Journal of Alloys and Compounds 478 (2009) 22–29

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Magnetic properties of Th_3P_4-type $Tb_4Sb_{3-X}\{Si, Ge, Bi\}_X$ solid solutions

A.V. Morozkin[a,*], D. Buddhikot[b], A.K. Nigam[b], O. Isnard[c,d], Y. Mozharivskyj[e]

[a] Department of Chemistry, Moscow State University, Leninskie Gory, House 1, Building 3, GSP-2, Moscow 119992, Russia
[b] Tata Institute of Fundamental Research, Mumbai 400005, India
[c] Institut Laue-Langevin, 6 Rue J. Horowitz, 38042 Grenoble, France
[d] Institut Néel du CNRS, Université Joseph.Fourier, BP166X, 38042 Grenoble, France
[e] Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

ARTICLE INFO

Article history:
Received 27 August 2008
Received in revised form 2 October 2008
Accepted 9 October 2008
Available online 27 November 2008

Keywords:
Rare earth intermetallics
Terbium bismuth antimonide
Terbium germanium antimonide
Terbium silicon antimonide
Magnetisation
Neutron diffraction
Magnetic structure

ABSTRACT

The magnetic properties of Tb_4Sb_2Bi, $Tb_4Sb_{2.75}Ge_{0.25}$ and $Tb_4Sb_{2.3}Si_{0.7}$ solid solutions (Th_3P_4-type, cubic; cI28, space group $I\bar{4}3d$, No. 220) have been investigated by means of magnetization and neutron diffraction studies. The magnetization measurements indicate that the Tb_4Sb_2Bi compound orders magnetically at 120 K (T_N) and 50 K (T_C). The magnetization vs. field isotherm at 5 K shows signature of ferromagnetic order. Neutron diffraction experiment in zero applied magnetic field shows that below $T_N = 125(4)$ K Tb_4Sb_2Bi exhibits a antiferromagnetic flat spiral type ordering with wave vector $\mathbf{K}_1 = [\pm K_X, \pm K_X, \pm K_X]$ (K_X value changes from 0.1033 up to 0.158 in the temperature interval down to 2 K). Below $T_m = 70(4)$ K the decreasing of antiferromagnetic component coincides with increasing of the ferromagnetic component and about $T_{CN} = 55(4)$ K, Tb_4Sb_2Bi shows ferromagnetic transition. At 2 K, the magnetic structure of Tb_4Sb_2Bi is ferromagnetic cone and the cone axis is along [1 1 1] direction.

Neutron diffraction study of $Tb_4Sb_{2.75}Ge_{0.25}$ indicate an antiferromagnetic ordering at 155(4) K (ferromagnetic cone with $\mathbf{K}_1 = [\pm 0.136(2), \pm 0.136(2), \pm 0.136(2)]$) and ferromagnetic ordering (sharp increasing of ferromagnetic component) at 145(4) K. The K_X value is nearly constant from 155 K down to 2 K. At 2 K, the magnetic structure of $Tb_4Sb_{2.75}Ge_{0.25}$ is ferromagnetic cone with a weak antiferromagnetic component and the cone axis is along [1 1 1] direction.

Low field magnetisation measurements on $Tb_4Sb_{2.3}Si_{0.7}$ indicate a ferromagnetic ordering at $T_C \sim 180$ K. Thus small substitutions of Bi, Ge and Si at Sb-site of Tb_4Sb_3 are found to increase the magnetic ordering temperature of the parent compound.

1. Introduction

It is known that R_4X_3 compounds having the cubic, Th_3P_4-type structure (cI28, space group $I\bar{4}3d$, No. 220) can be formed with R = rare earth element and X = Ge, Sb and Bi [1]. The Th_3P_4-type Gd_4Sb_3 and Gd_4Bi_3 compounds demonstrate ferromagnetic type ordering in an applied magnetic field at $T_C = 260$ K and $T_C = 335$ K, respectively [2–4]. It has been reported that Tb_4Bi_3 has paramagnetic Curie temperature $\Theta_P = 192$ K and effective magnetic moment $M_{Tb}^{eff} = 10.06\ \mu B$ [5].

The parent compound Tb_4Sb_3 orders antiferromagnetically at ~108 K in zero magnetic field and shows a field induced ferromagnetic ordering in a small critical field $H_C \sim 0.3$ T. Below 108 K in zero applied field the Tb_4Sb_3 has flat spiral ordering with wave vector $\mathbf{K}_1 = [\pm 1/8, \pm 1/8, \pm 1/8]$ (the cone axis arranges along [1 1 1] direction with cone angle $\beta = 90^\circ$). Also, below ~50 K, Tb_4Sb_3 shows the possibility of second magnetic transition with $\mathbf{K}_2 = \sim[1/2, 1/2, 1/2]$ with possible re-orientation of Tb magnetic moments [6].

The size factor and the effect of cell volume and hence bond distances on the magnetic properties of Tb_4Sb_3 were investigated by substituting Bi, Ge and Si for Sb in Tb_4Sb_3. A few $Tb_4Sb_{3-X}\{Si, Ge, Bi\}_X$ systems of selected compositions have been studied in the present work by magnetization and neutron diffraction experiments.

2. Experimental details

The Tb_4Sb_2Bi, $Tb_4Sb_{2.75}Ge_{0.25}$ and $Tb_4Sb_{2.3}Si_{0.7}$ compounds were made in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. Antimony (purity 99.99 wt.%), bismuth (purity 99.99 wt.%), germanium (purity 99.99 wt.%), silicon (99.99 wt.%) and terbium (purity 99.96 wt.%) were used as the starting components. Zirconium was used as a getter during the melting process. Subsequently, the compounds were annealed at 1170 K for 170 h in an argon atmosphere and quenched in ice-cold water.

The quality of the polycrystalline alloys was determined using X-ray powder diffraction and EDX microprobe techniques. A "Camebax" microanalyser was employed for the microprobe X-ray spectral analyses of the specimen. X-ray powder patterns were obtained on a diffractometer DRON-3 (Cu Kα radiation, $2\theta = 20.70^\circ$, step 0.05°, 1002 points). The obtained diffractograms were identified and intensity

* Corresponding author.
E-mail address: morozkin@general.chem.msu.ru (A.V. Morozkin).

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.10.168

calculations were made in the isotropic approximation using the Rietan-programs [7].

The neutron diffraction investigation was carried out from 250 K down to 2 K in zero magnetic field at the Institute Laue-Langevin, Grenoble, France, using the high resolution powder diffractometer *D1B* [8], operating at a wavelength $\lambda = 0.252$ nm ($2\theta = 2.8$–84°). The diffraction patterns were indexed, and the calculations were performed by using the FULLPROF 98-program [9].

The ac and dc magnetization was measured on a Physical Property Measurement System (PPMS, Quantum Design) and a commercial SQUID magnetometer (Quantum Design) in the temperature range of 5–300 K in fields up to 5 T.

3. Results and discussion

3.1. Crystal structure

In the Th_3P_4-type structure the Tb atoms occupy the 16(c) site (X_{Tb}, X_{Tb}, X_{Tb}) while the antimony atoms occupy the 12(a) site (3/8, 0, 1/4) [1]. The Tb atoms positions in the unit cell are given in Table 1. In Fig. 1 shows that Tb sublattice consists of two identical Tb sublattices (Tb1, 2, 3, 4, 9, 10, 11, 12 and Tb5, 6, 7, 8, 13, 14, 15, 16). The unit cell data and The Tbj–Tbj distances for $Tb_4Sb_{3-X}\{Si, Ge, Bi\}_X$ compounds are given in Table 2.

Table 1
Atomic positions of Tb atoms in the Th_3P_4-type $Tb_4Sb_{3-X}\{Si, Ge, Bi\}_X$ unit cells.

Atom	X/a	Y/b	Z/c
Tb1	X_{Tb}	X_{Tb}	X_{Tb}
Tb2	$X_{Tb} - 1/2$	$3/2 - X_{Tb}$	$1 - X_{Tb}$
Tb3	$1 - X_{Tb}$	$X_{Tb} - 1/2$	$3/2 - X_{Tb}$
Tb4	$3/2 - X_{Tb}$	$1 - X_{Tb}$	$X_{Tb} - 1/2$
Tb5	$X_{Tb} + 1/4$	$X_{Tb} + 1/4$	$X_{Tb} + 1/4$
Tb6	$3/4 - X_{Tb}$	$X_{Tb} - 1/4$	$5/4 - X_{Tb}$
Tb7	$X_{Tb} - 1/4$	$5/4 - X_{Tb}$	$3/4 - X_{Tb}$
Tb8	$5/4 - X_{Tb}$	$3/4 - X_{Tb}$	$X_{Tb} - 1/4$
Tb9	$X_{Tb} - 1/2$	$X_{Tb} - 1/2$	$X_{Tb} - 1/2$
Tb10	X_{Tb}	$1 - X_{Tb}$	$3/2 - X_{Tb}$
Tb11	$3/2 - X_{Tb}$	X_{Tb}	$1 - X_{Tb}$
Tb12	$1 - X_{Tb}$	$3/2 - X_{Tb}$	X_{Tb}
Tb13	$X_{Tb} - 1/4$	$X_{Tb} - 1/4$	$X_{Tb} - 1/4$
Tb14	$5/4 - X_{Tb}$	$1/4 + X_{Tb}$	$3/4 - X_{Tb}$
Tb15	$1/4 + X_{Tb}$	$3/4 - X_{Tb}$	$5/4 - X_{Tb}$
Tb16	$3/4 - X_{Tb}$	$5/4 - X_{Tb}$	$1/4 + X_{Tb}$

3.2. Magnetization

DC magnetization of Tb_4Sb_2Bi compound as a function of temperature is shown in Fig. 2. The data indicate an antiferromagnetic-like cusp in magnetization centered at 120 K followed by a second peak 50 K in an applied field of 0.01 T. The difference between zero-field-cooled and field-cooled magnetization data below the magnetic transition suggest possible presence of competing antiferromagnetic and ferromagnetic interactions. The paramagnetic susceptibility follows Curie–Weiss law. Magnetization as a function of field, $M(H)$, in fields up to 5 T is presented in

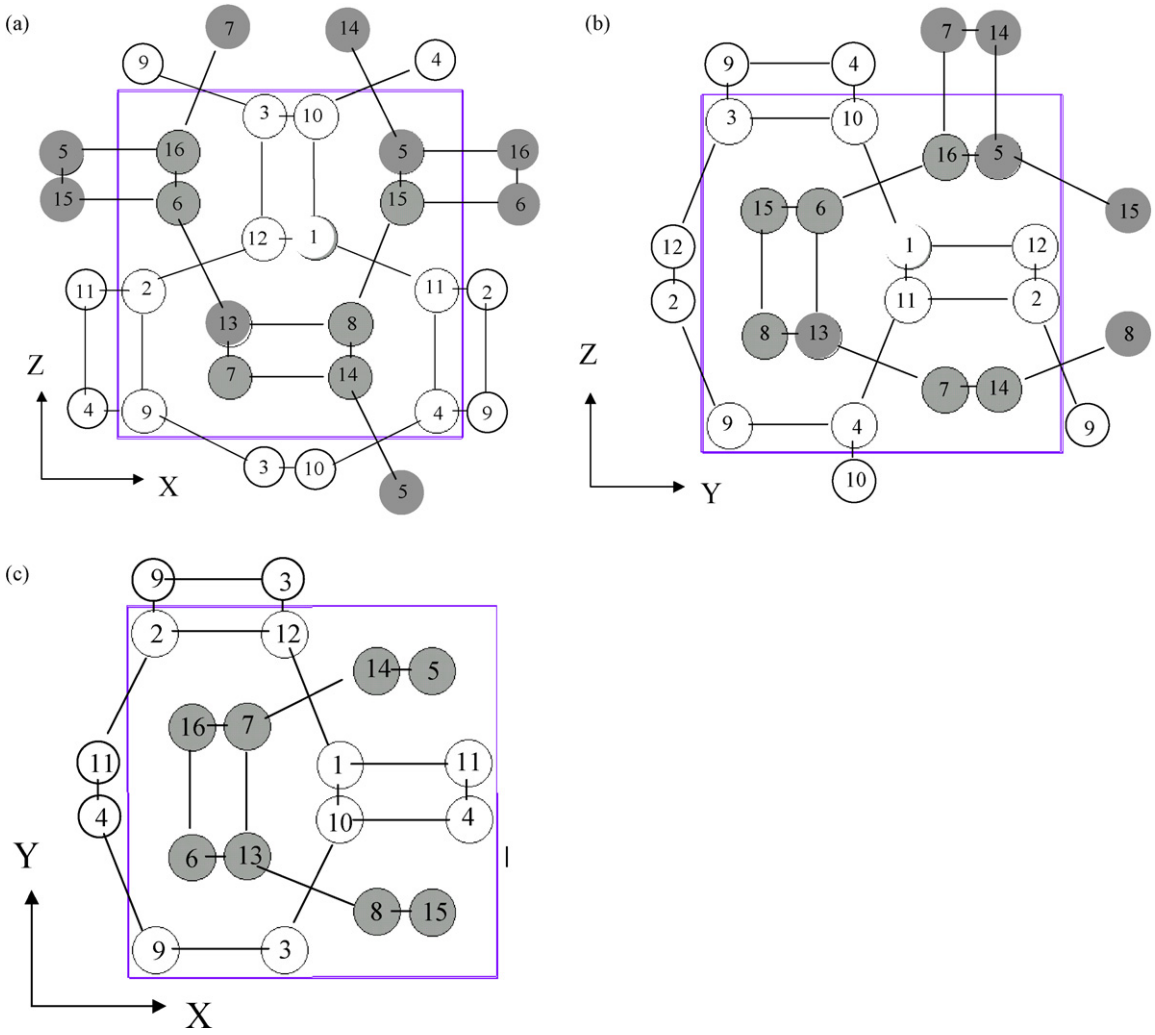

Fig. 1. Two same Tb sublattices in the Th_3P_4-type $Tb_4Sb_{3-X}\{Si, Ge, Bi\}_X$ unit cells: Tb1, 2, 3, 4, 9, 10, 11, 12 (white circle) and Tb5, 6, 7, 8, 13, 14, 15, 16 (gray circle) with shortest Tb–Tb distances: projection on *XZ* plane (a), projection on *YZ* plane (b) and projection on *XY* plane (c).