Magnetic ordering in the rare earth intermetallic compound Tb₂Ti₃Ge₄: Magnetization and neutron diffraction studies

Satish K. Malik
Jagat Lamsal
R. L. de Almeida
S. Quezado
William B. Yelon
Missouri University of Science and Technology, yelonw@mst.edu

Follow this and additional works at: http://scholarsmine.mst.edu/faculty_work
Part of the Materials Science and Engineering Commons

Recommended Citation
http://scholarsmine.mst.edu/faculty_work/1544

This Article is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. For more information, please contact weaverjr@mst.edu.
Magnetic ordering in the rare earth intermetallic compound \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \): Magnetization and neutron diffraction studies

S. K. Malik,1 Jagat Lamsal,2 R. L. de Almeida,1 S. Quezado,1 W. B. Yelon,3 V. O. Garlea,4 A. V. Morozkin,5 and R. Nirmala6,a)

1International Center for Condensed Matter Physics (ICCMP), University of Brasilia, Brasilia 70904-970, Brazil
2Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA
3Department of Chemistry and Materials Research Center, Missouri University of Science and Technology, Rolla, Missouri 65409, USA
4Neutron Scattering Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
5Department of Chemistry, Moscow Lomonosov State University, Moscow 119899, Russia
6Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India

(Presented 12 November 2008; received 24 September 2008; accepted 29 October 2008; published online 6 February 2009)

Magnetization and neutron diffraction studies on a polycrystalline \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \) sample (orthorhombic \( \text{Sm}_5\text{Ge}_4 \)-type structure, space group \( \text{Pnma} \), No. 62) have been carried out. This compound is found to order antiferromagnetically at \( \sim 18 \) K \( (T_N) \). The magnetization \( (M) \) versus field \( (H) \) isotherms obtained at 2, 3, 5, and 10 K indicate a field-induced antiferromagnetic to ferromagnetic transition in fields of the order of 0.5 T. The saturation magnetization value at 2.5 K extrapolated to \( 1/H = 0 \) is only \( -5.6 \mu_B/\text{Tb}^3^+ \), suggesting the possible presence of crystal field effects with or without a persisting antiferromagnetic component. Neutron powder diffraction data at 10 K confirm the existence of a magnetic long range order. Modeling of the magnetic scattering reveals a complex and incommensurate antiferromagnetic spin structure below \( T_N \). © 2009 American Institute of Physics. [DOI: 10.1063/1.3063073]

I. INTRODUCTION

Structure-property studies on rare earth intermetallic compounds of orthorhombic \( \text{Sm}_5\text{Ge}_4 \)-type structure have intensified ever since the observation of multifunctional properties such as giant magnetocaloric effect, colossal magnetostriiction, and large magnetoresistance in \( \text{R}_3(\text{Si}_x\text{Ge}_{1-x})_4 \) \( (R = \text{rare earth}) \) compounds.1,2 These properties are believed to emerge from the highly correlated lattice and spin degrees of freedom in these compounds. Attempts of titanium metal substitution for rare earth in \( \text{R}_3\text{Ge}_4 \) resulted in isostructural \( \text{R}_2\text{Ti}_3\text{Ge}_4 \) \( (R = \text{Gd, Tb, Dy, Ho, and Er}) \) compounds (orthorhombic, \( \text{Sm}_5\text{Ge}_4 \)-type).3,4 Among these, the compounds other than that with Gd display dominant antiferromagnetic interactions in their magnetically ordered state, and the magnetic ordering temperatures are comparatively much smaller than those of the parent \( \text{R}_3\text{Ge}_4 \) compounds. The Tb compound of this series exhibits considerably enhanced magnetocaloric effect at low temperatures.5 This observation has motivated us to study the magnetic properties of \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \) sample more systematically by means of magnetization and neutron diffraction (ND) experiments, the results of which are discussed below.

II. EXPERIMENTAL DETAILS

A polycrystalline sample of \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \) was prepared by arc melting under argon atmosphere starting from stoichiometric amounts of high purity constituent elements (Tb, 99.9% pure; Ti and Ge, 99.999% pure, Cerac, Inc., USA).

The sample was remelted several times to ensure the homogeneity and was further annealed in vacuum at 1100 K for 8 days. The sample was characterized by powder x-ray diffraction experiment at room temperature. Magnetization measurements were carried out in the temperature range of 2–300 K using commercial magnetometers (MPMS SQUID and PPMS-VSM, Quantum Design, USA) in various applied fields. For measurement of magnetization in zero-field-cooled (ZFC) state, the sample was cooled from the paramagnetic state in zero applied field and magnetization was measured while warming the sample. Then the sample was cooled in field and the magnetization data in the field-cooled (FC) state were collected while warming the sample in field.

To investigate crystal and magnetic structure, powder ND experiments on \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \) sample were carried out at a few selected temperatures between 300 and 10 K at the University of Missouri Research Reactor Facility using a position sensitive detector diffractometer (incident neutron wavelength of 1.478 961 Å). Refinement of the ND data was performed using the FULLPROF computer code.

III. RESULTS AND DISCUSSION

Temperature dependence of magnetization of \( \text{Tb}_2\text{Ti}_3\text{Ge}_4 \) in applied fields of 1 and 10 mT reveals that this compound orders antiferromagnetically at \( \sim 18 \) K \( (T_N) \) (Fig. 1). The difference between the ZFC and FC magnetization data below \( T_N \) in 1 mT field vanishes in applied fields larger than 10 mT. In addition, the ZFC and FC magnetization data bifurcate much above \( T_N \) in 1 mT field, indicating the presence of short range magnetic interactions [Fig. 1(a)]. This observation is indeed consistent with the behavior of several other
Sm$_2$Ge$_4$-type compounds. In these materials, the magnetic interactions between the moments within the layer and across the layer in the overall three dimensional layered structure and their dynamics are expected to play an important role.

The magnetization versus field ($M$-$H$) isotherm of Tb$_2$Ti$_3$Ge$_4$ compound, obtained at 2.5 K, displays a field-induced antiferromagnetic to ferromagnetic transition in fields of the order of 0.5 T (Fig. 2). This metamagnetic transition (MMT) is S-shaped (inset in Fig. 2) and is not a martensiticlike, sharp, first order magnetostructural transition as exhibited by isostructural Gd$_5$Ge$_4$-type compound and may be due to spin rotation. The occurrence of a crystal structure change in applied field could be ruled out because of the absence of hysteresis associated with MMT. The $M$-$H$ isotherms obtained at temperatures below 10 K also show the field-induced transition in a critical field of about 0.5 T (Fig. 3). The critical field value is nearly constant in the temperature range from 2 to 10 K; however, minor low field hysteresis develops only at 5 K. The metamagnetic behavior vanishes at temperatures above 15 K. This MMT may be responsible for the observed enhanced and broad magneto-caloric effect below the Néel temperature of this compound.

The saturation magnetization ($M_s$) value of Tb$_2$Ti$_3$Ge$_4$ at 2.5 K obtained by extrapolating the magnetization to infinite field ($1/H \to 0$) is only $\sim 5.6 \mu_B$/Tb$^{3+}$ (compared to 9$\mu_B$ of free ion $gJ$ value of Tb$^{3+}$). This reduced value of $M_s$ suggests a possible presence of crystal field effects and/or a persisting antiferromagnetic component (Fig. 2). In materials of layered structure, which show MMT from antiferromagnetic to ferromagnetic ordered state, anisotropic interactions are expected to compete with exchange interactions.

Analysis of the room temperature powder ND data of Tb$_2$Ti$_3$Ge$_4$ reveals the presence of small amounts of parasitic 1:1 phase ($\sim 7\%$ of TbGe). This was included as a secondary phase in the Rietveld refinements. However, the presence of trace amounts of TbGe (antiferromagnetic, $T_N \sim 56$ K) is realized neither in magnetization nor in the more sensitive heat capacity experiments. The results of the refinement of the primary Tb$_2$Ti$_3$Ge$_4$ component are given in Table I. A more complete discussion of the magnetic structure will be presented elsewhere. ND results confirm that at 10 K, the Tb$_2$Ti$_3$Ge$_4$ compound is antiferromagnetic. Figure 4 shows the low angle region of the ND pattern at room temperature and at the lowest measuring temperature (10 K). Clearly, a
number of new magnetic peaks appear at 10 K. These index neither on the crystallographic cell nor on any simple doubling of the cell axes. All magnetic reflections at 10 K appear to correspond to two wave vectors $K_1=[\pm 5/8,0,0]$ and $K_2=[0,0,\pm 1/4]$. A model for the incommensurate ordering has not yet emerged. Analysis of such a complex magnetic structure requires further ND data at smaller temperature intervals below $T_N$.

From the present experimental data one may conclude that the magnetic structure of Tb$_2$Ti$_3$Ge$_4$ compound is complex and close to an antiferromagnetic cone spin structure (with cone axis lying along the crystallographic c-axis). It may be of relevance to recollect that the parent, isostructural Tb$_2$Ge$_4$ compound ($T_N\sim 91$ K) also has a complex, canted antiferromagnetic structure. Thus substitution of nonmagnetic Ti for magnetic Tb ions (by 60 at. %) leads to a decrease in the magnetic transition temperature to about one-fifth of the initial value and a substantial increase in the magnetic unit cell volume. Indeed, various interatomic bond distances between the rare earth atoms and nonmagnetic Si and Ge atoms within the layered Sm$_5$Ge$_4$-type structure have been found to play a key role in determining the magnetism in $R_5(Si_{3-2x}Ge_{1+2x})_4$ compounds.

**IV. CONCLUSIONS**

Magnetic properties of the rare earth intermetallic compound Tb$_2$Ti$_3$Ge$_4$ have been studied by bulk magnetization and ND experiments. This compound is found to order antiferromagnetically at $\sim 18$ K and undergo a field-induced magnetic transition at $2.5$ K, giving rise to a saturation magnetization of $-5.6\mu_B$/Tb$^{3+}$. A complex incommensurate antiferromagnetic structure is observed below $T_N$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$n$</th>
<th>$R$ ($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>8d</td>
<td>0.000 59(77)</td>
<td>0.093 97(36)</td>
<td>0.830 94(63)</td>
<td>1.0</td>
<td>0.512(79)</td>
</tr>
<tr>
<td>Ti$_1$</td>
<td>4c</td>
<td>0.333 38(98)</td>
<td>$\frac{1}{8}$</td>
<td>0.012 18(112)</td>
<td>0.5</td>
<td>0.588(131)</td>
</tr>
<tr>
<td>Ti$_2$</td>
<td>8d</td>
<td>0.162 07(64)</td>
<td>0.128 16(66)</td>
<td>0.333 25(85)</td>
<td>1.0</td>
<td>1.162(125)</td>
</tr>
<tr>
<td>Ge$_1$</td>
<td>4c</td>
<td>0.192 59(83)</td>
<td>$\frac{1}{8}$</td>
<td>0.633 80(76)</td>
<td>0.5</td>
<td>0.518(64)</td>
</tr>
<tr>
<td>Ge$_2$</td>
<td>4c</td>
<td>0.963 04(85)</td>
<td>$\frac{1}{8}$</td>
<td>0.129 83(55)</td>
<td>0.5</td>
<td>0.518(64)</td>
</tr>
<tr>
<td>Ge$_3$</td>
<td>8d</td>
<td>0.169 89(66)</td>
<td>0.955 58(31)</td>
<td>0.541 29(43)</td>
<td>1.0</td>
<td>0.631(57)</td>
</tr>
</tbody>
</table>

**TABLE I. Results of Rietveld refinement of the ND data of Tb$_2$Ti$_3$Ge$_4$ at room temperature.** Space group is Pnma (No. 62); and $x$, $y$, and $z$ are the fractional coordinates; $n$ is the fractional site occupancy, and $R$ is the isotropic thermal parameter. The lattice parameters $a$, $b$, and $c$ are 7.004 18(64), 13.434 12(118), and 7.144 45(64) $\text{Å}$, respectively; $\chi^2$ is $(R_{exp}/R_{calc})^2=3.44$. 

**FIG. 4.** (Color online) ND patterns of Tb$_2$Ti$_3$Ge$_4$ at 300 K (paramagnetic state) and at 10 K (antiferromagnetic state) (a). The low angle region, at room temperature and at 10K, showing the appearance of incommensurate magnetic peaks below $T_N$ (b).