site is not available for hydrogen due to size restrictions. The Switendick criterion, confirmed in neutron measurements [55,56], largely determines the maximum content of absorbed hydrogen. The theoretically determined maximum hydrogen concentration in \(\text{RT}2\text{H}_6\) (\(R\): rare earth, \(T\): transition metal = Y, Mn) compounds is therefore 6.0 H/f.u. [57]. Only the use of ultra-high hydrogen pressures of the order of 10\(^{6}\) MPa led to the formation of RMn\textsubscript{2}H\textsubscript{6} hydrides; the first being YMnH\textsubscript{6} [58,59]. Highly hydrogenated \((x \geq 4.5\) H/f.u.) compounds show different physical properties compared to low-hydrogen compounds \((x \leq 4.5\) H/f.u.) [60,61] and will not be discussed in this study.

2.2. Sample Preparation and Dependence of \(\Delta V/V\) versus Hydrogen Content

In the discussed hydrides, the sample preparation was similar and usually involved the following scenario.

The host materials (RMn\textsubscript{2}) were prepared from high purity elements using the standard induction melting technique under argon atmosphere. Next, materials were usually annealed to obtain a single-phase compound. The RMn\textsubscript{2} samples were saturated with hydrogen using a standard volumetric method (Sievert) to obtain RMn\textsubscript{2}H\textsubscript{6} hydrides in the
typical range of $x$: $0 < x < 4.3$–$4.5$ [7–9, 55, 62–67]. The first test after hydrogen saturation was XRD measurements at 300 K. As a representative example, the HoMnH$_x$C$_{15}$ diffractogram is presented in Figure 5a. The most visible effect of hydrogen absorption by the sample is the shift of the diffraction lines towards smaller angles (in 2 theta), which means an increase in the distance between atoms in the cell, and consequently an increase in the unit volume of the cell with $x$.

![XRD patterns](image)

**Figure 5.** HoMnH$_x$. (a) The XRD patterns for different $x$; here, $\alpha$ represents the cubic phase $(Fd\bar{3}m)$, and $\beta$ represents the rhombohedral phase $(R\bar{3}m)$; (b) Relative change in the unit cell volume as a function of $x$ [66].

Even at room temperature, the RMnH$_x$ hydrides do not persist in the crystallographic structure of the host compound. For the HoMnH$_x$C$_{15}$ hydride, a combination of the cubic ($\alpha$) and rhombohedral distortion ($\beta$) is observed (Figure 5a). The obtained results are in agreement with [68]. To compare lattice parameters of hydrides with different crystallographic structures, their parameters were converted into parameters of the pseudo-cubic cell considering abundance phases, if the system is not a single-phase system. For example, the lattice parameters of the rhombohedral phase were converted into lattice parameters $a^*_\delta$ of the pseudo-cubic phase according to the relationship reported below:

$$a^*_\delta = \sqrt[3]{a^2_\delta c_\delta / \sqrt{3}}$$  \hspace{1cm} (3)

where $a_\delta$ and $c_\delta$ are lattice parameters of the rhombohedral phase (space group: $R\bar{3}m$, nr166, setting: 1) [66].

The relative volume change in unit cell versus hydrogen content in HoMn:H$_x$C$_{15}$ is depicted in Figure 5b. The first ‘model’ that attempted to describe the relation between $\Delta V/V_0$ and $x$ was just a linear relationship. The next one, the Hirata model, only correctly reproduces the lowest range of $x$ ($0 < x < 3.0$) (Figure 5b, dashed line) [69], and its development was proposed by Figiel et al. [51]. In the last one (farther: Hirata–Figiel model), the authors assume a two-stage approach to occupying interstitial sites (Figure 5b red line). Initially, with a characteristic parameter $X_c < 3.0$–$3.5$ H/f.u. (see below), the A2B2 type sites are filled (this part is identical with Hirata model). Next, above $X_c > 3.0$–$3.5$ H/f.u., the AB3 type sites are also occupied. It is represented by a characteristic break in the red curve ($x \sim 3.2$ H/f.u., Figure 5). The Hirata-Figiel model is described according to the relationship described below [51].
\[
\frac{\Delta V}{V_0} = \left[ \frac{B_0 + bx}{B_0} \right]^{1/b} - 1; \quad \text{for } x < X_c \tag{4}
\]
\[
\frac{\Delta V}{V_0} = \left[ \frac{B_0 + b(x_c + (1 - P)(x - X_c))}{B_0} \right]^{1/b} + \left[ \frac{B_0 + Pb(x - X_c)}{B_0} \right]^{1/b}; \quad \text{for } x \geq X_c \tag{5}
\]

where \(\Delta V/V_0\) is the relative increase in unit cell volume; \(B_0\) is a parameter of the lattice contraction, a quantity analogous to the bulk modulus at starting concentration related to the intrinsic pressure; \(b\) is the first derivative with respect to concentration \(x\): \((B_c = B_0 + b_x)\); and \(P\) is the probability of filling the AB3 sites by hydrogen atoms for concentrations greater than \(X_c\) \((P = 0 \text{ for } x \leq X_c)\) [34,51]. Fitted parameters for the \(R\)Mn\(\text{H}_x\) \((R: \text{Y, D}_{y}, \text{Gd}, \text{Tb}, \text{Ho})\) hydrides are presented in Table 2. For all compounds, the characteristic \(X_c\) belongs to the region of ~3.0–3.5 and probabilities of entering the AB3 interstitial sites \(P \sim 0.6–0.9\). This type of filling sites was also postulated in [50,51].

<table>
<thead>
<tr>
<th>Sample</th>
<th>(B_0)</th>
<th>(b)</th>
<th>(X_c)</th>
<th>(P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMn(\text{H}_x) (300 K) *</td>
<td>9.24</td>
<td>9.63</td>
<td>3.25</td>
<td>0.77</td>
</tr>
<tr>
<td>DyMn(\text{H}_x) (300 K) *</td>
<td>7.03</td>
<td>9.08</td>
<td>3.20</td>
<td>0.61</td>
</tr>
<tr>
<td>GdMn(\text{H}_x) (300 K) *</td>
<td>9.43</td>
<td>10.01</td>
<td>3.06</td>
<td>0.52</td>
</tr>
<tr>
<td>TbMn(\text{H}_x) (300 K) *</td>
<td>7.78</td>
<td>9.36</td>
<td>3.15</td>
<td>0.56</td>
</tr>
<tr>
<td>HoMn(\text{H}_x) (300 K) *</td>
<td>6.93</td>
<td>8.90</td>
<td>3.33</td>
<td>0.88</td>
</tr>
<tr>
<td>HoMn(\text{H}_x)_C14, (300 K) **</td>
<td>4.7(6)</td>
<td>13(1)</td>
<td>3.48(3)</td>
<td>0.9(1)</td>
</tr>
<tr>
<td>HoMn(\text{H}_x)_C14, (75 K) **</td>
<td>6.1(2)</td>
<td>9 (1)</td>
<td>3.41(3)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>HoMn(\text{H}_x)_C15, (300 K) ***</td>
<td>6.0(5)</td>
<td>10(1)</td>
<td>3.2(1)</td>
<td>0.6(1)</td>
</tr>
</tbody>
</table>

* [51] ** [7], *** [66].

The relative volume increase \((\Delta V/V_0)\) of unit cells of hydrides determined at room temperature and depending on the hydrogen content in the sample is non-linear and can be described by the same function, indicating that this effect is determined only by the presence of hydrogen. The fits of the Hirata–Figiel model to the change in \((\Delta V/V_0)\) depending on the hydrogen concentration for the various studied hydrides \(R\)Mn\(\text{H}_x\) are shown in Figure 6.

**Figure 6.** Comparison of relative volume change in unit cells for \(R\)Mn\(\text{H}_x\) versus hydrogen content at \(T = 300\) K. Based on [7,51,65–67].

For \(x < 3.0\) H/f.u., the curves, except for those corresponding to (Gd and Nd)Mn\(\text{H}_x\), are almost identical. At values greater than \(x = 3.0\) H/f.u., distinct behavior becomes visible.
with increasing $x$, especially for concentrations close to the maximum, where the relative increase in volume increases with the atomic number of the rare earth element.

2.3. Examples of Structural and Magnetic Transformations in $R$Mn$_2$H$_x$

With a temperature change, the $R$Mn$_2$H$_x$ hydrides undergo complex phase transformations in many cases, which, combined with the often occurring multi-phase states, makes the interpretation of their X-ray diffraction magnetic transformation results extremely difficult. Some authors have even argued that it will never be possible [39]. One of the first hydride families to be studied over a wide range of $x$ and temperature changes was YMn$_2$H$_x$, showing a very wide range of structural transformations as a function of temperature. In contrast, TbMn$_2$H$_x$ hydride families show a very ‘modest’ spectrum of structural transformations. Very interesting are the structural and magnetic properties of HoMn$_2$H$_x$ hydrides, in which the base compound can crystallize in a C14 or C15 Laves phase structure, depending on the sample preparation [10].

2.3.1. YMn$_2$H$_x$

Due to the similarity of its electronic structure to that of lanthanides, yttrium is classified as rare earth element. The host YMn$_2$ compound shows a large increase (about 5%) in elemental cell volume near 100 K in X-ray diffraction measurements. A temperature hysteresis of several degrees is also observed (compare with Figure 1a). Hydrogen in the YMn$_2$H$_x$ induces a number of structural and magnetic transformations that best are represented by the phase diagram (Figure 7). The structural and magnetic phase diagram for YMn$_2$H$_x$ hydrides can be distinguished into three ranges [50,70–74].

![Figure 7. Structural and magnetic phase diagram of YMn$_2$H$_x$ hydrides as a function of $x$ and temperature. The thick line separates the paramagnetic area from the magnetic ordering area. Para, Ferri and AF correspond to paramagnetic, ferrimagnetic and antiferromagnetic states, respectively. Based on [50,70–76]. Here, $\alpha$ represents phase type C15; $\alpha'$ indicates regular phase ($P-43m$); $\beta$ represents the tetragonal phase ($\varepsilon > 0$), which is a phase with very low hydrogen content (<0.1 H/f.u.); $\beta'$ is like...](image-url)
\(\beta\) but with a higher hydrogen content of 0.3 < \(x\) < 0.6; \(\gamma\) is a phase with tetragonal distortion but with \(\varepsilon < 0\); and \(\delta\) represents the rhombohedral phase.

Range 1: \(x \leq 1.2\) H/f.u.

A number of phase transformations are observed. In the range of 0.4 \(\leq x \leq 0.8\) and below ~245 K, the regular \(\alpha\) phase transforms to the tetragonal \(\beta'\) phase of the same type as noted in the case of YMn (at approx. 100 K). In the \(\beta'\) phase, the lattice parameters satisfy the inequality \(\varepsilon > 0\), where \(\varepsilon = 1 - \varepsilon_{\text{ultr}}\) (\(\varepsilon_{\text{ultr}}\) tetragonal structure parameters). On the other hand, below the temperature range ~100–150 K, there is a distortion to the tetragonal phase \(\gamma\), in which \(\varepsilon < 0\). The \(\alpha \rightarrow \beta\) transformation is accompanied by the antiferromagnetic magnetic ordering of the manganese sublattice. Below \(x = 0.4\) H/f.u. and above \(x = 0.8\) H/f.u., a combination of phases is observed: the host compound \((\alpha)\), the tetragonal \((\beta)\) with low hydrogen content \((x < 0.1\) H/f.u.) and the \(\gamma\) phase.

Range 2: \(1.15 \leq x \leq 3.5\)

A very wide range is noted in which hydrides retain the structure of the regular phase. In this area, the hydrides exhibit a ferrimagnetic order. The ordering temperature increases from ~250 K to ~350 K with increasing hydrogen concentration. Neutron diffraction measurements for YMn:D\(_{1.15}\) and YMn(H\(_{0.64}\)D\(_{0.36}\))\(_{1.15}\) \([72,73]\) indicate a structural transformation from the C15 phase to the regular phase described with lower symmetry (space group: \(P\bar{3}m1\)). From these measurements, it also follows that deuterium is located in A2B2 positions, and magnetic moments of Mn atoms create two magnetic sublattices. One of them forms a non-collinear antiferromagnetic canted structure, and the other one, which is very weak (\(\lesssim 0.1\) \(\mu_N\)), exhibits ferrimagnetic ordering. The abundance of the latter increases linearly as \(x\) increases \([70]\).

Range 3: \(3.5 \leq x \leq 4.5\)

Below the temperature range ~300–400 K and along with the increase in hydrogen content, a structural transformation from the regular phase \(\alpha'\) (from the range 2) to the rhombohedral phase \(\delta\) through the two-phase area \((\alpha' + \delta)\) occurs. The \(\delta\) phase is a rhombohedral phase belonging to the spatial group \(R\bar{3}m\) \([75]\).

Neutron diffraction studies for YMn:D\(_{3.45}\) and YMn:H\(_{1.3}\)\(_{3.45}\) \([71,72,75,76]\) showed an antiferromagnetic arrangement of the Mn sublattice below 360–398 K with propagation vector \(k = [\frac{1}{2} \frac{1}{2} \frac{1}{2}]\). Mn atoms occupy two different positions, and their nearest neighbors (H or D) are also different, which explains the alternative ferro- or antiferromagnetic coupling between Mn planes. Moreover, it was also observed that the magnetic ordering of the Mn sublattice and hydrogen/deuterium ordering appeared at the same temperature. Because there are no additional reflections from the deuterium atoms, the deuterium superstructure was described with the \(k = 0\) propagation vector. As the hydrogen content of the sample increases, the magnetic ordering temperature \((T_\text{c})\) of the hydride increases from about 230 K to about 400 K (the red line in Figure 7 conventionally separates the paramagnetic state from the magnetic ordering state). The reason for the increase in \(T_\text{c}\) is an increase in the elemental cell volume of the sample (by up to 30\% compared to YMn) and, consequently, an increase in the \(d_{\text{Mn-Mn}}\) interatomic distances above the critical distance \(d_\text{c}\). This results in an increase in the degree of localization of the Mn magnetic moments and therefore an increase in their exchange interaction, leading to an increase in the magnetic ordering temperature.

2.3.2. \(\text{TbMn}_{1.1-x}\text{H}_x\)

A characteristic feature of RMn:H\(_x\) hydrides is splitting of the structural line into two (or more) components (observed) with decreasing temperature. This process is a spinodal decomposition, as previously mentioned in Chapter 1, and is clearly visible in Figure 8a. With decreasing temperature (below ~360 K), the high-temperature regular phase \(\alpha\) splits into two phases \((\alpha_0 + \alpha_\text{f})\) with different hydrogen contents. In the temperature range of 220–250 K, even the third phase \((\alpha_\text{m})\) termed “intermediate” is observed (gray lines). The
$\alpha_0$ and $\alpha_1$ phases occur at the lowest temperatures. Comparing lattice parameters hydrides with $x = 0.5$ and 1.0 and below 200 K (Figure 8b), it can be noticed that the parameters of the $\alpha_0$ phase are very close to those of the host compounds (TbMn$_2$), also reflecting their characteristic behavior (increases in parameters). The $\alpha_0$ phase contains negligible amounts of hydrogen, less than $\sim$0.05 H/f.u. This phase can be treated as a solid solution of hydrogen in the metal. The parameters of the second rich-amount hydrogen phase ($\alpha$) were estimated as $\sim$1.6–1.8 H/f.u. [9,52]. The process of spinodal decomposition is reversible with temperature.

![Figure 8](image_url)

**Figure 8.** (a): Evolution of the (220) and (311) XRD lines versus temperature; (b): Lattice parameters for the TbMn$_2$H$_x$ hydrides as a function of temperature. Symbols $\alpha$ and $\beta$ correspond to cubic and rhombohedral distortion, respectively; $\alpha_0$, $\alpha_1$ and $\alpha_m$ correspond to the 'reach-amount' hydrogen phase, low-amount hydrogen phase and 'intermediate' phase, respectively. The lattice parameters of the rhombohedral structure are expressed in parameters of the pseudo-cubic structure (Equation (3)). Parameters of TbMn$_2$H$_x$ ($x = 3.5$ and 4.3 H/f.u.) hydrides were determined taking into account the abundance of regular and rhombohedral phases. The dashed lines for $x = 1.0$ indicate the probable change in parameter values (b). Based on [9,52].

For TbMn$_2$H$_x$, $1.8 \leq x \leq 3.3$, hydrides persist one regular phase ($\alpha$) in the whole temperature range. The increase in parameters for $x = 2.0$, 2.5, 3.0 is continuous, and weak jumps are observed (marked as black dots) only in the temperature range of 270–280 K (Figure 8b), which corresponds well to magnetic ordering temperature for these hydrides.

In the range $3.2 \leq x \leq 4.3$ and in addition to the regular $\alpha$ phase, the second phase rhombohedral distortion ($\beta$) is observed. This phase, which is initially recognized as an “inclusion” of another phase, becomes dominant at the expense of the $\alpha$ phase as the nominal hydrogen content increases [9].

The spinodal decompositions into two phases ($\alpha_0 + \alpha_1$) were confirmed using magnetic measurements. Figure 9a shows the dependence of magnetization as a function of temperature for TbMn$_2$H$_x$ ($x = 0.0$, 1.0 and 2.0 H/f.u.). The characteristic maximum for TbMn$_2$ at $\sim$50 K (compare the parameters that increase in Figure 1a) is also visible in the magnetization of hydride with $x = 1.0$ what corresponds to $\alpha_0$ phase. Magnetic ordering of the $\alpha_1$ phase is estimated at $\sim$240 K. For $x = 2.0$, hydride magnetization is a flat curve (100 Oe) in the whole range of temperatures with only exceedingly small irregularities at $\sim$280 K that clearly have been expressed/exposed in the external field of 50 kOe (insert in Figure 9a). This maximum indicates antiferromagnetic ordering, as confirmed in the neutron diffraction study for TbMn$_2$D$_{2.0}$ [52]. Magnetic ordering temperature increases with increasing...
hydrogen content \( x \) as represented by the gray thick line in Figure 9b. The increase of magnetic ordering temperature from \(-50\) K for host \( \text{TbMn}_2 \) to the range of \(-200\)–\(400\) K for its hydrides is fascinating.

![Figure 9](image)

**Figure 9.** (a) The dependence of the magnetization of \( \text{TbMn}_2 \text{H}_x \) hydrides versus temperature in the external magnetic field of \( 100\) Oe and \( 50\) kOe for \( \text{TbMn}_2\text{H}_{2.0} \) (insert). Para, Ferri and AF represent paramagnetic, ferrimagnetic and antiferromagnetic states, respectively; (b) Tentative magnetic and structural hydride phase diagrams for \( \text{TbMn}_2\text{H}_x \). The thick red line separates the paramagnetic state from the state of magnetic ordering. Descriptions in gray correspond to magnetism. Based on [9,52].

This effect is related to the magnetic properties of manganese. For magnetic interactions between the magnetic moments of manganese, an important critical distance is \( d_c = 2.71\) Å. Manganese atoms located closer than \( d_c \) do not form long-distance magnetic ordering, and atoms at a distance greater than \( d_c \) create large magnetic moments (about 3 \( \mu_B \)) and strongly magnetically couple together (compare with Section 1). Because hydrogen causes a strong increase in the volume of the unit cell, it also forces an increase of \( d_{Mn-Mn} \) above \( d_c \), which in turn causes the creation of magnetic order. Because the Mn-Mn interaction is strong and the ordering temperature is proportional to the exchange interaction, magnetic ordering is achieved in these hydrides at such high temperatures. Due to the nature of the exchange interaction, the magnetic moments of manganese are arranged antiferromagnetically. The influence of the interactions coming from rare earth magnetic moments is weak due to the effect of shielding their magnetic moments related to 4f electrons shells. It is reflected in weak dependence of magnetic ordering temperature of hydrides versus rare earth elements (Figure 6) [7–9,55,64–67].

2.3.3. \( \text{GdMn}_2\text{H}_x \)

The magnetic (Figure 10a) phase diagram of \( \text{GdMn}_2\text{H}_x \) is very similar to that for \( \text{TbMn}_2\text{H}_x \), and one can conventionally identify three \( x \)-ranges. In range (i) \( x \leq 1.8\) H/f.u., with decreasing temperature, there is a decay of the high-temperature regular phase into, initially, three phases with different hydrogen contents. The phase with intermediate hydrogen content rapidly disappears with decreasing temperature. The other two clearly segregate into “hydrogen-poor” \( (x \leq 0.05\) H/f.u.) and “hydrogen-rich” \( (x \approx 1.8\) H/f.u.) phases. In range (ii), corresponding to \( 1.8 \leq x \leq 3.2 \), there is only a regular phase throughout the temperature range. In the range (iii) above \( x = 3.2\) H/f.u., the regular phase is transformed to the rhombohedral phase through the area of coexistence of two phases, including the regular phase and the rhombohedral phase [8,55]. Also, the course of changes in lattice parameters versus temperature (Figure 10b) is very similar to those noted for \( \text{TbMn}_2\text{H}_x \). A clear spinodal decomposition is visible for \( x \leq 2\) H/f.u.
Figure 10. GdMnH₆. (a) Composite magnetic and structural hydride phase diagrams for GdMnH₆. The red line separates the paramagnetic state from the magnetic ordering state. Symbols α and β correspond to cubic and rhombohedral distortion, respectively; α₀, α₁ and α₂ correspond to the ‘reach-amount’ hydrogen phase, low-amount hydrogen phase and ‘intermediate’ phase, respectively; (b) The lattice parameters. The rhombohedral structure is expressed in parameters of the pseudo-cubic structure (Equation (3)). Parameters of GdMnH₆ (x = 3.5 and 4.3 H/f.u.) hydrides were determined by taking into account the abundance of regular and rhombohedral phases [8].

2.3.4. DyMnH₆

Structural hydride studies have also been carried out for a series of DyMnH₆ hydrides [63]. Their structural phase diagram is largely similar to the structural phase diagrams of (Gd or Tb)MnH₆, which have been reposted above. The phase diagram of the Dy hydrides (Figure 11) has been described using a combination of two phases: the regular (C15 type) phase denoted as α and the rhombohedral (R̅3m) phase denoted as β. The apostrophes (‘) next to the phase symbols refer to the different hydrogen concentrations in the phase or indicate the ordered magnetic state of the sample (e.g., α and α‘ for x = 2.0 H/f.u.).

Figure 11. Structural phase diagram of DyMnH₆ hydrides. Here, α indicates the regular phase of C15 type, and β represents the rhombohedral phase. The red line separates the paramagnetic state from the magnetic ordering state. PARA—paramagnetic state. Based on [63].
For samples with a nominal concentration of \( x \leq 1.6 \) H/f.u., the authors observed spinodal-type decays. For TbMnH\(_x\) (Figure 8b) in a temperature range of \(-200\) to \(-250\) K, a region of up to three regular phases with different hydrogen contents appears. As the temperature decreases (below \( 200 \) K), one of them disappears; there is, as already known from previous analyses, a decomposition into two regular phases with a minimum \( x \)-value (\( \alpha' \) phase) and a phase with \( x = 1.6 \) H/f.u. (\( \alpha'' \) phase).

The absence of structural transformations as a function of temperature can be seen for \( 1.8 \leq x \leq 2.8 \), which is very similar to the hydrides with Tb and Gd. Above \( x = 2.8 \) H/f.u., a very narrow interval \( x \) is observed in which spinodal type decay is again observed, and it is absent for \( x \geq 3.0 \) H/f.u. For \( x \approx 3.4 \), rhombohedral \( \beta \) phases with different \( x \) were observed below (320–380) K, and these phases transform to a regular \( \alpha \) phase with increasing temperature.

The red line separates the paramagnetic span from the state of magnetic order, and the temperature of magnetic order increases with increasing concentration \( x \) (Figure 11).

### 2.3.5. HoMnH\(_x\)_C15 and HoMnH\(_x\)_C14

The structural phase diagrams for HoMnH\(_x\)_C15 and HoMnH\(_x\)_C14 proved to be extremely interesting but at the same time complicated. Although both hydride series share a common HoMn host (crystallizing in the Laves C15 or C14 phase), their phase diagrams are quite different from each other [7,66,68,77].

The structural phase diagram of HoMnH\(_x\)_C15 hydrides can be divided into the following main areas (Figure 12a) [66]:

- \( x \leq 2.0 \). In this area, two phases are observed at the lowest temperatures: “hydrogen-poor” \( \alpha_0 \) and “hydrogen-rich” \( \varepsilon_1 \). The \( \alpha_0 \) phase is identical to the C15-type phase of the starting compound HoMnC15 and contains a negligible amount of dilute hydrogen (\( x \approx 0.04 \) H/f.u.). The \( \varepsilon_1 \) phase is monoclinic and contains \( \approx 1.6 \) H/f.u. As the

![Figure 12](image_url)

**Figure 12.** The proposed phase diagrams for (a) HoMnH\(_x\)_C15 and (b) C14 HoMnH\(_x\)_C14 hydrides (prepared on the basis of HoMn-host material crystallizing in C15 or C14 Laves types, respectively). The red lines separate the paramagnetic state (Para) from the magnetic ordering state. AF indicates antiferromagnetic, and Ferro and Ferri correspond to ferro- and ferrimagnetic ordering states, respectively. Blue symbols correspond to structural measurements and red ones to magnetic studies. Based on [7,66,77].
temperature increases (above ~200 K), the $\varepsilon$ phase undergoes a structural transformation to a rhombohedral $\delta$ phase and further, together with the $\omega$ phase, coexists up to the highest temperatures (for $x < 0.5$ H/f.u.) or transforms to a single rhombohedral $\delta$ phase (for $0.5 \leq x \leq 1.6$) to finally undergo a structural transformation to a regular $\alpha$ phase. For the hydride $x = 1.65$, no spinodal type decays were observed, only $\varepsilon \rightarrow \delta \rightarrow \alpha$ type transformations at ~230 K and ~250 K, respectively. For higher concentrations of $1.65 \leq x \leq 2.0$, a multiphase system is expected and noted as a hatched area:

- An area of an exclusively $\alpha$ phase. This is mainly a high-temperature area with the exception of a low-temperature narrow range of $2.0 \leq x \leq 2.2$ (yellow area);
- An area of $2.2 \leq x \leq 2.8$, where again a spinodal type decay is observed. The two phases $\alpha$ and $\delta$ occur from the lowest to room temperature;
- An area of $x \geq 2.8$. The $\delta$ phase occurs from the lowest temperatures up to ~300–360 K, above which it is transformed to the regular $\alpha$ phase through a narrow two-phase region ($\alpha + \delta$).

In the magnetic part of the diagram, the red line separates the paramagnetic state from the magnetic ordering state. The lowest magnetic ordering temperature of ~200 K is reached by the hydride $x = 1.6$. As the hydrogen content of the sample increases, $T_\text{i}$ increases to ~310 K ($x = 3.5$ H/f.u.). For $x > 3.5$, it is expected to increase further. Magnetic measurements indicate that only in hydrides with a hydrogen content close to 2.0 H/f.u. and greater than ~4.2 H/f.u. can relatively simple antiferromagnetic structures be expected. In the remaining cases, we are dealing with either biphasic or monophasic systems with complicated magnetization-temperature dependence $M(T)$, suggesting canted ferromagnetic ordering [66,77].

In the structural diagram of the HoMn:H$_{\text{C14}}$ hydrides (Figure 12b), the following areas can be distinguished:

- Area $x \leq 1.8$, in which there is the coexistence of a ‘hydrogen-poor’ $\beta$ phase that does not undergo any structural transformation from the lowest temperatures to temperatures ~270–400 K and a ‘hydrogen-rich’ phase in which structural transformations of the type ($\eta \rightarrow \gamma \rightarrow \beta$) are observed. The $\beta$ phase is structurally identical to the C14-type phase, with an estimated hydrogen content of less than 0.05 H/f.u. The $\eta$, $\gamma$, and $\beta$ phases correspond to the monoclinic, orthorhombic and hexagonal phases, respectively, with an estimated hydrogen content of ~1.8 H/f.u.;
- Area $1.8 \leq x \leq 3.4$, in which the low-temperature monoclinic phase $\eta$ is transformed to the high-temperature hexagonal phase $\beta$ via the orthorhombic phase $\gamma$. The temperatures of the structural transformations increase almost linearly with the hydrogen content of the sample;
- Area $3.4 \leq x \leq 3.6$, covering a narrow $x$-range, in which spinodal-type decay is again observed. Two phases ($\eta$ and $\gamma$) with similar hydrogen contents (~3.4 H/f.u. and ~3.55 H/f.u) coexist from the lowest temperatures up to ~200 K, above which a structural transformation of the $\eta \rightarrow \gamma$ type occurs (during which time $\gamma$ undergoes no structural transformation). The spinodal type decomposition ($\gamma \rightarrow \eta + \gamma$) disappears above ~300 K;
- Area $x \geq 3.6$, in which the low-temperature $\gamma$ phase transforms to the high-temperature $\beta$ phase in the temperature range ~320 (380) K;
- The high-temperature region of the $\beta$ phase only (yellow area).

The bold line in the magnetic phase diagram of HoMn:H$_{\text{C14}}$ hydrides (Figure 12b) separates the paramagnetic state from the magnetic ordering state. The magnetic ordering temperature increases monotonically (in the range of 200–330 K) with an increasing hydrogen concentration (up to $x = 3.7$ H/f.u.). Above $x = 3.7$ H/f.u., it is expected to increase further. In this series of hydrides, “pure” antiferromagnetic (AF) ordering is only to be expected for $1.8 \leq x \leq 2.2$ and $4.2 \leq x \leq 4.5$. For the remaining $x$ concentrations, either multiphase systems (with different types of magnetic ordering) or single-phase systems
showing non-trivial \( M(T) \) relations (including those with possible magnetic moment reorientation) are observed \([66,77]\).

It is interesting to note that in both series, the proportion of single-stranded phases is observed (\( \epsilon \) and \( \eta \)) in diagrams described by the same \( C2/m \) space group, but with completely different atomic arrangements and unit cell parameters \([66,77]\).

### 2.3.6. SmMn\(_2\)H\(_2\)

The compound SmMn\(_2\) crystallizes in the hexagonal structure of the Laves C14 phase type at room temperature. Below a temperature of \(~86\, \text{K}\), it undergoes a structural transformation from a hexagonal to an orthorhombic phase with a simultaneous transition to an antiferromagnetic ordering state (see Figure 1) \([16]\). Although it absorbs hydrogen quite readily, this compound is reluctant to form stable crystal structures for any hydrogen concentration. Figure 13a,b shows temperature X-ray diffractograms of SmMn\(_2\)H\(_{2.0}\) hydride, the only one of the SmMn\(_2\)H\(_x\) hydrides for which structural properties are reported in the literature \([78]\). Structural analysis of the diffractograms showed that the hydride, at room temperature, retains a C14-type phase (\( \beta \)), which decomposes into two hexagonal phases (\( \beta_1 \) and \( \beta_2 \)) with slightly different lattice parameters \( \sim 1.9\, \text{H/f.u.} \) and \( \sim 2.1\, \text{H/f.u.} \), respectively, below 248 K (Figure 13a). The structural transformation temperature correlates with the magnetic ordering temperature \( \sim 248\, \text{K} \) (Figure 13c) \([78]\).

![Figure 13. SmMn\(_2\)H\(_x\): (a,b) Temperature X-ray patterns; (c) Variation in magnetic moment as a function of temperature. Based on \([78]\).](image)

### 2.3.7. ErMn\(_2\)H\(_x\)

Also in ErMn\(_2\)H\(_x\) hydrides, for \( x \leq 1.8\, \text{H/f.u.} \), there is observed a characteristic decomposition into a ‘hydrogen-rich’ and a ‘hydrogen-poor’ phase, and the transition is rather complicated. The former phase (as in HoMn\(_2\)H\(_x\)_C14 hydrides) is monoclinic at the lowest temperatures and transforms to a hexagonal phase with increasing temperature (\( \eta \rightarrow \beta_1 \)), while the ‘hydrogen-poor’ phase \( \beta_0 \) does not undergo structural transformations (Figure 14).
Figure 14. Diffractograms of ErMn$_2$H$_{1.0}$ hydride as a function of temperature. Here, $\beta$ indicates the C14-type phase with nominal hydrogen content ($x = 1.0$ H/f.u.), $\beta_0$ represents the C14-type phase with minimal hydrogen content ($x < 0.05$ H/f.u.), $\beta_r$ denotes the ‘rich-hydrogen’ phase with the C14 structure, and $\eta_r$ represents the monoclinic phase (space group: C2/m). Based on [64].

The ErMn$_2$H$_x$ hydride diagram can be described as an alternation of two-phase and single-phase regions as a function of hydrogen content (Figure 15). At low temperatures and for $x \geq 1.8$ H/f.u., only monoclinic phases occur. The hydride $x = 2.0$ H/f.u. no longer retains the structure of the starting compound in the entire temperature range. At a temperature of ~200 K, it undergoes a structural transformation from the hexagonal phase to the phase with low symmetry along with a temperature decrease through the two-phase region (hexagonal $\beta^*$ + monoclinic $\eta^*$), as shown by neutron measurements [67]. The sample with maximum hydrogen content, nominally containing 4.3 H/f.u., shows continuous spinodal decomposition into two phases with hydrogen contents of ~3.8 H/f.u. and ~4.6 H/f.u. in the temperature range of 70–385 K (Figure 15).
The structural transformations are accompanied by transitions from the paramagnetic state to the magnetic ordering state. The lowest values of magnetic susceptibility are recorded for $x = 2.0$ H/f.u. (Figure 15). In this sample, antiferromagnetic ordering is also to be expected; however, this has not been clearly demonstrated so far. At higher hydrogen concentrations for $x \approx (2.7–4.0)$ H/f.u., the hydrides show a complex temperature dependence of magnetization, suggesting a complex magnetic structure including ferrimagnetic canted ordering [64].

The analysis of magnetic results of hexagonal hydrides is not easy or clear. For example, Mössbauer spectroscopy on $^{161}$Er nuclei at 4 K showed no magnetic order in the ErMn$_2$H$_{2.6}$ hydride, so a paramagnetic state of the rare earth sublattice was postulated [79]. On the other hand, neutron diffraction studies on deuterides ErMn$_2$D$_{1.2}$ and ErMn$_2$D$_{1.6}$ conducted by Makarova et al. [23] gave a different result—both samples showed antiferromagnetic ordering with the propagation vector $k = [1/3, 1/3, 0]$. Similar results were obtained for TmMn$_2$D$_{1.6}$ and (Lu$_{0.5}$Y$_{0.6}$)Mn$_2$D$_{1.6}$ [23].

2.3.8. NdMn$_2$H$_2$

The NdMn$_2$H$_2$ hydrides undergo structural transformations from the hexagonal phase (C14) to the monoclinic C2/m phase through the Cmcm orthorhombic phase and the disintegration of the spinodal phase. Due to the repeatability of the phases, the symbols used to describe the HoMn$_2$H$_2$–C14 and ErMn$_2$H$_2$ hydrides has been retained ($\beta$—C14-type phase, $\gamma$—orthorhombic phase, $\eta$—monoclinic phase).

An example of complex structural transformations is the temperature evolution of the high-temperature line (205) in the NdMn$_2$H$_{2.5}$ hydride (Figure 16). The high-temperature $\beta$ phase transforms into the orthorhombic $\gamma$ phase ($\approx$280 K) and then decomposes ($\approx$235 K) into two orthorhombic phases $\gamma_1$ and $\gamma_2$ with different hydrogen contents. With a further slight decrease in temperature, these phases clearly segregate and simultaneously transform into monoclinic phases $\eta_1$ and $\eta_2$. The estimated hydrogen contents in both phases were (at 80 K) $\approx$1.9 H/f.u. and $\approx$2.9 H/f.u, respectively [65].
Figure 16. Temperature evolution of the hexagonal structural line (205) in \( \text{NdMn}_2\text{H}_{2.5} \) hydride. Phase \( \gamma \) occurs between the red lines. Based on [63].

Figure 17 shows a simplified structural phase diagram for \( \text{NdMn}_x\text{H}_x \). Due to difficulties in the preparation of hydrides with \( x < 2.0 \) (tendency to form amorphous structures, multiphase systems), this area was not analyzed [65]. Similar difficulties in obtaining hydrides were also encountered with \( \text{SmMn}_x\text{H}_x \) samples (Section 2.3.6), which may suggest that \( R\text{Mn}_x \) compounds with light rare earths are reluctant to form structurally stable hydrides with low hydrogen concentrations. All studied \( \text{NdMn}_x\text{H}_x \) hydrides undergo a structural transformation according to a general sequence from the high-temperature hexagonal phase of the starting compound through the orthorhombic phase and ending with the low-temperature monoclinic phase (\( \beta \to \gamma \to \eta \)). Hydrides with \( x = 2.0 \) and \( 2.8 \leq x \leq 3.5 \) behave according to this sequence, while the \( \text{NdMn}_x\text{H}_x \) hydrides with \( 2.1 \leq x \leq 2.8 \) and \( 3.5 \leq x \leq 4.3 \) show spinodal-type decomposition into two phases with different hydrogen contents in different temperature ranges.

Figure 17. Structural (in black) and magnetic (in red) phase diagram of \( \text{NdMn}_x\text{H}_x \) hydrides. Here, \( \beta \) indicates the presence of a of a hexagonal phase, and \( \eta \) stands for the contribution of the monoclinic phase. The red lines in the region \( 2 \leq x < 5 \) separate the paramagnetic (Para) state from the magnetic.
ordering state (below lines), and the dashed line in the region \( x < 2 \) represents the probable separation of these states. Based on [65].

A red line running through the \( T_c \) temperatures was drawn on the structural phase diagram (Figure 17). It separates the paramagnetic state from the magnetic ordering state. The determined \( T_c \) temperatures are similar to those observed for other \( \text{RMn}_2\text{H}_x \) (Sections 2.3.1–2.3.7) and follow the general trend of their increase with increasing hydrogen concentration in the sample. However, the diagram does not even indicate the proposed magnetic ordering for specific values of \( x \) due to the ambiguous interpretation of magnetic measurements.

The transformations discussed here are represented only symbolically; a detailed description of the structural transformation analysis of the magnetic results for \( \text{NdMn}_2\text{H}_x \) is presented in [65].

3. Summary

The presented results of structural and magnetic measurements of \( \text{RMn}_2\text{H}_x \) hydrides (with \( x \) below \(-4.5 \) H/f.u.) indicate great similarity, but also differences depending on the rare earth element. We summarize them below.

3.1. Structural Changes in \( \text{RMn}_2\text{H}_x \) Hydrides

1. A linear increase in the relative volume of the unit cell (\( \Delta V/V_0 \)) with increasing hydrogen concentration \( x \) was not observed in any of the \( \text{RMn}_2\text{H}_x \) samples. The saturation of the hydrides is best described by the Hiura-Figiel function (Section 2.2).

2. \( \text{RMn}_2\text{H}_x \) compounds easily absorb hydrogen, which, depending on the concentration in the compound, forces a number of structural transformations. These transformations as a function of temperature are illustrated in structural phase diagrams.

3. The structural phase diagram of \( \text{GdMn}_2\text{H}_x \) hydrides is the simplest of all the tested \( \text{RMn}_2\text{H}_x \) hydrides. Hydrides of rare earth elements both lighter and heavier than gadolinium show more complicated structural diagrams.

- The phase diagram of \( \text{GdMn}_2\text{H}_x \) can be divided into three main areas. In the first area (\( x \leq 1.8 \) H/f.u.), as the temperature decreases, the high-temperature cubic phase decomposes into, initially, three phases with different hydrogen contents. The phase with intermediate hydrogen content quickly disappears as the temperature decreases. The remaining two are clearly segregated into phases: “poor in hydrogen” (\( x \leq 0.05 \) H/f.u.) and “rich in hydrogen” (\( x = 1.8 \) H/f.u.). The “hydrogen-poor” phase can be treated as a solid solution of hydrogen in the metal. In the second range, \( 1.8 \leq x \leq 3.2 \), there is only a cubic phase in the entire temperature range, which is increased in third area.

- The phase diagram of \( \text{TbMn}_2\text{H}_x \) is very similar to the hydride diagram of Gd. However, the boundary separating the areas of coexistence of rhombohedral and cubic phases from the highly hydrogenated rhombohedral phase is slightly different.

- In the phase diagram of \( \text{DyMn}_2\text{H}_x \) hydrides, below \( x = 1.6 \) H/f.u., the same type of phase transformations observed in hydrides with Tb and Gd are noted. However, the middle region (single phase, without structural transformations) narrows (\( 1.6 \leq x \leq 2.4 \)). For \( x \geq 2.4 \) H/f.u., additional two-phase regions appear, which are a combination of cubic and rhombohedral phases with different hydrogen contents.

- In hydrides with \( \text{HoMn}_2\text{H}_x \), C14 and C15 and for \( x \leq (1.6–1.7) \) H/f.u., there are, as noted above, spinodal-type decays into two phases “rich and poor in hydrogen” (no “intermediate” phase is observed). However, here the “hydrogen-rich” phase undergoes structural transformations as the temperature increases from the monoclinic through orthorhombic to hexagonal phase.

The central range of occurrence of one phase over the entire temperature range in the C15 series is reduced to an almost symbolic range \((2.0 \leq x \leq 2.2)\). In the C14 series, such
an area no longer exists. Instead, a wide area (1.8 < x < 3.2) of transformations in structural
structures occurs, such as monoclinic phase → orthorhombic phase → hexagonal phase. For higher x, areas dominated by rhombohedral or orthorhombic phases appear in both series.

- Also in ErMnHₓ hydrides, for x ≤ 1.8 H/f.u., there is a decomposition into phases
  “rich” and “poor” in hydrogen (without the “intermediate” phase). The “hydrogen-rich” phase (as in HoMnHₓ C14 hydrides) crystallizes in the monoclinic structure at the lowest temperatures. As the temperature increases, it transforms into the hexagonal phase. The erbium hydride diagram can be described as the alternation of two-phase and single-phase regions as a function of hydrogen content. At low temperatures, only monoclinic phases occur above x = 1.8 H/f.u.
- In the hexagonal hydride SmMnHₓ₂₀, spinodal-type decomposition into two hexagonal phases with slightly different hydrogen contents (-1.9 H/f.u. and ~2.1 H/f.u.) was observed; such a small difference in x concentrations in the area of spinodal decay does not occur for other RMnHₓ.
- The NdMnHₓ phase diagram is filled mainly with two-phase systems, even for x ≈ 4.0 H/f.u., which makes it similar to the erbium hydride diagram in this respect.
- The occurrence of monoclinic phases is observed only for hydrides with Ho, Er and Nd.
- The observed decompositions of phases with different hydrogen contents are of the spinodal type.
- YMnHₓ hydrides behave differently from lanthanide hydrides. In the range of low hydrogen contents (x ≤ 1.15 H/f.u.), the spinodal-type decomposition into two phases with significantly different hydrogen contents, typical of hydrides with lanthanides, does not occur. Instead, a number of structural transformations occur.
- Based on the conducted research, a synthetic picture of phase transformations under the influence of hydrogen can be presented in the form of a general structural model of the phase diagram of hydrides RMnHₓ (Figure 18), which allows easier understanding of the characteristic features of the observed structural changes.

![Phase diagram](image)

**Figure 18.** General sketch of the structural phase diagram for RMnHₓ hydrides. I—Area corresponding to the solid solution of hydrogen in the metal. Estimated hydrogen concentration is below ~0.1 H/f.u. II—Area of occurrence of spinodal-type decomposes into poor and hydrogen-rich phases (Gd, Tb, Dy, Er, Ho)MnHₓ. For YMnHₓ, this region ends at x = 1.15 H/f.u. and includes more complicated structural changes. III—High-temperature area of occurrence of the phase corresponding to the phase of the starting compound. IV—Area of occurrence of phase combinations of regular/hexagonal and their distortions. V—For RMnHₓ hydrides with R: Y, Gd, Tb, Ho (C15), this area is structurally identical to area III, and the x range has a different width depending on the rare earth element. For other hydrides with R: Ho(C14), Nd and Er, spinodal decays or transformations to monoclinic phases occur in this area.
3.2. Magnetic Transformations and Properties

1. In all discussions on RMn:H$_x$ hydrides, there is a strong increase in the magnetic ordering temperature $T_c$ from the range of 14–105 K corresponding to the starting compounds to the range of 0–200 K for their hydrides, depending on the hydrogen content. The course of ordering temperatures for RMn:H$_x$ hydrides is shown in Figure 19. The highest magnetic ordering temperatures in the range of $1.5 \leq x \leq 4.0$ are exhibited by GdMn$_2$H$_x$ hydrides, and the lowest are observed for ErMn$_2$H$_x$ and HoMn$_2$H$_x$-C14 hydrides. In this $x$ range, the different $T_c$ curves of the HoMn$_2$H$_x$-C14 and C15 hydrides indicate the influence of the structure of the starting compound on the magnetic properties of the hydrides.

![Figure 19](image-url)

Figure 19. The course of the magnetic ordering curves of the discussed RMn:H$_x$ hydrides.

2. The reason for the increase in the magnetic ordering temperature of hydrides is the increase in Mn–Mn exchange interactions and a greater degree of localization of the Mn magnetic moments due to the increase in the $d_{Mn-Mn}$ distance resulting from hydrogen doping.

3. All the RMn:H$_x$ hydrides in a magnetically ordered state are ferrimagnetic, and their net magnetization strongly depends on the hydrogen concentration.

4. Hydrogen significantly affects the magnetic structure of hydrides/deuterides. In the deuteride TbMn$_2$D$_{2.9}$, a collinearly ordered antiferromagnetic structure appears with a propagation vector $k = [1/2, 1/2, 1/2]$, which is significantly simpler than the magnetic structure of the initial compounds. This is one of the most interesting phenomena occurring under the influence of hydrogen in these systems.

5. It can be concluded that the share of f-electron elements in the formation of magnetic properties is similar and depends only slightly on the rare earth element.

6. It can be concluded that the magnetism of hydrogenated RMn$_2$ compounds originates from the electron band.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en16217383/s1, Figure S1: Arrangement of atoms in C14; Figure S2: Arrangement of atoms in C15; Table S1: Atom positions in C14; Table S2: Atom positions in C15; File S1: C14 and C15-type Laves phases: details of crystal structures. References [4,80–85] are cited in the supplementary file.

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References


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