2011

Critical magnetic transition in TbNi₂Mn-magnetization and Mossbauer spectroscopy

Jianli Wang

University of Wollongong, jianli@uow.edu.au

S J. Campbell

UNSW, stewart.campbell@adfa.edu.au

S J. Kennedy

Bragg Institute ANSTO Australia

Rong Zeng

University of Wollongong, rzeng@uow.edu.au

S. X. Dou

University of Wollongong, shi@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>

Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/1354>

Recommended Citation

Wang, Jianli; Campbell, S J.; Kennedy, S J.; Zeng, Rong; Dou, S. X.; and Wu, Guangheng: Critical magnetic transition in TbNi₂Mn-magnetization and Mossbauer spectroscopy 2011, 1-11.
<https://ro.uow.edu.au/engpapers/1354>

Authors

Jianli Wang, S J. Campbell, S J. Kennedy, Rong Zeng, S. X. Dou, and Guangheng Wu

Critical Magnetic Transition in TbNi₂Mn – Magnetization and Mössbauer Spectroscopy

J.L. Wang^{1,2}, S.J. Campbell¹, S.J. Kennedy², R. Zeng³, S.X. Dou³ and G.H. Wu⁴

¹School of Physical, Environmental and Mathematical Sciences, The University of New South
Wales, The Australian Defence Force Academy, Canberra ACT 2600, Australia

²Bragg Institute, ANSTO, Lucas Heights, NSW 2234, Australia

³Institute for Superconductivity and Electronic Materials, University of Wollongong,
Wollongong, NSW 2522, Australia

⁴Institute of Physics, Chinese Academy of Science, Beijing 100190, P. R. China

Abstract: The structural and magnetic properties of the TbNi₂Mn_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 ⁵⁷Fe Mössbauer spectroscopy (5-300 K). TbNi₂Mn_x crystallize in the MgCu₂-type structure (space group *Fd-3m*). 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 RNi₂Mn contribute to their increased magnetic ordering temperatures compared with RNi₂ and RMn₂. 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 TbNi₂Mn around the Curie temperature *T_C*=147 K confirm the magnetic transition is second order with critical exponents $\beta=0.77\pm0.12$, $\gamma=1.09\pm0.07$ and $\delta=2.51\pm0.06$. These exponents establish that the magnetic interactions in TbNi₂Mn 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. Mössbauer spectra above *T_C* are fitted by two

subspectra 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.

Key Words: Rare earth metals and alloys, magnetic phase transition, magnetization, magnetic susceptibility, Mössbauer spectroscopy

PACS: 71.20.Eh, 77.80.Bh, 75.30.Cr, 82.80.Ej

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_2X_2 ($\text{X}=\text{Ge}$ or Si) [4] and RMn_2 [5] are of particular interest due to interplay between the 3d and 4f magnetism and the sensitive dependence of the Mn moment and sublattice structures on Mn-Mn interatomic distances. In the RMn_2 system for example, there is a critical Mn-Mn spacing $d_{\text{Mn-Mn}}$ (~ 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_2Mn compounds with $\text{R}=\text{Tb}$, Dy , Ho , and Er have been reported to crystallize in the MgCu_2 -type structure of space group $Fd\bar{3}m$ with TbNi_2Mn found to exhibit the largest magnetic ordering temperature T_C [8, 9]. For TbNi_2Mn , 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 TbNi_2Mn has the MgCu_2 -structure, although Mushnikov *et al.* [11] concluded that the crystal structure of TbNi_2Mn is described by the AuBe_5 -type structure of space group $F4\bar{3}m$. Table I lists the main preparation conditions for these TbNi_2Mn 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 TbNi_2Mn samples exhibit lattice parameters ranging from 7.123 Å [10] to 7.184 Å [11] with Curie temperatures ranging from $T_C \sim 131$ K [9] to $T_C \sim 151$ 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, RNi_2Mn has been found to exhibit considerably higher Curie temperatures than the corresponding isostructural compounds RNi_2 and RMn_2 [9]. TbNi_2Mn , has been found to exhibit the highest Curie temperature with reported values in the range $T_C \sim 140(\pm 10)$ K (Table I) compared with $T_C \sim 37.5$ K and $T_C \sim 54$ K for TbNi_2 and TbMn_2 , respectively [9].

In order to clarify the factors that contribute to the range of structural and magnetic properties reported for TbNi_2Mn (Table I), we have carried out a systematic investigation of a series of TbNi_2Mn_x compounds ($0.9 \leq x \leq 1.10$) prepared in the same manner. A further aim of the present work is therefore to clarify the magnetic interactions occurring in TbNi_2Mn compared with TbNi_2 and TbMn_2 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. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [12], TbCo_2 and $\text{TbCo}_{1.9}\text{Fe}_{0.1}$, [13], $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (divalent cation A), $\text{La}_{0.73}\text{Ba}_{0.27}\text{MnO}_3$, $\text{Tl}_2\text{Mn}_2\text{O}_7$, Ni-Mn-Ga and CeFe_2 -related compounds [14-17]); here we apply a similar approach in detailed critical analyses of the magnetic phase transition at T_C in TbNi_2Mn .

2. Experimental

The TbNi_2Mn_x ($x = 0.90, 0.97, 1.00, 1.03$ and 1.10), $\text{Tb}_{1-y}\text{Ni}_2$ ($y = 0.00, 0.02$ and 0.05) and TbMn_2 samples were prepared using starting elements of purities $\geq 99.9\%$. Ingots of mass ~ 2 g were prepared at UNSW@ADFA by standard argon arc-melting procedures with each ingot melted at least five times for improved homogeneity. The $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ sample for the Mössbauer study was prepared from an ingot doped with ~ 0.5 wt% ^{57}Fe . We have also investigated the behaviour of an ~ 8 g TbNi_2Mn sample (identified as TbNi_2Mn^*). 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 (CuK α radiation; $\lambda = 1.5418$ Å). The structure of the TbNi₂Mn* sample was further checked by neutron diffraction at 300 K (high intensity diffractometer Wombat, OPAL, Lucas Heights; $\lambda = 2.4072$ Å) for comparison with the x-ray diffraction data. Magnetization measurements were carried out over the temperature range 5-340 K in a SQUID magnetometer ($\mu_0 H = 0-5$ T). The DC field dependences of the magnetic ac susceptibility were recorded using a conventional physical properties measurement system (PPMS-9, Quantum Design, $\mu_0 H = 0 - 8$ T) over the temperature range 5–340 K. The ⁵⁷Fe Mössbauer spectra were obtained between 5 K 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 TbNi₂Mn_x 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 ($Fd-3m$) in which Cu are located at the 16d site and Mg at the 8a site [5, 8]. A small impurity phase <2 % (reflections around $2\theta \sim 29^\circ$) is observed, as in the case of HoNi₂Mn and ErNi₂Mn [9]. The skewing of the high angle peaks indicates the presence of large strains in these un-annealed samples. As discussed below, it is noted that the (200) reflection of space group ($F4-3m$) [11] is absent for all TbNi₂Mn_x samples of Fig. 1(a). The lattice constants were derived using the Le Bail method with a maximum indicated around Mn composition $x \sim 1.0$ (Fig. 2 (a)). Similar behaviour has been detected in ErNi₂Mn_x [18].

Mushnikov *et al.* [11] observed additional (200) and (420) reflections in the room temperature and 4.2 K neutron diffraction patterns of TbNi₂Mn annealed at 870°C for 7 days. They concluded that the crystal structure of TbNi₂Mn is described by the AuBe₅-type structure of space group $F4-3m$, a superstructure of $Fd-3m$. It should be noted that a (200) peak can also be discerned with CuK α

radiation for a TbNi₂Mn sample annealed at 750°C for 7 days [9] and with CrK α radiation for TbNi₂Mn annealed at 870°C for 7 days [11]. On the other hand a (200) peak is not observed with CrK α radiation for their other TbNi₂Mn_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 TbNi₂Mn_x samples which exhibit the MgCu₂-type structure, it is clear that the final structure adopted by TbNi₂Mn_x compounds depends sensitively on the preparation conditions, the Mn composition and sample heat treatments. The MgCu₂-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 AuBe₅-type structure with Tb in the 4c site and 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 MgCu₂-type structure for TbNi₂Mn [9], optimal refinements to the AuBe₅-type structure resulted in the off-stoichiometric composition TbNi_{2.09}Mn_{0.81} with the introduction of vacancies leading to increase in refinements agreement values [11]. Similar behaviour - with sensitive dependence of the structure on composition and sample preparation conditions - has also been exhibited by the RNi₂ system [21] where a temperature induced phase transition (and pressure-induced transition for YNi₂) is detected from *F*-43*m* to *Fd*-3*m* [21]. A full crystallographic investigation of the conditions under which the different structures are obtained for TbNi₂Mn – MgCu₂-type or AuBe₅-type – and the factors governing the transformation from one structure to the other is required.

The room temperature neutron diffraction pattern for TbNi₂Mn* sample is shown in Fig. 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 space groups *Fd*-3*m* and *F*4-3*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 patterns (Fig. 1(a)), the neutron diffraction pattern of as-prepared TbNi₂Mn* (Fig. 1(b)) exhibits the MgCu₂-type structure with no

evidence of the (200) and (420) reflections of the AuBe₅-type structure [11]. Rietveld refinement of the room temperature neutron diffraction pattern (well above the magnetic-ordering temperature of TbNi₂Mn*~147 K as discussed below), confirms that the space group of the as-prepared TbNi₂Mn* sample is *Fd-3m*. The quality of fit parameters are: pattern factor, $R_p=3.24\%$ weighted pattern factor, $R_w=4.23\%$ and the expected pattern factor $R_{exp}=0.53\%$.

3.2 Magnetic Behaviour

The magnetic behaviour of all TbNi₂Mn_x samples ($x=0.90, 0.97, 1.00, 1.03$ and 1.10) have been investigated. Given the ~8 g available for the as-prepared TbNi₂Mn* sample, we chose to investigate this sample in detail to ensure consistency for measurements using the variety of magnetic methods.

Fig. 3 (a) shows the temperature dependences of the low field DC magnetization ($\mu_0 H=0.005$ T) for TbNi₂Mn* on warming and cooling after first cooling in zero field (ZFC). The Curie temperatures T_C^{DC} for all TbNi₂Mn_x samples were determined as the temperature at which the dM/dT versus T curve exhibits a minimum (e.g. inset to Fig. 3(a)). The T_C values for the set of TbNi₂Mn_x samples (Fig. 2(b)) exhibit a similar dependence on Mn composition as the lattice parameter a (Fig. 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 TbNi₂Mn_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 TbNi₂Mn [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 TbNi₂Mn_x, and using $B_0=128$ GPa and $dT_C/dP = -1.96$ K/GPa for TbNi₂Mn [10], the change of T_C with $x=1.0$ (unit

cell volume $V=373.5 \text{ \AA}^3$), compared with $x=0.9$ ($V=365.4 \text{ \AA}^3$), is estimated as $\Delta T_C \sim 5.4 \text{ K}$. This calculated change in the critical temperature - based solely on the volume change of $\Delta V/V=2.17\%$ from $\text{TbNi}_2\text{Mn}_{0.9}$ to $\text{TbNi}_2\text{Mn}_{1.0}$ – compares well with the experimentally measured difference of $\Delta T_C \sim 7 \pm 1 \text{ K}$. (Fig. 2(b)) and confirms the occurrence of strong magnetostructural coupling in TbNi_2Mn_x .

For a given set of preparation conditions, differences in T_C values for TbNi_2Mn_x (Table I) are concluded to be due mainly to both 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_2Mn for which $T_C^{\text{DC}} = 148 \pm 2 \text{ K}$ for the present TbNi_2Mn^* sample (Fig 3(a)) compared with $T_C = 151 \text{ K}$ [10], $T_C = 131 \text{ K}$ [9] and $T_C = 142 \text{ K}$ [11]. Just as variations in the sample compositions and preparation conditions alter the structural behaviour of TbNi_2Mn as discussed above, these effects account for the observed spread in T_C values (Table I).

Independent of the T_C value for a particular sample, a key feature in the magnetism of TbNi_2Mn compared with TbNi_2 and TbMn_2 , is the significantly higher transition temperature exhibited by TbNi_2Mn ($T_C \sim 140(10) \text{ K}$) compared with those of TbNi_2 ($T_C \sim 37.5 \text{ K}$) and TbMn_2 ($T_C \sim 54 \text{ K}$) [9, 21, 22]. Fig 3(c) shows a graph of T_C values versus the de Gennes factor, $G_R=(g-1)^2J(J+1)$, for RNi_2Mn [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 approximation, the Curie temperature T_C in R-T compounds can be expressed by [25, 26]:

$$T_C = \frac{T_{T-T} + T_{R-R} + \sqrt{(T_{T-T} - T_{R-R})^2 + 4T_{R-T}^2}}{2}, \quad (1)$$

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-j} ($i, j=R, T$) where $T_{T-T} = \frac{2Z_{T-T}A_{T-T}G_T}{3}$, $T_{R-R} = \frac{2Z_{R-R}A_{R-R}G_R}{3}$ and $T_{R-T} = \frac{2A_{R-T}\sqrt{Z_{R-T}Z_{T-R}G_RG_T}}{2}$. 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 $(g-1)^2J(J+1)$ 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]), 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 Fig. 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 (~ 1.6 K) for $TbNi_2$ and $A_{Er-Er}=1.6 \times 10^{-23}$ J (~ 1.2 K) for $ErNi_2$ [25].

Fig. 3(c) demonstrates that T_C for RNi_2Mn is not predicted by the de Gennes rule alone. Extrapolation of T_C values for RNi_2Mn versus G_R leads to an intercept of ~ 26.6 K, indicating a J_{T-T} contribution. Assuming that the A_{R-R} values in RNi_2Mn 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 $R=Er$ the unit cell volumes are: $V=366.8$

$\text{\AA}^3$ for TbNi_2Mn and $V=367.1 \text{ \AA}^3$ for TbNi_2 (c.f. $V=445.1 \text{ \AA}^3$ for TbMn_2) [9, 22], and $V=361.8 \text{ \AA}^3$ for ErNi_2Mn and $V=361.6 \text{ \AA}^3$ for ErNi_2 (c.f. $V=421.9 \text{ \AA}^3$ for ErMn_2) [9, 22]. Using $T_{R-R} = \frac{2Z_{R-R}A_{R-R}G_R}{3}$ this leads to $T_{\text{Tb-Tb}} = 28 \text{ K}$ ($Z_{\text{Tb-Tb}}=3$ in TbNi_2Mn while $Z_{\text{Tb-Tb}}=4$ in TbNi_2). This demonstrates that the J_{R-T} and J_{T-T} components in the magnetic energy terms for RNi_2Mn contribute significantly to the increase of magnetic ordering temperatures compared with corresponding RNi_2 and RMn_2 compounds. This finding is supported by the moment values $\mu_{\text{Ni}}=0.3(2) \mu_B$ and $\mu_{\text{Mn}}=1.4(2) \mu_B$ determined for TbNi_2Mn at 4.2 K [11]. It is concluded that the presence of Ni and Mn magnetic moments in RNi_2Mn leads to stronger R-T and T-T exchange interactions, resulting in the higher T_C values for the series of RNi_2Mn compounds compared with RNi_2 and RMn_2 . This behaviour agrees well with the general tendency detected in R_mT_n compounds that, with decreasing m/n ratio (i.e. from T-poor to T-rich compounds), the contribution T_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 with Mn composition for TbNi_2Mn_x (Fig. 2(b)) are due to variations in the R-T and T-T interactions resulting from the strong magnetostructural 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_2Mn^* in Fig. 3(b) is similar to that reported previously [9]. The Curie temperature $T_C^{\text{ac}} = 147 \pm 2 \text{ K}$ (minimum of $d\chi/dT$; inset to Fig. 3(b)) agrees well with $T_C^{\text{DC}} = 148 \pm 2 \text{ K}$ obtained from the DC magnetization measurements of Fig. 3(a). The ac susceptibility data also indicate an extended shoulder as the temperature approaches $\sim 200 \text{ K}$ as also reflected by the inflection in $d\chi/dT$ around $\sim 185 \text{ K}$. This feature may be associated with the slight impurity noted above in the x-ray diffraction pattern of Fig 1(a) although its origin remains unclear.

We have analyzed the high field ($\mu_0 H_{DC} > 0.5$ T) ac susceptibility data measured around the Curie temperature (Fig 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 analyzed. 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 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]:

$$\chi_M(H, T_M) \propto H^{1/\delta-1}, \quad (2)$$

$$\chi_M(H, T_M) \propto ((T_M - T_C)/T_C)^{-\gamma}, \quad (3)$$

$$(T_M - T_C)/T_C \propto H^{1/(\gamma+\beta)}. \quad (4).$$

The exponent $\delta = 2.51 \pm 0.06$ was obtained on fitting equation (2) to a double-logarithmic plot of $\chi_M(H, T_M)$ as a function of DC field (Fig. 5(a)). Following the approach described in [14, 31], we have determined the critical temperature to be $T_C^{\text{crit}} = 147.0 \pm 1.7$ K on extrapolation of the graph of T_M against $(\mu_0 H)^{0.57}$ (Fig. 5(b); equation (4)). This value of $T_C^{\text{crit}} = 147.0 \pm 1.7$ K is in very good agreement with the values $T_C^{\text{DC}} = 148.0 \pm 1$ K and $T_C^{\text{ac}} = 147 \pm 2$ K determined directly from the magnetization and ac magnetic susceptibility measurements (Figs. 3(a), 3(b) respectively) (as a further check it should be noted that $T_C^{\text{crit}} = 148.4 \pm 1.3$ 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 TbNi₂Mn system. For the remainder of the critical exponent analyses we apply $T_C = 147.0$ K.

Figs. 5(c) and 5(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 Figs. 5(c) and 5(d) indicates that these power laws apply to TbNi₂Mn 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 TbNi₂Mn 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 TbNi₂Mn is quite extended (~ 0.1 to 0.3 ; Fig. 5(c)), data could only be measured to within $(T_M - T_C)/T_C \sim 0.1$ of the transition 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 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 TbNi₂Mn. This finding agrees with previous conclusions based on analyses of the Curie temperatures for the RNi₂Mn system (R=Tb, Dy, Ho, Er), that the magnetic ordering is dominated by the 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}MnO₃ [33] with this relatively high value ascribed to the formation of ferromagnetic clusters above T_C . According to Halder *et al.* [13], β describes the rate of change of the ordered moment below T_C with a smaller β indicating more rapid the growth of the ordered moment. In the case of TbNi₂Mn, $\beta = 0.77$ indicates a slower growth of the ordered moment with decreasing temperature as is evident in the DC magnetic data (Fig. 3(a)). The slow growth of the ordered

moment in TbNi₂Mn 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 TbNi₂Mn (102-186 K) and the resultant Arrot-plots of M^2 as a function of H/M are shown in Figs. 6(a) and 6(b) respectively. The Arrot-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 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 TbNi₂Mn at 146 K and 150 K (Fig. 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] and [31], M-H curves well below T_C show an upward curvature away from linearity (leading to a larger value of δ), M-H curves well above T_C exhibit a downward curvature (leading to a smaller δ) while for temperatures close to T_C , the M-H curves show linear behaviour. On this basis the δ values derived at 146 K ($\delta = 2.66 \pm 0.01$) and 150 K ($\delta = 2.41 \pm 0.01$) indicate that the δ 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 Fig 5(a) as based on the ac susceptibility data.

The modified Arrot-plots, $M^{1/\beta}$ as a function of $(H/M)^{1/\gamma}$, shown in Fig. 6(d) provide a cross-check of our critical exponent analyses. Using $\beta = 0.77 \pm 0.12$ and $\gamma = 1.09 \pm 0.07$ derived from the susceptibility data, these modified Arrot-plots exhibit isothermal curves which are parallel to a high degree for DC fields $\mu_0 H > 2$ T. The average slope is 905 ± 10 (emu/g) ^{$1/\gamma + 1/\beta$} T ^{$-1/\gamma$} with slopes of 892 ± 14 (emu/g) ^{$1/\gamma + 1/\beta$} T ^{$-1/\gamma$} at the lowest temperature 102 K (~ -1.4 %) and 917 ± 9 (emu/g) ^{$1/\gamma + 1/\beta$} T ^{$-1/\gamma$} at

the highest temperature, 186 K ($\sim +1.3\%$). This analysis demonstrates that the critical exponent values determined for δ , β and γ from the ac susceptibility data, also describe the DC magnetic behaviour.

3.4 Magnetocaloric Effect

Given that many Laves phase compounds exhibit large magnetocaloric effects (MCE) [34-36], we investigated the magnetic entropy change for TbNi₂Mn*. The isothermal entropy change $-\Delta S_M$ for magnetic field change ΔH from $H = 0$ to H , was derived from the Maxwell relation [1, 37]:

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (6).$$

The magnetic entropy curves $-\Delta S_M$ (Fig. 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 K and $-\Delta S_M \sim 3.0$ J/kg K for $\Delta\mu_0 H = 0-3$ T and $\Delta\mu_0 H = 0-5$ T respectively. By comparison, for TbNi₂ where a sharp MCE peak was found around $T_C = 37.5$ K, $-\Delta S_M \sim 14.5$ J/kg K for field change $\Delta\mu_0 H = 0-5$ 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 TbNi₂Mn, leading to the reduced value of $-\Delta S_M$ compared with TbNi₂.

Mean field theory predicts that $-\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ at second order phase transitions [37, 38]. The linear fit to data in Fig. 7(b) demonstrates that the relationship $-\Delta S_M \propto (\mu_0 H/T)^{2/3}$ is valid around T_C , in agreement with the conclusion from magnetization measurements that the magnetism of TbNi₂Mn is governed by long range interactions.

3.5 Mössbauer spectroscopy

Examples of Mössbauer spectra and fits for the ⁵⁷Fe-doped TbNi₂Mn sample over the temperature range 5-300 K are shown in Fig. 8. As outlined below the fits allow the average values of the

hyperfine parameters of $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ to be determined above and below the transition temperature (Fig 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_2Mn 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 (Fig. 8(a)) have fractional areas $D_1 \sim 10(1) \%$ and $D_2 \sim 90(2) \%$. Rietveld refinements of room temperature TbNi_2Mn 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 (Fig. 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 Fig. 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 Fig 9(a) results from contributions to the exchange interactions present in the Tb and transition metal (Ni, Mn) sublattices and correspondingly reflect the magnetic order in the Tb and (Ni, Mn) sublattices [11, 37, 38]. The spectra for magnetically split spectra 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 $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ spectra 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 Fig. 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 Fig. 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 Fig 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 $\sim 90\%$, correspond to the contribution from ^{57}Fe at 16d sites with the third sextet S_3 representing ^{57}Fe located at the 8a site of fractional area $\sim 10\%$. The spectral fits are found to be consistent with our conclusion that the $\text{Mn}(^{57}\text{Fe})$ atoms occupy both 16d and 8a sites in RNi_2Mn .

It should be noted that similar behaviour has been found for RMn_2 compounds ($\text{R}=\text{Tb}, \text{Dy}, \text{Ho}$) 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 $d_{\text{Mn-Mn}} \sim 2.66 \text{ \AA}$), 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].

Fig. 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]:

$$B_{hf}(T) = B_{hf}(0)(1 + bT^{\frac{3}{2}} + cT^{\frac{5}{2}} + dT^2) \quad (7).$$

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 Fig 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 waves interactions dominate, while the T^2 term indicates that Stoner-type interactions also contribute to the magnetic behaviour of $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ 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 $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ [42] and MnSi [45] systems but differs from that in the R_2Fe_{17} -based systems where T^2 dependence of the hyperfine field was obtained [46].

As shown in Fig. 9(b) the average value of the quadrupole interaction $\varepsilon \sim 0.26 \text{ mm/s}$ for $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ above T_C (the quadrupole shift $\varepsilon = |\Delta|/2$ for quadrupole splitting Δ [6]) is similar to values reported for the RMn_2 system ($\varepsilon = 0.171 \text{ mm/s}$ and $\varepsilon = 0.127 \text{ mm/s}$ 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 (Fig 8(a)), is consistent with a positive value for the quadrupole interaction ε . A positive ε also accounts well for the asymmetry observed in the predominantly quadrupolar spectra around T_C .

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

$$IS(T) = IS_0(T) + IS_{sods}(T) \quad (8).$$

$IS_0(T)$ represents the temperature dependence of the charge density at the probe nucleus which is generally weakly temperature dependent. The second term, IS_{SODS} , the so-called second-order Doppler shift, can be described in terms of the Debye model for the phonon spectrum by,

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

m is the mass of the ^{57}Fe nucleus, k Boltzmann's constant, c the velocity of light and $\tau = \theta_D/T$ the reduced temperature [46, 48, 49]. The Debye temperature θ_D has been derived to be $\theta_D = 200 \pm 20$ K on fitting the mean isomer shift data of Fig. 9(c) to equation (9). The present value for the Debye temperature is similar to the value of $\theta_D = 188 \pm 5$ K reported by Jackson *et al.* [10] from specific heat measurements. The Debye temperature value of $\theta_D \sim 200$ K for TbNi_2Mn is consistent with the difference in θ_D values for TbNi_2 ($\theta_D = 264$ K) [50] and TbMn_2 ($\theta_D = 145$ K) [51] with the reduced value for TbMn_2 compared with TbNi_2 resulting in the intermediate value for TbNi_2Mn . Similar behaviour has also been found for ErNi_2Mn related system [18].

4 Conclusions

In summary, the MgCu_2 -type Laves phase of space group $\text{Fd-}3\text{m}$ can be formed for the TbNi_2Mn_x 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_2Mn_x 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, reported differences in T_C values for TbNi_2Mn_x (e.g. Table I) 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 RNi_2 and RMn_2 compounds is governed by R-R interactions whereas additional T-T and R-T contributions are present in RNi_2Mn . These additional T-T and R-T components in the

magnetic energy terms for RNi_2Mn contribute to their increased values of magnetic ordering temperatures compared with corresponding RNi_2 and RMn_2 compounds. A strong magneto-structural 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 $dT_C/dP \sim -1.96 \text{ K/GPa}$ for TbNi_2Mn [10]).

The magnetic phase transition at $T_C = 147 \pm 1.7 \text{ K}$ in TbNi_2Mn 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_2Mn 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 J/kg K for a magnetic field change of 0 T to 5 T. The combined magnetic field and temperature dependence of the entropy (Fig 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_2Mn has a Debye temperature $\theta_D = 200(20) \text{ K}$ as determined from the temperature dependence of the mean isomer shift.

Acknowledgements

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:

- [1] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
- [2] P. Kumar, K. G. Suresh, A. K. Nigam, A. Magnus, A. A. Coelho, and S. Gama, Phys. Rev. B **77**, 224427 (2008).
- [3] S. Gama, A. A. Coelho, A. de Campos, A. M. Carvalho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004); E. J. R. Plaza, V. S. R. de Sousa, P. J. von Ranke, A. M. Gomes, D. L. Rocco, J. V. Leitão and M. S. Reis, J. Appl. Phys. **105**, 013903 (2009).
- [4] J.L. Wang, S.J. Campbell, A.J. Studer, M. Avdeev. R. Zeng and S.X. Dou, J. Phys.: Condens. Matter **21**, 124217 (2009).
- [5] R. Hauser, E. Bauer, E. Gratz, Th. Häufler, G. Hilscher and G. Wiesinger, Phys. Rev. B **50**, 13493 (1994); M. Dzevenko, L. Havela, J. Prokleska, P. Svoboda, K. Miliyanchuk and Y. Kalychak, Physica B **321**, (2007).
- [6] J.L. Wang, S.J. Campbell, A.J. Studer, M. Avdeev, M. Hofmann, M. Hoelzel and S.X. Dou, J. Appl. Phys. **104**, 103911 (2008).
- [7] I. Dincer, A. Elmali, Y. Elerman, H. Ehrenberg, H. Fuess, and O. Isnard, J. Phys.: Condens. Matter **16**, 2081 (2004).
- [8] J. L. Wang, C. C. Tang, G. H. Wu, Q. L. Liu, N. Tang, W. Q. Wang, W. H. Wang, F. M. Yang, J. K. Liang, F. R. de Boer, and K. H. J. Buschow, Solid State Commun. **121**, 615 (2002).
- [9] J. L. Wang, C. Marquina, M. R. Ibarra, and G. H. Wu, Phys. Rev. B **73**, 094436 (2006).
- [10] D. D. Jackson, S. K. McCall, S. T. Weir, A. B. Karki, D. P. Young, W. Qiu, and Y. K. Vohra, Phys. Rev. B **75**, 224422 (2007).
- [11] N. V. Mushnikov, V. S. Gaviko, J. Park, and A. N. Pirogov, Phys. Rev. B **79**, 184419 (2009).
- [12] A. Berger, G. Campillo, P. Vivas, J. E. Pearson, and S. D. Bader, *J. Appl. Phys.* **91**, 8393 (2002).
- [13] M. Halder, S. M. Yusuf, M. D. Mukadam and K. Shashikala Phys. Rev. B **81**, 174402 (2010).

- [14] Wei Li, H. P. Kunkel, X. Z. Zhou, G. Williams, Y. Mukovskii, and D. Shulyatev, Phys. Rev. B **75**, 012406 (2007)
- [15] J. H. Zhao, H. P. Kunkel, X. Z. Zhou, G. Williams, and M. A. Subramanian, Phys. Rev. Lett. **83**, 219 (1999). W.J. Jiang, X. Z. Zhou, G. Williams, R. Privezentsev and Y. Mukovskii, Phys. Rev. B **79**, 214433 (2009).
- [16] X.Z. Zhou, W. Li, H.P. Kunkei and G. Williams, Phys. Rev. B **73**, 012412 (2006); A.G. Berndt, X. Chen, H.P. Kunkei and G. Williams, Phys. Rev. B **52**, 10160 (2006); D. Wang, H.P. Kunkei and G. Williams, Phys. Rev. B **51**, 2872 (1995).
- [17] B. Padmanabhan, H. L. Bhat, S. Elizabeth, S. Rößler, U. K. Rößler, K. Dörr, and K. H. Müller, Phys. Rev. B **75**, 024419 (2007) and references therein.
- [18] J.L. Wang, S.J. Campbell, R. Zeng, S.X. Dou and S.J. Kennedy, J. Appl. Physics, in press.
- [19] J. H. Zhu and C. T. Liu, Acta mater. **48**, 2339 (2000)
- [20] N.V. Mushnikov, V.S. Gaviko, E.G. Gerasimov, P.B. Terent'ev, J.G. Park, A.N. Pirogov, J. Phys. Conf. Series **200**, 032049 (2010).
- [21] E. Gratz, E. Goremychkin, M. Latroche, G. Hilscher, M. Rotter, H. Muller, A. Lindbaum, H. Michor, V. Paul-Bonocour, and T. Fernandez-Dias, J. Phys.: Condens. Matter **11**, 7893 (1999).
- [22] A. V. Morozkin, Yu. D. Seropeign, A. V. Gribanov, and J. M. Barakatova, J. Alloys Compd. **256**, 175 (1997).
- [23] M.R. Ibarra, J.I. Arnaudas, P.A. Algarabel and A. del Moral, J. Magn. Magn. Mat. **46**, 167(1984).
- [24] S. Labroo, N. Ali, and P. Robinson, J. Appl. Phys. **67**, 5292 (1990).
- [25] E. Belorizky, M.A. Fremy, J.P. Gavigan, D. Givord and H.S. Li. J. Appl. Phys. **61**, 3971. (1987); N.H. Duc, Phys. Stat. Sol. (b) **164**, 545 (1991); N.H. Duc, T.D. Hien, D. Givord, J.J. Franse and F.R. de Boer, J. Magn. Magn. Mat. **124**, 305 (1993).

- [26] J. L. Wang, N. Tang, Y. P. Shen, D. Yang, C. P. Yang, B. Fuquan and F. M. Yang, J. Magn. Magn. Mat. **204**,185 (1999); J.L. Wang, R.W. Zhao, N. Tang, W.Z. Li, Y.H. Gao, F.M. Yang and F.R. de Boer. J. Appl. Phys. **76**, 6740 (1994).
- [27] J. J. M. Franse and R. J. Radwanski, *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier Science, B.V., Amsterdam, 1993), Vol. **7**, p. 307.
- [28] M. Mizumaki, K. Yano, I. Umehara, F. Ishikawa, K. Sato, A. Koizumi, N. Sakai, and T. Muro Phys. Rev. B **67**, 132404 (2003).
- [29] Sava Milosević and H. Eugene Stanley, Phys. Rev. B **6**, 986 (1972).
- [30] H. E. Stanley, in *Introduction to Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).
- [31] M. Campostrini, M. Hasenbusch, A. Pelissetto, P. Rossi, and E. Vicari, Phys. Rev. B **65**, 144520 (2002).
- [32] S. N. Kaul, J. Magn. Magn. Mater. **53**, 5 (1985).
- [33] R. Venkatesh, M. Pattabiraman, S. Angappane, G. Rangarajan, K. Sethupathi, J. Karatha, M. Fecioru-Morariu, R. M. Ghadimi and G. Guntherodt, Phys. Rev. B **75**, 224415 (2007).
- [34] N. K. Singh, S. Agarwal, K. G. Suresh, R. Nirmala, A. K. Nigam, and S. K. Malik, Phys. Rev. B **72**, 014452 (2005); N.K. Singh, K.G. Suresh, D S Rana, A K Nigam, S.K. Malik, J. Phys.: Condens. Matter. **18**, 10775 (2006).
- [35] N.A. de Oliveira, J. Phys.: Condens. Matter **20**, 175209 (2008).
- [36] S. Ma, W. B. Cui, D. Li, N. K. Sun, D. Y. Geng, X. Jiang and Z. D. Zhang, Appl. Phys. Lett. **92**, 173113 (2008).
- [37] J.L. Wang, S.J. Campbell, R. Zeng, C.K. Poh, S.X. Dou and S.J. Kennedy, J. Appl. Phys. **105**, 07A909 (2009).
- [38] H. Oesterreicher and F. T. Parker, J. Appl. Phys. **55**, 4334 (1984).
- [39] J. Marzec, J. Przewoźnik, J. Żukrowski and K. Krop, J. Magn. Magn. Mater. **157/158**, 413 (1996).

- [40] P. Stoch, J. Pszczoła, L. Dąbrowski, J. Suwalski and A. Pańta, *J. Alloy. Comp.* **337**, 33 (2002).
- [41] J.L. Oddou, C. Jeandey, R. Ballou, J. Deportes and B. Ouladdiaf, *Solid State Commum.* **85**, 419 (1993).
- [42] M. K. Chattopadhyay, S. B. Roy, Sujeet Chaudhary, and Kanwal Jeet Singh, and A. K. Nigam, *Phys. Rev. B* **66**, 174421 (2002)
- [43] B.E. Argyle, S.H. Charap, and E.W. Pugh, *Phys. Rev.* **132**, 2051 (1963)
- [44] C.L. Chien and R. Hasegawa, *Phys. Rev. B* **16**, 2115 (1977).
- [45] M.K. Chattopadhyay, P. Arora and S.B. Roy, *J. Phys.: Condens. Matter* **21**, 296003 (2009).
- [46] J. L. Wang, S. J. Campbell, O. Tegus, C. Marquina and M. R. Ibarra, *Phys. Rev. B* **75**, 174423 (2007).
- [47] J. Przewoźnik, J. Żukrowski and K. Krop, *J. Magn. Magn. Mater.* **119**, 150 (1993).
- [48] J. Cieślak, S. M. Dubiel, J. Żukrowski, M. Reissner and W. Steiner, *Phys. Rev. B* **65**, 212301 (2002).
- [49] G.J. Long, D. Hautot, F. Grandjean, D.T. Morelli and G.P. Meisner, *Phys. Rev. B* **60**, 7410 (1999).
- [50] M.R. Ibarra, A. Del Moral and J.S. Abell, *J. Phys. Chem. Solid.* **45**, 789 (1984).
- [51] M. Shiga and H. Wada, *J. Magn. Magn. Mater.* **151**, 225 (1995).

Table I Structure and magnetic transition temperatures of TbNi₂Mn_x compounds together with information on sample preparation.

Composition	Structure	Preparation conditions	Space group	Lattice parameter a (Å)	T _C (K)	Reference
TbNi ₂ Mn	MgCu ₂ (C15)	Annealed at 750 °C for 7 days	<i>Fd-3m</i>	7.158 Å	131 K	[9]
TbNi ₂ Mn	MgCu ₂ (C15)	Annealed at 900 °C for 5 days	<i>Fd-3m</i>	7.123 Å	151 K	[10]
TbNi ₂ Mn	AuBe ₅ (C15b)-	Annealed at 870 °C for 7 days	<i>F-43m</i>	7.1842 Å	142 K	[11]
TbNi ₂ Mn _x with x=0.25, 0.5, 0.75	MgCu ₂ (C15)	Annealed at 870 °C for 7 days	<i>Fd-3m</i>			[18]
TbNi ₂ Mn _x with x=0.90, 0.97, 1.00, 1.03, 1.10	MgCu ₂ (C15)	As prepared	<i>Fd-3m</i>	7.149 Å, 7.177 Å, 7.202 Å, 7.190 Å, 7.190 Å	144 K, 149 K, 150 K, 145 K, 141 K.	Present work
TbNi ₂ Mn*	MgCu ₂ (C15)	As prepared	<i>Fd-3m</i>	7.178 Å	147	Present work

Figure Captions

Fig. 1 (a) X-ray diffraction patterns for as prepared TbNi_2Mn_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_2Mn^* sample ($\lambda = 2.4072 \text{ \AA}$). 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.

Fig 2 (a) Variation of the lattice constant a with Mn composition for as-prepared TbNi_2Mn_x .

(b) Variation of the Curie temperature T_C , with Mn composition. T_C was derived from the minimum in the dM/dT versus T curve e.g. Fig 3(a).

Fig. 3 (a) Cooling and warming curves of the DC magnetization for TbNi_2Mn^* ($\mu_0 H_{DC}=0.005 \text{ T}$).

The warming data were measured after first cooling in zero field (ZFC); the cooling data were then measured in the magnetic field (FC). The warming and cooling directions are indicated by the arrows with the Curie temperature marked for each sample. The dM/dT versus T curve as derived from the cooling data is shown in the inset.

(b) Temperature dependence of the ac susceptibility on warming for TbNi_2Mn^* ($\mu_0 H_{DC}=0.01 \text{ T}$) with the $d\chi/dT$ data shown as the inset.

(c) The magnetic ordering temperatures T_C as a function of the de Gennes factor,

$G_R=(g-1)^2 J(J+1)$ for RNi_2Mn , RNi_2 and RMn_2 compounds (adapted from Fig 4 [9]). The

dashed lines represent linear fits for RNi_2Mn ($T_C=9.89 \times G_R+26.6$), RNi_2 ($T_C = 3.39 \times G_R$) and

RMn_2 ($T_C = 5.14 \times G_R$).

Fig. 4 Temperature dependence of the ac magnetic susceptibility as measured in the DC magnetic

fields indicated ($\mu_0 H_{DC} = 0.5 \text{ T to } 8 \text{ T}$) for TbNi_2Mn^* . The dashed line shows the locus of T_M , the temperatures of maximum susceptibility in the $\chi'_m(H, T)$ curves.

Fig. 5 (a) Values of χ_M , the maxima in susceptibility for the different DC field values ($0.5 \text{ T} < \mu_0 H < 8 \text{ T}$), 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 temperature at which the maxima in susceptibility occurs in Fig. 4 plotted against $H^{1/(\gamma+\beta)}$, where $1/(\gamma+\beta) = 0.57$ are exponents based on the Heisenberg model. The zero field intercept yield a value of $T_C = 147.0 \pm 1.7 \text{ K}$.

(c) Values of χ_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_C was determined as indicated in Fig. 5(b). The line represents a fit to the power law of equation (4).

Fig. 6 (Colour online) (a) Magnetization as a function of applied DC field ($\mu_0 H = 0 - 5 \text{ T}$) for TbNi_2Mn^* around the Curie temperature T_C .

(b) Arrot-plots of M^2 as a function of $\mu_0 H/M$ for the magnetisation data of Fig 6(a). The positive slopes indicate that the transition at T_C is second-order.

(c) Magnetisation for TbNi_2Mn^* at $T = 146 \text{ K}$ and $T = 150 \text{ K}$ versus DC field plotted on a double-logarithmic scale. The lines represents fits of M versus H resulting with $\delta = 2.66 \pm 0.01$ at 146 K and $\delta = 2.41 \pm 0.01$ at 150 K based on $M \sim H^{1/\delta}$, equation (5).

(d) Modified Arrot-plots of $M^{1/\beta}$ as a function of $(H/M)^{1/\gamma}$ for $\gamma = 1.09$ and $\beta = 0.77$ (exponents derived from fits to equations (3) and (4) in Figs 5(c) and (d) respectively).

Fig. 7 (Color online) (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$ for TbNi_2Mn^* as measured in magnetic fields up to 5 T and derived from equation (6).

(b) Dependence of the entropy change $-\Delta S_M(T, H)$ on the parameter $(\mu_0 H/T_C)^{2/3}$. The full line represents a linear fit to the data.

Fig. 8 (Color online) ^{57}Fe Mössbauer spectra of $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ 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 $B_{\text{hf}1}$, dash-dot line; S_2 - medium hyperfine field $B_{\text{hf}2}$; dotted line; S_3 - smallest hyperfine field $B_{\text{hf}3}$; dashed line).

Fig. 9 (Color online) Temperature dependences of the Mössbauer hyperfine parameters of $\text{TbNi}_2\text{Mn}(^{57}\text{Fe})$ derived from the fits to the spectra shown in Fig 8.

- (a) The average hyperfine field values $\langle B_{\text{hf}} \rangle$ determined using a distribution of hyperfine fields (open triangles) and three sextets (half filled diamond). As discussed in the text, the dashed line represents the best fit to the equation: $B_{\text{hf}}(T) = B_{\text{hf}}(0)(1 + bT^{3/2} + cT^{5/2} + dT^2)$.
- (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.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9