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Magnetic behaviour of TbMnFe

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Abstract. Neutron diffraction and Mössbauer measurements have been carried out on the cubic Laves phase intermetallic TbMnFe. The magnetic moment on the transition metal atom is found to be low, 0·2 μ_B, at room temperature. This moment is temperature independent down to 10 K. Magnetic moment on the rare earth atom varies from 2·5 μ_B at 296 K to 7·27 μ_B at 10 K. Mössbauer spectra recorded at 298 K and 78 K have magnetic character but there is a large distribution of hyperfine field values. Both these features arise due to magnetic frustration created in the sample due to the competing ferro and antiferromagnetic interactions between the transition metal atoms.

Keywords. Rare earth intermetallics; neutron diffraction; Mössbauer; magnetic structure.

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1. Introduction

Numerous investigations of magnetic properties of heavy rare earth (R) transition metal (T) intermetallics have been carried out using different probes [1]. Amongst these intermetallics, those having the formula RT_2 crystallize in the Laves phase structure. The presence of three different competing exchange interactions namely $4f$–$4f$, $4f$–$3d$ and $3d$–$3d$ [1–3], makes the study of their magnetic properties interesting in spite of their simple crystal structure.

RMn_2 compounds crystallize in the C15 cubic Laves phase structure for R = Y, Gd, Tb, and Dy while a C14 hexagonal Laves phase structure exists for R = Er, Tm and Lu. $HoMn_2$ and $SmMn_2$ can have either of the two structures depending on the heat treatment. RFe_2 compounds, on the other hand, crystallize in the C15 cubic Laves phase structure for all these heavy lanthanides.

Some of the RMn_2 intermetallics show large magnetovolume anomalies at their magnetic ordering temperatures [4]. Large changes in the cell constant are found in YMn_2 and $TbMn_2$ [5]. The cause of these large magnetovolume anomalies has been attributed to the Mn–Mn inter-atomic distance, d_{Mn-Mn} [6, 7]. There is a critical distance, $d_c = 2{\cdot}66$ Å, between Mn atoms to sustain the magnetic moment at Mn sites for both cubic and hexagonal structure. For $d_{Mn-Mn} > 2{\cdot}66$ Å, the Mn atom has a localized magnetic moment and for $d_{Mn-Mn} < 2{\cdot}66$ Å, there is no local magnetic moment. However, when d_{Mn-Mn} is close to 2·66 Å, the Mn moment is unstable and the magnetic properties become sensitive to external parameters like pressure, temperature, alloying,

etc. [8–10]. Unlike RMn_2 intermetallics, a ferromagnetic ordering exists between Fe atoms in all RFe_2 alloys, with the moment on R aligned antiparallel to Fe moment, resulting in a ferrimagnetic structure [11]. The ordered moment on Fe site is close to $1{\cdot}6\,\mu_B$ at low temperatures.

The magnetization and Mössbauer measurements on the compound $Ho(Fe_{2-x}Mn_x)$ [12] have revealed that the magnetic moment on Fe decreases from $1{\cdot}43\,\mu_B$ to $0{\cdot}96\,\mu_B$ with increase in Mn concentration from $x = 0{\cdot}0$ to $x = 0{\cdot}6$. This concentration dependence of the magnetic moment is not linear. The moment on Mn, assuming an antiferromagnetic alignment of Fe and Mn moments, has been shown to be very low [12]. Similar observations are reported in $Y(Fe_{2-x}Mn_x)$ [13] where the two end members with $x = 0$ and $x = 2$ have ferromagnetic and helical antiferromagnetic ordering, respectively. The mixed system has two types of Mn atoms, one of high spin with moment of $2{\cdot}7\,\mu_B$ and the other of low spin with moment decreasing from $0{\cdot}6\,\mu_B$ to $0{\cdot}08\,\mu_B$ as the Mn concentration is increased.

The intermetallics $TbMn_2$ and $TbFe_2$ form a solid solution over the entire concentration range [14]. $TbFe_2$ has a ferrimagnetic ordering with $T_C = 697$ K with Fe moment of $1{\cdot}6\,\mu_B$ at low temperatures aligned along $\langle 111 \rangle$ direction [11, 15]. $TbMn_2$ exhibits a complex magnetic behaviour [16–20]. For $40\text{ K} < T < 45\text{ K}$, there is a ferrimagnetic ordering of rare earth and transition metal atoms. Below 40 K, the structure is antiferromagnetic, characterized by the propagation vector (2/3, 2/3, 0). At 2 K, magnetic ordering with propagation vector (1/2, 1/2, 1/2) is observed with magnetic peaks at (1/2, 1/2, 1/2), etc. The structure scheme is modified by application of external magnetic field [16, 17]. The replacement of 4% Mn by Fe changes the magnetic structure drastically [17, 18] where rhombohedral distortion below 70 K is reported.

To understand the magnetic behaviour of the mixed system, where an interplay of ferro and antiferromagnetic interactions could lead to frustration, we have undertaken a neutron diffraction study of TbMnFe. The results of neutron diffraction on TbMnFe and Mössbauer measurements on TbMnFe and $TbFe_2$ are reported here. In TbMnFe the T–T distance, $d_{T-T} = 2{\cdot}646$ Å, which is close to d_c. Hence, it would be interesting to study the behaviour of magnetic moments on T atom site.

2. Experimental

The sample was prepared by repeated arc melting of the constituents of 99·9% purity in an ultra pure argon atmosphere and then annealed for 200 h at temperature of 1150 K. Single phase formation for the annealed samples was tested by X-ray diffraction. The total weight loss due to evaporation of the constituents and the intermetallic formed during melting was less than 2·5%. For neutron measurements, well powdered sample was packed in a cylindrical vanadium container. For the low temperature experiments, the sample was packed in an aluminium container. Powder diffraction profiles were recorded using the PSD-based powder diffractometer at Dhruva reactor [21] with a wavelength of 1·1 Å. Diffraction patterns were recorded at a series of temperatures in the range of 10 K to 300 K using a two-stage closed cycle refrigerator (CCR).

Mössbauer spectra ^{57}Fe were recorded at room temperature and at 78 K, using a constant acceleration drive and a ^{57}Co source in a Rh matrix. The $TbFe_2$ spectra were

least squares fitted using a computer program which solves the complete nuclear hyperfine Hamiltonian matrix. The isomeric shift values are reported with respect to Fe metal at room temperature.

3. Experimental results

3.1 *Neutron diffraction*

The diffraction pattern recorded at room temperature could be indexed using C15 cubic Laves phase structure. The X-ray as well as neutron diffraction patterns showed the presence of weak Fe lines. The sample being magnetically ordered at 300 K, refinement of the neutron diffraction pattern was carried out using higher angle data [22]. The structure of TbMnFe conforms to the space group Fd3m. The parameters varied were scale factor, zero angle of the detector, half width parameters, cell constant, temperature factor and the occupancies of the different atoms in the unit cell. The occupancies obtained were found to be consistent with the stoichiometry TbMnFe. Variation of Mn occupancy parameter yielded no change in its value. The analysis gave the cell constant as 7·485 Å, and a temperature factor (B) of 0·90 Å^2. The refinement converged to an agreement factor of 3·4%.

A particularity of the C15 Laves phase structure factors is that the magnetic part of the intensity of (220) reflection depends only on the magnetic moment of *R*-site while that of (222) reflection depends only on the magnetic moment of the *T*-metal site. The (222) reflection was found to be weak and hence was not used in our calculation of magnetic moment. The reflections (220), (111) and (311) were used to obtain the *R*- and *T*-site magnetic moments and were found to be $2{\cdot}50(3)\mu_B$ and $0{\cdot}20(4)\mu_B$ at *RT*, respectively. The form factors used were from Lander *et al* [23] and Watson *et al* [24]. The intensities of the remaining reflections were calculated using these moments and were found to be in good agreement with the observed intensities. Table 1 gives the comparison between observed and calculated intensities.

Figure 1 shows the neutron diffraction patterns of TbMnFe as a function of temperature from 10 K to 300 K. The patterns have been corrected for background and

Table 1. Observed and calculated intensities of different reflections of TbMnFe at 300 K with error bars in bracket using $M_A = 2{\cdot}5\,\mu_B$ and $M_B = 0{\cdot}2\,\mu_B$ for calculations.

hkl	I_{obs}	I_{calc}
(111)	3274(57)	3275
(220)	6504(81)	6206
(311)	8739(94)	8766
(222)	1323(36)	1208
(400)	378(19)	430
(422)	2922(54)	3358
(511)*		
(333)	3924(62)	4166
(440)	3195(56)	3195

*Fe (200) also contributes to these reflections.

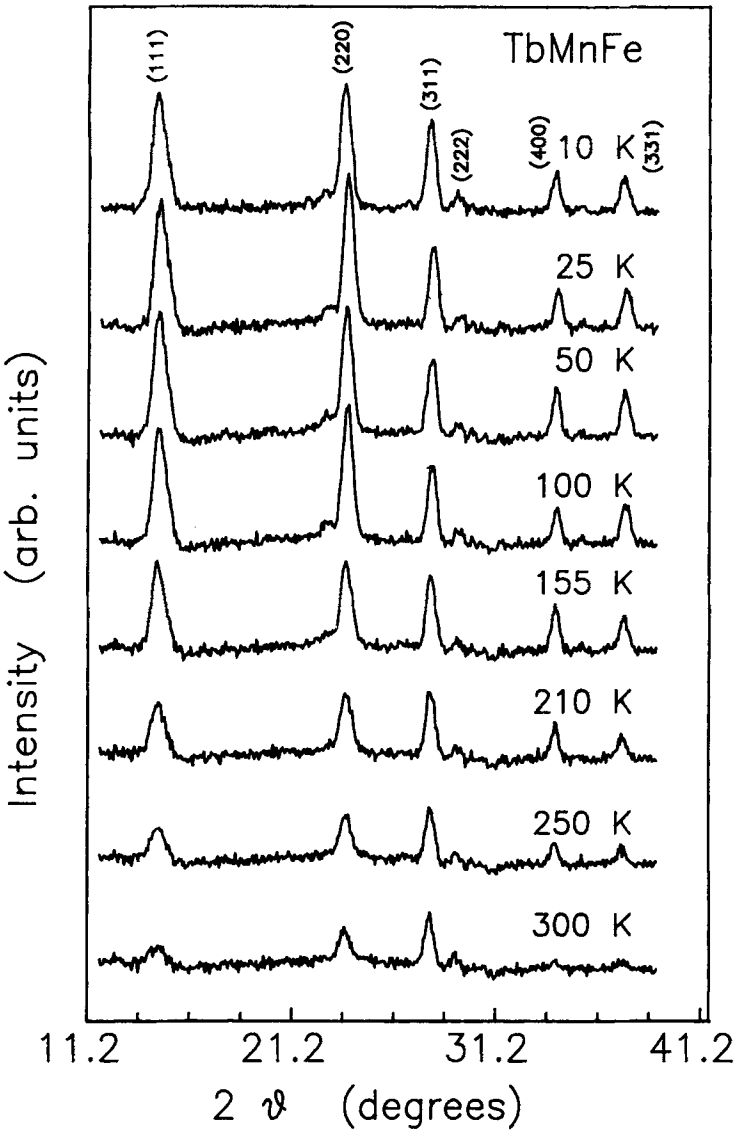

Figure 1. Temperature dependence of neutron diffraction patterns for TbMnFe.

contribution from Al peaks of the sample holder. As seen from the figure, the intensities of the (111), (220), (311), (400) and (331) reflections increase as the temperature is lowered to 10 K, but there is no observable change in the intensity of (222) reflection. No additional line suggestive of antiferromagnetic ordering was observed down to 10 K. The structure remains cubic down to 10 K. The moment obtained on *R*-site was found to be 7·27(3)μ_B at 10 K. The moment on *T*-site remains unchanged as indicated by the constant value of the intensity of the (222) reflection. Temperature dependence of the peak intensities of some of the reflections is shown in figure 2. It is of interest to note

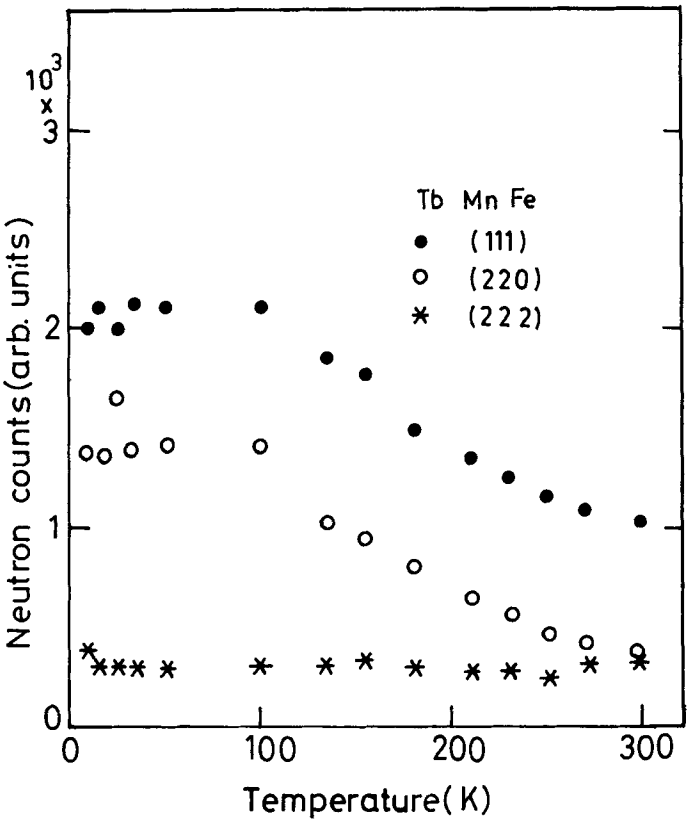

Figure 2. Temperature dependence of peak intensities of (111), (220) and (222) reflections in TbMnFe.

that the ordered Tb site moments for $TbFe_2$ and $TbMn_2$ below the Curie and Néel temperatures are 9·0 μ_B and 8·7 μ_B, respectively [11].

3.2 *Mössbauer measurements*

Mössbauer spectra of $TbFe_2$ and TbMnFe recorded at room temperature and 78 K are shown in figure 3. The observed spectrum consists of two magnetic sextets having an intensity ratio 1:3 which implied that the magnetization is along the (111) direction [25,26]. These two sextets originate from Fe atoms which are crystallographically equivalent sites of trigonal symmetry ($\bar{3}m$) but magnetically inequivalent as the two values of the angle θ between the two principal efg axis $\langle 111 \rangle$ and the magnetization direction [111] are 0° and 70°32′, respectively. This observation is in conformity with the observations of earlier investigators [25]. From the analysis of the RT spectrum, the values of isomeric shift, δ, and quadrupole splitting ΔE_q observed were found to be $-0{\cdot}07\,\text{mms}^{-1}$ and $-0{\cdot}49\,\text{mms}^{-1}$, respectively, and the internal hyperfine field values for the two [25–27] Fe sites characterized by $\theta = 70°32'$ and $\theta = 0°$ were $h_1 = 215\,\text{kOe}$ and $h_2 = 197\,\text{kOe}$, respectively. The analysis of the 78 K data gave $\delta = 0{\cdot}03\,\text{mms}^{-1}$, $\Delta E_q = -0{\cdot}52\,\text{mms}^{-1}$, $h_1 = 228\,\text{kOe}$ and $h_2 = 200\,\text{kOe}$. The consistency between the

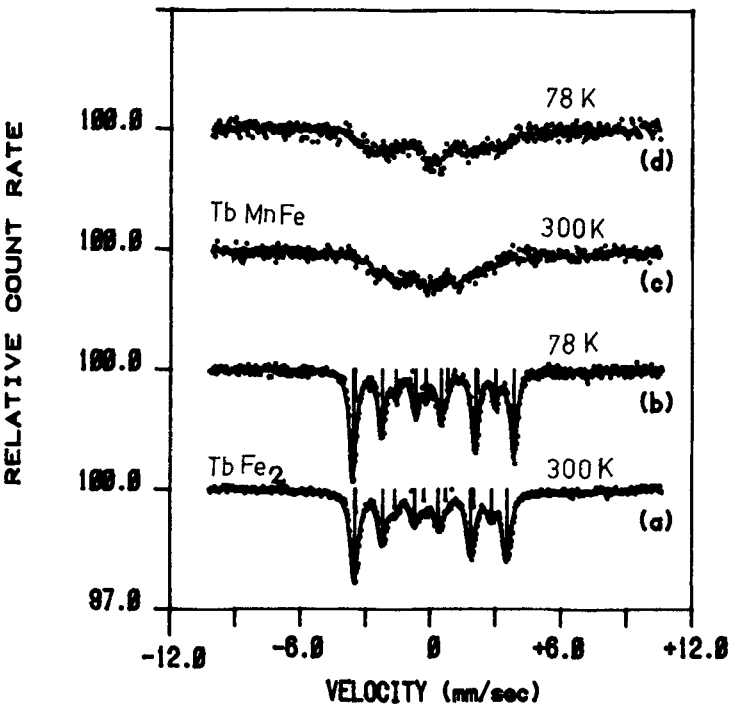

Figure 3. Mössbauer spectra of $TbFe_2$ (**a**, **b**) and TbMnFe (**c**, **d**) at 300 K.

RT and 78 K data was found to be very good. These values of internal hyperfine field correspond to $\mu_{Fe} \cong 1{\cdot}7\,\mu_B$ at 78 K assuming a value of $\cong$ 120 kOe per Bohr magneton.

The TbMnFe spectra, though magnetic in nature at both the temperatures, do not exhibit well resolved patterns and show a broad distribution of internal hyperfine field values, making the analysis complicated. Hence the Fe spin orientation cannot be uniquely defined for this system. However, the average internal hyperfine field value observed at 78 K suggests that the average moment on Fe site must be more than 1 μ_B. TbMnFe spectra recorded with an external magnetic field of 1 kOe did not show any appreciable change in the line shape, hence ruling out the possibility of superparamagnetism. The spectra in paramagnetic state for both the samples showed well-defined quadrupole doublets. These observations suggest that there is a distribution of internal hyperfine fields in TbMnFe due to different types of magnetic interactions resulting in the frustration of magnetic system.

4. Discussion

Antiferromagnetic coupling has been observed between Mn and any other 3d-transition metal atom when the separation between them is less than 2·8 Å [28]. In the present system this distance was found to be 2·64 Å, which is very close to the critical value of 2·66 Å. The interaction between Mn–Mn and Fe–Mn is negative while the Fe–Fe interaction is positive. Mn and Fe atoms are randomly distributed on *T*-sites,

leading to topological frustration. This frustration weakens the interaction between transition metal atoms leading to low moment. Hence no change in the intensity of scattered neutrons from the (222) planes is observed (within the instrument resolution) with lowering of temperature. In a similar system, namely $Tb(Mn_{0.96}Fe_{0.04})_2$ [17, 18], the moment on Mn, i.e., T-site, is found to be low. In this system, however, there is a progressive rhombohedral distortion below the magnetic ordering temperature, conforming to the space group ($R\bar{3}m$) which decouples the Mn moments into two sites, 1b and 3d. The neutron observations have been interpreted on the basis of magnetic moment on one Mn site (1b) and nonmagnetic Mn atoms on the other site (3d). In TbMnFe, the present neutron measurements do not show any crystallographic distortion and all T sites (16d) are randomly occupied by Fe and Mn atoms. The neutron observations at 300 K are in accordance with the Mössbauer results which do not show well-split spectra indicating distribution of hyperfine fields and thus no unique value of moment on T-site. Also, as the temperature is lowered to 78 K, the Mössbauer pattern does not improve much and thus it can be concluded that frustration persists at low temperatures. This is also inferred from neutron diffraction results at low temperatures. Only the Tb site moment is ordered at 296 K and its magnetic moment increases as the temperature is lowered.

5. Conclusion

Neutron diffraction measurements on TbMnFe show that the transition site moment is low and temperature independent. The rare earth moment increases from 2·5 μ_B at 296 K to 7·27 μ_B at 10 K. Mössbauer spectra suggest a distribution of hyperfine fields and their direction at the T-metal atom site. The observation that the magnetic moment on T-site remains unchanged with respect to temperature is in conformity with earlier observations in similar systems [29, 30].

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