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Structural and magnetic properties of C15 $HoMn_2$ hydrides

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ABSTRACT

Powder samples of cubic $HoMn_2H_x$ hydrides, with $0 \le x \le 4.3$, have been investigated by X-ray diffraction and AC/DC magnetometry as a function of temperature and external magnetic field. Hydrogen is demonstrated to strongly modify structural and magnetic properties. X-ray studies revealed many structural transformations placed at low temperatures. In particular, a transformation from the cubic to the monoclinic structure was detected, which so far has not been reported for other cubic RMn_2H_x (R – rare earth or Yttrium) compounds. The structural transformations are reflected in the magnetic behavior. The change in ordering temperatures implies a very strong relationship between the magnetic interactions and the Mn–Mn distance modified at hydrogen absorption. Tentative magnetic and structural phase diagrams are proposed. The presented results are compared with the properties of other cubic and hexagonal RMn_2H_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 above $x \sim 3.0$ [1,2]. Significant increase of the relative volume of the unit cell due to hydrogen absorption causes strong modifications of structural and magnetic properties of those hydrides.

Systematic research of the rare earth compounds with Mn shows the important role of Mn–Mn distance, which determines the magnetic interactions in the RMn_2H_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 strong localization of the magnetic moment at manganese sites is observed leading to a frustrated Mn sublattice [4]. The lattice parameter of our host material $HoMn_2$ $a \approx 7.531$ Å at RT gives Mn–Mn distance ($d_{Mn-Mn} = 2.66$ Å) slightly below the critical value d_c, and therefore after the hydrogenation process we should expect many complex magnetic structures in this system.

The present paper is a next step in a comprehensive work concerning the structural and magnetic properties of RMn_2H_x hydrides (R–Y, Gd, Tb, Dy, Er and Sm).

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 carried out for the C15 structure (space group: *Fd-3m*). We tried to find the similarities to the other RMn_2 cubic structures, simultaneously having 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 samples of $HoMn_2H_x$ with different hydrogen concentration $x = 0.55$, 1.0, 1.65, 2.0, 2.5, 3.0, 3.5, and 4.3 were prepared. The standard technique for the sample preparation and hydrogenation process was used as reported elsewhere [8,9]. The quality of the $HoMn_2H_x$ hydrides were checked by X-ray diffraction technique.

The X-ray powder diffraction (XRD) measurements have been carried out on the Siemens D5000 diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å), and with continuous flow cryostat in the temperature range from 70 to 380 K. The data were collected in a process of heating. At each step the temperature was stabilized (at least 40 min) in order to reach the thermal equilibrium. For identification of the XRD patterns the FullProf program [10] based on the Rietveld method [11] was used.

The AC/DC susceptibility at the temperature range 4–300 K and the field dependence of the magnetization $M(H)$ of the samples were measured with the LakeShore VSM 7225 magnetometer. The temperature dependence of magnetization was obtained using both ZFC and FC modes. The magnetic measurements were done in a process of heating as well.

Additionally, the field dependence of the magnetization $M(H)$ was recorded for hysteresis loops in ±10 kOe field mode using the Lake Shore 7300 magnetometer at 77 K.

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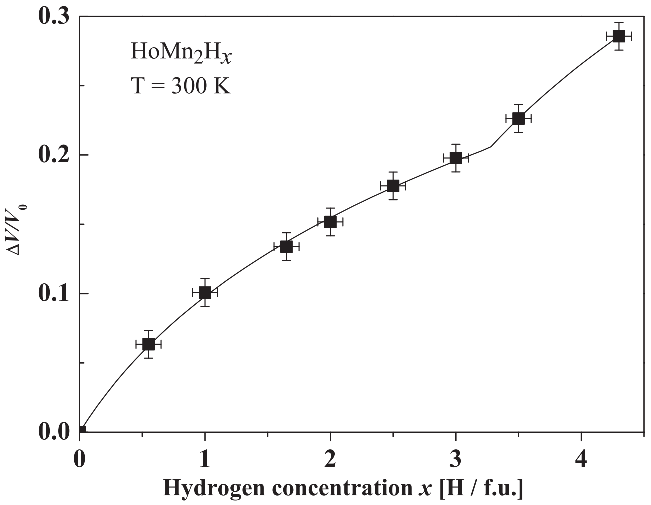

Fig. 1. The relative change of the unit cell volume as a function of hydrogen concentration for $HoMn_2H_x$. The solid line represents the fit to the model from [15].

In the paramagnetic state above the ordering temperature the magnetic behavior was characterized by the Curie–Weiss relation:

$$\chi(T) = \chi_{\mathrm{dia}} + \frac{C}{(T-\Theta)} \qquad (1)$$

with $\chi_{\mathrm{dia}} = -1.6 \times 10^{-7}$ cm^3/g estimated from the tabulated data [12].

3. Results

3.1. The X-ray diffraction results

Most of the $HoMn_2H_x$ (with $x \le 3.5$) hydrides revealed the single-phase C15 cubic structure at room temperature. Only the sample with $x = 0.55$ consisted of two phases with a different hydrogen content at RT. The disproportion between the H concentrations allows us to suggest the spinodal decomposition of the sample with $x = 0.55$ into hydrogen deficient and hydrogen rich phases. The fully hydrogenated sample with $x = 4.3$ have revealed well-defined rhombohedral structure (space group: $R\bar{3}m$, no. 166). This behavior is very similar to the other cubic systems with Gd, Y and Dy [9,13,14] where that type of structural distortion for saturated hydrides was found.

The increase of hydrogen concentration in the system causes the expansion of the lattice parameters and consequently the growth of the unit cell volume. The relative volume $\Delta V/V_0$ as a function of hydrogen content (Fig. 1) was fitted with Eq. (2) according to the model proposed in [15] yielding parameters: $B_0 = 6 \pm 0.5$, $b = 10 \pm 1$, $X_C = 3.2 \pm 0.1$, $P = 0.6 \pm 0.1$.

$$\begin{cases} \dfrac{\Delta V}{V_0} = \left[\dfrac{B_0 + bx}{B_0}\right]^{1/b} - 1; & \text{for} \quad x < X_C \\ \dfrac{\Delta V}{V_0} = \left[\dfrac{B_0 + b\,(X_C + (1-P)(x - X_C))}{B_0}\right]^{1/b} & \\ \qquad + \left[\dfrac{B_0 + Pb\,((x - X_C))}{B_0}\right]^{1/b} - 2; & \text{for} \quad x \ge X_C \end{cases} \qquad (2)$$

The value of the X_C parameter indicates that the filling of AB3 interstitial sites by hydrogen occurs for hydrogen concentrations $x > \sim 3.2$.

The set of lattice parameters gained from diffraction patterns at 70 K and 300 K for all analyzed samples is listed in Table 1. The lattice parameters of rhombohedral and monoclinic structures are converted to the pseudo-cubic system according to the relations: $(a_{rh}{}^* = [2(a_{rh})^2 c_{rh}/(3)^{1/2}]^{1/3}$, $a_m{}^* = [a_m b_m c_m\,(\sin\beta)]^{1/3}$.

3.1.1. The $0 \le x < 2$ range

In this hydrogen concentration range the sample with $x = 1.0$ reveals the most interesting behavior. The XRD-patterns for this hydride taken at different temperatures are presented in Fig. 2. Two characteristic temperatures of 295 K and 205 K are clearly visible. From the highest temperatures down to 295 K we observe only one cubic structure (the α phase, *Fd-3m* space group) and below this temperature we can see the splitting of it into two structurally different phases. In contrast to other hydrides based on Gd, Tb or Er [9,16,17], only one of them keeps the host structure down to the lowest temperatures. We found that the lattice parameters of this phase are comparable with those of pure $HoMn_2$ (the α_0 phase) compound. However, the other component transforms from the cubic structure to the rhombohedral one (the δ_r phase, $R\bar{3}m$ space group) at 295K and next to the monoclinic one (the ε_r phase, $C2/m$ space group) at ~205 K, which is signaled by a large splitting of the $(2\,2\,0)_{m,r}$ line (Fig. 2). These structural transformations are fully reversible, so heating the sample above the transition point leads to the reconstruction of the uniform cubic structure. These types of transformations were not observed for any RMn_2H_x (R: Gd, Y, Dy, Tb, Er, Sm) hydrides [9,13,14,16–18].

More detailed information of the structural transformations for $x = 1.0$ and other samples with $x \le 1.65$ are presented in Fig. 3. For the sake of clarity and easier comparison, all lattice parameters of the monoclinic and rhombohedral structures are presented as converted to the pseudo-cubic structure (Section 3.1). In the $HoMn_2H_{1.0}$ hydride abundances of the component phases are almost equal at low temperatures with a little advantage of the hydrogen rich phase (Fig. 3d). The δ_r phase is interesting because it can be understood as an intermediate phase between ε_r and α. Its lattice parameters decrease with temperature (range: 200–290 K) and its abundance increases. It can be related to a gradual diffusion of hydrogen from the δ_r to the α_0 phase. Above ~290 K both phases transform to the single α phase.

For $x = 0.55$ two separate phases exist, also structurally different in the whole temperature range (Fig. 3a and b). The lattice parameters of one of them tend again towards those of pure $HoMn_2$ (the α_0 phase) system at lower temperatures (Fig. 3a). For the other phase only one structural transformation at ~200 K is observed, from the monoclinic (ε_r) to the rhombohedral (δ_r) phase which holds to the highest temperatures.

On the basis of the comparison of the lattice parameters of the pure $HoMn_2$ compound and its hydrides with $x = 0.55$ and 1.0 and their relative abundances (Fig. 3a–d) we could calculate the amount of hydrogen in α_0 as ~0.04 H at./f.u. and in ε_r as ~1.6 H at./f.u. The corresponding values are almost identical for both hydrides below ~200 K and comparable with those obtained for (Gd, Tb, Er)Mn_2H_x [9,16,17]. The corresponding abundances of the α_0 and ε_r phases change with the nominal hydrogen concentration of the sample, which is in agreement with the requirement of constant total hydrogen amount in the sample. It is interesting that for the systems with Ho we do not observe the intermediate phase like for hydrides with Tb and Gd but the distortion to lower symmetry for the hydrogen rich phase. We explain the low temperature splitting into two phases, the hydrogen deficient (α_0) and the hydrogen rich (δ_r or ε_r), as being due to the spinodal decomposition, which was already reported for the RMn_2H_x Laves phases [9,16–18] and other RH_x hydrides [19].

For hydride with $x = 1.65$ on cooling a sequence of single-phase transformations ($\alpha \to \delta_r \to \varepsilon_r$) is observed like that detected for $x = 0.55$ and 1.0 (Fig. 3e and f). One can see that the temperatures of transformations are insignificantly shifted towards lower temperatures in comparison with those for $x = 1.0$. 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