

**$^{55}\text{Mn}$  nuclear-magnetic-resonance study of the  $\text{GdMn}_2$  hydrides**

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The  $^{55}\text{Mn}$  NMR spin-echo spectra for the cubic  $\text{GdMn}_2\text{H}_x$  compounds with  $x=0, 0.5, 1, 2, 2.5, 3, 3.4, 3.5$  and for the rhombohedral  $\text{GdMn}_2\text{H}_{4.3}$  are reported. For the samples with  $x=0, 0.5,$  and  $1$  spectra with a single broad line at 129, 132, and 135 MHz, respectively are observed. Satellite patterns with up to three lines are observed for  $2 < x < 3.5$ . The effect is attributed to a diversification of manganese moments caused by hydrogen neighbors leading to up to three values of the Mn moment in the cubic hydrides with  $x > 2.5$ . For  $\text{GdMn}_2\text{H}_{3.5}$  the directions of Mn magnetic moments with respect to the magnetization are derived from the line shifts in an applied magnetic field. The two narrow lines observed for the rhombohedral compound  $\text{GdMn}_2\text{H}_{4.3}$  at 186 and 423 MHz are attributed to the two Mn sites in the structure. The observed effects are explained by the presence of four different magnetic structures and four manganese spin states in the series. [S0163-1829(96)05741-4]

**INTRODUCTION**

A variety of magnetic structures revealed by the  $\text{RMn}_2$  compounds ( $R$ =rare earth and yttrium) has recently attracted a considerable interest in research, involving magnetic and transport measurements, neutron diffraction,  $\mu\text{SR}$ , and other techniques. The magnetic behavior of the manganese sublattice in these systems is strongly dependent on the Mn-Mn distance. The  $\text{GdMn}_2$  compound crystallizes in the cubic  $C15$  structure and orders magnetically at 110 K.<sup>1</sup> In a recent paper<sup>2</sup> a model of the ground-state magnetic structure of  $\text{GdMn}_2$  was proposed, assuming a canted ferrimagnetic Gd moment alignment within the Gd sublattice and an antiferromagnetic order within the Mn sublattice. From the hyperfine field measured on Mn nuclei in a NMR experiment<sup>3</sup> the Mn magnetic moment value of  $2.6\mu_B$  is derived, close to that of  $2.7\mu_B$  obtained in neutron-diffraction measurements for  $\text{YMn}_2$ .<sup>4</sup>

Although similar lattice parameters and close ordering temperatures of  $\text{GdMn}_2$  and  $\text{YMn}_2$  can be attributed to the crucial influence of the Mn-Mn distance, the difference in magnetic structure between the compounds is quite significant and is attributed to the large  $4f$  magnetic moments of gadolinium, whereas yttrium bears a small or zero moment. In  $\text{GdMn}_2$  the volume anomaly at the ordering temperature is small and no distortion of the cubic crystal lattice is observed, in contradiction to  $\text{YMn}_2$ , where the anomaly is huge and a tetragonal distortion of the lattice appears. This distortion is the result of a release of frustration arising in the antiferromagnetic structure of the manganese sublattice in  $\text{YMn}_2$ . A lack of such distortion in  $\text{GdMn}_2$  can be attributed to the presence of gadolinium magnetic moments of  $7\mu_B$

acting towards removal of the frustrated state. The recent Moessbauer studies of  $\text{GdMn}_2$  indicate that the Gd sublattice is magnetically ordered below 110 K and that the canting angle of Gd moments changes considerably with temperature.<sup>2,5</sup>

The  $\text{GdMn}_2$  compound easily absorbs hydrogen.<sup>6</sup> The maximum hydrogen content achieved is  $x=4.3$  atoms per formula unit.<sup>7</sup> A continuous range of  $x$  up to 3.5 can be obtained and at room temperature these hydrides retain the cubic  $C15$  structure of the host compound, similarly to  $\text{YMn}_2\text{H}_x$ .<sup>8</sup> The increase of lattice parameter, and thus the interatomic distances with hydrogen uptake amounts to 5.9% for  $x=3.5$ . In the recent neutron-diffraction study of cubic  $\text{YMn}_2\text{H}_x$  it was found that hydrogen atoms occupy exclusively tetragonal  $A_2B_2$  (96g in the  $Fd\ 3m$  space group) sites with two rare-earth and two manganese atoms as the nearest neighbors to a hydrogen atom.<sup>9</sup> As the structure and interatomic distances in both series are similar, it is assumed that hydrogen occupies  $A_2B_2$  sites also in  $\text{GdMn}_2\text{H}_x$ . An uptake of hydrogen to its maximum content  $x=4.3$  leads to a rhombohedral distortion of the cubic lattice.<sup>7</sup> In the crystallographic structure of this hydride (space group  $R\ 3m$ ) manganese occupies two inequivalent sites  $3b$  and  $9e$ .

The lattice expansion together with the chemical effect of hydrogen result in dramatic changes of the properties of hydrides as compared to the host intermetallics. The magnetic ordering temperature generally rises considerably with increasing hydrogen content. The increase of ordering temperature, however, is not monotonous in  $\text{YMn}_2\text{H}_x$ , with a huge rise at low  $x < 1$  and a steep drop at  $x=1$  followed by a linear increase for  $1 < x < 3.5$ .<sup>10,11</sup> A peculiar temperature behavior of the crystal lattice at the low hydrogen concentra-

tion range  $x < 1$  is observed. A second crystallographic transition, corresponding to a tetragonal lattice distortion, appears below the temperature of magnetic ordering ( $T_0$ ) in addition to the anomaly at  $T_0$  observed for the host  $\text{YMn}_2$ .<sup>12</sup> The type of magnetic structure also changes, e.g., in  $\text{YMn}_2\text{H}_x$  a weak ferrimagnetic component appears with increasing H content.

In the magnetic measurements on the cubic  $\text{GdMn}_2\text{H}_x$  the ferrimagnetic component observed for  $\text{GdMn}_2$  initially decreases with  $x$ , leading to a small antiferromagnetic susceptibility for  $\text{GdMn}_2\text{H}_2$ , and the ferrimagnetic behavior reenters for  $x > 2.5$ .<sup>13</sup> A very small susceptibility of  $\text{GdMn}_2\text{H}_{4.3}$  persisting down to 4.2 K indicated that the compound was either not ordered magnetically or antiferromagnetic.

In our previous  $^{55}\text{Mn}$  NMR study of  $\text{YMn}_2\text{H}_x$ , satellite patterns corresponding to a large increase of the hyperfine field from about 12 T for  $\text{YMn}_2$  to above 40 T for  $\text{YMn}_2\text{H}_3$  were observed.<sup>14,15</sup> In the present work we report the  $^{55}\text{Mn}$  NMR data of the Gd-based series.

### EXPERIMENTAL

The sample of  $\text{GdMn}_2$  was prepared by induction melting of an appropriate amount of 99.9% purity gadolinium and 99.99% purity manganese. The ingots were annealed for 2 weeks at 800 °C and subsequently hydrided at 25 °C in a reactor with thermostated and calibrated volume. The amount of absorbed hydrogen was determined from the pressure difference before and after the hydrogenation. All the hydrides were homogenized for about 16 h at 200 °C.

The  $^{55}\text{Mn}$  NMR spin-echo spectra were taken at 4.2 K, using an automated spin-echo spectrometer.<sup>16</sup> The sequence of two radio frequency pulses of 1 and 2  $\mu\text{s}$  length, spaced at 15  $\mu\text{s}$  was applied. The spectra shown in Fig. 1 are corrected by frequency squared for the electronic factor and the population of nuclear levels.

### RESULTS

In the NMR spectrum of  $^{55}\text{Mn}$  of the host  $\text{GdMn}_2$  (Fig. 1) a single broad line of 40 MHz width centered at 129 MHz is observed, which is in agreement with the literature data.<sup>3</sup> The single line pattern persists for the hydrides with  $x = 0.5$  and 1, with the line position shifted to 132 and 135 MHz, respectively. A satellite at 218 MHz appears in  $\text{GdMn}_2\text{H}_2$  besides the main line which is centered at 144 MHz. For  $\text{GdMn}_2\text{H}_{2.5}$  a two-line spectrum is also observed. A very intense line of 20 MHz width is located at 213 MHz and a satellite is centered at 307 MHz. For  $\text{GdMn}_2\text{H}_3$  three structured broad lines at 221, 314, and 413 MHz are obtained. For  $\text{GdMn}_2\text{H}_{3.4}$  and  $\text{GdMn}_2\text{H}_{3.5}$  also a three broad line pattern is observed, with the line positions at 188, 300, and 419 MHz for the latter sample. In the rhombohedral compound  $\text{GdMn}_2\text{H}_{4.3}$  a very narrow line at 186 MHz and a double line centered at 423 MHz are obtained.

Using for the conversion factor between the frequency and the magnetic field the value of 10.50 MHz/T for  $^{55}\text{Mn}$  we get the values of magnetic-field induction  $B_e$  at Mn nucleus from the line frequencies.

In order to analyze the influence of interatomic distances on the local magnetic states of manganese the values of  $B_e$

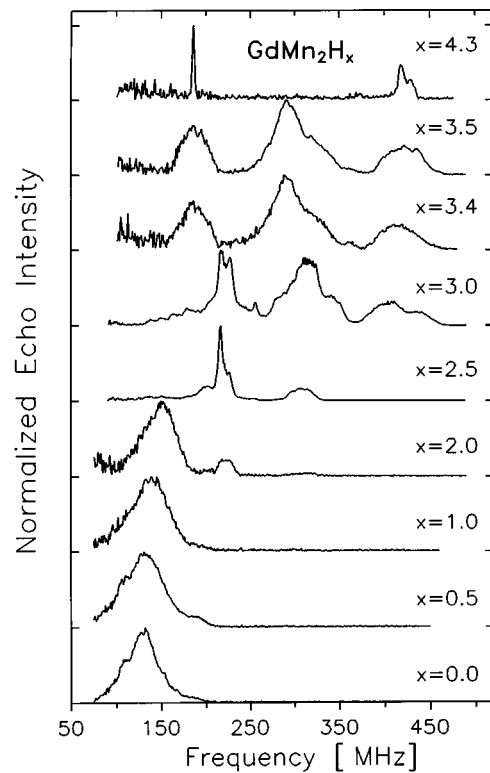


FIG. 1. The  $^{55}\text{Mn}$  NMR spin-echo spectra of the  $\text{GdMn}_2\text{H}_x$  compounds for the pulse sequence 1/15/2  $\mu\text{s}$  at 4.2 K.

for each sample are plotted in Fig. 2 versus manganese-manganese nearest-neighbor distance obtained from the lattice constant  $a$  using formula  $d_{\text{Mn-Mn}} = 2^{-3/2}a$ . Looking at the evolution of  $B_e$  four different regions can be distinguished. The first one includes samples with  $x = 0, 0.5, 1, 2$  the second one: 2.5, 3, the third one: 3.4, 3.5, and the fourth corresponds to the maximum  $x$  of 4.3.

In the first region a smooth increase of the main line  $B_e$  with  $d_{\text{Mn-Mn}}$  is observed. This region corresponds to a single Mn moment value, possibly in an antiferromagnetic structure

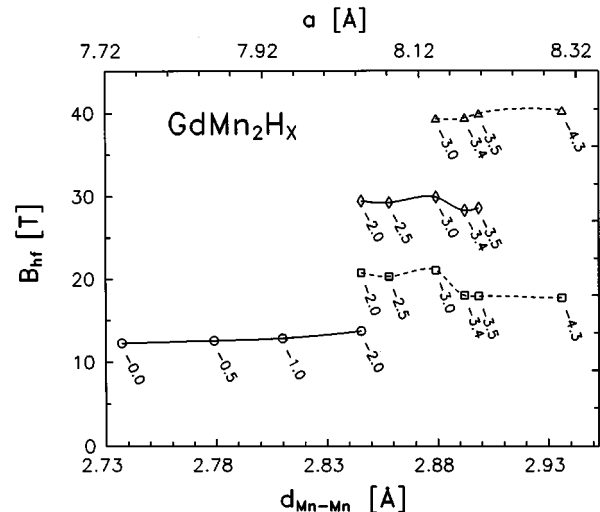


FIG. 2. The  $^{55}\text{Mn}$  hyperfine fields  $B_{\text{hf}}$  versus manganese-manganese nearest-neighbor distance  $d_{\text{Mn-Mn}}$ .

of the manganese sublattice. Weak satellite lines observed for  $x=2$  indicate appearance of some additional different values of  $B_e$  at this hydrogen content. The second region reflects changes of  $B_e$  values and a large increase of the number of Mn atoms with modified  $B_e$ . In the spectra for  $x=2.5$  and 3 the strongest lines correspond to much higher values of  $B_e$  than for  $x<2$ . For  $x=3$  the 314 MHz line becomes much more intense and an additional line centered at 413 MHz appears. In the third region, for  $x=3.4$  and 3.5 the spectra are very similar and the two lower lines are shifted towards lower fields comparing to the samples with  $x=2.5$  and 3. The fourth region includes the fully hydrided samples, where only two values of  $B_e$  are detected with their much narrower distributions reflected by their linewidths being much lower than for the other samples. It is worth noting here that the values of  $B_e$  corresponding to the uppermost lines in the third and fourth regions are more than three times larger than  $B_e$  in the host  $\text{GdMn}_2$  and a similar effect was observed for  $\text{YMn}_2$ .<sup>15</sup>

### DISCUSSION

In order to explain the observed changes in the spectra we have to consider the origin of the magnetic field at the Mn nucleus. Its induction  $B_e$  can be expressed as a sum:

$$B_e = B_{\text{hf}} + B_{\text{loc}}, \quad (1)$$

where  $B_{\text{hf}}$  is the hyperfine field and  $B_{\text{loc}}$  is the local magnetic field being usually of order of 1 T and including the Lorentz contribution and the dipolar contribution from the neighboring moments. As  $B_{\text{hf}}$  is usually dominant,  $B_e$  is often called synonymously the hyperfine field and abbreviated as HFF.  $B_{\text{hf}}$  consists of the core polarization term  $B_c$ , orbital field  $B_{\text{orb}}$ , and the valence electron contribution  $B_v$ :

$$B_{\text{hf}} = B_c + B_{\text{orb}} + B_v, \quad (2)$$

where  $B_c$  arises from the core electrons polarized by the moment of the parent atom,  $B_{\text{orb}}$  originates from the unquenched orbital moment of the 3d electrons and  $B_v$  is the contribution of the valence electrons polarized by the magnetic moments of the parent atom and magnetic neighbors.

The above contributions can be related to the corresponding partial magnetic moments  $\mu_i$  through the hyperfine coupling:  $B_i = A_i \mu_i$  where  $A_i$  are the hyperfine coupling constants and  $i$  stands for the  $c$ ,  $\text{orb}$ , or  $v$  indexes.

In both intermetallic compounds  $\text{GdMn}_2$  and  $\text{YMn}_2$  similar values of Mn hyperfine fields are found. If the manganese moments of  $2.7\mu_B$  in  $\text{YMn}_2$  and  $2.6\mu_B$  in  $\text{GdMn}_2$  were exclusively due to 3d electron spin, it would lead to hyperfine fields more than twice as large as are observed, since the hyperfine coupling constant  $A_c$  for the core polarization term is of  $-10 \text{ T}/\mu_B$ .<sup>17</sup> We tentatively explained the discrepancy as a result of compensation between the negative core polarization term  $B_c$  and the positive orbital field  $B_{\text{orb}}$  combined with the valence electron contribution  $B_v$  which is also positive.<sup>15</sup> The recent theoretical paper<sup>18</sup> reports a large and positive  $B_v$  for Mn in  $\text{YMn}_2$ . We assume that this interpretation is also valid for  $\text{GdMn}_2$ . Similar values of the hyperfine fields between the gadolinium-based and nonmagnetic yttrium-based compounds indicate also a negligible contribution to  $B_v$  from the Gd moments at zero-field measurements

as compared to the dominant self-contribution. The value of  $B_v$  in the NMR measurements at applied field<sup>3</sup> was estimated at 3 T.

Introduction of interstitial hydrogen causes a global effect of an increase of interatomic distances. However, in the analysis of the influence of hydrogen on local magnetic properties its chemical influence on the electronic structure via bonding effects has to be also considered. In our NMR studies of the interstitially modified magnetic materials (see review paper<sup>19</sup>) we find a large influence of the light interstitial atom neighbors such as N, C or H on the valence electron distribution and polarization. The influence becomes effective at the mutual distance comparable with the sum of atomic radii. It leads to a decrease of the valence electron density and polarization at the atom neighboring to a light interstitial one, and results in a change of its magnetic moment and the magnetic coupling with the neighbors. Such an effect was also observed for Mn in  $\text{YMn}_2\text{H}_x$  and the diversification of the hyperfine fields with hydrogen content  $x$  was detected already for  $x=1$ . For  $\text{GdMn}_2\text{H}_x$  those changes start at a higher  $x$  of 2 and a possible explanation of the difference, as already mentioned, is the influence of large Gd magnetic moments removing frustration of the antiferromagnetic manganese sublattice. An effect on the difference between the two systems could also have the slightly larger lattice constants of the corresponding Gd containing hydrides as compared to the Y-based ones, and, thus, a larger H-Mn distance and in consequence a weaker hydrogen influence on the Mn site.

For the hydrogen content  $x=3, 3.4$ , and 3.5 the three values of the hyperfine field reflect the presence of three groups of Mn moments in the compounds. In order to obtain a deeper insight into the origin of the three manganese magnetic moment values the NMR spin-echo spectrum for  $\text{GdMn}_2\text{H}_{3.5}$  was measured at an applied magnetic field of 1 T. The spectrum at 1 T compared to the zero field one reveals a shift of the lowermost 188 MHz line to higher frequencies, whereas the remaining two lines shift in the opposite direction.

The opposite direction of the shifts for the lower line from those for the two higher lines means the opposite sense of the hyperfine field of the lower line and the two upper lines. As the appearance of a positive hyperfine field with respect to the Mn moment direction is very unlikely because it would imply a huge, unphysical orbital moment or an enormous valence electron polarization, we conclude that all three lines correspond to a negative hyperfine field dominated by the core polarization contribution  $B_c$ . Thus, the shift of the two upper lines to lower frequencies corresponds to the two manganese moments having a considerable component parallel to the magnetization direction of the sample. Consequently, the lowermost line corresponds to the Mn moment with their component antiparallel to the other two and to the magnetization of the sample. Since in the recent x-ray magnetic circular dichroism measurements at the Gd  $L_3$  edge it was found that the Gd sublattice magnetization is dominant throughout the series,<sup>20</sup> the above effect means that the magnetic structure of the Mn sublattice here, unlike the host  $\text{GdMn}_2$  is not antiferromagnetic, but ferrimagnetic, as in  $\text{YMn}_2\text{H}_3$ .<sup>21</sup>

Having in mind that the influence of hydrogen neighbors tends to reduce the valence electron polarization of the Mn neighbors we can expect the highest number of hydrogen nearest neighbors for manganese atoms to correspond to the uppermost line for  $x=3.5$ . Assuming a complete suppression of the valence electron polarization and orbital contribution to the hyperfine field for these atoms and using  $A_c = -10 T/\mu_B$ ,<sup>17,18</sup> one comes to the value for the Mn moment of  $4\mu_B$ .

In the NMR spectra of rhombohedral  $GdMn_2H_{4.3}$  a two-line pattern is observed. This means that at low temperatures the compound is magnetically ordered, similar to the isostructural  $YMn_2H_{4.3}$ .<sup>11</sup> The weak intensity of the NMR signal and the recent magnetic measurements indicate an antiferromagnetic type of order. It is also confirmed by the recent Mössbauer results which show that  $GdMn_2H_{4.3}$  is magnetically ordered up to 145 °C.<sup>22</sup> From the very narrow lines in the NMR spectrum we conclude that the magnetic structure of the compound is a collinear, well compensated, antiferromagnetic one. In the cubic hydrides the lines are much broader reflecting more complex structures.

The two lines in the spectrum of  $GdMn_2H_{4.3}$  can be attributed to the two inequivalent manganese crystallographic sites  $3b$  and  $9e$  in this structure. Comparing the intensities of the lines with the site abundancies one can attribute the 186 MHz line which has a lower integral intensity to the  $3b$  site and the 423 MHz line to the  $9e$  site. The much different hyperfine fields indicate the difference between Mn moments on those sites possibly related with the difference of valence electron moments. As it was discussed above, assuming the pure spin origin of the hyperfine field for the upper 40 T line we arrive at the value of  $4\mu_B$  for the magnetic moment of Mn  $9e$  site.

## CONCLUSIONS

Four different regions of the magnetic structure of manganese sublattice and four different groups of Mn HFF reflecting the appearance of different Mn sites in  $GdMn_2H_x$  are observed with changing hydrogen content  $x$ . For  $x < 2$  a single value of HFF is obtained and some additional different HFF values appear at the hydrogen concentration  $x=2$ , higher than for the isostructural  $YMn_2H_x$ . The difference between  $YMn_2H_x$  and  $GdMn_2H_x$  is attributed to the influence of the Gd magnetic sublattice.

Three different Mn sites with similar population appear in the cubic hydride with  $x=3.5$ , two of them have moments with a component parallel to the total magnetization, and the third one has an antiparallel component.

A huge difference, more than a factor of 3, between the lowest and the highest hyperfine field in the series is attributed to the cancellation of the valence electron polarization. Significant differences of this contribution are attributed to the local influence of hydrogen neighbors.

The rhombohedral  $GdMn_2H_{4.3}$  is found to be magnetically ordered with the two inequivalent manganese crystallographic sites  $3b$  and  $9e$  in an antiferromagnetic structure. At least one of the manganese sites in  $GdMn_2H_{3.5}$  and  $GdMn_2H_{4.3}$  has a magnetic moment which is  $4\mu_B$  or larger.

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