

## High pressures studies on hydrides of selected manganese alloys

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**Abstract** Specific behavior found in hydrides formed in manganese, Mn-Ni and  $YMn_2$  under high pressure is presented and discussed. The synthesis of ferromagnetic fcc-manganese was proved. Parameters of the equations of state (EOS) derived from measurements in the diamond anvil cell (DAC) are summarized for manganese hydrides and for hydrides derived from  $YMn_2$  Laves phase. It was found that the compression behavior of recently discovered  $YMn_2H_6$  is different from  $YMn_2$ -based hydrides with lower hydrogen content.

**Key words** deuterides/hydrides • high pressure • ferromagnetic fcc-manganese • Laves phases • equation of state

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### Introduction

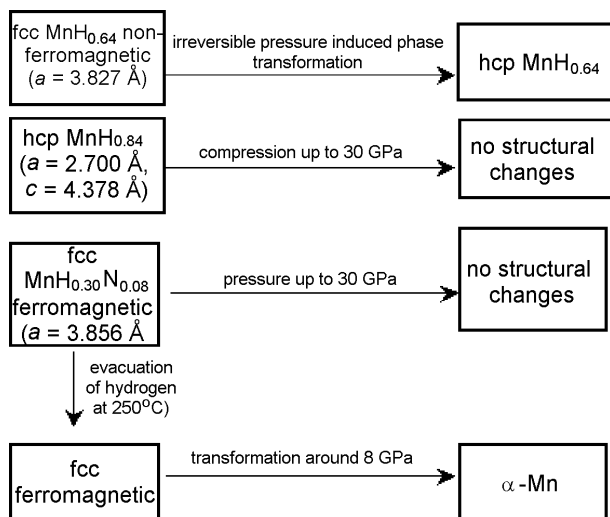
Manganese located at the centre of 3d series of transition metals has a very unique behavior when alloyed with other metals to form substitutional alloys or intermetallic compounds. Furthermore, new interesting phenomena occur when hydrogen is involved to form hydrides. Salient features of these systems will be briefly described below.

### Manganese hydrides

$\alpha$ -Manganese, one of the four allotropic structures of this element existing at atmospheric pressure, undergoes a para-antiferromagnetic transition at low temperatures. On the other hand it was predicted [9] that the cubic phase of manganese, stable between 1090 and 1137°C should be ferromagnetic if stabilized at lower temperature and lattice parameter higher than 3.84 Å.

Manganese hydride (hcp), discovered by Krukowski and Baranowski [11], was the first hydride obtained exclusively by high hydrogen pressure technique. Its fcc structure was synthesized at higher temperature by Fukai *et al.* [8] and Filipek *et al.* [4]. The Mn-H(D) system was also investigated by Ponyatovsky and Belash [16] and Antonov *et al.* [1] who described its T-P phase diagram in large pressure (to 4.4 GPa) and temperature (to 1000°C) conditions.

Compression of manganese hydrides in Bridgman anvils [6] and then in DAC [7] confirmed that the hcp



**Fig. 1.** Influence of hydrostatic pressure on structural and magnetic properties of manganese hydrides.

hydride does not change its crystal symmetry up to 30 GPa. However, it was revealed that above 5 GPa the fcc  $\text{MnH}_{0.64}$  irreversibly transforms into the hcp structure. Very surprising was the behavior of nitrogen-doped fcc hydride. The fcc  $\text{MnH}_{0.30}\text{N}_{0.08}$  sample, in spite of its largest molecular volume, preserved original structure up to 30 GPa showing stabilizing effect of coexistent nitrogen and hydrogen atoms in the metal lattice. This fcc phase was ferromagnetic in agreement with theoretical prediction for fcc manganese with sufficiently large molecular volume. It was even more interesting that ferromagnetism associated with this fcc structure remained after desorption of hydrogen (and nitrogen) by annealing the sample in vacuum. After annealing the material can be considered as “quenched” fcc-manganese. However, removing of interstitial atoms (H and N) destabilizes this structure which after application of hydrostatic pressure of 8 GPa transforms back into  $\alpha$ -manganese. The influence of hydrostatic pressure on structural and magnetic properties of manganese hydrides and procedure leading to formation of ferromagnetic manganese are summarized in Fig. 1.

### Hydrides of nickel-manganese alloys

Interesting electronic properties were observed for hydrides in the nickel-manganese system formed under hydrogen pressure within the range up to 1.5 GPa [3]. They are related to a virtual bound state, passing through the Fermi level when the 3d solute atoms belong to the left midrange of the 3d transition series [2]. Manganese is located just in the middle of 3d series. For smaller concentration of manganese ( $\text{Ni}_{90.7}\text{Mn}_{9.3}$ ), the initial thermoelectric power value, as well as its steep and large (from  $-20$  to about  $0 \mu\text{V/K}$ ) change during hydride formation, are just like in the case of pure nickel or nickel doped with metals which do not influence too much its electronic structure. However, at higher concentration ( $\text{Ni}_{82.5}\text{Mn}_{17.5}$ ) manganese behaves as the

left 3d midrange elements like Cr, V or Ti. Initial thermopower of  $\text{Ni}_{82.5}\text{Mn}_{17.5}$  alloy is less negative (only  $-4 \mu\text{V/K}$ ) as compared with nickel and the positive jump during the formation of hydride is strongly reduced (from 20 to  $6 \mu\text{V/K}$ ). This can be attributed to a virtual bound state (VBS), passing through the Fermi level (in the hydrogen-free alloy) and the shift of the Fermi level beyond the position of the VBS peak, when the empty bands of the alloy are filled by electrons from hydrogen atoms dissolving as protons in the metallic lattice. A similar tendency has been observed also for palladium doped with 4d metals like rhodium and ruthenium.

### Laves phase $\text{YMn}_2$ based hydrides

At room temperature,  $\text{YMn}_2$  has a typical C15 Laves phase structure with a lattice parameter of  $7.684 \text{ \AA}$ . Magnetic first order transition into a helimagnetic structure occurs near 100 K [14, 18] with Mn moments of  $2.7 \mu\text{B}$ . This transition is accompanied with a large (about 5%) volume expansion due to the localization of the Mn moments.

Hydrogen readily dissolves in the C15 cubic lattice of  $\text{YMn}_2$ . At 300 K, the lattice parameter continuously increases with increasing hydrogen concentration without change of symmetry up to  $\text{YMn}_2\text{H}_{3.5}$  composition [17]. Above this composition a rhombohedral distortion of the cubic cell was found described in the  $R3m$  space group. The rhombohedral  $\text{YMn}_2\text{H}_{4.3}$  was considered so far as a hydride with highest hydrogen concentration available in the  $\text{YMn}_2\text{H}_x$  system [10, 12]. However, recently we synthesized a novel hydride [5, 15, 21]  $\text{YMn}_2\text{H}_6$  which crystallize in a fluorite type cubic structure isostructural to  $\text{Mg}_2\text{FeH}_6$  and cannot be derived simply from initial C15 structure.

This hydride was synthesized in 0.2 GPa and  $200^\circ\text{C}$  thus not in extreme pressure-temperature conditions. It is worth of noting that, unexpectedly,  $\text{YMn}_2\text{H}_6$  is more stable than hydrides with lower H content and decomposes at higher temperature (620 K) [15].

Pure Laves compounds were studied at high hydrostatic pressures from several years [13], but it seems that the first DAC compression experiments with Laves phase-based hydrides were undertaken recently by our group. Compression of  $\text{YFe}_2\text{H}_5$  and  $\text{ErFe}_2\text{H}_5$  in DAC apparatus revealed phase transformations for both hydrides [19]. In this paper, we report the data obtained with the same technique and related to hydrides derived from  $\text{YMn}_2$ .

### Experimental

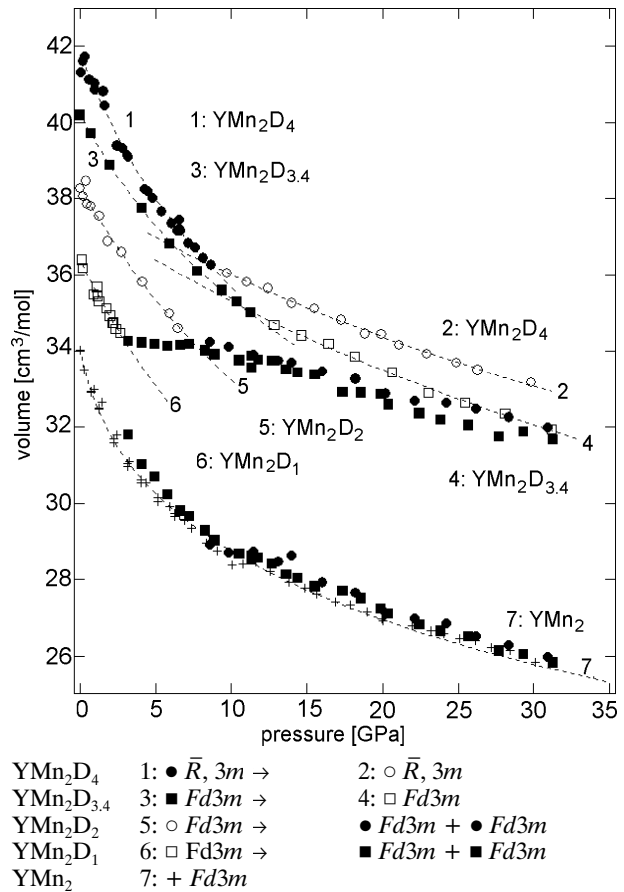
Synthesis and characterization of hydrides were done as in Ref. [5]. Powder samples were pressurized in a diamond anvil cell with methanol and ethanol mixtures as pressure transmitting medium. Experiments were carried out at  $25^\circ\text{C}$  up to 30 GPa. Diffraction patterns were measured by an energy dispersive type X-ray diffraction system with a tungsten tube operating at 47.5 kV and 27.5 mA and a pure Ge detector.

## Results and discussion

Figure 2 shows recently published [20] compressibility data obtained for parent  $\text{YMn}_2$  and its deuterides within the concentration range up to 4 D/f.u.

The fitting done for  $\text{YMn}_2$  in the pressure range up to 30 GPa with the second order Birch-Murnaghan equation of state gave extremely high  $K_0'$  (25.7) value which seems not adequate. Therefore, we divided the compression curve into two segments, below and above 8 GP. In Table 1, the numerical data for  $\text{YMn}_2$  are given with values for other hydrides (deuterides). The  $K_0$  (21.6) and  $K_0'$  (13.2) values for low pressure segment are in good agreement with the data reported by Lindbaum [13] (19 and 15.2, respectively) for a fit procedure up to 10 GPa. For  $\text{YMn}_2\text{D}_1$  and  $\text{YMn}_2\text{D}_2$ , a spinodal-like decomposition starting near 5 GPa has been observed. The  $\text{YMn}_2\text{D}_{3,4}$  and  $\text{YMn}_2\text{D}_4$  preserved the initial structures but, like for parent  $\text{YMn}_2$ , two sets of parameters were necessary to describe their compression behavior. It means that the large compressibility of  $\text{YMn}_2$  as well as  $\text{YMn}_2\text{D}_x$  or  $\text{YMn}_2\text{H}_x$  (where  $x \leq 4.3$ ) is basically related to the character of the metallic lattice; we guess that specifically the manganese sublattice is involved here. In view of these results it seemed interesting to extend the research to  $\text{YMn}_2\text{H}_6$ , a novel hydride synthesized under high hydrogen pressure.

The X-ray diffraction patterns of  $\text{YMn}_2\text{H}_6$  before compression, at 31 GPa and after pressure release to atmospheric value are shown in Fig. 3. This hydride did not change its  $Fm\bar{3}m$  cubic structure within the whole range investigated. The most intriguing, however, is the fact that in contrast to parent  $\text{YMn}_2$  and all hydrides (deuterides) with smaller hydrogen concentration, the behavior of  $\text{YMn}_2\text{H}_6$  can be described (as can be seen



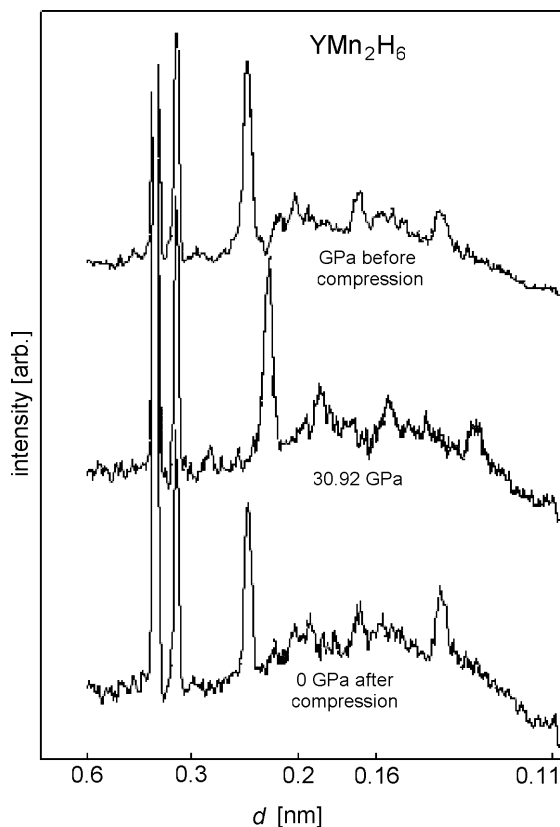
**Fig. 2.** Compression curves for C15  $\text{YMn}_2$  and deuterides derived from this structure [20].

in Fig. 4) in the whole pressure range with only one set of parameters of the Birch-Murnaghan equation.

**Table 1.** High pressure behavior of manganese hydrides and hydrides of several manganese related compounds

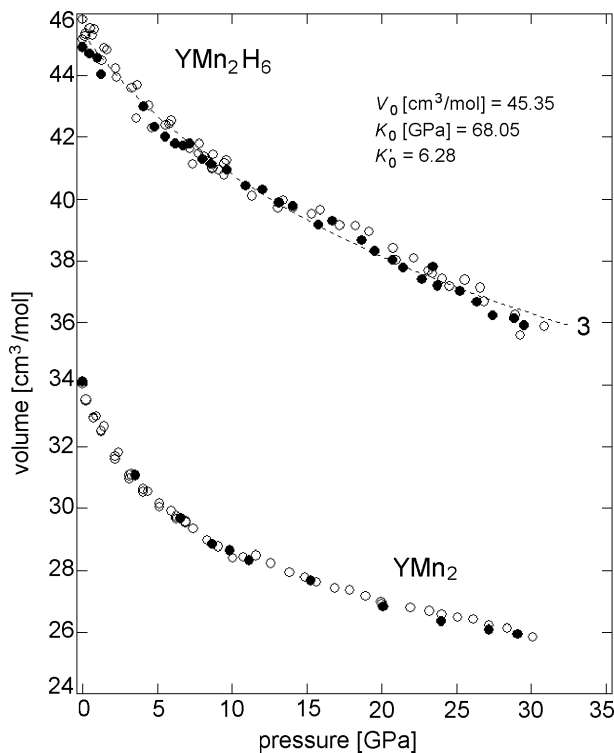
Sample	$V_0$ [cm <sup>3</sup> /mol]	$K_0$ [GPa]	$K_0'$	$n$	Remarks
hcp $\text{MnH}_{0.84}$	8.297	92.7	8.77		hcp structure (whole range)
fcc $\text{MnH}_{0.64}$	8.436	84.1	8.77		irreversible transition into hcp hydride at 6 GPa
fcc $\text{MnH}_{0.30}\text{N}_{0.08}$	8.639	107.0	3.93		fcc structure (whole range)
$\text{YMn}_2$	34.11	14.1	25.7	50	cubic (whole range)
	34.02	21.6	13.2	21	cubic (low pressure segment $P < 8$ GPa)
	31.24	83.1	7.13	29	cubic (high pressure segment $P > 8$ GPa)
$\text{YMn}_2\text{D}_1$	36.37	44.1	4.0 fixed	12	cubic (spinodal-like reversible decomposition around 5 GPa)
$\text{YMn}_2\text{D}_2$	38.29	52.99	4.0 fixed	9	cubic (spinodal-like reversible decomposition around 6 GPa)
$\text{YMn}_2\text{D}_{3,4}$	40.11	60.28	4.0 fixed	11	cubic (low pressure segment)
	37.80	133.9	4.0 fixed	20	cubic (high pressure segment)
$\text{YMn}_2\text{D}_4$	41.65	46.07	4.0 fixed	27	rhombohedral (low pressure segment)
	38.22	153.0	4.0 fixed	17	rhombohedral (high pressure segment)
$\text{YMn}_2\text{D}_6$	45.35	68.05	6.28		cubic $Fm\bar{3}m$ (whole range)

$n$  – total number of data.



**Fig. 3.** X-ray diffraction patterns of  $\text{YMn}_2\text{H}_6$ .

We guess that different compression behavior of  $\text{YMn}_2\text{H}_6$  is related not only to different symmetry, but also to different bonding character between hydrogen and



**Fig. 4.** Compression curve for  $\text{YMn}_2\text{H}_6$  (data for  $\text{YMn}_2$  are given for comparison).

metal in this hydride. This is supported also by calorimetric data showing unusually high thermal stability.

Table 1 reports the data of our DAC measurements on hydrides (deuterides) of manganese and several manganese related compounds.

Compressibility of manganese hydrides does not differ too much from that observed for other hydrides of transition metals. Pressure-induced fcc-hcp irreversible transition was observed for hydride, but a small amount of nitrogen stabilizes the fcc structure.

A specific interaction between yttrium and manganese is responsible for the unusual compressibility in the low pressure range observed in  $\text{YMn}_2$  and related hydrides (deuterides) up to 4.3 H/f.u.

The particular behavior of  $\text{YMn}_2\text{H}_6$  compared to the other  $\text{YMn}_2$  hydrides indicates that at this concentration the hydrogen suppresses the unique character of the parent  $\text{YMn}_2$  intermetallic.

## References

- Antonov VE, Antonova TE, Chirin NA *et al.* (1996) T-P phase diagram of the Mn-H system at pressures to 4.4 GPa and temperatures to 1000°C. *Scripta Mater* 34:1331–1336
- Blatt FJ, Schroeder PA, Foiles CL *et al.* (1976) *Thermoelectric power of metals*. Plenum Press, New York
- Filipek SM (1997) Thermoelectric power of (NiMn)-H and (NiCo)-H systems. *Pol J Chem* 71:1777–1786
- Filipek SM, Majchrzak S, Sawaoka AB *et al.* (1991) Phase diagram of the Mn-H system. *High Pressure Res* 7:271–273
- Filipek SM, Paul-Boncour V, Percheron-Guegan A *et al.* (2002) Synthesis of novel deuterides in several Laves phases by using high pressure of gaseous deuterium. *J Phys-Condens Matter* 14:11261–11264
- Filipek SM, Sugiura H, Sawaoka AB (1990) Phase transformations in the manganese hydride. In: Holzapfel WB, Johannsen PG (eds) *Proc of the 12th Int Conf AIRAPT and 27th Int Conf EHPRG (July, 1989 Paderborn, RFN)*. Gordon and Breach Science Publishers, New York–London, p 493
- Filipek SM, Sugiura H, Skoskiewicz T (2000) Pressure induced phase transformations in the Mn-H and Mn-H/N. In: Manghnani MH, Nellis WJ, Nicol MF (eds) *Proc of the 17th Int Conf Science and Technology of High Pressure AIRAPT, 25 July, 1999, Honolulu, Hawaii*. Universities Press, Hyderabad, India, pp 550–554
- Fukai Y, Ishikawa H, Goto T *et al.* (1989) High-pressure synthesis and magnetic properties of cubic manganese hydride. *Phys Chem N F* 163:479–482
- Fuster G, Brener NE, Callaway J *et al.* (1988) Magnetism in bcc and fcc manganese. *Phys Rev B* 38:423–432
- Goncharenko IN, Mirebeau I, Irodova AV *et al.* (1997) Interplay of magnetic and hydrogen orders in the laves hydride  $\text{YMn}_2\text{H}_{4.3}$ . *Phys Rev B* 56:2580–2584
- Krukowski M, Baranowski B (1975) Formation of manganese hydride from metallic manganese and high pressure gaseous hydrogen. *Roczniki Chemii* 49:1183–1186
- Latroche M, Paul-Boncour V, Percheron-Guégan A *et al.* (1998) Temperature dependence study of  $\text{YMn}_2\text{D}_{4.5}$  by means of neutron powder diffraction. *J Alloys Compd* 274:59–64
- Lindbaum A, Gratz E, Heathman S *et al.* (1999) Compressibility of  $\text{YMn}_2$ ,  $\text{Y}_6\text{Mn}_{23}$ ,  $\text{YMn}_{12}$  and  $\text{ScMn}_2$

- studied by synchrotron powder diffraction. *J Phys-Condens Matter* 11:1189–1198
14. Nakamura Y (1983) Magnetovolume effects in Laves phase intermetallic compounds. *J Magn Magn Mater* 31/34:829–834
  15. Paul-Boncour V, Filipek SM, Dorogova M *et al.* (2005) Neutron diffraction study, magnetic properties and thermal stability of  $YMn_2D_6$  synthesized under high deuterium pressure. *J Solid State Chem* 178:356–362
  16. Ponyatovsky EG, Belash IT (1975) Synthesis and physical and chemical properties of manganese hydride. *Dokl Akad Nauk SSSR* 224:607–608
  17. Przewoźnik J, Paul-Boncour V, Latroche M *et al.* (1998) Hydrogen induced phase transitions in  $YMn_2$ . *J Alloys Compd* 274:29–37
  18. Shiga M, Wada H, Nakamura Y *et al.* (1983) Magnetism and thermal expansion anomaly of  $RMn_2$  ( $R = Y, Gd, Tb, Ho$  and  $Er$ ). *J Magn Magn Mater* 31/34:119–120
  19. Sugiura H, Marchuk I, Paul-Boncour V *et al.* (2003) Pressure induced phase transitions and EOS of several Laves phase hydrides. *J Alloys Compd* 356/357:32–35
  20. Sugiura H, Paul-Boncour V, Percheron-Guégan A *et al.* (2004) High pressure studies of  $YMn_2$  Laves phase and its deuterides. *J Alloys Compd* 367:230–234
  21. Wang Chien-Yuan, Paul-Boncour V, Kang Chia-Cheng *et al.* (2004) The novel  $YMn_2D_6$  deuteride synthesized under high pressure of gaseous deuterium. *Solid State Commun* 130:815–820