

# High pressure studies of $\text{GdMn}_2$ and its hydrides

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## Abstract

High pressure energy dispersive X-ray diffraction (EDXD) studies have been performed on  $\text{GdMn}_2$  and its  $\text{GdMn}_2\text{H}_x$  ( $x = 1, 2$ ) hydrides up to 20 GPa at room temperature in a diamond anvil cell. The C15 structure of  $\text{GdMn}_2$  is retained in the whole pressure range. Structural transformations from the C15 to a yet unidentified phase were observed for both hydrides in the 4–10 GPa pressure range. For higher hydrogen content, the transition pressure region shifts to higher values. Equations of state of pure  $\text{GdMn}_2$  and its hydrides have been determined. For all these compounds, an unusually high compressibility at lower pressures has been revealed.

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**Keywords:** Rare earth compounds; Hydrogen absorbing materials; High pressure; X-ray diffraction; Metal hydrides; Transition metal elements

## 1. Introduction

Laves phases have been the subject of intensive investigations since their discovery. The research of  $\text{RMn}_2$  (R: rare earth or yttrium, M: transition metal element) is recently mostly aimed at determining their structural and magnetic properties related to hydrogen absorption and the capacity of particular Laves phase for hydrogen storage. Some compounds showed relatively good hydrogen storage capacity up to five hydrogen atoms per formula unit [1]. It was observed that introduction of a certain amount of hydrogen can cause a structural transformation of the initial compound [2,3]. Although there are numerous papers dealing with structural and magnetic properties of particular Laves phases, there are very few reports on pressure investigations of the Laves phase hydrides.

The aim of the present research was to investigate the influence of hydrogen on the structural behavior of  $\text{GdMn}_2$  and  $\text{GdMn}_2\text{H}_x$  ( $x = 1, 2$ ) Laves phases under high pressure. The effect of pressure factor can be considered as also affecting the magnetic structure. Therefore, the research deals with the studies of pressure induced structural transformations and their relation with the magnetic behavior.

## 2. Experimental

The host  $\text{GdMn}_2$  was prepared of high-purity materials using the standard induction melting technique in an argon atmosphere. It crystallizes in the cubic C15 type Laves phase ( $\text{Fd } \bar{3}m$  space group) structure with a lattice parameter equal to 7.704 Å.

The  $\text{GdMn}_2\text{H}_x$  ( $x = 1, 2$ ) hydrides were obtained by saturation of  $\text{GdMn}_2$  with hydrogen gas under certain pressure and temperature conditions [3]. In fact, the samples were the same as those investigated in [3]. The cubic C15 structure is retained for both hydrides but the lattice parameters increase to 7.973 and 8.078 Å, respectively. These compounds are stable under normal conditions.

The pressure-dependent X-ray measurements were performed using the energy dispersive X-ray diffraction method (EDXD) in a diamond anvil cell (DAC), which allowed to obtain pressures up to 20 GPa. A tungsten target tube operating at 40 KeV and 25 mA was used as the X-ray source. The average acquisition time, at each pressure, was around 24 h. For each compound, at least two pressure runs were carried out. We paid special attention to the pressure regions where some unexpected behavior was detected.

The gasket with a 300  $\mu\text{m}$  drilled hole was made of Inconel. Mineral oil was used as pressure transmitting medium. The hole was loaded with the sample and a ruby chip. Ruby fluorescence was used for the determination of pressure.

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### 3. Results and discussion

It was assumed, that the contraction of the unit volume under pressure in the investigated compounds could be described in the same way as in metals. Thus, we used the Murnaghan model [4] to express the equation of state (EOS)

$$P = \frac{B_0}{B'_0} \left[ \left( \frac{V_0}{V(P)} \right)^{B'_0} - 1 \right] \quad (1)$$

where  $B_0$  is the bulk modulus,  $B'_0$  the first derivative of bulk modulus,  $V_0$  the molar volume at ambient pressure and  $V(P)$  the molar volume at pressure  $P$ .

Using this equation, we analyzed and fitted our experimental data.

#### 3.1. $GdMn_2$ compound

For this pure compound, no structural transition was observed up to 19.9 GPa at room temperature. The volume changes as function of pressure were reversible. However, an unusual large compressibility was detected in the low pressure region (from ambient to  $\sim 5.0$  GPa) (Fig. 1). We noticed that at higher pressure the compressibility of this compound became smaller, more likely to normal solids. Thus, we came to the idea of two ranges: low and high pressure parts. We could select two regions of different compressibility below and above a transition point around 4.8 GPa, leading for both ranges to a bulk modulus of  $B_0 = 14$  and 60 GPa, respectively as calculated from Eq. (1). The differences in compressibility may suggest some phase transition of second order. Considering the fact that the C15 structure is retained throughout the experiment, some kind of transformation of electron density of states seems to be possible. It is in accordance with literature data for intermetallics of

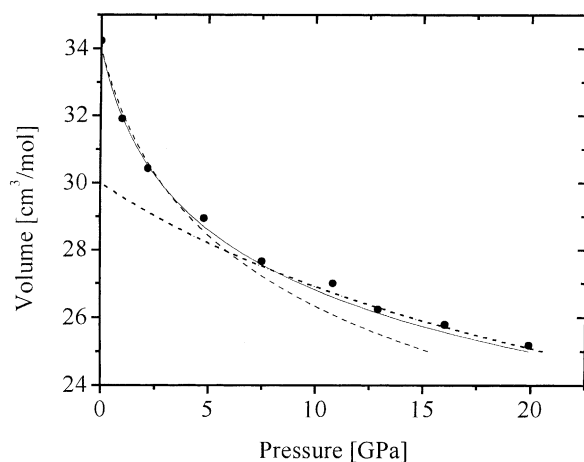


Fig. 1. Molar volume of  $GdMn_2$  as function of pressure: (—) solid line in the whole pressure range under which  $GdMn_2$  was investigated,  $B_0 = (12.1 \pm 0.6)$  GPa,  $B'_0 = 9.0 \pm 0.4$ ; (-·-) short dash dot up to 4.8 GPa,  $B_0 = (69.3 \pm 3.5)$  GPa,  $B'_0 = 5 \pm 0.3$ ; (---) dash from 4.8 GPa,  $B_0 = (14 \pm 0.7)$  GPa,  $B'_0 = 7 \pm 0.4$ .

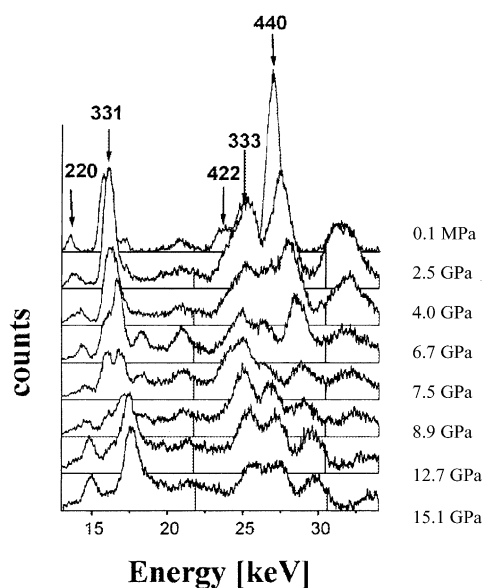


Fig. 2. EDXRD patterns of  $GdMn_2H_1$  taken under sequential increasing pressure. ( $E \times d_{hkl} = 37.80$  KeV Å).

Gd [5], where an unusually large compressibility was also detected in a low pressure region.

#### 3.2. $GdMn_2H_1$ and $GdMn_2H_2$ hydrides

Structural X-ray diffraction studies for  $GdMn_2H_1$  and  $GdMn_2H_2$  hydrides were undertaken at room temperature in the pressure range from ambient to 15.1 and 14.0 GPa, respectively.

The energy dispersive X-ray diffraction patterns (EDXRD) are presented in Figs. 2–4 for increasing and decreasing

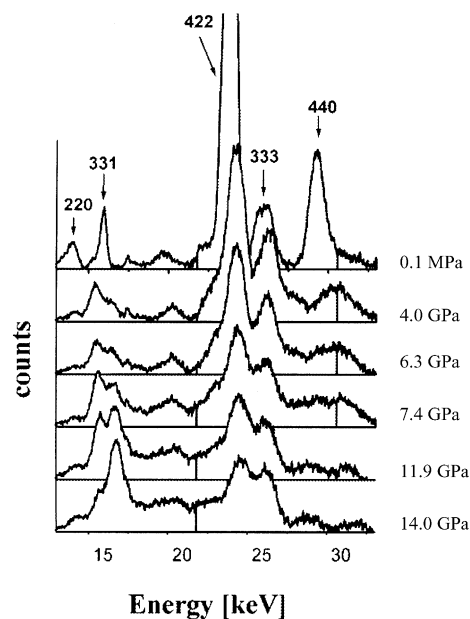


Fig. 3. EDXRD patterns of  $GdMn_2H_2$  taken under sequential increasing pressure. ( $E \times d_{hkl} = 37.15$  KeV Å).

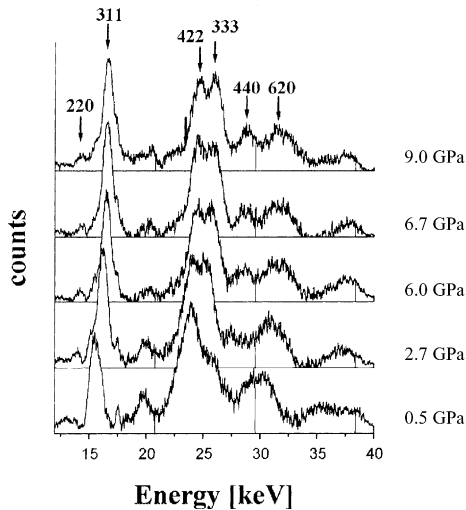


Fig. 4. EDXRD patterns of GdMn<sub>2</sub>H<sub>1</sub> taken under sequential decreasing pressure. ( $E \times d_{hkl} = 37.80 \text{ KeV \AA}$ ).

pressure. The patterns revealed some structural changes that took place during the increase of pressure only. As one can see in Fig. 2, some structural changes were observed in the pressure range from  $\sim 4.0$  to  $\sim 8.0$  GPa for GdMn<sub>2</sub>H<sub>1</sub> and from  $\sim 5.5$  to  $\sim 10$  GPa for GdMn<sub>2</sub>H<sub>2</sub> (Fig. 3) but when the pressure was reduced, the structure remained the same. For better visualization of these changes, the interplanar distances for GdMn<sub>2</sub>H<sub>1</sub> as function of pressure are presented in Fig. 5. Clearly, new peaks can be seen associated with a new structure of unknown origin. We have tried to identify this structure using different fitting programs but at least seven structure types including orthorhombic and hexagonal ones were indicated with comparable fitting parameters. The main reason for this uncertainty is the limited number and the relatively small intensity of the diffraction lines as well as peak broadening. All these obstacles might probably be overcome by using synchrotron radiation and a more

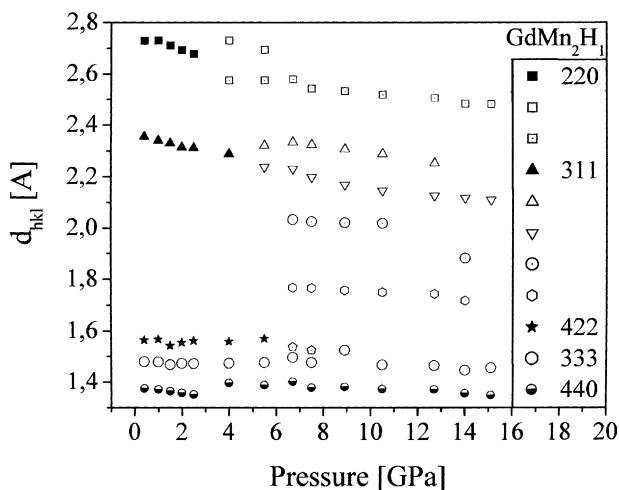


Fig. 5. The change of interplanar distances of GdMn<sub>2</sub>H<sub>1</sub> as pressure increases. Indices not marked are due to appearance of a new phase.

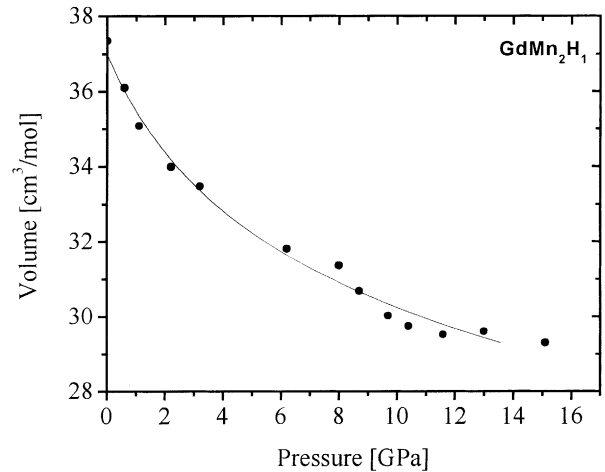


Fig. 6. Molar volume of GdMn<sub>2</sub>H<sub>1</sub> when pressure decreases  $B_0 = 19.8 \text{ GPa}$ ;  $B'_0 = 8$ .

precise detection of the diffracted X-rays. These structural changes show a strange reversibility. When pressure was being released no structural transformation took place for both GdMn<sub>2</sub>H<sub>1</sub> and GdMn<sub>2</sub>H<sub>2</sub>, and the apparent structure was C15 (see Fig. 3) with the lattice parameter close to the starting material. As mentioned above, it was difficult to determine the structure after the pressure induced transformations due to line broadening and the small number of peaks, but the XRD patterns obtained seem to be similar to those obtained by Strecker for the C14 structure [7]. The occurrence of two pressure values dividing the range into three regions where different XRD patterns are visible, is similar to those obtained during an investigation of the Mössbauer effect as function of pressure for GdMn<sub>2</sub> [7]. However, according to our results, the structure after the phase transition for both hydrides is rather cubic than hexagonal so we considered this explanation with caution.

The parameters of EOS calculated on the basis of Murnaghan's model also showed unusual large compressibility of the samples containing hydrogen similarly to the pure compound (Fig. 6).

It is interesting to point out that the compressibility of both hydrides is comparable though the hydrogen concentration is significantly different (Fig. 7). Also, the shape of curves of molar volume of both hydrogenated compounds as function of pressure seem to be parallel to that of the pure compound. This behavior follows the well known phenomena observed in many transition metal hydrides where hydrogen atoms in the hosts lattice are incompressible. For the first time, such a result was reported by Fukizawa and Fukai [8] for vanadium and niobium hydrides and was later confirmed for other transition metal hydrides [9].

It is interesting that the volume increase during the introduction of the first hydrogen atom per formula unit into the GdMn<sub>2</sub> lattice is much bigger than that for the next ones [3].

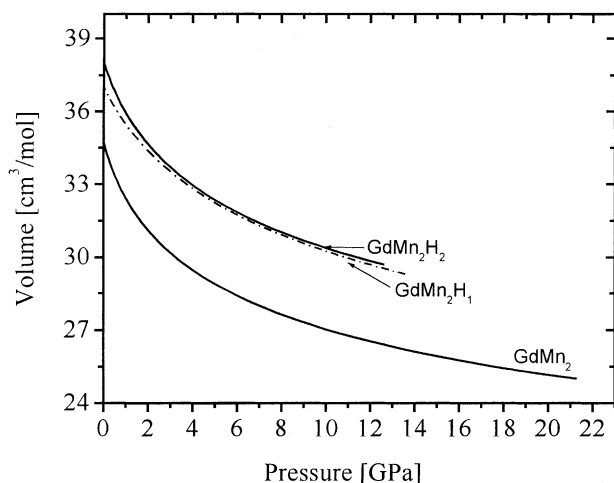


Fig. 7. Comparison of compressibility of  $\text{GdMn}_2$  and its hydrides. For the clarity, only fits of corresponding equations of state are given in the figure.  $\text{GdMn}_2\text{H}_1$ :  $B_0 = (19.8 \pm 0.9)$  GPa;  $B'_0 = 8 \pm 0.4$ .  $\text{GdMn}_2\text{H}_2$ :  $B_0 = (13.8 \pm 0.7)$  GPa;  $B'_0 = 8$  fixed.  $\text{GdMn}_2$ :  $B_0 = (12.1 \pm 0.6)$  GPa;  $B'_0 = 9 \pm 0.4$ .

#### 4. Interpretation

Based on the experimental results and the literature data, let us analyse possible explanations for such pressure induced structural behaviour.

As we stated above, due to peak broadening and the small number of peaks, it was difficult to estimate exactly what structural transformation took place during the increase of pressure. But regarding the influence of hydrogen, it is quite clear that with the increase of the hydrogen content the region of phase transition shifts to higher pressure.

According to literature data, reported so far, one can discuss some possible mechanisms of the observed structural transformation for  $\text{GdMn}_2\text{H}_x$  ( $x = 1, 2$ ) under pressure.

The first one is based on the fact that  $\text{GdMn}_2\text{H}_1$  splits into two phases with different hydrogen content and one of this phases orders magnetically as the temperature decreases [3]. Since decreasing temperature causes a unit cell volume contraction, it is believed that it has a similar effect on the structure as pressure increase. However, as proved in [3], such a transformation would have resulted in two cubic phases with different lattice parameters that would have been detected by our method. However, the new phase or phases that appear in the range of transitions in our studies are not cubic.

The next considered mechanism is related to the structure change from C15 to C14 for  $\text{GdMn}_2$  and similar compounds under pressure as reported by Reiß [6].

It is valuable for further analysis to compare the pressure and temperature induced phase transformations in  $\text{RM}_2$  ( $R = \text{Gd, Y}$ ;  $M = \text{Fe, Mn}$ ) Laves phase compounds and their hydrides. A brief compilation of the literature data is presented in Table 1.

Table 1  
Pressure and temperature induced phase transitions in some Laves-phases and its hydrides

| Compound                  | Temperature (K) | Pressure (GPa)                | Occurrence of transition            |
|---------------------------|-----------------|-------------------------------|-------------------------------------|
| $\text{YMn}_2$            | 300             | At 150                        | From C15 to C14 [6]                 |
| $\text{YFe}_2$            | 300             | At 150                        | From C15 to C14 [6]                 |
| $\text{GdMn}_2$           | 300             | Up to 50                      | No transition                       |
|                           | 4.2             | From $\sim 2$ to $\sim 4$     | From C15 to C14 [7]                 |
| $\text{GdFe}_2$           | 300             | At 50                         | From C15 to C14 [6]                 |
| $\text{GdMn}_2\text{H}_1$ | 300*            | Range $\sim 4$ to $\sim 8^*$  | Unidentified transition*            |
|                           | 4.2             | Ambient pressure              | Splitting into two cubic phases [3] |
| $\text{GdMn}_2\text{H}_2$ | 300*            | Range $\sim 6$ to $\sim 10^*$ | Unidentified transition*            |
|                           | 4.2             | Ambient pressure              | No transition [3]                   |

\* This work.

Having analyzed the data from the Table 1, an interesting feature of the compounds under consideration can be figured out related to magnetic interactions.

Regarding the magnetic interactions, it is well known that Gd atoms possess well-localized magnetic moments, but the interactions between them are weak due to large separation distances. But in the light of the above mentioned experimental data, it is the Gd sublattice which drives the structural transformation (C15–C14) whereas the Mn sublattice remains unchanged. The magnetic interactions contribute to the free energy of the system, and because they are distance dependent, they can also contribute to the structural phase transformations. Therefore, one can try to find out a possibility to change magnetic interaction of Gd atoms in such a way that would result in a structural transformation. Although the decreasing Gd–Gd distance would lead to an increase of the temperature of magnetic ordering, the pressure required to induce such a transformation at room temperature is outside our experimental capability. In fact, such a transformation can occur at a Laves phase cell volume of about  $276 \text{ \AA}^3$ , which corresponds to a volume reduction of about 40%.

In this context, the pressure behaviour of Laves phase compounds listed in Table 1 can be compared. For  $\text{YMn}_2$  and  $\text{YFe}_2$ , the transition (C15–C14) occurs at a very high pressure. However, the compounds with Gd instead of Y undergo the C-15–C14 phase transformation at much lower pressures which can be correlated with the role of the Gd–Gd magnetic interactions not existing in the compounds with Y. For Gd based compounds, a difference occurs also depending on the 3d metal, Fe or Mn. For  $\text{GdFe}_2$  that has better localized Fe magnetic moment than Mn, the pressure required to initiate a structural transformation is reduced to 50 GPa [Table 1]. The magnetic ordering temperature  $T_C$  for Gd sublattice in  $\text{GdFe}_2$  reaches  $\sim 300$  K at this pressure [6]. For  $\text{GdMn}_2$  no C15–C14 transition at room temperature and 50 GPa is observed, but at 4.2 K it appears under very small pressure  $\sim 2$  GPa [7]. A linear approximation of  $T_C$  as function of pressure for  $\text{GdMn}_2$  taken from [7] gives  $T_C \sim 300$  K

at pressures above 50 GPa. That is why no phase transformation is visible in our experiment for GdMn<sub>2</sub>.

A more complicated situation appears in the GdMn<sub>2</sub> hydrides. Two opposite tendencies take place when hydrogen atoms penetrate the structure. First, the expansion of the unit cell results in a decreasing Gd–Gd magnetic interaction which leads to an increase rather than a decrease of the C15 structure stability. A typical increase of the lattice volume is about 2.9 Å<sup>3</sup> per hydrogen atom in transition metal hydrides. Secondly, while the cell expands a process modifying the Mn magnetism takes place as the Mn–Mn distance exceeds the critical value [3]. With respect to of magnetic order, the Mn–Mn interaction becomes dominant in relation to Gd–Gd interaction. Based on experimental results, we understand that the second process dominates at ambient pressure. As it is visible from Fig. 7, the maximal pressure for the hydrides reduces their volume to the value corresponding to the volume of the pure GdMn<sub>2</sub> at about 4 GPa. The phases induced in the hydrides correspond to GdMn<sub>2</sub> volumes below 2 GPa. By comparing it with the data on the pressure dependence of the magnetic interactions in GdMn<sub>2</sub> [7], one can see that at this pressures the magnetic interactions of the Gd atoms can be stronger than the Mn interactions also for the hydrides. However, they cannot affect the structural changes at room temperature.

Increasing of the amount of hydrogen in the structure causes, at room temperature, an increase of the pressure required for initiation of the structural transformation as it was observed for the hydride with higher content of hydrogen. That means, that in the investigated hydrides the observed structure transformations are not related to magnetism. However, the problem of finding the reasons for the observed pressure induced phase transformations remains. It is worth noting here, that the appearance of the new phases occurs at pressures (~4 to 10 GPa) where there is a transition range between the weak and strong compressibility ranges. So treating it as instability range and taking into account the tendency of the hydrogen atoms to order,

we can assume, that at these pressures metastable structures appear, which allow the system to find the free energy minimum.

## 5. Summary

High pressure energy dispersive X-ray diffraction (EDXD) was performed on GdMn<sub>2</sub> and its GdMn<sub>2</sub>H<sub>x</sub> ( $x = 1, 2$ ) hydrides. The C15 structure of GdMn<sub>2</sub> is retained in the whole pressure range. Structural transformations from C15 to a yet unidentified phase were observed for both hydrides in the 4–10 GPa range. For higher hydrogen content, the transition pressure region shifts to higher values. For all these compounds an unusually high compressibility at lower pressures was revealed.

To solve the problem of the unknown structural phases, we plan a structural investigation with use of the synchrotron radiation technique giving the possibility of better X-ray resolution.

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