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LETTER TO THE EDITOR

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Abstract
The results of neutron diffraction investigations of TbMn$_2$D$_2$ deuteride are
presented and analysed. The location of deuterium atoms in the lattice was
determined. Magnetic ordering in this compound appears below 300 K. The
magnetic structure can be described by the propagation vector $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$. The
Tb sublattice couples antiferromagnetically, with magnetic moments equal
to 4.8 μ_B, and the Mn sublattice is also coupled antiferromagnetically, with
different magnetic moments.

1. Introduction

The Laves phases RMn$_2$ (R = rare earth, Y and Th) exhibit a variety of new magnetic properties
associated with peculiarities of Mn magnetism, frustration related to the lattice symmetry
and interactions with rare-earth magnetic moments. These compounds crystallize in cubic
C15 ($Fd\bar{3}m$) and hexagonal C14 ($P6_3mmc$) structures at room temperature. The systems
easily absorb hydrogen, which locates in the interstitial positions. Hydrogen (deuterium)
introduced into these compounds not only causes distinct changes of their structures, but also
strongly influences their magnetic properties. It is well established that the hydrogen atoms
locate at the tetrahedral g-type interstitials. As a result, their unit cell at room temperature is
expanded in proportion to the hydrogen content, as has already been reported for YMn$_2$H$_x$ [1],
GdMn$_2$H$_x$ [2], DyMn$_2$H$_x$ [3] and SmMn$_2$H$_2$ [4]. However, the role of hydrogen, especially
in the modification of the magnetic structure, is still not clear. Many neutron diffraction
experiments have been performed on RMn$_2$D$_x$ deuterides at low temperatures. It is observed
that both magnetic and deuterium ordering take place, at the same temperature. For YMn$_2$D$_{1.15}$,
the magnetic and nuclear structures are described in the $P\bar{4}3m$ space group [5]. However, for
large values of the hydrogen concentration x, the magnetic ordering is accompanied by a
rhombohedral distortion. The propagation vector of the magnetic structure is $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ for all the
compounds, YMn$_2$D$_{4.5}$ [6, 7] and RMn$_2$H$_{4.5}$ (R = Y, Gd, Tb, Dy and Ho) [8, 9].

From the results of the neutron diffraction experiments on the $TbMn_2$ single crystal [10] we know that in this compound there exists a complicated noncollinear magnetic structure of antiferromagnetic type. To find out the influence of hydrogen (deuterium) on the magnetic structure of this compound we performed a neutron diffraction study for $TbMn_2D_2$ deuteride. This deuterium concentration was chosen on the basis of structural and magnetic investigations of the $TbMn_2H_x$ series [11]. For this concentration the hydride retains the cubic structure over the whole temperature range. The magnetic measurements gave evidence of a ferrimagnetic-type ordering with $M = 42$ G cm^3 g^{-1} at 4.2 K and 55 kOe field and the magnetic ordering temperature was 284 ± 6 K.

2. Experimental details

The sample was prepared from high-purity materials using the standard induction melting technique. Before deuteration the material was monitored by an x-ray technique. The deuteration was carried out using the standard technology described in e.g. [1]. The x-ray measurements on the prepared sample were performed at room temperature on a SIEMENS D5000 diffractometer using Cu Kα radiation ($\lambda = 1.540\,56$ Å). The measurements proved that the sample consisted of a single phase of C15 Laves-phase-type structure ($Fd\bar{3}m$) with a small admixture (less than 1%) of the Tb_2O_3 oxide. The sample used for the experiment was powdered, with a mean grain size of about 50 μm.

The neutron diffraction experiments were performed at ILL using the high-resolution diffractometer D1A with an incident neutron wavelength $\lambda = 1.9114$ Å. The data were collected at temperatures of 1.5 K, 100 K, 200 K and 320 K in the angular range $0 < 2\theta < 160°$. The fitting and refinement of the diffraction spectra were performed using the FULLPROF program based on the Rietveld method [12]. The scattering lengths used in the refinement were taken from the internal table of the FULLPROF program: $b_{Tb} = 0.738 \times 10^{-12}$ cm, $b_{Mn} = -0.6671 \times 10^{-12}$ cm, $b_D = 0.6671 \times 10^{-12}$ cm. The form factors were also taken from the FULLPROF manual: for Mn^{3+}, $\langle j_0 \rangle$ was used, while for Tb, $\langle j_0 \rangle + c_2 \langle j_0 \rangle$ was used, where c_2 was calculated in the dipolar approximation.

3. Results

The diffraction pattern obtained at 320 K (figure 1) is characteristic for nuclear Bragg reflections associated with $MgZn_2$-type structure ($Fd\bar{3}m$) with the lattice parameter $a = 7.955(2)$ Å. This is in very good agreement with the value 7.948(4) Å obtained from the x-ray measurement using FULLPROF refinement as well. In addition to the Tb- and Mn-atom positions in the lattice, which were obtained from the x-ray data, it was possible to determine the positions of the deuterium atoms in the structure, from the neutron diffraction patterns. They are randomly distributed at 96g sites and shifted from the centre of 2Mn–2Tb tetrahedra. The calculated position of the deuterium atoms is then (x, y, z), with $x = 0.42(2)$, $y = 0.42(2)$, $z = 0.14(1)$, and with the origin of the unit cell at the centre ($\bar{3}m$). The agreement between the calculated and observed pattern is very good, with a Bragg reliability factor $R_B = 4\%$.

At 1.5 K, in addition to the nuclear Bragg peaks, new reflections characteristic of the magnetic ordering are observed (figure 2). They can be indexed with the propagation vector $k = [\frac{1}{2} \frac{1}{2} \frac{1}{2}]$, leading to a magnetic cell eight times larger than the chemical one. The low-temperature magnetic structure was determined by trying different models of collinear and noncollinear arrangements. The only model which gave a good fit of the neutron data can be described as follows. All the magnetic moments pointing along the [110] direction are
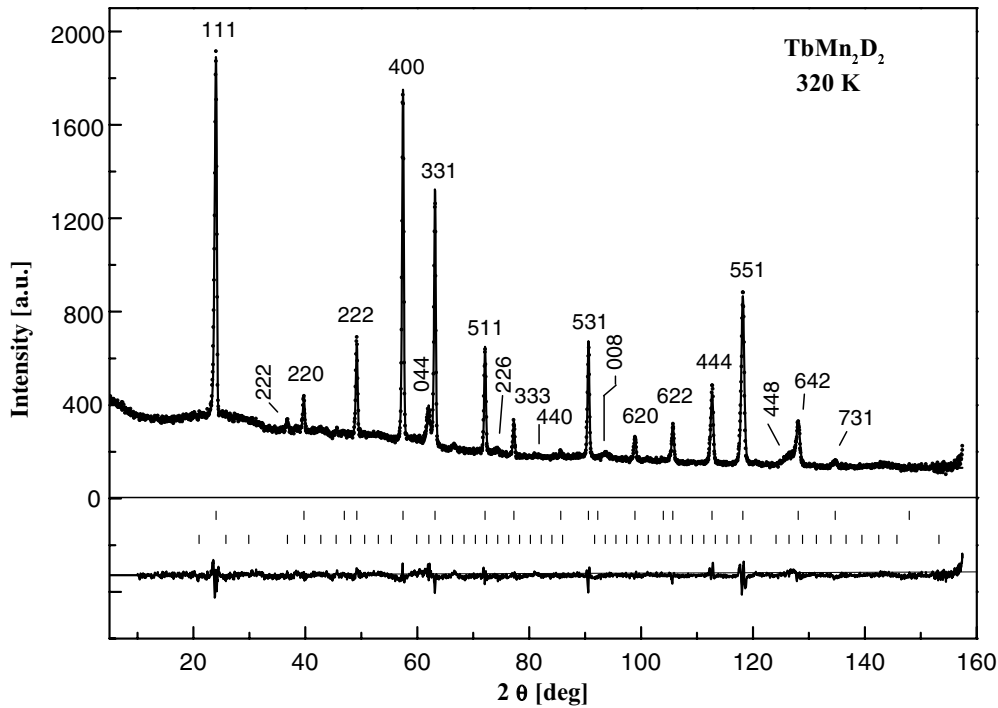
Figure 1. The neutron diffraction pattern taken at 320 K with the indexed lines for the $Fd\bar{3}m$ structure and the Tb_2O_3 oxide.

in the (111) planes perpendicular to the propagation vector. The magnetic structure can be described as a stacking of ferromagnetic (111) layers, where there is antiferromagnetic coupling between successive layers. We deduced this taking it into account that with a propagation vector $k = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$, the first magnetic peak $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ is very relevant for the determination of the direction of the magnetic moments. The multiplicity of this reflection in the powder pattern is 8, but the only nonzero reflection for this peak is that at $\pm(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, whereas the remaining reflections at $\pm(\frac{\bar{1}}{2}\frac{1}{2}\frac{1}{2})$, $\pm(\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2})$ and $\pm(\frac{1}{2}\frac{1}{2}\frac{\bar{1}}{2})$ are exactly zero because the fcc lattice translations are antitranslations for the propagation vector $k = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$. Having in mind that the proposed solution might not be unique, we assume our model as the most probable. In figure 2 only the magnetic reflections are indexed. No crystal distortion is observed in the nuclear reflections. The results of the refinement are presented in table 1. The refinement carried out with one Mn crystallographic site gives a magnetic reliability factor of $R_M = 13\%$. However, the refinement is significantly improved when using a rhombohedral description of the four positions of the Mn atoms. That is, Mn_1 possess a magnetic moment of 3.3(1) μ_B, while Mn_2, Mn_3 and Mn_4 have the same magnetic moment of 1.2(1) μ_B, and the Tb magnetic moment has a value of 4.8(1) μ_B. The magnetic reliability factor reaches $R_M = 8.5\%$. The values obtained from the fit are presented in table 1. It is important to mention that at low temperature, the background is not flat, but indicates the persistence of short-range correlation. The diffraction patterns taken at 100 K and 200 K consist of the same magnetic peaks as were observed at 1.5 K, with magnitudes decreasing with temperature. The fits gave the same magnetic structure at 100 K and 200 K as for 1.5 K with magnetic moments of Tb of 4.1(1) μ_B and 3.6(1) μ_B respectively. The Mn magnetic moments remained almost unchanged (at 100 K,
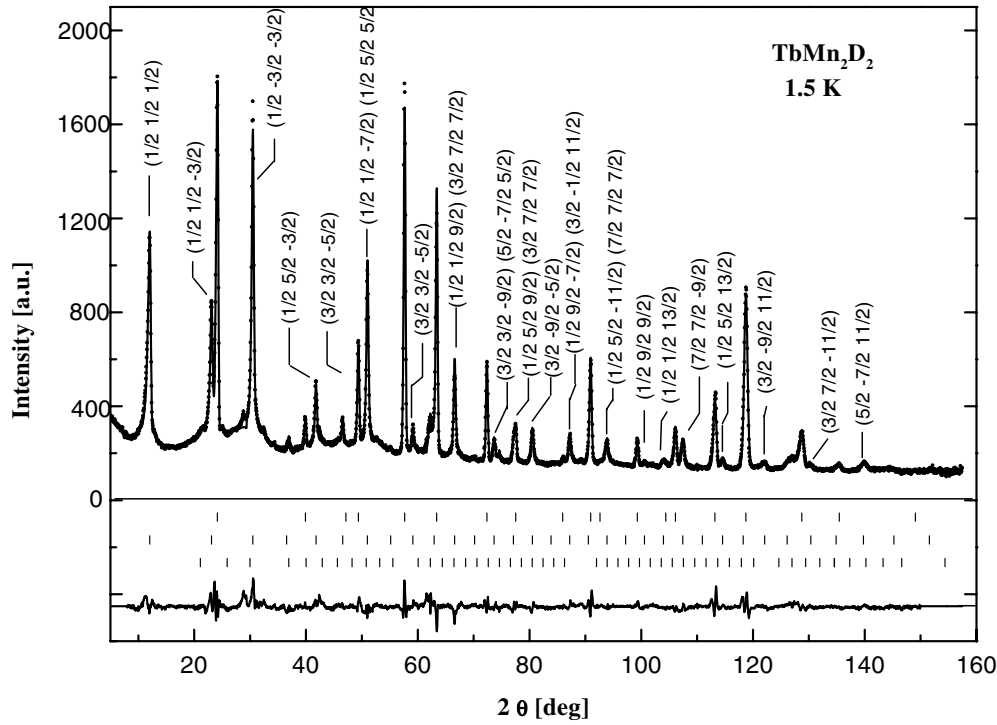
Figure 2. The neutron diffraction pattern taken at 1.5 K with the indexed lines for the magnetic structure only. The structural lines are the same as in figure 1.

Table 1. $TbMn_2D_2$ at 1.5 K. Lattice constant $a = 7.934$ Å. Propagation vector $k = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$. Fitted position of deuterium (at 300 K): (0.42, 0.42, 0.14).

| Atom	Magnetic moment (μ_B)			
	M_x	M_y	M_z	M
Tb_1	3.38	−3.38	0	4.8(1)
Tb_2	−3.38	3.38	0	4.8(1)
Mn_1	−2.30	2.30	0	3.3(1)
Mn_2	0.85	−0.85	0	1.2(1)
Mn_3	0.85	−0.85	0	1.2(1)
Mn_4	−0.85	0.85	0	1.2(1)

$Mn_1 = 3.0(1)$, $Mn_{-2,-3,-4} = 0.8(1)$, while at 200 K, $Mn_1 = 3.4(1)$, $Mn_{-2,-3,-4} = 1.0(1)$). The magnetic reliability factors were $R_M = 19\%$ and 23% for 100 K and 200 K respectively.

4. Discussion

The positions of deuterium atoms not being in the centre of the 2Tb–2Mn tetrahedra obtained in our experiment is in agreement with similar observations for YMn_2D_x deuterides [7]. More interesting and unexpected however is the magnetic structure. It is much simpler than for pure $TbMn_2$, where precise measurements on the single crystal [10] gave a complicated magnetic structure, which appeared to be metastable, poised between the structure S_1 with propagation

vector $[\frac{2}{3}\frac{2}{3}0]$ and another structure S_2 with propagation vector $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$. A similar collinear magnetic structure has been proposed for $TbMn_2H_{4.3}$ [8]. So it seems that the expansion of the unit cell caused by deuterium leads to simplification and stabilization of the magnetic structure. In figure 3 a view of the proposed magnetic structure is presented. The magnetic structure for the $TbMn_2D_2$ deuteride investigated is also different to and simpler than that proposed for a single-phase $YMn_2D_{1.15}$ deuteride [5], which suggests that, like the deuterium, the Tb sublattices play an important role in stabilizing this magnetic structure.
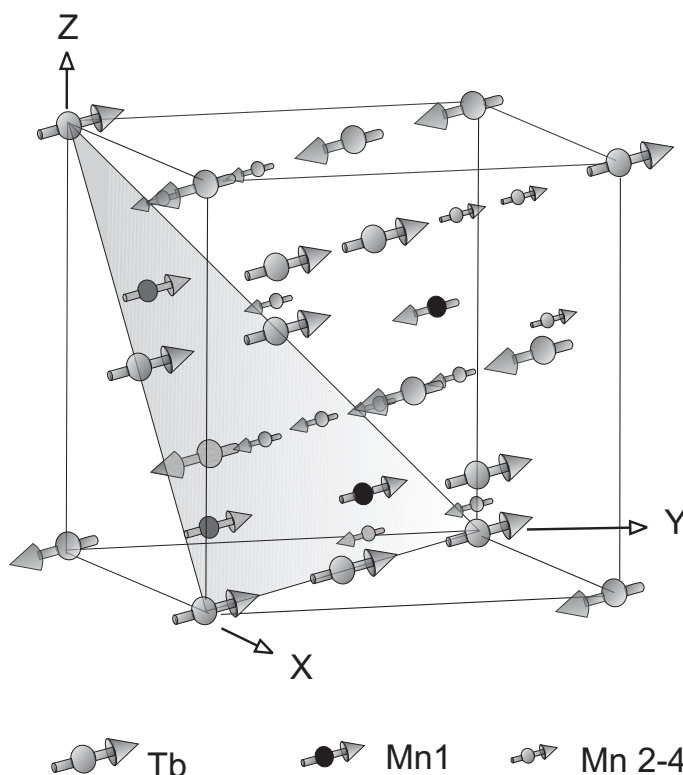
Figure 3. A view of the magnetic structure. The shaded area is the (111) plane.

The values of the Mn moments ($Mn_{2,3,4}$; table 1) are larger than those of the moments in $Tb(Mn_{0.96}Fe_{0.04})_2$ [10]. Such an increase of the Mn magnetic moments can result from the increase of the Mn–Mn distances caused by deuterium, due to the more highly localized character of the Mn magnetic moments. The observation of smaller magnetic moments (1.2 μ_B) at three Mn sites and a bigger one for the fourth Mn site (3.3 μ_B) can also be correlated with deuterium content. The bigger magnetic moments are possessed by the Mn atoms with deuterium atoms as nearest neighbours, whereas the rest of the Mn atoms with no D in the NN shell have smaller magnetic moments. Such an interpretation finds support from NMR investigations. In the NMR measurements on ^{55}Mn nuclei in YMn_2H_x [13, 14] and in $GdMn_2H_x$ [15] for $x = 2$, two clear resonant lines were observed: one at the position corresponding to the pure compound; and a second weaker satellite line at a frequency about two times higher. This supports our interpretation, that there exist Mn atoms with different magnetic moments. In the neutron diffraction study [8] of $TbMn_2D_{4.5}$ the Mn magnetic moments are even bigger (3.6 and 2.8 μ_B). It is worth noting also that the Mn_1 moments

being different from each other can be understood if one takes into account the frustration problem. The Mn moments tend to have an antiferromagnetic coupling and, in the C15 structure, this leads to well known frustration effects such as crystal distortion. This distortion lowers the local symmetry of Mn-atom sites and eliminates frustration, but on the other hand leads to a complicated magnetic structure, as was found in $TbMn_2$ [10]. Another possibility for eliminating frustration while maintaining unchanged crystal structure and symmetry is to have different Mn moments, and such a case is observed for the $TbMn_2D_2$ system. The Mn magnetic moments seem not to change as functions of temperature, which corresponds well to the behaviour observed in $TbMn_2H_{4.3}$ [8], where slightly smaller values of the Mn magnetic moments at $\sim$100 K were also observed.

From the fit presented we have Tb magnetic moments at 1.5 K equal to 4.8 μ_B, which is much less than the values obtained for $TbMn_2$ (8.7 μ_B) [10] and for $TbMn_2D_{4.5}$ (9 μ_B) and also the free-ion value. Due to the properties of the Tb magnetic moments and their local character, one should expect for $TbMn_2D_2$ a value that is also about 9 μ_B. Thus we have also made an attempt to fit the spectrum with Tb magnetic moments fixed at the value 8.7 μ_B as for the $TbMn_2$ compound [10]. As a result, the arrangement of the magnetic moments remained unchanged, and the values of the Mn moments were different: $\mu(Mn_2) = \mu(Mn_3) = \mu(Mn_4) = 0.82\ \mu_B$, whereas $\mu(Mn_1)$ increased to 5.89 μ_B, and the magnetic reliability factor was $R_M = 11.3\%$. In this case we got a very big magnetic moment for Mn_1, which is in fact almost equal to the value, $p_{eff} = 5.9\ \mu_B$, for the Mn^{2+} ion, but it is difficult to accept this here, because the maximal value of the Mn moment (3.9(5) μ_B) is reported for $HoMn_2D_{4.5}$ [8]. Also, in the NMR data mentioned above [13–15] for $x = 2$, there are no traces of corresponding high-frequency resonant lines, and only for $x \sim 4$ is a value of the Mn moment of about 4 μ_B suggested, which in fact agrees well with the conclusions from neutron diffraction data [8]. So we need instead to explain the small values of the Tb magnetic moments. Assuming them to have weak magnetic coupling and a stronger temperature dependence than for $TbMn_2D_{4.5}$, we can envisage them fluctuating or rotating at 1.5 K to get the fitted value of 4.8 μ_B. The crystal-field influence due to the cubic symmetry can be neglected, but the presence of deuterium atoms in the NN shell can lower the local symmetry and as a result also influence the Tb magnetic moment. The low value of the Tb magnetic moment can also be explained by the presence of the strong diffuse scattering observed at low temperature due the partial disorder of the Tb moments. In contrast to the Mn magnetic moments, the Tb moments decrease with temperature, which is also in agreement with their behaviour observed in $TbMn_2H_{4.3}$ [8]. The higher magnetic reliability factors for elevated temperatures can be related to the decrease of the relative intensity of the reflections.

It is also interesting that the mean magnetic moment per formula unit as calculated from the neutron data equals $\mu = 1.05\ \mu_B$/f.u., which is in agreement with the results from the magnetization measurements on $TbMn_2D_2$ ($\mu = 0.95\ \mu_B$/f.u. at 5.5 T and 4.2 K) [16].

References

[1] Figiel H, Przewoźnik J, Paul-Boncour V, Lindbaum A, Gratz E, Latroche M, Escorne M H, Percheron-Guegan A and Mietniowski P 1998 *J. Alloys Compounds* **274** 29
[2] Żukrowski J, Przewoźnik J, Krop K, Strecker M and Wortmann G 1997 *J. Alloys Compounds* **261** 47
[3] Przewoźnik J, Żukrowski J, Freindl K, Japa E and Krop K 1999 *J. Alloys Compounds* **284** 31
[4] Figiel H, Budziak A and Żukrowski J 1999 *Solid State Commun.* **111** 519

[5] Latroche M, Paul-Boncour V, Percheron-Guegan A, Bourée-Vigneron F and Andre J 2000 *Physica* B **276–278** 666

[6] Latroche M, Paul-Boncour V, Percheron-Guegan A and Bourée-Vigneron F 1998 *J. Alloys Compounds* **274** 59

[7] Latroche M, Paul-Boncour V, Przewoźnik J, Percheron-Guegan A and Bourée-Vigneron F 1995 *J. Alloys Compounds* **231** 99

[8] Goncharenko I N, Mirebeau I, Irodova A V and Suard E 1999 *Phys. Rev.* B **59** 9324

[9] Makarova O L, Goncharenko I N and Mirebeau I 1999 *Phys. Rev.* B **59** 11 826

[10] Brown P J, Ouladdiaf B, Ballou R, Deportes J and Makrosjan A S 1992 *J. Phys.: Condens. Matter* **4** 134

[11] Figiel H, Budziak A, Żukrowski J, Kelemen M C, Fischer G and Dormann E 2001 to be published

[12] Rodriguez-Carvajal J 1990 *Satellite Mtg on Powder Diffraction of the 15th Congr. of the International Union of Crystallography (Toulouse, France, 1990)* abstracts, p 127

[13] Kapusta Cz, Przewoźnik J, Żukrowski J, Spiridis N, Figiel H and Krop K 1990 *Hyperfine Interact.* **59** 353

[14] Figiel H, Kapusta Cz, Spiridis N, Riedi P C and Lord J S 1993 *Z. Phys. Chem.* **179** 467

[15] Kapusta Cz, Przewoźnik J, Żukrowski J, Figiel H, Lord J S, Riedi P C, Paul-Boncour V, Latroche M and Percheron-Guegan A 1996 *Phys. Rev.* B **54** 14 922

[16] Leyer S, Fischer G, Dormann E, Budziak A and Figiel H 2001 *J. Phys.: Condens. Matter* at press