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Magnetic structures and magnetic phase transitions in $TbMn_{0.33}Ge_2$

A. Gil[a], M. Hofmann[b], B. Penc[c], A. Szytuła[c,*]

[a]*Department of Mathematics and Natural Sciences, Pedagogical University, Armii Krajowej 13/15, 42-200 Częstochowa, Poland*
[b]*Berlin Neutron Scattering Center, Hahn-Meitner Institute, D-14 109 Berlin-Wannsee, Germany*
[c]*Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland*

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Abstract

A study of the magnetic structure of $TbMn_{0.33}Ge_2$ has been made using a neutron diffractometer of better resolution and new results have been obtained. The paramagnetic neutron diffraction data confirmed the $CeNiSi_2$-type of crystal structure reported earlier for this compound. The magnetic moments are located on terbium. At 1.5 K the Tb magnetic moments have two components: a collinear and sine wave modulated one so the magnetic order at this temperature has a complex character. With increasing temperature, the change of the magnetic structure to the sine wave modulated one is observed near the Néel temperature $T_N = 28$ K.

Keywords: Rare earth compounds; Crystal structure; Magnetically ordered materials; Neutron diffraction; Phase transition

1. Introduction

Ternary rare earth compounds of composition RTX_2 (R is a rare earth, T is a 3d element, and X is (Si, Ge, Sn)), form a large family of compounds. They crystallize in the $CeNiSi_2$-type structure [1] (*Cmcm* space group). These compounds display a variety of magnetic behaviours that have been the subject of numerous investigations (see bibliography in Ref. [2]).

X-ray [3] and neutron diffraction [4] data confirm that the RMn_xGe_2 compounds exhibit a defected $CeNiSi_2$-type crystal structure. Magnetic susceptibility and neutron diffraction data show that the compounds with R=Nd, Gd–Ho are antiferromagnets with a simple collinear structure at low temperatures [4].

$TbMn_{0.33}Ge_2$ was earlier reported to exhibit a collinear antiferromagnetic structure at 4.2 K [4]. However, in this experiment the neutron diffraction data were collected using an instrument with poor resolution. Now the study of the magnetic structure of $TbMn_{0.33}Ge_2$ has been repeated using the E6 diffractometer installed at the BER II reactor at the Hahn-Meitner Institute, Berlin. This instrument offers excellent resolution and is equipped with multichannel detectors. Additionally, it is possible to obtain full diffraction patterns at selected temperatures, so the temperature variations of the magnetic peak intensities and positions could be traced.

2. Results

The experiment was performed on the same samples as were used in our previous study [4]. The incident neutron wavelength was 2.44 Å. The data were processed by the Rietveld method using the FULLPROF program [5] with neutron scattering lengths taken from Ref. [6] and the Tb^{3+} form factor was adopted from Ref. [7].

The diffraction patterns collected in the paramagnetic state at 28 and 35 K, respectively, are shown in Fig. 1. Processing of neutron data confirmed that the space group is *Cmcm*. The atoms occupy the 4(*c*) positions: 0, *y*, 1/4; 0, $\bar{y}$, 3/4; 1/2, 1/2 + *y*, 1/4; 1/2, 1/2 − *y*, 3/4 (Table 1).

At 28 K a broad peak near $2\theta = 18°$ is observed in the neutron diffraction pattern which indicates short range ordering at this temperature.

In the low temperature (1.5–19 K) patterns two sets of magnetic reflections are observed. The dominant intensity contributions come from a reciprocal lattice position of the C-centered lattice ($\mathbf{k}_1 = 0$). The Tb magnetic moments are located at the following positions in the crystal unit cell:

*Corresponding author.
E-mail address: szytula@if.uj.edu.pl (A. Szytuła).

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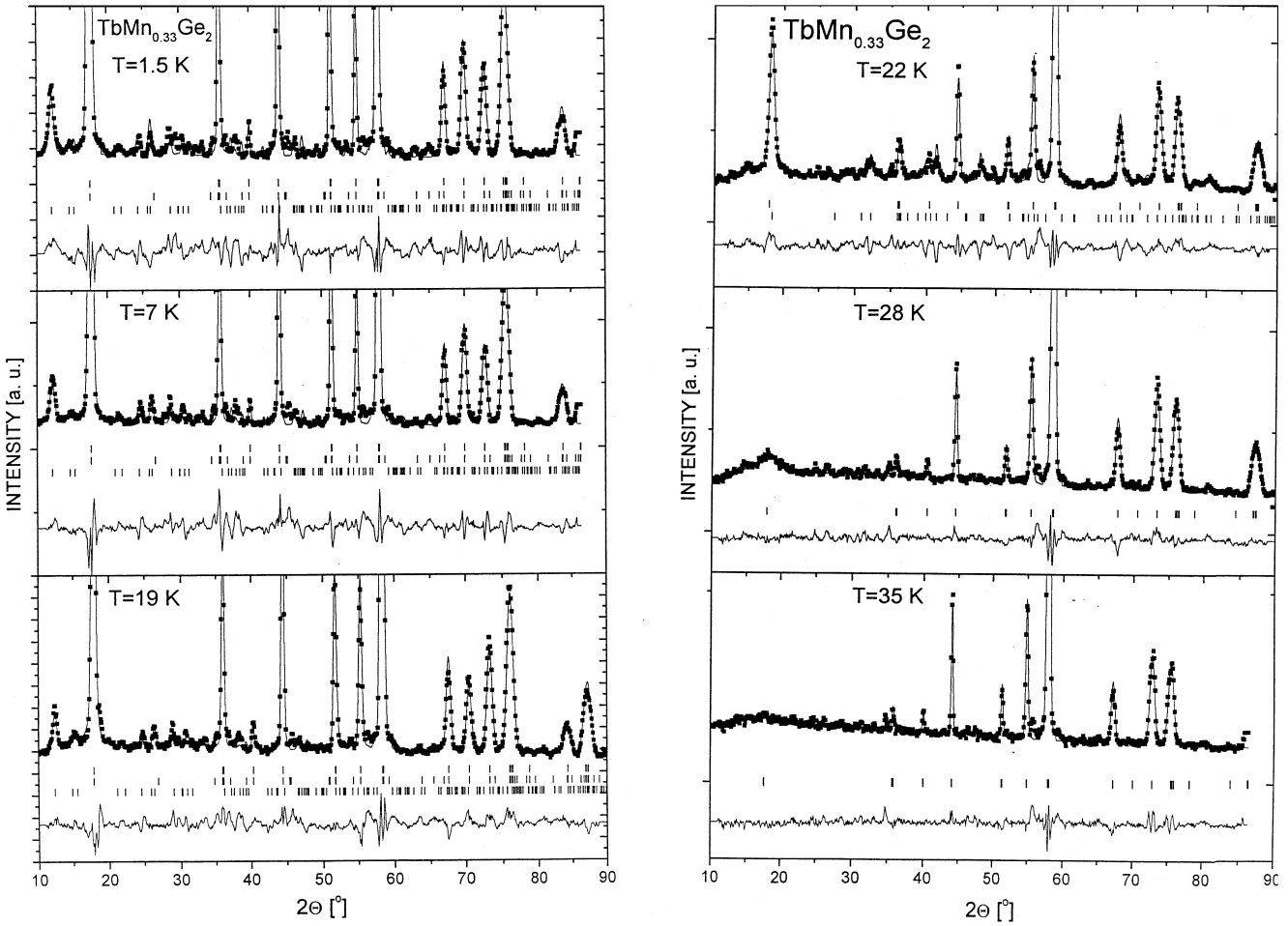

Fig. 1. Observed, calculated and difference neutron diagrams of $TbMn_{0.33}Ge_2$ obtained in paramagnetic state at 28 and 35 K and magnetic state at 1.5, 7, 19 and 22 K.

Table 1
Refined crystal and magnetic structure parameters of $TbMn_{0.33}Ge_2$

T (K)	1.5	7	19	22	24	28	35
a (Å)	4.1105(6)	4.1177(6)	4.1144(5)	4.1146(5)	4.1149(8)	4.1145(13)	4.1143(15)
b (Å)	15.8682(29)	15.8896(27)	15.8760(22)	15.8761(22)	15.8763(30)	15.8736(51)	15.8794(60)
c (Å)	3.9886(6)	3.9917(6)	3.9887(5)	3.9895(5)	3.9905(7)	3.9905(10)	3.9907(12)
V (Å^3)	260.16(13)	261.14(13)	260.54(12)	260.61(12)	260.70(16)	260.63(25)	260.72(27)
y_{Tb}	0.0987(12)	0.1004(12)	0.0997(8)	0.1003(9)	0.1015(9)	0.1053(7)	0.1042(9)
y_{Mn}	0.3178(155)	0.3046(146)	0.3170(69)	0.3125(37)	0.3001(42)	0.2997(7)	0.2994(52)
y_{Ge1}	0.4513(18)	0.4498(18)	0.4501(6)	0.4518(5)	0.4498(5)	0.4484(5)	0.4499(10)
y_{Ge2}	0.7448(17)	0.7457(15)	0.7497(8)	0.7519(9)	0.7515(7)	0.7493(6)	0.7480(8)
μ_1 (μ_B)[a]	6.95(10)	6.94(10)	4.93(4)				
k_x	0.6885(6)	0.6905(6)	0.6891(7)	0.1097(4)	0.1134(6)		
k_y	0.0660(30)	0.0658(30)	0.0729(42)	0	0		
k_z	0.1701(8)	0.1722(8)	0.1693(11)	0	0		
μ_2 (μ_B)[b]	4.5(2)	4.3(2)	3.03(13)	3.7(1)	3.1(1)		
$R_{n,Bragg}$ (%)	2.01	1.95	3.85	3.89	2.05	5.95	4.47
$R_{n,prof.}$ (%)	1.58	1.79	3.14	4.05	1.87	7.17	7.41
$R_{mag.}1$ (%)	3.67	4.97	6.75				
$R_{mag.}2$ (%)	48.0	42.5	48.2	19.3	28.9		

[a] μ_1, $R_{mag.}1$, Tb magnetic moment and reliability factor refined for the collinear magnetic structure.
[b] μ_2, $R_{mag.}2$, Tb magnetic moment and reliability factor refined for the sine wave modulated magnetic structure.

$\mathbf{S}_1(0, y, 1/4)$; $\mathbf{S}_2(0, \bar{y}, 3/4)$; $\mathbf{S}_3(1/2, 1/2+y, 1/4)$ and $\mathbf{S}_4(1/2, 1/2-y, 3/4)$.

Three antiferromagnetic collinear structures are possible [8]:

$\mathbf{G} = \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4$, $\mathbf{C} = \mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$ and $\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$

but the analysis of the obtained diffraction pattern confirms that the G-mode structure is preferred. The absence of the M001 reflection indicates that the magnetic moments are aligned along the *c*-axis. The Tb moments equal 6.95(10) μ_B at 1.5 K and at the positions $\pm(0, y, 1/4)$ have opposite signs (G_z mode) [4].

The question of localization of the Mn magnetic moments cannot be answered on the basis of the present measurements.

The set of small intensity reflections have been analysed by the FULLPROF program for the following models of the magnetic order in the Tb or Mn sublattices:

- sine wave modulated structure
- helicoidal structure.

The best agreement between calculated and experimental data was obtained for the sine wave modulated structure with the propagation vector $\mathbf{k} = (0.6885(6), 0.0660(30), 0.1701(8))$ and magnetic moments localized on the Tb sites.

Summarising, the Tb-magnetic moments give rise to two components:

- a collinear antiferromagnetic G_z structure with moments parallel to the *c*-axis and equal to 6.95(10) μ_B
- a sine wave modulated structure with moments parallel to the *a*-axis and equal to 4.5(2) μ_B.

The total Tb-magnetic moment of 8.2(2) μ_B is close to the free Tb^{3+} ion value.

The diffraction patterns for 2θ ranging from 10° to 30° and for temperatures ranging between 15 and 35 K are collected in Fig. 2. From this picture a change in the intensities of the magnetic peaks near $T_t = 21$ K is clearly

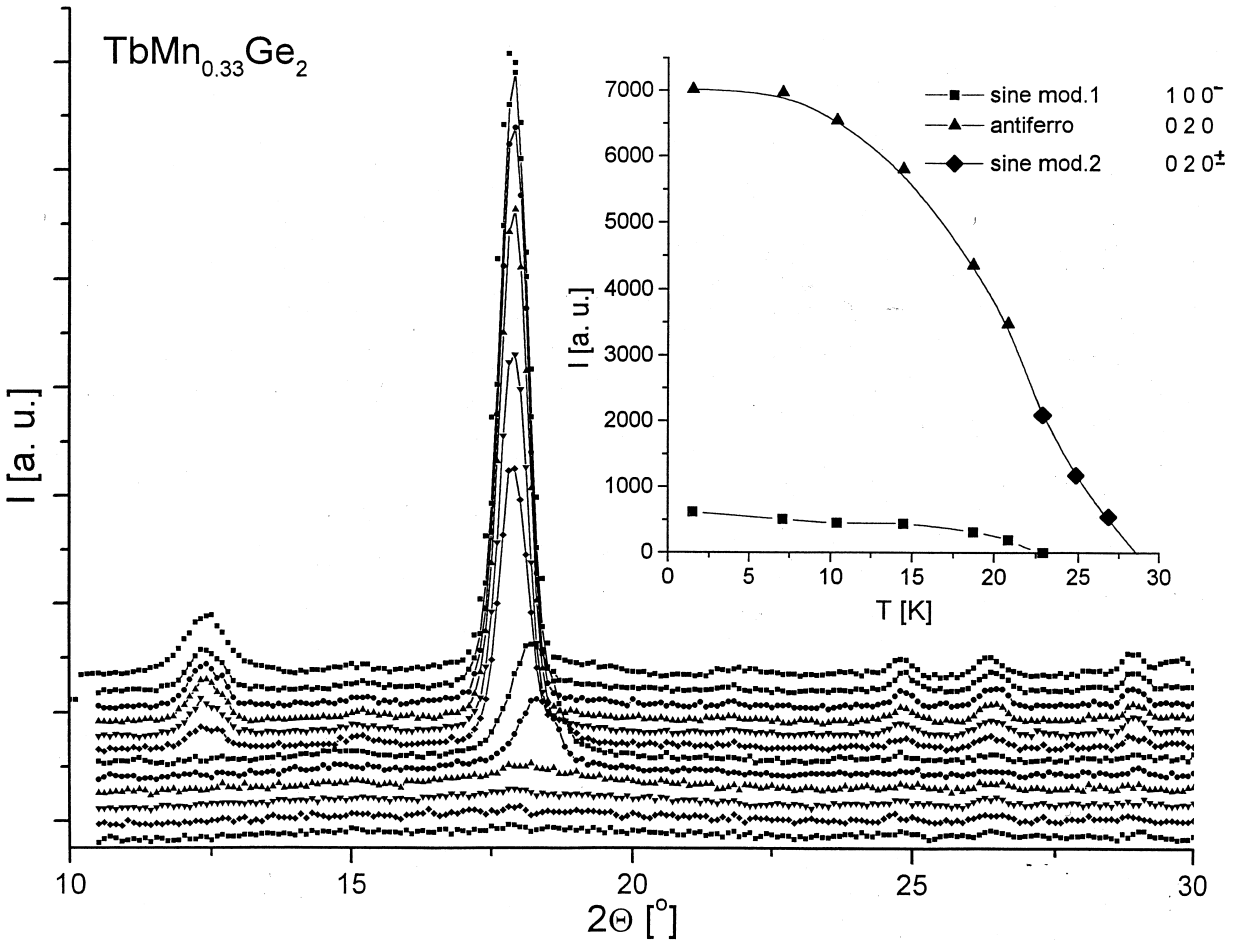

Fig. 2. Neutron diffraction patterns of $TbMn_{0.33}Ge_2$ in the 2θ range between 10° and 30° and temperatures ranging from 1.5 to 35 K. The inset shows the temperature dependence of the intensities of the magnetic peaks corresponding to the collinear magnetic structure 020 and to the sine wave modulated one (100^- and $020^{\pm}$).

visible. At this temperature the intensity of the most intense satellite at $2\theta = 12.4°$ decreases to zero while the very strong peak corresponding to the collinear structure at $2\theta = 17.6°$ changes the angle position. The position of the magnetic peaks on the neutron diffraction pattern at 22 and 24 K are indexed using the propagation vector $\mathbf{k} = (0.1097(4), 0, 0)$ at 22 K and (0, 0.1134(6), 0) at 24 K. The best agreement between observed and calculated intensities are obtained for the sine wave modulated structure accompanied by the antiferromagnetic G_z-type structure with magnetic moments equal to 3.7(1) μ_B at 22 K and 3.1(1) μ_B at 24 K.

The temperature dependence of the 020 and $020^{\pm}$ magnetic peak intensities gives a Néel temperature equal to 28 K (the inset in Fig. 2). Above this temperature a broad peak corresponding to short-range order effects is observed (Fig. 2).

3. Discussion

The data presented in this work, obtained on a better diffractometer, indicate a complicated magnetic structure of $TbMn_{0.33}Ge_2$: a complex magnetic structure at low temperatures and a sine wave modulated one near the Néel temperature. The low temperature magnetic structure is similar to those observed in isostructural $TbNi_xGe_2$ ($x = 0.6$ and 0.8) [9]. In this work, below the Néel temperature, the magnetic order is described by the two wave vectors $\mathbf{k}_1 = 0$ and $\mathbf{k}_2 = (0.237, 0, 0.2941)$ and the authors suggest a complex complicated magnetic structure at low temperatures or the presence of one of the known binary Tb–Ge or Tb–Ni or ternary Tb–Ni–Ge compounds which have ordering temperatures near $T_t = 21$ K. The existence of some parasitic phases in our sample could not be excluded. The neutron diffraction data for $TbMn_{0.33}Ge_2$ presented in this work show also the phase transition to the new sine wave modulated magnetic structure near the Néel temperature. This effect has been also detected in a large number of intermetallic rare earth compounds [10]. It arises as a result of a temperature-dependent free energy for the different propagation vectors.

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