Critical magnetic transition in TbNi$_2$Mn—magnetization and Mössbauer spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2011 J. Phys.: Condens. Matter 23 216002
(http://iopscience.iop.org/0953-8984/23/21/216002)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 159.226.35.191
The article was downloaded on 29/10/2011 at 07:54

Please note that terms and conditions apply.
Critical magnetic transition in TbNi$_2$Mn—magnetization and Mössbauer spectroscopy

J L Wang$^{1,2}$, S J Campbell$^1$, S J Kennedy$^2$, R Zeng$^3$, S X Dou$^3$ and G H Wu$^4$

$^1$ School of Physical, Environmental and Mathematical Sciences, The University of New South Wales, The Australian Defence Force Academy, Canberra ACT 2600, Australia
$^2$ Bragg Institute, ANSTO, Lucas Heights, NSW 2234, Australia
$^3$ Institute for Superconductivity and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia
$^4$ Institute of Physics, Chinese Academy of Science, Beijing 100190, People’s Republic of China

Received 24 January 2011, in final form 15 March 2011
Published 9 May 2011
Online at stacks.iop.org/JPhysCM/23/216002

Abstract
The structural and magnetic properties of the TbNi$_2$Mn$_x$ series (0.9 $\leq$ x $\leq$ 1.10) have been investigated using x-ray diffraction, field- and temperature-dependent AC magnetic susceptibility, DC magnetization (5–340 K; 0–5 T) and $^{57}$Fe Mössbauer spectroscopy (5–300 K). TbNi$_2$Mn$_x$ crystallizes in the MgCu$_2$-type structure (space group $Fd\bar{3}m$). The additional contributions to the magnetic energy terms from transition-metal–transition-metal interactions (T–T) and rare-earth–transition-metal interactions (R–T) in RNi$_2$Mn compounds contribute to their increased magnetic ordering temperatures compared with RNi$_2$ and RMn$_2$. Both the lattice constant $a$ and the Curie temperature $T_C$ exhibit maximal values at the x = 1 composition indicating strong magnetostructural coupling. Analyses of the AC magnetic susceptibility and DC magnetization data of TbNi$_2$Mn around the Curie temperature $T_C = 147$ K confirm that the magnetic transition is second order with critical exponents $\beta = 0.77 \pm 0.12$, $\gamma = 1.09 \pm 0.07$ and $\delta = 2.51 \pm 0.06$. These exponents establish that the magnetic interactions in TbNi$_2$Mn are long range despite mixed occupancies of Tb and Mn atoms at the 8a site and vacancies. The magnetic entropy $-\Delta S_M$ around $T_C$ is proportional to $(\mu_0 H / T_C)^{2/3}$ in agreement with the critical magnetic analyses. The Mössbauer spectra above $T_C$ are fitted by two sub-spectra in agreement with refinement of the x-ray data while below $T_C$ three sub-spectra are required to represent the three inequivalent local magnetic environments. (Some figures in this article are in colour only in the electronic version)

1. Introduction
Interest in rare-earth–transition-metal (R–T) intermetallic compounds has continued unabated in recent years due in part to their continuing technological importance and potential applications (e.g. [1, 2]). Compounds rich in the rare earths have attracted interest as several series exhibit a large magnetocaloric effect (e.g. [3]). Compounds of rare earths with Mn such as RMn$_2$X$_2$ (X = Ge or Si) [4] and RMn$_2$ [5] are of particular interest due to the interplay between the 3d and 4f magnetism and the sensitive dependence of the Mn moment and sublattice structures on the Mn–Mn interatomic distances. In the RMn$_2$ system, for example, there is a critical Mn–Mn spacing $d_{Mn–Mn} ($~2.66 Å) below which the Mn moments become unstable [5]. Substitution of a third element for Mn can lead to significant modification of the magnetic properties leading to the development of materials with interesting magnetic and physical properties (e.g. [2, 6, 7]). RNi$_2$Mn compounds with R = Tb, Dy, Ho and Er have been reported to crystallize in the MgCu$_2$-type structure of space group $Fd\bar{3}m$ with TbNi$_2$Mn$_2$ found to exhibit the largest magnetic ordering temperature $T_C$ [8, 9]. For TbNi$_2$Mn, Wang...
et al [9] reported mixed occupancies of Ni (74%) and Mn (26%) at the 16d sites with mixed occupancies of Tb (74%) and Mn (22%) at the 8a site together with 4% vacant 8a sites. Jackson et al [10] also reported that TbNi2Mn has the MgCu2-type structure, although Mushnikov et al [11] concluded that the crystal structure of TbNi2Mn is described by the AuBe5-type structure of space group Fd3m. Table 1 lists the main preparation conditions for these TbNi2Mn samples along with structural information and magnetic transition temperatures. It is interesting to note that despite the nominal compositional equivalence and similarities in heat treatments, the TbNi2Mn samples exhibit lattice parameters ranging from 7.123 Å [10] to 7.184 Å [11] with Curie temperatures ranging from TC ∼ 131 K [9] to TC ∼ 151 K [10]. The high vapour pressure of Mn (leading to possible variations in the nominal Mn composition under different preparation and heat treatment conditions), together with the sensitive dependence of the Mn magnetism on Mn–Mn interatomic distances [5–7] is likely to contribute to the observed range in properties. Moreover, RNi2Mn has been found to exhibit considerably higher Curie temperatures than the corresponding isostructural compounds RNi3 and RMn2 [9]. TbNi2Mn, has been found to exhibit the highest Curie temperature with reported values in the range TC ∼ 140 (±10) K (table 1) compared with TC ∼ 37.5 K and TC ∼ 54 K for TbNi3 and TbMn2, respectively [9].

In order to clarify the factors that contribute to the range of structural and magnetic properties reported for TbNi2Mn (table 1), we have carried out a systematic investigation of a series of TbNi2Mn1–x compounds (0.9 ≤ x ≤ 1.10) prepared in the same manner. A further aim of the present work is therefore to clarify the magnetic interactions occurring in TbNi2Mn compared with TbNi2 and TbMn2 to account for this increased Curie temperature. The samples have been investigated by x-ray and neutron diffraction, DC magnetization, AC susceptibility (5–340 K) and Mössbauer spectroscopy (5–300 K). Critical exponent analyses have been applied successfully to investigate the magnetic behaviour of a wide range of materials (e.g. La1−xA15 MCO3 [12], TbCo2 and TbCo1+yFe1−y [13], R1−xA2O3 [14], La0.7Ca0.3MnO3, Tl2Mn2O7, Ni–Mn–Ga, and CeFe2-related compounds [14–17]); here we apply a similar approach in detailed critical analyses of the magnetic phase transition at TC in TbNi2Mn.

### 2. Experimental details

The TbNi2Mnx (x = 0.90, 0.97, 1.00, 1.03 and 1.10), Tb1−xNi3 (y = 0.00, 0.02 and 0.05) and TbMn2 samples were prepared using starting elements of purities ≥99.9%. Ingots of mass ∼2 g were prepared at UNSW@ADF with standard argon arc-melting procedures with each ingot melted at least five times for improved homogeneity. The TbNi2Mnx(57Fe) sample for the Mössbauer study was prepared from an ingot doped with ∼0.5 wt% 57Fe. We have also investigated the behaviour of an ∼8 g TbNi2Mn sample (identified as TbNi2Mn∗). This relatively large sample was prepared at the Institute of Physics, Beijing in a similar manner (argon arc-melting with five melts for improved homogeneity) for forthcoming neutron diffraction experiments. All samples, which have been studied in the as-prepared state, were characterized by x-ray diffraction (Cu Kα radiation; λ = 1.5418 Å). The structure of the TbNi2Mn∗ sample was further checked by neutron diffraction at 300 K (high intensity diffractometer Wombat, OPAL, Lucas Heights; λ = 2.4072 Å) for comparison with the x-ray diffraction data. Magnetization measurements were carried out over the temperature range 5–340 K in a superconducting quantum interference device (SQUID) magnetometer (μ0H = 0–5 T). The DC field dependences of the magnetic AC susceptibility were recorded using a conventional physical properties measurement system (PPMS-9, Quantum Design, μ0H = 0–8 T) over the temperature range 5–340 K. The 57Fe Mössbauer spectra were obtained between 5 and 300 K using a standard constant acceleration spectrometer and a 57CoRh source. The spectrometer was calibrated at room temperature with an α-iron foil.

### 3. Results and discussion

#### 3.1. Structural properties

Figure 1(a) shows the x-ray diffraction patterns of the set of five TbNi2Mnx samples (x = 0.90, 0.97, 1.00, 1.03 and 1.10) studied in the as-prepared state. All samples can be indexed with the MgCu2-type structure (Fd3m) in which Cu is located at the 16d site and Mg at the 8a site [5, 8]. A small impurity phase of <2% (reflections around 2θ ∼ 29°) is observed, as in the case of HoNi2Mn and ErNi2Mn [9].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Preparation conditions</th>
<th>Space group</th>
<th>Lattice parameter a (Å)</th>
<th>TC (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbNi2Mn</td>
<td>MgCu2 (C15)</td>
<td>Annealed at 750 °C for 7 days</td>
<td>Fd3m</td>
<td>7.158</td>
<td>131</td>
<td>[9]</td>
</tr>
<tr>
<td>TbNi2Mn</td>
<td>MgCu2 (C15)</td>
<td>Annealed at 900 °C for 5 days</td>
<td>Fd3m</td>
<td>7.123</td>
<td>151</td>
<td>[10]</td>
</tr>
<tr>
<td>TbNi2Mn</td>
<td>AuBe5 (C15b)</td>
<td>Annealed at 870 °C for 7 days</td>
<td>F43m</td>
<td>7.1842</td>
<td>142</td>
<td>[11]</td>
</tr>
<tr>
<td>TbNi2Mn, with x = 0.25, 0.5, 0.75</td>
<td>MgCu2 (C15)</td>
<td>Annealed at 870 °C for 7 days</td>
<td>Fd3m</td>
<td>7.149, 144, Present work</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TbNi2Mn, with x = 0.89, 0.97, 1.00, 1.03, 1.10</td>
<td>MgCu2 (C15)</td>
<td>As-prepared</td>
<td>Fd3m</td>
<td>7.177, 149,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.202, 150,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.190, 145,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.190, 141,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TbNi2Mn∗</td>
<td>MgCu2 (C15)</td>
<td>As-prepared</td>
<td>Fd3m</td>
<td>7.178</td>
<td>147</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Figure 1. (a) X-ray diffraction patterns for as-prepared TbNi$_2$Mn$_x$ samples with $x = 0.90, 0.97, 1.0, 1.03$ and $1.10$. (b) Room temperature neutron diffraction pattern of the as-prepared TbNi$_2$Mn$^*$ sample ($\lambda = 2.4072$ Å). The full line through the data corresponds to the Rietveld refinement with the residuals line also shown. The Bragg peak positions are indicated by the markers.

The skewing of the high angle peaks indicates the presence of large strains in these unannealed samples. As discussed below, it is noted that the (200) reflection of space group (F43m) [11] is absent for all the TbNi$_2$Mn$_x$ samples of figure 1(a). The lattice constants were derived using the Le Bail method with a maximum indicated around the Mn composition $x \sim 1.0$ (figure 2(a)). Similar behaviour has been detected in ErNi$_2$Mn$_x$ [18] and Zr$_x$Co$_2$ [19].

Mushnikov et al [11] observed additional (200) and (420) reflections in the room temperature and 4.2 K neutron diffraction patterns of TbNi$_2$Mn$^*$ annealed at 870°C for 7 days. They concluded that the crystal structure of TbNi$_2$Mn is described by the AuBe$_5$-type structure of space group F43m, a superstructure of Fd$ar{3}$m. It should be noted that a (200) peak can also be discerned with Cu Ka radiation for a TbNi$_2$Mn sample annealed at 750°C for 7 days [9] and with Cr Ka radiation for TbNi$_2$Mn annealed at 870°C for 7 days [11]. On the other hand, a (200) peak is not observed with Cr Ka radiation for their other TbNi$_2$Mn$_x$ samples with $x = 0.25$, 0.50 and 0.75 annealed at 870°C for 7 days [20]. Given the absence of the (200) reflection in the present as-prepared TbNi$_2$Mn$_x$ samples which exhibit the MgCu$_2$-type structure, it is clear that the final structure adopted by TbNi$_2$Mn$_x$ compounds depends sensitively on the preparation conditions, the Mn composition and the sample heat treatments. The MgCu$_2$-type structure is obtained for random distributions of Tb and Mn in the 8a site and Ni and Mn in the 16d site [9], whereas site ordering leads to the AuBe$_5$-type structure with Tb in the 4c site, Tb and Mn in the 4a site and Ni and Mn distributed in the 16e site [11]. The occurrence of vacancies is also likely to influence the structure: while 4% of vacant 8a sites were reported for the MgCu$_2$-type structure for TbNi$_2$Mn [9], optimal refinements to the AuBe$_5$-type structure resulted in the off-stoichiometric composition TbNi$_2$Mn$_{0.95}$.81, with the introduction of vacancies leading to an increase in the refinements’ agreement factors [11]. Similar behaviour—with sensitive dependence of the structure on composition and sample preparation conditions—has also been exhibited by the RNi$_2$ system [21], where a temperature-induced phase transition (and pressure-induced transition for YNi$_2$) is detected from F43m to Fd$ar{3}$m [21]. A full crystallographic investigation of the conditions under which the different structures are obtained for TbNi$_2$Mn–MgCu$_2$-type or AuBe$_5$-type—and the factors governing the transformation from one structure to the other—is required.

The room temperature neutron diffraction pattern for the TbNi$_2$Mn$^*$ sample is shown in figure 1(b). Since the
neutron-scattering lengths of Tb, Ni and Mn atoms are substantially different [11], the neutron pattern is expected to demonstrate more clearly the differences between the space groups $Fd\bar{3}m$ and $F4\bar{3}m$, as mentioned in [11], via, for example, the presence or absence of reflections such as (200) and (420). As expected on the basis of our x-ray diffraction example, the presence or absence of reflections such as (200) is expected to demonstrate more clearly the differences between the space groups $Fd\bar{3}m$ and $F4\bar{3}m$, as mentioned in [11], via, for example, the presence or absence of reflections such as (200) and (420). As expected on the basis of our x-ray diffraction example, the presence or absence of reflections such as (200) confirms that the space group of the as-prepared TbNi$_2$Mn$^*$ sample is $Fd\bar{3}m$. The quality of fit parameters are as follows: pattern factor, $R_p = 3.24\%$; weighted pattern factor, $R_w = 4.23\%$; and expected pattern factor, $R_{\text{exp}} = 0.53\%$.

3.2. Magnetic behaviour

The magnetic behaviour of all TbNi$_2$Mn$_x$ samples ($x = 0.90, 0.97, 1.00, 1.03$ and $1.10$) has been investigated. Given the ~8 g available for the as-prepared TbNi$_2$Mn$^*$ sample, we chose to investigate this sample in detail to ensure consistency for measurements using a variety of magnetic methods.

Figure 3(a) shows the temperature dependences of the low field DC magnetization ($\mu_0 H = 0.005$ T) for TbNi$_2$Mn$^*$ on warming and cooling after first cooling in zero field (ZFC). The Curie temperatures $T_C^{\text{DC}}$ for all TbNi$_2$Mn$_x$ samples were determined as the temperature at which the $dM/dT$ versus $T$ curve exhibits a minimum (e.g. inset to figure 3(a)). The $T_C$ values for the set of TbNi$_2$Mn$_x$ samples (figure 2(b)) exhibit a similar dependence on Mn concentration to the lattice parameter $a$ (figure 2(a)) with a maximum around $x = 1.0$. The compositional dependences of $a$ and $T_C$ indicate that the distance of separation of Mn atoms plays a critical role in governing the magnetic behaviour of TbNi$_2$Mn$_x$.

The changes in transition temperature resulting from a change in the unit cell volume due to the variation of Mn composition can be estimated from recent pressure studies of TbNi$_2$Mn [10]. Assuming that values of $B_0$, the bulk modulus and $dT_C/dP$, the rate of change of transition temperature with pressure $P$, do not change significantly with Mn composition in TbNi$_2$Mn$_x$, and using $B_0 = 128$ GPa and $dT_C/dP = -1.96$ K GPa$^{-1}$ for TbNi$_2$Mn [10], the change of $T_C$ with $x = 1.0$ (unit cell volume $V = 373.5$ Å$^3$) is estimated as $\Delta T_C \sim 5.4$ K. This calculated change in the critical temperature—based solely on the volume change of $\Delta V/V = 2.17\%$ from TbNi$_2$Mn$_{0.9}$ to TbNi$_2$Mn$_{1.0}$—compares well with the experimentally measured difference of $\Delta T_C \sim 7 \pm 1$ K (figure 2(b)) and confirms the occurrence of strong magnetostructural coupling in TbNi$_2$Mn$_x$.

For a given set of preparation conditions, differences in $T_C$ values for TbNi$_2$Mn$_x$ (table 1) are concluded to be due mainly to the concentration of Mn atoms and chemical pressure effects related to variations in the spacing between magnetic atoms. This is evident in the case of TbNi$_2$Mn.
Independent of the $T_C$ value for a particular sample, a key feature in the magnetism of TbNi$_2$Mn compared with TbNi$_2$ and TbMn$_2$ is the significantly higher transition temperature exhibited by TbNi$_2$Mn ($T_C \sim 140$ (10) K) compared with those of TbNi$_2$ ($T_C \sim 37.5$ K) and TbMn$_2$ ($T_C \sim 54$ K) [9, 21, 22]. Figure 3(c) shows a graph of $T_C$ values versus the de Gennes factor, $G_R = (g - 1)^2 J / (J + 1)$, for RNi$_2$Mn [9], RNi$_2$ [22, 23] and RMn$_2$ [24]. There are three exchange interactions in R–T compounds: indirect R–R interactions, indirect R–T interactions and direct T–T interactions. According to a molecular field approach, the Curie temperature $T_C$ in R–T compounds can be expressed by [25, 26]

$$
T_C = \frac{T_{T–T} + T_{R–R} + \sqrt{(T_{T–T} - T_{R–R})^2 + 4T_{G–T}^2}}{2},
$$

where $T_{T–T}$, $T_{R–R}$ and $T_{R–T}$ represent the contributions to $T_C$ resulting from the T–T, R–R and R–T interactions, respectively. $T_{T–T}$, $T_{R–R}$ and $T_{R–T}$ are given by the microscopic exchange coupling parameters $A_i$ (i, j = R, T) where $T_{T–T} = \frac{2\Delta_0}{2\Delta_0 + 1}$, $T_{R–R} = \frac{2\delta_0}{2\delta_0 + 1}$, and $T_{R–T} = \frac{2\mu_0}{2\mu_0 + 1}$.

Here $Z_{i–j}$ is the number of j atoms nearest the i atom (for the RT$_2$ system, $Z_{R–R}$, $Z_{R–T}$, $Z_{T–R}$ and $Z_{T–T}$ are 4, 12, 6 and 6, respectively [9, 25]) and $G_R$ is the de Gennes factor $(g - 1)^2 J / (J + 1)$ for rare earth atoms while $G_T$ is the corresponding de Gennes factor for transition-metal atoms [25, 26]. Assuming that Ni does not carry a moment in RNi$_2$ compounds [27] (or carries a small moment, e.g. $\mu_{Ni} = 0.2 \mu_B$ for GdNi$_2$ [28]), the R–T and T–T interactions are very weak or absent and the magnetism in RNi$_2$ is dominated by R–R exchange [27]. For RMn$_2$ the magnetic state of the Mn atoms depends critically on the rare earth element: the Mn moment is small in RMn$_2$ with R = Dy, Ho and Er while the Mn moment is estimated to be $\mu_{Mn} = 0.25 \mu_B$ in TbMn$_2$ [24]. Moreover, the transition temperatures in RMn$_2$ with R = Gd–Tm are in fairly good agreement with the de Gennes rule [9, 24], indicating that the magnetism is driven primarily by the rare earth element [24]. This is supported by figure 3(c) which shows that the transition temperatures $T_C$ for RNi$_2$ and RMn$_2$ exhibit linear relationships with the de Gennes factor $G_R$ and a temperature intercept close to zero for both compounds. The changes in volume which occur in RNi$_2$ and RMn$_2$ for different rare earths also play a role in the strength of the R–R interaction. For example, from R = Tb to R = Er, the fractional changes in unit cell volumes for RNi$_2$ and RMn$_2$ are $\Delta V / V \sim 0.15\%$ and $\Delta V / V \sim 0.52\%$, respectively [9]. These volume changes lead to differences between the $A_{R–R}$ exchange coupling parameters which in turn affect the transition temperatures. For example, for RNi$_2$ compounds, $A_{Tb–Tb} = 2.2 \times 10^{-23}$ J ($\sim 1.6$ K) for TbNi$_2$ and $A_{Er–Er} = 1.6 \times 10^{-23}$ J ($\sim 1.2$ K) for ErNi$_2$ [25].

Figure 3(c) demonstrates that $T_C$ for RNi$_2$Mn is not predicted by the de Gennes rule alone. Extrapolation of $T_C$ values for RNi$_2$Mn versus $G_R$ leads to an intercept of $\sim 26.6$ K, indicating a $T_{T–T}$ contribution. Assuming that the $A_{R–R}$ values in RNi$_2$Mn are the same as those deduced from RNi$_2$ compounds of similar unit cell volumes [25], the $T_{Tb–Tb}$ contribution resulting from the $J_{Tb–Tb}$ interaction can be estimated. As examples, for R = Tb and Er the unit cell volumes are $V = 366.8$ Å$^3$ for TbNi$_2$Mn, $V = 367.1$ Å$^3$ for TbNi$_2$ (cf V = 445.1 Å$^3$ for TbMn$_2$) [9, 22], $V = 361.8$ Å$^3$ for ErNi$_2$Mn and $V = 361.6$ Å$^3$ for ErNi$_2$ (cf V = 421.9 Å$^3$ for ErMn$_2$) [9, 22]. Using $T_{R–R} = 2\mu_0 / 2\mu_0 + 1$ for rare earth atoms while $G_T$ is the corresponding de Gennes factor for transition-metal atoms [25, 26]. This behaviour agrees well with the general tendency detected in RNi$_2$Mn compounds that, with decreasing $m / n$ ratio (i.e. from T-poor to T-rich compounds), the contribution $T_{R–R}$ of the R–R interactions to $T_C$ decreases while the T–T and R–T become dominant [25]. Similarly the changes in $T_C$ in Mn composition for TbNi$_2$Mn (figure 3(b)) are due to variations in the R–R and T–T interactions resulting from the strong magnetostuctural coupling and modifications of the Mn magnetic state due to volume changes (similar changes are observed in the RMn$_2$ system [5]).

3.3. Magnetic transition—mean field analysis

3.3.1. Exponents—AC magnetic susceptibility. The AC magnetic susceptibility of TbNi$_2$Mn$^+$ in figure 3(b) is similar to that reported previously [9]. The Curie temperature $T_C = 1477 \pm 2$ K (minimum of $d\chi / dT$; inset to figure 3(b)) agrees well with $T_{Cbc} = 148 \pm 2$ K obtained from the DC magnetization measurements of figure 3(a). The AC susceptibility data also indicate an extended shoulder as the temperature approaches $\sim 200$ K as also reflected by the inflection in $d\chi / dT$ around $\sim 185$ K. This feature may be associated with the slight impurity noted above in the x-ray diffraction pattern of figure 1(a), although its origin remains unclear.

We have analysed the high field ($\mu_0 H_{DC} > 0.5$ T) AC susceptibility data measured around the Curie temperature (figure 4) by mean field theory. Application of large DC fields eliminates the AC susceptibility response to technical magnetization effects such as domain walls while suppressing the background [14–16], thereby ensuring that only critical data are analysed. Figure 4 reveals several features of the AC susceptibility with increasing DC field: (i) the magnitude decreases; (ii) the width of the predominant peak increases and (iii) the position of the broad peak shifts to higher temperatures. The critical behaviour can be derived from the maxima $\chi_M(H, T)$ in the temperature dependence of the AC susceptibility $\chi(H, T)$ in DC fields, with $T_M$ defined as the temperature of maximum $\chi_M(H, T)$ [14]. According to the conventional static scaling law ([14–16, 29, 30] and references therein), the temperature dependence of maxima $\chi_M(H, T)$ is governed by power laws [14–16]:
as a function of DC field (figure 5(a)). Following the approach described in [14, 31], we have determined the critical temperature to be $T_{\text{crit}} = 147.0 \pm 1.7$ K on extrapolation of the graph of $T_M$ against $(\mu_0 H)^{0.57}$ (figure 5(b); equation (4)). This value of $T_{\text{crit}} = 147.0 \pm 1.7$ K is in very good agreement with the values $T_{\text{DC}} = 148.0 \pm 1$ K and $T_{\text{crit}}^e = 147 \pm 2$ K determined directly from the magnetization and AC magnetic susceptibility measurements (figures 3(a) and (b), respectively). (As a further check it should be noted that $T_{\text{crit}}^e = 148.4 \pm 1.3$ K was obtained from a graph of $T_M$ versus $(\mu_0 H)^{0.538}$. The exponent value 0.538 is based on $\gamma + \beta = 1.86$ derived below from equation (4).) The agreement between the $T_C$ values determined directly from the magnetization data and from critical exponent analysis confirms the applicability of the power laws to the TbNi$_2$Mn system. For the remainder of the critical exponent analyses we apply $T_C = 147.0$ K.

Figures 5(c) and (d) are double-logarithmic plots of $\chi_M(\mu_0 H, T_M)$ versus $(T_M - T_C)/T_C$ and $(T_M - T_C)/T_C$ versus $\mu_0 H$, respectively. The high degree of linearity obtained on fitting equations (3) and (4) to figures 5(c) and (d) indicates that these power laws apply to TbNi$_2$Mn with exponent values of $\gamma = 1.09 \pm 0.07$ and $\gamma + \beta = 1.86 \pm 0.12$, $\beta = 0.77 \pm 0.12$ determined respectively. Description of the critical magnetic behaviour of TbNi$_2$Mn by the above power laws confirms that the transition is second order. However, it should be noted that while the region of reduced temperature $(T_M - T_C)/T_C$ over which equation (3) applies to TbNi$_2$Mn is quite extended ($\sim 0.1$–0.3; figure 5(c)), data could only be measured to within $(T_M - T_C)/T_C \sim 0.1$ of the transition.

Figure 4. Temperature dependence of the AC magnetic susceptibility as measured in the DC magnetic fields indicated ($\mu_0 H_{\text{DC}} = 0.5$–8 T) for TbNi$_2$Mn*. The dashed line shows the locus of $T_M$, the temperatures at which the maxima in susceptibility occur in figure 4 plotted against $\chi_M(H, T_M)$ versus $T/\mu_0 H_{\text{DC}}$ for a double-logarithmic scale. The line represents a fit to the power law of equation (2). (b) $\chi_M(H, T_M)$ versus $T_M$ on a double-logarithmic scale. The line represents a fit to the power law of equation (4). This value of $T_{\text{crit}} = 147.0 \pm 1.7$ K is in very good agreement with the values $T_{\text{DC}} = 148.0 \pm 1$ K and $T_{\text{crit}}^e = 147 \pm 2$ K determined directly from the magnetization and AC magnetic susceptibility measurements (figures 3(a) and (b), respectively). (As a further check it should be noted that $T_{\text{crit}}^e = 148.4 \pm 1.3$ K was obtained from a graph of $T_M$ versus $(\mu_0 H)^{0.538}$. The exponent value 0.538 is based on $\gamma + \beta = 1.86$ derived below from equation (4).) The agreement between the $T_C$ values determined directly from the magnetization data and from critical exponent analysis confirms the applicability of the power laws to the TbNi$_2$Mn system. For the remainder of the critical exponent analyses we apply $T_C = 147.0$ K.

Figures 5(c) and (d) are double-logarithmic plots of $\chi_M(H, T_M)$ versus $(T_M - T_C)/T_C$ and $(T_M - T_C)/T_C$ versus $\mu_0 H$, respectively. The high degree of linearity obtained on fitting equations (3) and (4) to figures 5(c) and (d) indicates that these power laws apply to TbNi$_2$Mn with exponent values of $\gamma = 1.09 \pm 0.07$ and $\gamma + \beta = 1.86 \pm 0.12$, $\beta = 0.77 \pm 0.12$ determined respectively. Description of the critical magnetic behaviour of TbNi$_2$Mn by the above power laws confirms that the transition is second order. However, it should be noted that while the region of reduced temperature $(T_M - T_C)/T_C$ over which equation (3) applies to TbNi$_2$Mn is quite extended ($\sim 0.1$–0.3; figure 5(c)), data could only be measured to within $(T_M - T_C)/T_C \sim 0.1$ of the transition.

Figure 5. (a) Values of $\chi_M$, the maxima in susceptibility for the different DC field values (0.5 T < $\mu_0 H < 8$ T), plotted against DC field on a double-logarithmic scale. The line represents a fit to the power law of equation (2). (b) $T_M$, the temperatures at which the maxima in susceptibility occur in figure 4 plotted against $H^{1/(\gamma + \beta)}$, where $1/(\gamma + \beta) = 0.57$ are exponents based on the Heisenberg model. The zero field intercept yields a value of $T_{\text{crit}} = 147.0 \pm 1.7$ K. (c) Values of $\chi_M$ plotted against the reduced temperature $(T_M - T_C)/T_C$ on a double-logarithmic scale. The line represents a fit to the power law of equation (3). (d) Values of the reduced peak temperature $(T_M - T_C)/T_C$ plotted against the DC field on a double-logarithmic scale. The value of $T_{\text{crit}}$ was determined as indicated in (b). The line represents a fit to the power law of equation (4).
temperature $T_C$. The mean field model corresponding to long range order has theoretical values of $\beta = 0.5$, $\gamma = 1.0$ and $\delta = 3.0$ while the theoretical values based on the three-dimensional Heisenberg model corresponding to short range interactions are $\beta = 0.365$, $\gamma = 1.386$ and $\delta = 4.80$ [32]. The present results of $\beta = 0.77 \pm 0.12$, $\gamma = 1.09 \pm 0.07$ and $\delta = 2.51 \pm 0.06$ indicate that, even though there are mixed occupancies of Tb and Mn atoms and vacancies on the 8a site [9], long range interactions dominate the critical behaviour of TbNi$_2$Mn. This finding agrees with previous conclusions based on analyses of the Curie temperatures for the RNi$_2$Mn system (R = Tb, Dy, Ho, Er), that the magnetic ordering is dominated by the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between localized moments [9, 10]. However, the present exponent $\beta = 0.77$ compared with $\beta = 0.5$ for long range order is surprisingly large. $\beta = 0.57$ has been reported for single crystal Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [33], with this relatively high value ascribed to the formation of ferromagnetic clusters above $T_C$. According to Halder et al [13], $\beta$ describes the rate of change of the ordered moment below $T_C$ with a smaller $\beta$ indicating more rapid growth of the ordered moment. In the case of TbNi$_2$Mn, $\beta = 0.77$ indicates a slower growth of the ordered moment with decreasing temperature as is evident in the DC magnetic data (figure 3(a)). The slow growth of the ordered moment in TbNi$_2$Mn is likely to be due to disorder of the local environments created by the presence of the mixing occupancy of Tb and Mn and vacancies at the 8a site [9].

3.3.2. Exponents—DC field magnetization. The variation of magnetization with applied DC field for TbNi$_2$Mn (102–186 K) and the resultant Arrott plots of $M^2$ as a function of $H/M$ are shown in figures 6(a) and (b), respectively. The Arrott plots exhibit positive slopes, as expected for the second-order transition at $T_C$ [4]. The field dependence of magnetization for a second-order system at $T_C$ can be expressed by equation (5) [17, 31] and provides a cross-check of the exponent $\delta = 2.51 \pm 0.06$ derived from the DC field dependence of AC susceptibility:

$$M \sim H^{1/\delta}. \quad (5)$$

The double-logarithmic $M$–$H$ curves for TbNi$_2$Mn at 146 and 150 K (figure 6(c); temperatures just above and below $T_C$) are well described by the power relation $M \sim H^{1/\delta}$ at both temperatures with linear fits leading to the values $\delta = 2.66 \pm 0.01$ and $\delta = 2.41 \pm 0.01$, respectively. As indicated in [17, 31], the $M$–$H$ curves well below $T_C$ show an upward curvature away from linearity (leading to a larger value of $\delta$), the $M$–$H$ curves well above $T_C$ exhibit a downward curvature (leading to a smaller $\delta$), while for temperatures close to $T_C$ the $M$–$H$ curves show linear behaviour. On this basis the $\delta$ values derived at 146 K ($\delta = 2.66 \pm 0.01$) and 150 K ($\delta = 2.41 \pm 0.01$) indicate that the $\delta$ value at $T_C = 147.0 \pm 1.7$ K from the DC magnetization data would be very close to the value $\delta = 2.51 \pm 0.06$ derived from equation (5) and figure 5(a) as based on the AC susceptibility data.

The modified Arrott plots, $M^{1/\gamma}$ as a function of $(H/M)^{1/\delta}$, shown in figure 6(d) provide a cross-check of equation (5).
The magnetic entropy curves $-\Delta S_M$ (figure 7(a)) exhibit broad peaks around $T_C$ (typical for a second-order phase transition [1]) with maximum values of $-\Delta S_M \sim 1.9$ J kg$^{-1}$ K$^{-1}$ and $-\Delta S_M \sim 3.0$ J kg$^{-1}$ K$^{-1}$ for $\mu_0H = 0$–3 T and $\Delta \mu_0H = 0$–5 T, respectively. By comparison, for TbNi$_2$ where a sharp MCE peak was found around $T_C = 37.5$ K, $-\Delta S_M \sim 14.5$ J kg$^{-1}$ K$^{-1}$ for field change $\Delta \mu_0H = 0$–5 T [3]. The local disorder created by the mixed occupancy of Tb and Mn at the 8a site and vacancies is likely to contribute to increased broadening of $-\Delta S_M$ for TbNi$_2$Mn, leading to the reduced value of $-\Delta S_M$ compared with TbNi$_2$.

Mean field theory predicts that $-\Delta S_M$ is proportional to $(\mu_0H/T_C)^2/3$ at second-order phase transitions [37, 38]. The linear fit to data in figure 7(b) demonstrates that the relationship $-\Delta S_M \propto (\mu_0H/T_C)^2/3$ is valid around $T_C$, in agreement with the conclusion from magnetization measurements that the magnetism of TbNi$_2$Mn is governed by long range interactions.

3.5. Mössbauer spectroscopy

Examples of Mössbauer spectra and fits for the $^{57}$Fe-doped TbNi$_2$Mn sample over the temperature range 5–300 K are shown in figure 8. As outlined below, the fits allow the average values of the hyperfine parameters of TbNi$_2$Mn($^{57}$Fe) to be determined above and below the transition temperature (figure 9). In the paramagnetic region above $T_C \sim 147$ K the spectra indicate features consistent with quadrupolar effects, while below $T_C$ the spectra exhibit magnetic hyperfine splitting. As Mn atoms enter both 8a and 16d sites in RNi$_2$Mn compounds [9–11], it is assumed that the dopant $^{57}$Fe atoms also enter these sites. Consistent with this two-site occupancy, the spectra above $T_C$ are found to be fitted best using two doublets $D_1$ and $D_2$ ($\chi^2 \sim 1.16$) rather than one doublet ($\chi^2 \sim 1.25$). The optimal fits to spectra above $T_C$ (figure 8(a)) have fractional areas $D_1 \sim 10(1)\%$ and $D_2 \sim 90(2)\%$. Rietveld refinements of room temperature TbNi$_2$Mn x-ray diffraction patterns show that $\sim 10.0(0.5)\%$ of the transition-metal atoms occupy the 8a site with 90.0(0.5)\% in the 16d site [9]. We therefore identify doublet $D_1$ as representing the behaviour of the 8a site with $D_2$ representing the behaviour of the 16d sites.

The spectra below $T_C$ (figure 8) show magnetic hyperfine splitting. The magnetically split spectra were fitted assuming a distribution of hyperfine fields leading to the graph of average field values versus temperature shown in figure 9(a). As discussed below, we have also fitted the magnetic spectra using two or three sextets to approximate the possible site transition-metal occupancies of the 16d and 8a sites for comparison with refinement results [9].

The average hyperfine field shown in figure 9(a) results from contributions to the exchange interactions present in the Tb and transition-metal (Ni, Mn) sublattices and correspondingly reflects the magnetic order in the Tb and (Ni, Mn) sublattices [11, 37, 38]. The spectra for magnetically split structures would therefore be expected to be fitted using two sub-sextets to represent $^{57}$Fe atoms in the 8a and 16d sites. In practice, we found that at least three sub-sextets are needed to provide optimal fits for the spectra below the magnetic ordering temperature $T_C$. For analysis of the TbNi$_2$Mn($^{57}$Fe) spectra
Figure 8. $^{57}\text{Fe}$ Mössbauer spectra of TbNi$_2$Mn($^{57}\text{Fe}$) over the temperature range 5–300 K. As discussed in the text, the spectra above $T_C \sim 147$ K were fitted with two doublets (D$_1$—dashed line; D$_2$—dotted line) while the magnetic spectra below $T_C$ were fitted using three sextets (S$_1$—largest hyperfine field $B_{hf1}$, dash-dot line; S$_2$—medium hyperfine field $B_{hf2}$, dotted line; S$_3$—smallest hyperfine field $B_{hf3}$, dashed line). 

below $T_C$, we assume that the line width and isomer shift are the same for all three sub-sextets with the magnetic hyperfine field and quadrupole interaction allowed to vary. As shown in figure 9(a), the average hyperfine field values derived from fits based on three sextets (half-filled diamonds) agree well with the average values derived from the field distribution fit (open triangles). The spectral fits using three sextets are shown in figure 8, as they allow comparison with site occupancies of the transition-metal atoms determined from the earlier x-ray diffraction refinements [9]. The fit to the 5 K spectrum of figure 8, for example, is represented by three sub-spectral sextets: S$_1$ of largest hyperfine field $B_{hf1}$ and fractional area $A_1 \sim 40$ ($\pm 6$)%; S$_2$ of medium hyperfine field $B_{hf2}$ with $A_2 \sim 49$ ($\pm 7$)% and S$_3$ of smallest hyperfine field $B_{hf3}$ with $A_3 \sim 11$ ($\pm 3$)%.

Following the transition-metal occupancies of the 16d and 8a sites [9, 10], we conclude that sextets S$_1$ and S$_2$, of combined fractional area ~90%, correspond to the contribution from $^{57}\text{Fe}$ at 16d sites, with the third sextet S$_3$ representing $^{57}\text{Fe}$ located at the 8a site of fractional area ~10%. The spectral fits are found to be consistent with our conclusion that the Mn($^{57}\text{Fe}$) atoms occupy both 16d and 8a sites in RNi$_2$Mn.

Figure 9. Temperature dependences of the Mössbauer hyperfine parameters of TbNi$_2$Mn($^{57}\text{Fe}$) derived from the fits to the spectra shown in figure 8. (a) The average hyperfine field values ($B_{hf}$) determined using a distribution of hyperfine fields (open triangles) and three sextets (half-filled diamonds). As discussed in the text, the dashed line represents the best fit to the equation $B_{hf}(T) = B_{hf}(0)(1 + bT^3/2 + cT^5/2 + dT^2)$. (b) The average quadrupole shift of the two sub-spectral components used to fit spectra above $T_C$ and the average quadrupole interaction values of the three sub-spectral components below $T_C$. The line is a guide to the eye. (c) The mean isomer shift values; the dashed line represents the best fit to equation 8 resulting in the Debye temperature $\theta_D = 200 \pm 20$ K.

It should be noted that similar behaviour has been found for RMn$_2$ compounds (R = Tb, Dy, Ho) where two sub-spectra rather than a single sub-spectrum are required [39–41] even though there exists only one transition-metal crystallographic site for magnetic state spectra. In the case of DyMn$_2$ it was reported that magnetic and non-magnetic Mn atoms coexist below the ordering temperature [39] (this behaviour is linked with the strong dependence of the magnetic state of the Mn atoms on the critical Mn–Mn distance $d_{\text{Mn-Mn}} \sim 2.66$ Å), whereas for TbMn$_2$ and HoMn$_2$ the Mössbauer spectra below the magnetic ordering temperatures were fitted using at least two sub-sextets which are related to the nearest neighbour environment of the Fe atoms and/or the direction of the easy axis of magnetization [40, 41].
Figure 9(a) also shows a fit of the average magnetic hyperfine field values to equation (7), which incorporates a superposition of collective electron and spin-wave effects [42]:

\[ B_{hf}(T) = B_{hf}(0)(1 + bT^2 + cT^4 + dT^6). \] (7)

As outlined by Chattopadhyay et al [42], the \( T^{3/2} \) term is due to excitations of long wavelength spin waves and the \( T^5/2 \) term results from spin-wave–spin-wave interactions [43], with the \( T^2 \) term arising from Stoner band excitations [44]. The dashed line in figure 9(a) represents the best fit to the average magnetic hyperfine field values leading to constants \( b = 1.16 \times 10^{-3} \text{ K}^{-3/2} \), \( c = 1.64 \times 10^{-5} \text{ K}^{-5/2} \), and \( d = 2.47 \times 10^{-4} \text{ K}^{-2} \). This fit shows that the \( T^{3/2} \) term, and therefore spin wave interactions, dominate, while the \( T^2 \) term indicates that Stoner-type interactions also contribute to the magnetic behaviour of TbNi\(_2\)Mn\(_2\)Mn\(_2\) with this itinerant character probably linked with the band magnetism of Ni. This type of temperature-dependent behaviour—dominant \( T^{3/2} \) but with \( T^2 \) contributions—is similar to that reported for the Fe\(_{1-x}\)Co\(_x\)Si [42] and Mn\(_x\)Si [45] systems, but differs from that in the R\(_2\)Fe\(_{17}\)-based systems, where \( T^2 \) dependence of the hyperfine field was obtained [46].

As shown in figure 9(b), the average value of the quadrupole interaction \( \varepsilon \approx 0.26 \text{ mm s}^{-1} \) for TbNi\(_2\)Mn\(_2\)(\(^{57}\)Fe) above \( T_C \) (the quadrupole shift \( \varepsilon \approx |\Delta|/2 \) for quadrupole splitting \( \Delta \)) is similar to values reported for the RMn\(_2\) system (\( \varepsilon \approx 0.171 \text{ mm s}^{-1} \) and \( \varepsilon \approx 0.127 \text{ mm s}^{-1} \) for GdMn\(_2\) and YMn\(_2\), respectively [47]). While the sign of the quadrupole interaction cannot be derived from fits to spectra in the paramagnetic state above \( T_C \), the asymmetry in the magnetic splittings below \( T_C \), particularly evident in the sub-spectral sextets S\(_1\), S\(_2\) and S\(_3\) (figure 8(a)), is consistent with a positive value for the quadrupole interaction \( \varepsilon \). A positive \( \varepsilon \) also accounts well for the asymmetry observed in the predominantly quadrupolar spectra around \( T_C \).

The Debye temperature of TbNi\(_2\)Mn\(_2\)(\(^{57}\)Fe) has been determined from the temperature dependence of the isomer shift IS\( (T) \) shown in figure 9(c). The isomer shift is given by [48, 49]

\[ IS(T) = IS(0) + IS_{\text{SODS}}(T). \] (8)

\( IS(0) \) represents the temperature dependence of the charge density at the probe nucleus which is generally weakly temperature-dependent. The second term, \( IS_{\text{SODS}} \), the so-called second-order Doppler shift, can be described in terms of the Debye model for the phonon spectrum by

\[ IS_{\text{SODS}}(T) = \frac{3kT}{2mc} \left[ \frac{3}{8T^3} + \frac{3}{T^5} \right] \int_0^T \frac{x^3}{e^x - 1} \, dx. \] (9)

where \( m \) is the mass of the \(^{57}\)Fe nucleus, \( c \) is Boltzmann’s constant, \( T \) is the velocity of light and \( \tau = \theta_D/T \) is the reduced temperature [46, 48, 49]. The Debye temperature \( \theta_D \) has been derived to be \( \theta_D = 200 \pm 20 \text{ K} \) by fitting the mean isomer shift data of figure 9(c) to equation (9). The present value for the Debye temperature is similar to the value of \( \theta_D = 188 \pm 5 \text{ K} \) reported by Jackson et al [10] from specific heat measurements. The Debye temperature value of \( \theta_D \approx 200 \text{ K} \) for TbNi\(_2\)Mn\(_2\) is consistent with the difference in \( \theta_D \) values for TbNi\(_2\) (\( \theta_D = 264 \text{ K} \)) [50] and TbMn\(_2\) (\( \theta_D = 145 \text{ K} \)) [51], with the reduced value for TbMn\(_2\) compared with TbNi\(_2\) resulting in the intermediate value for TbNi\(_2\)Mn\(_2\). Similar behaviour has also been found for the related system ErNi\(_2\)Mn [18].

4. Conclusions

In summary, the MgCu\(_2\)-type Laves phase of space group \( Fd\overline{3}m \) has been formed for the TbNi\(_2\)Mn\(_2\) system with Mn compositions in the range \( 0.9 \leq x \leq 1.10 \). The variations of the lattice parameter \( a \) and the Curie temperature \( T_C \) of TbNi\(_2\)Mn\(_2\) with Mn composition show similar behaviours to \( x = 1.0 \). This strong correlation between the lattice constant and the Curie temperature is due to the sensitive dependence of both the RKKY interaction between Tb moments [9] and the Mn–Mn interactions on the distance between magnetic atoms. For a given set of preparation conditions, the reported differences in \( T_C \) values for TbNi\(_2\)Mn\(_2\), (e.g. table 1) are due to the concentration, \( x \), of Mn atoms and chemical pressure effects related to the variation in the spacing between magnetic atoms. As demonstrated by the variation of transition temperature with the de Gennes factor \( G_R \) (figure 3(c)), the magnetic behaviour of RNil\(_2\) and RmNil\(_2\) compounds is governed by R–R interactions, whereas additional T–T and R–T contributions are present in RmNil\(_2\). These additional T–T and R–T components in the magnetic energy terms for RNil\(_2\)Mn compounds contribute to increased values of magnetic ordering temperatures compared with corresponding RNil\(_2\) and RmNil\(_2\) compounds. A strong magnetostructural coupling exists in this system, as reflected by the dependence of the lattice constant \( a \) and transition temperature \( T_C \) on composition and our calculation of the change of \( T_C \) with unit cell volume (using \( dT_C/dP \approx −1.96 \text{ K GPa}^{-1} \) for TbNi\(_2\)Mn [10]).

The magnetic phase transition at \( T_C = 147 \pm 1.7 \text{ K} \) in TbNi\(_2\)Mn has been determined to be second order. DC magnetization curves (0–5 T; 102–186 K) and AC susceptibility curves (100–200 K) taken at DC magnetic fields in the range 0.5–8.0 T have been analysed in detail based on the conventional static scaling law. The resultant three critical exponents of the second-order phase transition in TbNi\(_2\)Mn are \( \beta = 0.77 \pm 0.12 \), \( \gamma = 1.09 \pm 0.07 \), and \( \delta = 2.51 \pm 0.06 \), indicating that long range ordering interactions dominate this system. The magnetic entropy change around \( T_C \) has been found to be \( 3.0 \text{ J kg}^{-1} \text{ K}^{-1} \) for a magnetic field change of 0–5 T. The combined magnetic field and temperature dependence of the entropy (figure 8(b)) is also consistent with long range interactions. The temperature dependence of the average magnetic hyperfine field values indicates that spin-wave interactions dominate, with Stoner-type interactions also contributing to the overall magnetic behaviour. TbNi\(_2\)Mn has a Debye temperature \( \theta_D = 200(20) \text{ K} \) as determined from the temperature dependence of the mean isomer shift.
Acknowledgments

The work is supported in part by an award from UNSW and the Australian Institute of Nuclear Science and Engineering, Australian Research Council Discovery Grant (DP0879070) and Australian Research Council LIEF Grant (LE0775559).

References