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Magnetic ordering in the rare earth intermetallic compound Tb$_2$Ti$_3$Ge$_4$: Magnetization and neutron diffraction studies

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Magnetization and neutron diffraction studies on a polycrystalline Tb$_2$Ti$_3$Ge$_4$ sample (orthorhombic Sm$_5$Ge$_4$-type structure, space group *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 (M extrapolated to $1/H \rightarrow 0$) is only $\sim$5.6μ_B/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 Sm$_5$Ge$_4$-type structure have intensified ever since the observation of multifunctional properties such as giant magnetocaloric effect, colossal magnetostriction, and large magnetoresistance in R_5(Si$_x$Ge$_{1-x}$)$_4$ (R =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 R_5Ge$_4$ resulted in isostructural R_2Ti$_3$Ge$_4$ (R=Gd, Tb, Dy, Ho, and Er) compounds (orthorhombic, Sm$_5$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 R_5Ge$_4$ 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 Tb$_2$Ti$_3$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 Tb$_2$Ti$_3$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 Tb$_2$Ti$_3$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 Tb$_2$Ti$_3$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
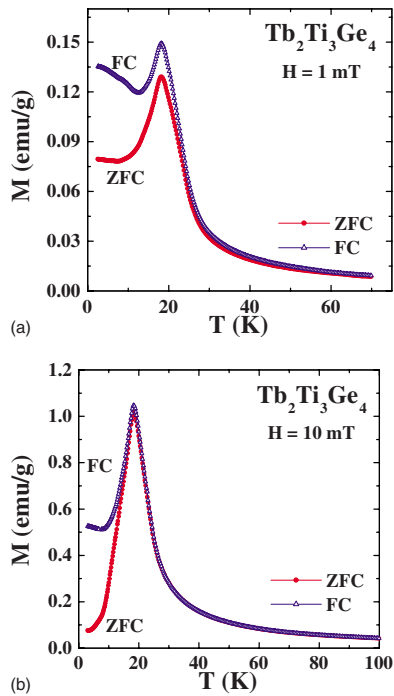
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FIG. 1. (Color online) Magnetization of $Tb_2Ti_3Ge_4$ vs temperature in applied fields of 1 mT (a) and 10 mT (b) in ZFC and FC conditions.

Sm_5Ge_4-type compounds.[6–8] 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.[6–8]

The magnetization versus field (*M-H*) isotherm of $Tb_2Ti_3Ge_4$ 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_5Ge_4-type compound[8] 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* iso-
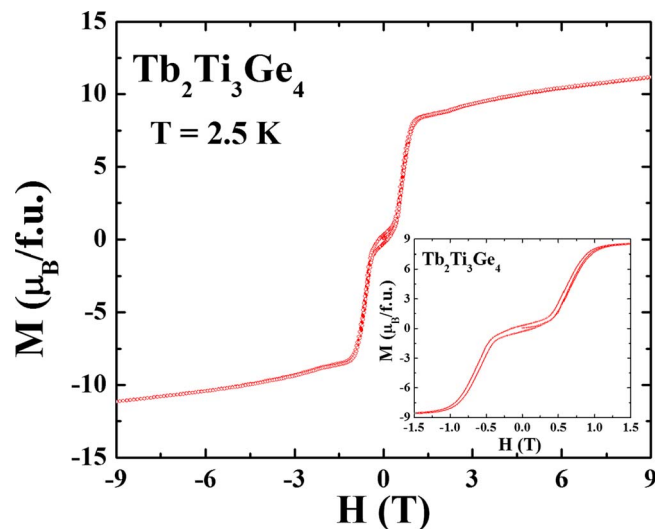

FIG. 2. (Color online) Magnetization of $Tb_2Ti_3Ge_4$ vs field at 2.5 K up to 9 T field. The inset shows a closer view in low fields.
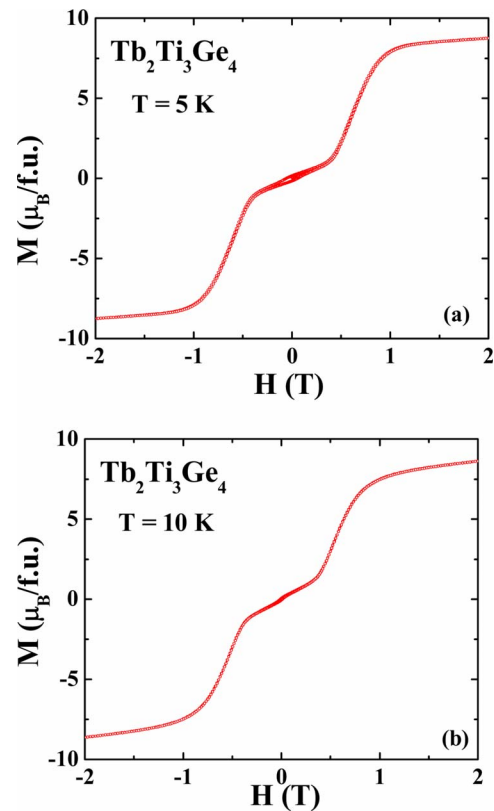

FIG. 3. (Color online) Magnetization of $Tb_2Ti_3Ge_4$ vs field at 5 K (a), and 10 K (b) in fields up to 2 T.

therms 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 magnetocaloric effect below the Néel temperature of this compound.[4]

The saturation magnetization (M_S) value of $Tb_2Ti_3Ge_4$ at 2.5 K obtained by extrapolating the magnetization to infinite field ($1/H \rightarrow 0$) 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 $Tb_2Ti_3Ge_4$ 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)[9] is realized neither in magnetization nor in the more sensitive heat capacity experiments.[5] The results of the refinement of the primary $Tb_2Ti_3Ge_4$ 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 $Tb_2Ti_3Ge_4$ 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

TABLE I. Results of Rietveld refinement of the ND data of $Tb_2Ti_3Ge_4$ 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 *B* is the isotropic thermal parameter. The lattice parameters *a*, *b*, and *c* are 7.004 18(58), 13.434 12(118), and 7.144 45(64) Å, respectively; χ^2 is $(R_{wp}/R_{expt})^2 = 3.44$.

Atom	Site	X	Y	Z	n	B (Å^2)
Tb	8*d*	0.000 59(77)	0.093 97(36)	0.830 94(63)	1.0	0.512(79)
Ti$_1$	4*c*	0.333 38(98)	$\frac{1}{4}$	0.012 18(112)	0.5	0.588(131)
Ti$_2$	8*d*	0.162 07(64)	0.128 16(66)	0.333 25(85)	1.0	1.162(125)
Ge$_1$	4*c*	0.192 59(83)	$\frac{1}{4}$	0.633 80(76)	0.5	0.518(64)
Ge$_2$	4*c*	0.963 04(85)	$\frac{1}{4}$	0.129 83(55)	0.5	0.518(64)
Ge$_3$	8*d*	0.169 89(66)	0.955 58(31)	0.541 29(43)	1.0	0.631(57)

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 $\mathbf{K}_1 = [\pm 5/8, 0, 0]$ and $\mathbf{K}_2 = [0, 0, \pm 1/9]$. 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.
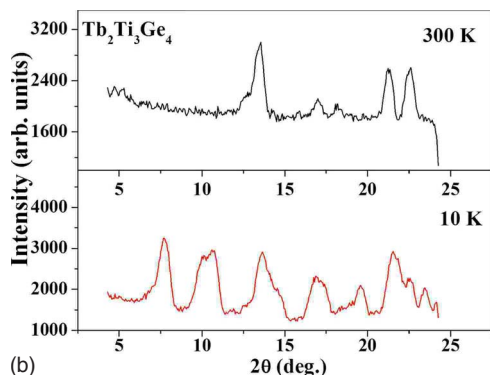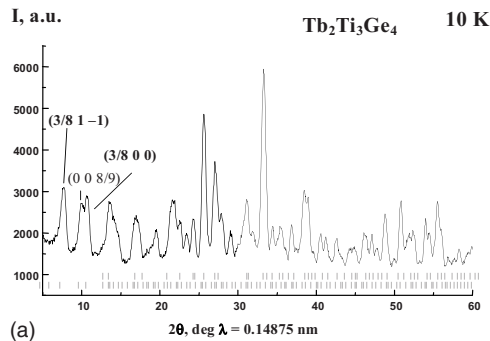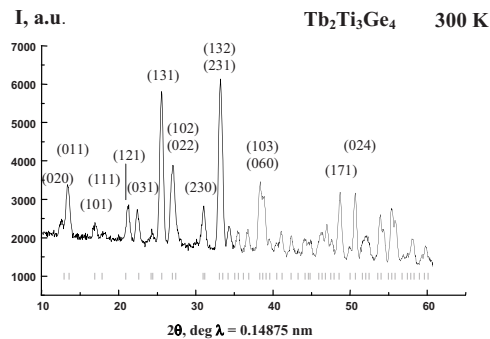

FIG. 4. (Color online) ND patterns of $Tb_2Ti_3Ge_4$ at 300 K (paramagnetic state) and at 10 K (antiferromagnetic state) (a). The low angle region, at room temperature and at 10K, showing the appearance of incommensurate magnetic peaks below T_N (b).

From the present experimental data one may conclude that the magnetic structure of $Tb_2Ti_3Ge_4$ 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_5Ge_4 compound ($T_N \sim 91$ K) also has a complex, canted antiferromagnetic structure.[10] 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_5Ge_4-type structure have been found to play a key role in determining the magnetism in $R_5(Si_xGe_{1-x})_4$ compounds.[11]

IV. CONCLUSIONS

Magnetic properties of the rare earth intermetallic compound $Tb_2Ti_3Ge_4$ have been studied by bulk magnetization and ND experiments. This compound is found to order antiferromagnetically at ~ 18 K and undergo a field-induced magnetic transition at 2.5 K, giving rise to a saturation magnetization of $\sim 5.6 \mu_B/Tb^{3+}$. A complex incommensurate antiferromagnetic structure is observed below T_N.

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