Structural and magnetic transformations in HoMn$_2$H$_x$ hydrides

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Abstract. The HoMn$_2$ compound crystallizes in the C15 or C14 Laves phases depending on preparation. The effect of hydrogen absorption on structural, magnetic and thermodynamic properties of HoMn$_2$H$_x$ hydrides for both phases has been investigated by XRD, AC/DC magnetometry, and calorimetry in the temperature range of 80–300 K. In addition to general features revealed by RMn$_2$H$_x$ compounds (R = rare earth or Yttrium), unusual behavior of these hydrides was found. In particular, a transformation from the cubic to the monoclinic structure was detected, which so far has not been reported for other cubic RMn$_2$H$_x$ (R = rare earth or Yttrium) compounds. The structural transformations are reflected in the magnetic behavior. The change in ordering temperatures indicates a strong correlation between the magnetic interactions and the Mn–Mn distance modified by hydrogen absorption. Tentative magnetic and structural phase diagrams are proposed. The presented results are compared with the properties of other cubic and hexagonal RMn$_2$H$_x$ hydrides.

1. Introduction

The hydrides of Laves phase type intermetallic compounds RMn$_2$ (R - rare earth or Yttrium) have been intensively studied due to their unusual physical properties. These compounds can easily absorb large amounts of hydrogen (about 4.5 H atoms per formula unit). In recent years, many investigations have proved that H atoms usually occupy tetrahedral A2B2 and AB3 sites. In most of the Laves phase hydrides H atoms occupy only A2B2 sites at low hydrogen concentration, whereas AB3 sites start to be filled if H-concentration is higher than $x \sim 3.0$ [1,2]. Significant increase of the volume of the unit cell due to hydrogen absorption causes a strong modification of structural and magnetic properties of those hydrides.

Systematic research of RMn$_2$ compounds shows the important role of Mn–Mn distance which determines the magnetic interactions in the RMn$_2$H$_x$ systems and leads to complicated patterns of magnetic ordering. Above the critical value of Mn–Mn distance $d_c \approx 2.7$ Å [3] a localized magnetic moment at manganese sites is observed leading to a frustrated Mn sublattice [4]. The lattice parameter of the parent material HoMn$_2$ determined at room temperature is $a \approx 7.531$ Å implying that the Mn-Mn distance ($d_{Mn-Mn} = 2.66$ Å) is slightly smaller than the critical value $d_c$. Therefore upon the hydrogenation we would expect complex magnetic structures in this system.
The pure HoMn$_2$ compound crystallizes either in the cubic C15 or in the hexagonal C14 structure, depending on the heat treatment [5]. Structural and magnetic results presented here were obtained for the C15 structure (space group: \textit{Fd-3m}). We tried to find the similarities to the other R$\text{Mn}_n$ cubic structures, bearing in mind a strong affinity of both the C15 and C14 polytypes [6,7]. It is well known that those structures are closely related to each other, however, it is still unclear whether the difference in cubic or hexagonal packing affects the properties of hydrides.

2. Experimental details
The cubic C15 parent material HoMn$_2$ and its hydrides HoMn$_2$H$_x$, with hydrogen concentrations $x = 0.55, 1.0, 1.65, 2.0, 2.5, 3.0, 3.5,$ and $4.3$ and the hexagonal C14 parent material HoMn$_2$ and its hydrides with $x = 1.0, 1.5, 2.0, 2.5, 3.0, 3.5,$ and $4.5$ were prepared by the standard technique for sample preparation and hydrogenation process reported elsewhere [8,9].

The x-ray powder diffraction (XRD) measurements have been carried out on the Siemens D5000 diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å), and with continuous flow cryostat in the temperature range from 70 to 385 K. The data were collected during the heating-up of samples. At each step the temperature was stabilized (at least 40 min) in order to reach the thermal equilibrium. For identication of the XRD patterns the FullProf program [10] based on the Rietveld method [11] was used.

The AC/DC susceptibility at the temperature range of $4 \div 300$ K were measured with the LakeShore VSM 7225 magnetometer. The magnetic measurements were performed during heating up.

In the paramagnetic state, the magnetic behavior was characterized by the Curie-Weiss law taking into account the correcting diamagnetic term $\chi_{\text{dia}}$ according to the equation $\chi(T) = \chi_{\text{dia}} + C/(T - \Theta)$.

3. Results
Because of many similarities between both series (C15 and C14) the results and their discussion is focused mainly on the C15 hydrides. Some selected results for the C14-type hydrides as well as the most important differences between the C15 and C14 series will be also presented.

3.1. The x-ray diffraction results
3.1.1. The $0 \leq x < 2$ range
For this hydrogen concentration range, the sample with $x = 1.0$ (C15\_HoMn$_2$H$_{1.0}$) reveals the most interesting behavior. The XRD-patterns for this hydride taken at different temperatures are presented in Figure 1.

![Figure 1](image-url)  
**Figure 1.** The temperature evolution of the (220), (311) and (222) diffraction lines for HoMn$_2$H$_{1.0}$ (more in text)
From 385K down to 295 K only one cubic structure was observed (the $\alpha$ phase, $Fd\cdot3m$ space group). Below 295 K we see a splitting of it into two structurally different phases, which is in contrast to other hydrides based on Gd,Tb or Er [9,12,13], where two structurally identical phases persisted down to the lowest temperatures. The lattice parameters of one of those phases are comparable with those of pure HoMn$_2$ compound (the $\alpha_0$ phase). However, the other component transforms from the cubic structure to the rhombohedral one (the $\delta_r$ phase, $R\cdot3m$ space group) at 295 K and then to the monoclinic one (the $\epsilon_r$ phase, $C2/m$ space group) at $\sim$ 205 K. These structural transformations are fully reversible, i.e. heating the sample above the transition temperature leads to the reconstruction of the uniform cubic structure. These types of transformations were not observed for any RMn$_3$H$_x$ ($R$: Gd,Tb,Er,Y,Dy,Sm) hydrides [9,12-16]. More detailed information of the structural transformations for $x = 1.0$ and other samples with $x \leq 1.65$ (C15) are presented in Figure 2a. For comparison Figure 2b shows results obtained for the C14-hydrides. For the sake of comparison, all the presented lattice parameters of monoclinic, rhombohedral, and hexagonal structures are converted to the pseudo-cubic system according to the relations: 

$$a_{in} = |a_{in} b_{in} c_{in} (\sin \beta)|^{1/2}, a_{in} = [2 (a_{in})^2 c_{in} / (3)^{1/2}]^{1/3}, a_{in} = [(3)^{1/2} (a_{in})^2 c_{in}]^{1/3}.$$

![Figure 2](image_url)

**Figure 2.** The lattice parameters of HoMn$_2$H$_x$ hydrides as a function of temperature: (a) C15, (b) C14.

For $x = 0.55$ (C15) two separate phases exist (Figure 2 a). The lattice parameters of one of them tend again towards those of the pure HoMn$_2$ system (the $\alpha_0$ phase) at lower temperatures. For the other phase only one structural transformation at $\sim$200 K is observed, from the monoclinic ($\epsilon_r$, $sg$: $C2/m$) to the rhombohedral ($\delta_r$, $sg$: $R\cdot3m$) phase which holds to the highest temperatures. Comparing the lattice parameters of the pure HoMn$_2$ compound and its hydrides with $x = 0.55$ and 1.0 and their relative abundances, we could calculate the amount of hydrogen in the $\alpha_0$ phase as $\sim$ 0.04 H at./f.u. and in the $\epsilon_r$ phase as $\sim$ 1.6 H at./f.u.

For hydride with $x = 1.65$ (C15) upon cooling, a sequence of single-phase transformations ($\alpha \rightarrow \delta \rightarrow \epsilon$) is observed, similar to those detected for $x = 0.55$ and 1.0 (Figure 2a). The temperatures of these transformations are insignificantly shifted towards lower temperatures. The lattice parameters do not change monotonically but reveal characteristic jumps which correspond to structural transformations. The comparison of the lattice parameters for $x = 1.65$ with those of hydrogen rich phase for $x = 0.55$ and 1.0 (Figure 2a) below 205 K shows their mutual overlapping, which confirms the presence of the same monoclinic $\epsilon_r$ structure for all the hydrides. Such reversible transformations could be of martensitic type.

The spinodal decomposition is also observed for $x = 1.0$ (C14). More surprising is the structural transformation of the type $\beta \rightarrow \delta \rightarrow \epsilon$, where $\beta$ corresponds to the hexagonal structure ($sg$: $P6\cdot3mmc$). It means that independently of the initial structure (C15 or C14) the same structural transformations to the rhombohedral phases ($\delta$) and then to the monoclinic structures ($\epsilon$) in both the series are observed.
3.1.2. The $2 \leq x \leq 4.3$ range

The temperature dependences of the lattice parameters for $2 \leq x \leq 4.3$ (for C15 and C14) are presented in Figure 3 a and b.

![Figure 3. The lattice parameters of HoMn$_2$H$_x$ vs. temperature: (a) C15, (b) C14.](image)

For this $x$ range, for the C15 hydrides, a combination of two structures, the cubic one ($\alpha$) and the rhombohedral one ($\delta$) is observed. Lattice parameters of the $\delta$ phase were converted to the pseudo-cubic system. Only for the sample with $x = 2.0$, the cubic C15 structure persists in the whole temperature range without any traces of distortion. A small jump of the lattice parameters of the sample is visible at $\sim 290$ K, which will be shown to be related to a magnetic transition in what follows. The most complicated behavior is observed for the $x = 2.5$ hydride. From the lowest temperature up to $\sim 305$ K a splitting into two phases occurs again, which was not observed for any cubic RMn$_2$H$_x$ hydrides with $2 < x < 3$.

The HoMn$_2$H$_{3.0}$ and HoMn$_2$H$_{3.5}$ hydrides show the same structural transitions but in different temperature ranges. For sample with $x = 3.0$ the rhombohedral unit cell exists up to $275$ K and for $x = 3.5$ up to $\sim 300$ K. For the sample with hydrogen concentration $x = 4.3$ the single rhombohedral phase $\delta$ is observed from the lowest temperatures up to $\sim 365$ K (Figure 3a). Between $\sim 365$ K and $\sim 380$ K two phases ($\alpha + \delta$) are expected. Further increase of temperature leads to the appearance of the $\alpha$ phase. The process is reversible, i.e. decreasing temperature leads to a return to the $\delta$ structure.

The C14 hydrides reveal more complicated behavior than the C15 ones (Figure 3 b). The hydrides with $x = 2.0$, 2.5, 3.0 undergo the same type of structural transformations ($\beta \rightarrow \delta \rightarrow \epsilon$). The sample with $x = 3.5$ splits into two rhombohedral phases ($\delta$) with different H content below $\sim 270$ K which then transform to monoclinic structures ($\epsilon$). However, the HoMn$_2$H$_{4.5}$ maintains the rhombohedral structure almost for the whole temperature range. The structural transformation to the hexagonal phase is observed above $\sim 385$ K.

3.2. The magnetic results

The $M(T)$ curves for different HoMn$_2$H$_x$ hydrides (C15 and C14) recorded at the external field of 200 Oe are presented in Figure 4 a and b.

The temperature dependence of $M/H$ curves for the hydrides with $x = 1.0$ (both for C15 and C14) prove the two-phase decomposition. Beside the magnetic anomaly at $T_N = 195 \pm 5$ K, which corresponds to a magnetic ordering in the hydrogen rich phase $\alpha$, the second very clear maximum at $T \approx 20$ K appears related to $T_C$ of the pure HoMn$_2$ compound [17,18]. For the hydride with $x = 1.65$ (C15) a magnetic transition was also observed. For $x = 2.0$ the estimated magnetic ordering temperatures are $\sim 265$ K and $\sim 218$ K (for C15 and C14, respectively), which is in agreement with a general tendency: increasing hydrogen content implies increasing $T_{N,C}$. The samples with $x = 2.0$ and 2.5 (both C15 and C14) reveal antiferromagnetic character of ordering. The hydrides (C15 and C14)
Figure 4 a and b. Magnetic susceptibility of the HoMn$_2$H$_x$ hydrides versus temperature in the external field of 200 Oe, for different hydrogen concentrations.

with $x = 3.5$ show the most complicated behavior, which can be also related to their complicated structural transformations. The samples with a maximal H content ($x \geq 4.3$, C15 and C14) reveal again a purely antiferromagnetic character and their magnetic ordering temperatures are expected to be higher than 370 K.

3.3. Comparison of XRD and magnetic results with Specific Heat (SH) measurements

The results and discussion of the SH measurements of the HoMn$_2$H$_x$ (C15) are reported in [19]. It is interesting to compare them with the XRD and magnetic results presented above.

Only for the HoMn$_2$ sample the phase transition was revealed by a single SH peak at $T_N = 20K$, which corresponds very well to the left maximum observed in the temperature dependence of the AC magnetic susceptibility measured along the crystal growth direction [001] [17]. Almost all the SH anomalies observed for the HoMn$_2$H$_x$ have a peculiar double-peak (or even triple-peak) structure.

As hydrogenation involves additional degrees of freedom a contribution to the specific heat in the whole temperature range may be expected. The increase of hydrogen concentration causes a large increase of the magnetic ordering temperature (e.g. $R$Mn$_2$H$_{1.0}$, $T_N \sim 200$ K), which was confirmed above by the magnetic and x-ray measurements. For example, the broad maxima of $C_{mol}(T)$ for the $x = 1.0$ and 1.65 hydrides between $\sim 170$ and 250 K [19] are located in the same temperature range where both the structural (monoclinic$\rightarrow$rhombohedral$\rightarrow$cubic) and magnetic transformations are observed (Figure 2 and 4). An additional peak at $\sim 215$ K is observed for the single-phase $x = 2.0$ hydride

Figure 5. Specific heat of HoMn$_2$H$_x$ (C15) vs. temperature.
In our opinion, it may be related to hydrogen ordering. The more H atoms in a system the more energy (heat) should be invested to disorder them. That is why the SH values rise with increasing hydrogen concentration \[19\]. Also, for higher hydrogen concentrations, the transformations and characteristic temperatures (especially magnetic ones) are reflected in $C_{\text{mol}}(T)$ curves and their maxima. We expect magnetic ordering at $\sim (370 - 375) \text{ K}$ for the HoMn$_2$H$_{1.3}$ as well.

4. Conclusions

Both structural and magnetic properties of HoMn$_2$H$_x$ (C15 and C14) are strongly dependent on hydrogen concentration. On the basis of the x-ray measurements we propose structural phase diagrams shown in Figure 6 a and c. Generally, they can be divided into three areas: (1) the areas where parent phases exist ($\alpha$ and $\beta$), (2) the areas below $x \sim (1.6-1.7)$ where the splitting into two phases of the same type ($\alpha/\beta + \varepsilon_r$) are observed, and (3) the areas with $x > \sim (1.9-2.0)$ where different structural transformations appear depending on the structure of the parent material.

The structural transformations are reflected in the magnetic phase diagrams (Figure 6 b and d). One can see that these diagrams are more similar to each other than the structural ones. The most important elements of both the diagrams are gray lines separating paramagnetic and ordered phases. A huge jump of the magnetic ordering temperature from $\sim 24 \text{ K}$ to $\sim (200-400) \text{ K}$ for the parent compound and its hydrides, respectively, is apparent.

Figure 6. The proposed phase diagrams for the HoMn$_2$H$_x$ hydrides: (a,c) structural; (b,d) magnetic.

The steady increase of the magnetic ordering temperature with increasing hydrogen concentration was also observed for (Gd,Y,Tb)Mn$_2$H$_x$ \[9,13,16\]. Such a correlation indicates that the magnetic transitions are predominantly determined by the magnetic interactions within the Mn sublattice. Increase of the Mn-Mn distance, much more than the critical distance $d_c$, leads to a better localization of the Mn magnetic moments and as a consequence to a substantial increase of the ordering temperatures in the hydrides.

The analysis of the complete set of data for these hydrides is in progress.
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