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$Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$: Crystal structure, magnetic properties and magnetocaloric effect. Structural transformation and magnetic properties of hexagonal Gd_5Bi_3

Volodymyr Svitlyk, Fan Fei, Yurij Mozharivskyj*

Department of Chemistry, McMaster University, ABB 423, 1280 Main Street west, Hamilton, Ontario, Canada, L8S 4M1

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Abstract

Nickel was successfully introduced into the Gd_5Sb_3 and Gd_5Bi_3 binaries to yield the $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ phases. Both Ni-substituted compounds adopt the orthorhombic Yb_5Sb_3-type structure. While the $Gd_5Ni_{0.71}Bi_{2.29}$ phase is thermodynamically stable at 800 °C and decomposes at lower temperatures upon annealing, it can be easily quenched to room temperature by rapid cooling from 800 °C. The $Gd_5Ni_{0.96}Sb_{2.04}$ phase is found to be thermodynamically stable till room temperature. Through annealing at different temperatures, Gd_5Bi_3 was proven to undergo the Mn_5Si_3-type (LT) $\leftrightarrow$ Yb_5Sb_3-type (HT) transformation reversibly, whereas Gd_5Sb_3 was found to adopt only the hexagonal Mn_5Si_3-type structure. Orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ and low-temperature hexagonal Gd_5Bi_3 order ferromagnetically at 115, 162 and 112 K, respectively. In Gd_5Bi_3, the ferromagnetic ordering is followed by spin reorientation below 64 K. Magnetocaloric effect in terms of ΔS was evaluated from the magnetization data and found to reach the maximum values of -7.7 J/kgK for $Gd_5Ni_{0.96}Sb_{2.04}$ and -5.6 J/kgK for $Gd_5Ni_{0.71}Bi_{2.29}$ around their Curie temperatures.

Keywords: Gadolinium bismuthide; Gadolinium nickel antimonide; Gadolinium nickel bismuthide; Phase transitions; Structure; Magnetic properties; Magnetocaloric effect

1. Introduction

Discovery of the giant magnetocaloric effect in $Gd_5Si_2Ge_2$ and related phases [1,2] showed that cooling efficiency of a ferromagnetic material increases significantly if a ferromagnetic ordering is coupled to a first-order structural transition. For such materials, the total entropy change, ΔS, can be divided in two parts: ΔS_{mag} and ΔS_{str} associated with the magnetic and structural transitions, respectively. While it is difficult to introduce and control structural transformations and associated with them ΔS_{str} in inorganic solid-state materials, it is possible to optimize the magnetic entropy part, ΔS_{mag}. In general, large ΔS_{mag} is associated with metal-rich phases, consisting of magnetically active 3*d*- or 4*f*- elements. Besides, the 4*f*-elements are likely to yield a larger ΔS_{mag} as the maximum entropy change during the ferromagnetic ordering depends on the total quantum number through $\Delta S_{mag}=R\ln(2J+1)$ [3]. Driven by this argument, we initiated exploration of structural and magnetic properties of the Ni-substituted Gd_5Sb_3 and Gd_5Bi_3 phases. The study was also inspired, in part, by the fact that the structurally related Y_5Sb_3 phase and its derivative $Y_5Ni_xSb_{3-x}$ were found to undergo a first-order orthorhombic-to-hexagonal structural transition at elevated temperatures [4].

Similar to Y_5Sb_3, Gd_5Bi_3 was found to adopt two structural modifications [5]. The stoichiometric Gd_5Bi_3 phase was believed to adopt a hexagonal Mn_5Si_3-type structure, while a Gd-richer phase, $Gd_{5+x}Bi_3$, was suggested for the orthorhombic Yb_5Sb_3-type polymorph [5]. No other literature data were found to substantiate existence of $Gd_{5+x}Bi_3$, instead recent results by Szade and Drzyzga [6] indicated that a Yb_5Sb_3-type structure is

*Corresponding author. Fax: +1 905 521 2773.
E-mail address: mozhar@mcmaster.ca (Y. Mozharivskyj).

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adopted by stoichiometric Gd_5Bi_3 at higher temperatures. This high-temperature modification was found to exhibit a ferromagnetic-like transition at 110 K, followed by spin reorientation or freezing below 60 K [6]. The magnetic behavior of the low-temperature hexagonal Gd_5Bi_3 polymorph was not studied. In contrast to Gd_5Bi_3, only a hexagonal Mn_5Si_3-type phase has been reported for Gd_5Sb_3 [7]. This hexagonal Gd_5Sb_3 phase orders ferromagnetically at 187 K and then undergoes a possible ferrimagnetic transition below 50 K [8]. Presence of structural and/or magnetic transitions in Gd_5Sb_3 and Gd_5Bi_3 was another motivation for us to explore the properties of the Ni-substituted phases. Here we report on the structural features and magnetocaloric effect of these phases.

2. Experimental

2.1. Synthesis and X-ray structure analysis

The starting materials were Gd (99.9%, CERAC Incorporation), Ni (99.93% Alfa Aesar), Bi (99.9999%, CERAC Incorporation) and antimony (99.999%, CERAC Incorporation). The samples with initial compositions Gd_5Sb_3, Gd_5Bi_3, Gd_5NiSb_2 and Gd_5NiBi_2 and a total mass of 1 g were arc melted in argon atmosphere, then turned over and remelted to achieve homogeneity. Two milligrams of Sb or Bi was added extra to the samples to compensate for losses during melting. For annealing at 800 °C and lower temperatures, the samples were sealed in evacuated silica tubes, kept at the required temperature for 1 or 2 weeks and then quenched in cold water. For annealing at 1350 °C, the samples were sealed in tantalum tubes with argon inside and heated in dynamic vacuum (10^{-6} Torr) in an induction furnace.

Phase composition and lattice constants of the prepared samples (Table 1) were determined from the X-ray powder diffraction patterns recorded on a Huber image plate Guinier camera with the Cu$K\alpha_1$ radiation. The lattice constants were derived through a full-profile Rietveld analysis using the Rietica software [9]. Single crystal studies were performed on a STOE IPDS II diffractometer with the Mo$K\alpha$ radiation. Small crystals with a shape of rectangular plates and silver luster were picked up from the Gd_5NiSb_2 and Gd_5NiBi_2 samples annealed at 800 °C for 2 weeks. The diffraction data were collected in the whole reciprocal sphere. Using the SHELXL program [10], the compositions were refined to $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ for the Gd_5NiSb_2 and Gd_5NiBi_2 samples, respectively (Tables 2 and 3). While during the refinements Ni was found to occupy the 4*c* site, we also check for the Ni presence on the 8*d* Sb1 or Bi1 site by refining their occupancies (Ni presence would lead to a lower electron density and thus lower occupancies for the pure Sb1/Bi sites). The refined occupancies were 0.993(3) for the 8*d* Sb1 site in $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and 0.995(6) for the 8*d* Bi1 site $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$. The occupancies are close to one within three standard deviations and thus the

Table 2
Crystal data and structure refinements for $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ at 293 K, Mo$K\alpha_1$ radiation, STOE IPDS II diffractometer

Composition	$Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$	$Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$
Space group	*Pnma*	*Pnma*
Lattice parameters (Å)	$a = 12.136(1)$	$a = 12.228(2)$
	$b = 8.9472(7)$	$b = 9.241(1)$
	$c = 7.9546(7)$	$c = 8.137(1)$
Volume (Å^3)	863.7(3)	919.5(3)
Z	4	4
Density (calculated) (g/cm^3)	8.389	9.665
Crystal size (mm^3)	$0.017 \times 0.054 \times 0.079$	$0.009 \times 0.046 \times 0.065$
2θ range for data collection	6.12–58.22°	6.02–58.28°
Index ranges	$-16 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 11$, $-10 \leqslant l \leqslant 10$	$-16 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 12$, $-11 \leqslant l \leqslant 11$
Reflections collected	8646	8896
Independent reflections	1227 [$R_{int} = 0.0603$]	1306 [$R_{int} = 0.2325$]
Completeness to max 2θ (%)	99.5	99.5
Data/restraints/parameters	1227/0/45	1306/0/45
Goodness-of-fit on F^2	0.812	0.699
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0286$, w$R_2 = 0.0335$	$R_1 = 0.0479$, w$R_2 = 0.0547$
R indices (all data)	$R_1 = 0.0375$, w$R_2 = 0.0522$	$R_1 = 0.0727$, w$R_2 = 0.1345$
Extinction coefficient	0.00054(3)	0.00013(2)
Largest diff. peak/hole, (e/Å^3)	1.60/−2.18	2.93/−4.30

Table 1
Crystal data for the phases annealed at 800 and 1350 °C

Phase	Annealing temperature (°C)	Structure type	Space group	Lattice constants, Å
Gd_5Sb_3	800	Mn_5Si_3	$P6_3/mcm$	$a = 9.0243(1)$, $c = 6.3241(1)$
$Gd_5Ni_{0.96}Sb_{2.04}$	800	Yb_5Sb_3	*Pnma*	$a = 12.133(1)$, $b = 8.9528(8)$, $c = 7.9561(8)$
Gd_5Bi_3	800	Mn_5Si_3	$P6_3/mcm$	$a = 9.1842(7)$, $c = 6.4177(8)$
Gd_5Bi_3	1350	Yb_5Sb_3	*Pnma*	$a = 12.106(1)$, $b = 9.549(1)$, $c = 8.261(1)$
$Gd_5Ni_{0.71}Bi_{2.29}$	800	Yb_5Sb_3	*Pnma*	$a = 12.230(1)$, $b = 9.222(1)$, $c = 8.102(1)$

Table 3
Atomic and isotropic temperature (U) parameters for $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ from single crystal diffraction data

Atom		Occupancy	x/a	y/b	z/c	U (Å^2)
$Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$						
Gd1	4*c*	1	0.2907(1)	1/4	0.6576(1)	0.010(1)
Gd2	4*c*	1	0.1991(1)	1/4	0.1299(1)	0.010(1)
Gd3	4*c*	1	0.5005(1)	1/4	0.9609(1)	0.010(1)
Gd4	8*d*	1	0.4338(1)	0.0390(1)	0.3156(1)	0.011(1)
Sb1	8*d*	1	0.3269(1)	0.9926(1)	0.9277(1)	0.009(1)
Sb2/Ni	4*c*	0.04/0.96(1)	0.5148(1)	1/4	0.5775(2)	0.012(1)
$Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$						
Gd1	4*c*	1	0.2880(2)	1/4	0.6622(2)	0.019(1)
Gd2	4*c*	1	0.2025(2)	1/4	0.1331(3)	0.021(1)
Gd3	4*c*	1	0.4986(2)	1/4	0.9646(2)	0.016(1)
Gd4	8*d*	1	0.4352(1)	0.0446(2)	0.3165(2)	0.025(1)
Bi1	8*d*	1	0.3264(1)	0.9906(1)	0.9274(1)	0.014(1)
Bi2/Ni	4*c*	0.29/0.71(1)	0.0215(2)	1/4	0.9119(3)	0.015(1)

corresponding 8*d* site can be assumed to be fully occupied by Sb or Bi.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository CSD number 418769 for $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and 418770 for $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ and also from the supporting information.

2.2. Magnetic measurements

Magnetization for the field cooled (FC) polycrystalline pieces of hexagonal Gd_5Bi_3, orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ phases (all annealed at 800 °C) was measured at 100 Oe field between 2 and 320 K (350 K for $Gd_5Ni_{0.96}Sb_{2.04}$ compound) on a Quantum Design SQUID magnetometer (Fig. 1). The transition temperatures were derived from the $\partial M/\partial T$ vs. T plots and correspond to the maxima in these plots. To explore the nature of the magnetic ordering in hexagonal Gd_5Bi_3, magnetization curves were measured at 4.2 and 100 K in increasing and decreasing magnetic fields (Fig. 2).

Magnetocaloric effect for $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ was evaluated from the magnetization data. For this purpose, a series of magnetization versus magnetic field (M vs. H) measurements was done around the ordering temperature with 5 K increments (Fig. 3). The magnetic field changed from 0 to 50,000 Oe with a 1000 and 2000 Oe step for $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$, respectively.

3. Results and discussion

3.1. Thermal stability and structures of Gd_5Sb_3, Gd_5Bi_3, $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$

Temperature stability of Gd_5Sb_3, Gd_5Bi_3, $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ is summarized in Fig. 4 (see also Table 1). From the initial annealing at 800 °C, both Gd_5Sb_3 and Gd_5Bi_3 were found to adopt the hexagonal Mn_5Si_3-type structure at 800 °C, while $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ were found to crystallize in the orthorhombic Yb_5Sb_3-type structure at 800 °C. Since hexagonal Mn_5Si_3-type and orthorhombic Yb_5Sb_3-type structures have been identified as low-temperature (LT) and high-temperature (HT) forms, respectively, for Y_5Sb_3 [4], the

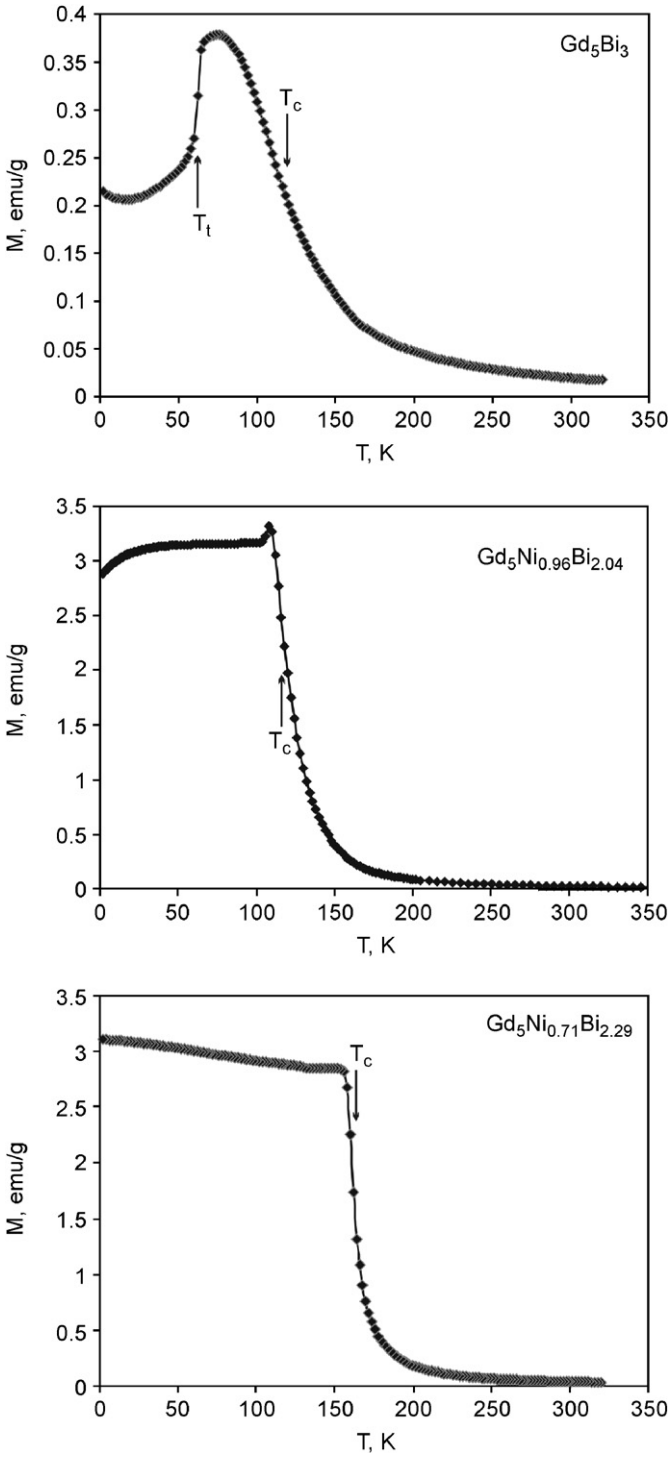

Fig. 1. Magnetization as a function of temperature at $H = 100$ Oe for hexagonal Gd_5Bi_3 and orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$.

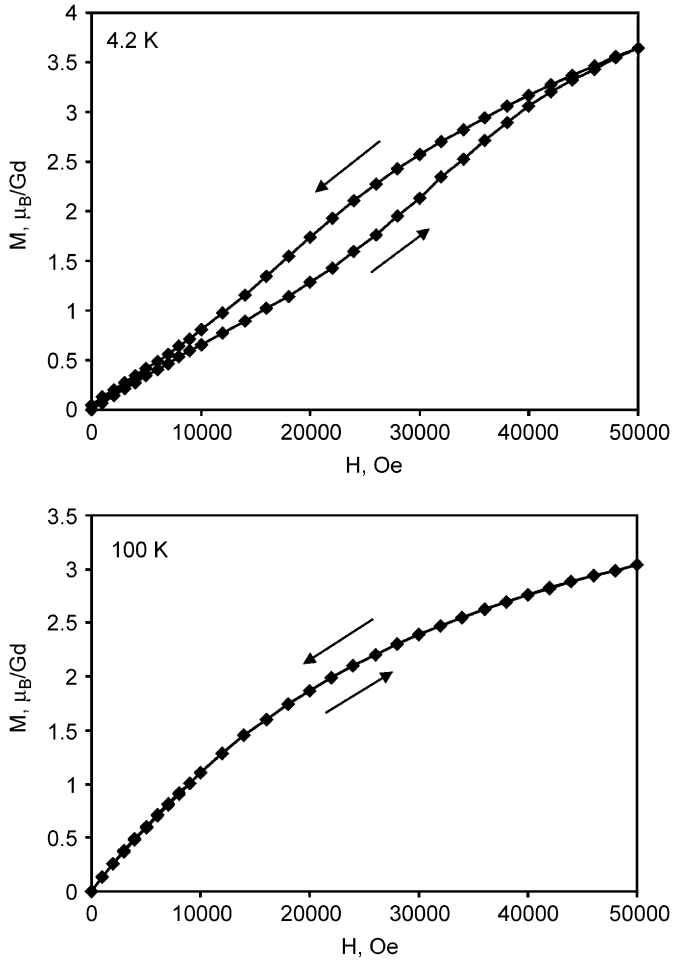

Fig. 2. Magnetization as a function of field for hexagonal Gd_5Bi_3 at 4.2 and 100 K.

same could be assumed for Gd_5Sb_3 and Gd_5Bi_3. Also based on the literature data for Gd_5Bi_3 [5,6], it could be hypothesized that the same structural sequence is followed by Gd_5Bi_3, but this was never rigorously proven. To check for the existence of the HT Yb_5Sb_3-type polymorphs, the two binaries Gd_5Sb_3 and Gd_5Bi_3, annealed at 800 °C, were sealed in tantalum tubes and annealed at 1350 °C in dynamic vacuum. After annealing at 1350 °C for 1.5 h, Gd_5Bi_3 showed complete transformation from the Mn_5Si_3-type polymorph into the Yb_5Sb_3-type one. If Gd_5Bi_3 treated at 1350 °C is annealed again at 800 °C for 2 weeks, it transforms back into the hexagonal polymorphs, proving that the Mn_5Si_3-type ↔ Yb_5Sb_3-type transformation is fully reversible. On the other hand, Gd_5Sb_3 showed no signs of structural rearrangements even after 6 h at 1350 °C, thus indicating that the orthorhombic structure is not accessible for Gd_5Sb_3 at least at this temperature. Annealing of the Gd_5Sb_3 and Gd_5Bi_3 samples at 600 and 400 °C produced the same phases as annealing at 800 °C.

The "A_5Pn_3" pnictides (A = a divalent electropositive atom such as Ca, Sr, Ba, Sm, Eu, Yb, Pn = Sb, Bi) with the Yb_5Sb_3-type structure have been shown to be, in reality, hydrogen-stabilized A_5Pn_3H phases, with hydrogen coming

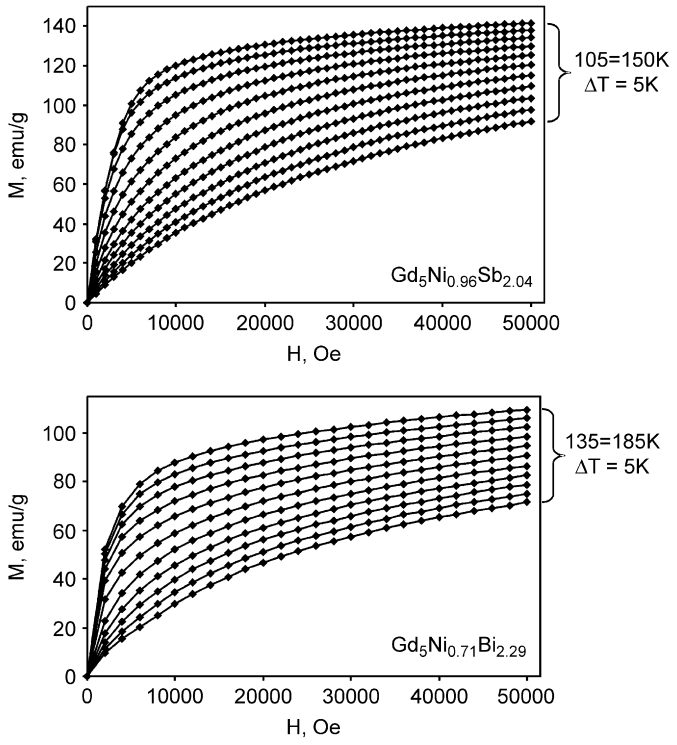

Fig. 3. Magnetization versus field curves for orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$.

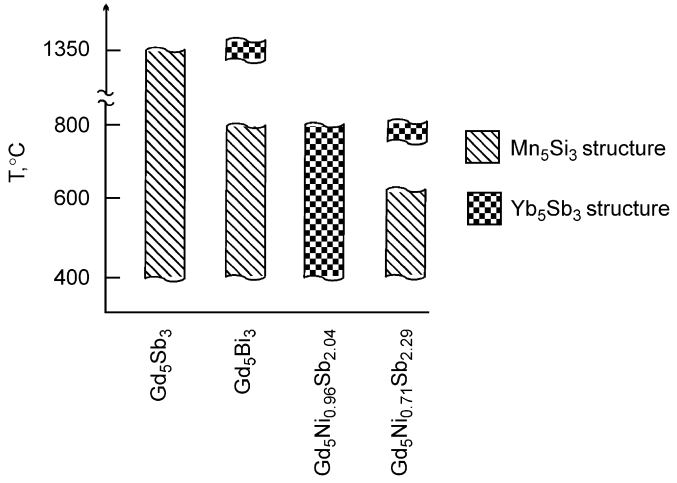

Fig. 4. Schematic phase diagram for Gd_5Sb_3, Gd_5Bi_3, $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$.

from the commercial A metals [11,12]. As Ta becomes relatively transparent to H_2 above 550 °C, annealing under the dynamic vacuum at higher temperatures dehydrogenates the samples and results in the formation of the hexagonal A_5Pn_3 phases (the Mn_5Si_3-type) [11]. While hydrogen presence is proven to be an important factor in the chemistry of pnictides with a divalent metal, A, its role in the stability of analogous pnictides with a trivalent rare-earth elements, RE, is not fully understood. Even if hydrogen tends to stabilize the RE_5Pn_3 pnictides, the conditions of our experiment (1350 °C and dynamic

vacuum) are expected to dehydrogenate and, thus, preclude hydrogen stabilization of the high-temperature form of Gd_5Bi_3 and also of the hexagonal Gd_5Sb_3 phase.

The compositions $Gd_5Ni_{0.96(1)}Sb_{2.04(1)}$ and $Gd_5Ni_{0.71(1)}Bi_{2.29(1)}$ obtained from the single crystal refinements were Ni poorer than the initial ones used for the synthesis, therefore it was assumed that the Ni amounts in these phases were the largest ones accessible under our experimental conditions. Thermal stability of the $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ phases was studied through annealing at 600 °C for 1 week, followed by annealing at 400 °C for 2 weeks. At 600 and 400 °C, $Gd_5Ni_{0.71}Bi_{2.29}$ was found to decompose into the hexagonal binary Gd_5Bi_3 and an unidentified Ni-containing phase. The lattice constants of the obtained Gd_5Bi_3 binary were in good agreement with those of the pristine Gd_5Bi_3 sample, thus indicating that there was no nickel left in the resulting Gd_5Bi_3 binary. We could not find suitable single crystals of hexagonal Gd_5Bi_3 to confirm that no nickel is present. In contrast, $Gd_5Ni_{0.96}Sb_{2.04}$ showed no signs of a structural transformation/decomposition at either 600 °C or 400 °C. While $Gd_5Ni_{0.96}Sb_{2.04}$ may still undergo a phase transition at lower temperatures, this could require a very long annealing time as the atomic rearrangements associated with this transition are very significant (see the discussion below).

In addition to $Gd_5Ni_{0.96}Sb_{2.04}$, and $Gd_5Ni_{0.71}Bi_{2.29}$ reported here, the orthorhombic Yb_5Sb_3-type structure is observed for other transition-metal substituted $RE_5T_xSb_{3-x}$ and $RE_5T_xBi_{3-x}$ phases annealed at 830 °C (*RE* is a rare earth and T = Fe–Cu) [4,13]. Out of all possible $RE_5T_xSb_{3-x}$ and $RE_5T_xBi_{3-x}$ phases, only few representatives and only those without gadolinium were prepared. Besides, the thermal stability of these phases was not investigated. Based on our current studies and the literature data [4], it can be concluded that the substitution of a late 3*d*-metal for Sb or Bi tends to stabilize the orthorhombic polymorphs of the corresponding binaries at high temperatures (exception is $Gd_5Ni_{0.96}Sb_{2.04}$). But this substitution by the transition metal is limited. The limited amount of Ni and the stability of the corresponding Ni-substituted orthorhombic phase were analyzed in details for $Y_5Ni_xSb_{3-x}$ [4]. It has been concluded that Ni incorporation reduces the strength of the Y–Sb interactions, which in turn limits the maximum amount of Ni in the structure. The structure can be stabilized only at high temperatures due to the entropy contribution stemming from the Ni/Sb statistical mixture. We can argue that the same is true for $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$.

The two structural polymorphs, the Mn_5Si_3 and Yb_5Sb_3 ones, differ significantly in terms of atomic arrangements (Fig. 5), and as pointed by Brunton and Steinfink [14] who first discovered the Yb_5Sb_3 phase, there is little resemblance between the two structure types. In the "classical" presentation by Guloy et al. [15], the Mn_5Si_3-type structure of Gd_5Bi_3 is constructed from the Gd1 octahedra that are fused along the *c* direction to form hexagonal columns. The columns are interconnected through the Bi atoms, which in turn form channels filled with Gd2 chains. While hexagonal channels can be also identified in the Yb_5Sb_3-type structure of Gd_5Bi_3, they are irregular and filled with both Gd and Bi atoms (Fig. 5). There are also the trigonal channels filled with the Bi atoms and attached to the hexagonal ones. No simple atomic rearrangement is found to transform one structure into the other, besides the space groups of the two structures are not in a group–subgroup relationship. Such different atomic arrangements may explain the fact that the HT orthorhombic polymorphs could be easily quenched into room temperature and that a long annealing time is required to obtain a LT hexagonal polymorph.

3.2. Magnetic properties and magnetocaloric effect

The LT hexagonal polymorph of Gd_5Bi_3 exhibits a complex magnetic behavior (Fig. 1) which is analogous to that found in hexagonal Gd_5Sb_3 [8]. While the overall shape of the curve may be representative of an antiferromagnetic ordering, the Weiss temperature derived from the paramagnetic region clearly indicates that interactions at higher temperatures are ferromagnetic in nature. These ferromagnetic interactions yield a ferromagnetic ordering at 112 K, followed by a significant decrease in magnetization below 64 K which is indicative of spin reorientation. A

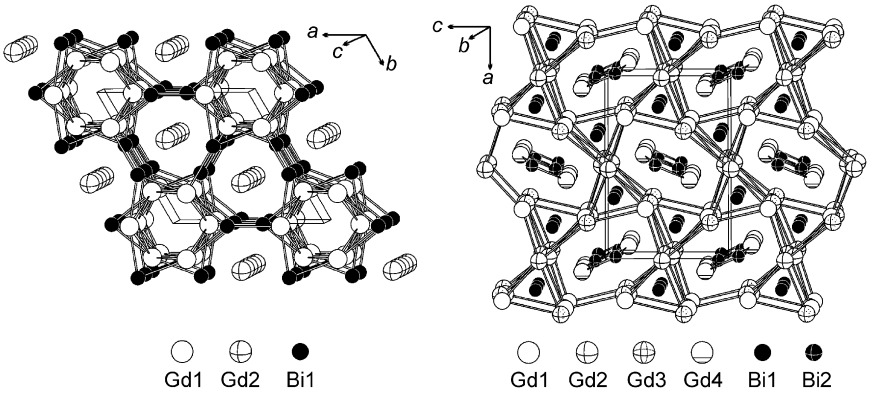

Fig. 5. Structures of the hexagonal Mn_5Si_3-type (left) and orthorhombic Yb_5Sb_3-type (right) polymorphs of Gd_5Bi_3.

step-like change in M vs. H at 4.2 K also points at spin reorientation at low temperatures (Fig. 2). This step-like feature is expected to be absent above 64 K, and this is verified by a M vs. H scan at 100 K. At both temperatures 4.2 and 100 K, magnetization in 50 kOe did not reach the gJ value of 7.00 μ_B expected for a Gd^{3+} free ion. Above 200 K, Gd_5Bi_3 follows the Curie–Weiss law with $\Theta_p = 137$ K and $\mu_{eff/Gd} = 8.57\,\mu_B$ (Table 4). For comparison, at the paramagnetic region the HT orthorhombic form of Gd_5Bi_3 obeys the Curie–Weiss law with $\Theta_p = 120$ K and $\mu_{eff/Gd} = 8.43\,\mu_B$ [6], while hexagonal Gd_5Sb_3 follows the Currie–Weiss law with much larger $\Theta_p = 267$ K and $\mu_{eff/Gd} = 10.9\,\mu_B$ [8].

The orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ compounds undergo ferromagnetic orderings at 115 and 162 K, respectively. Interestingly, the Currie temperature for the Ni-substituted $Gd_5Ni_{0.71}Bi_{2.29}$ is 50 K higher than that of the pure orthorhombic Gd_5Bi_3 binary. At higher temperatures, both Ni-substituted phases obey the Curie–Weiss relationship with $\Theta_p = 161$ K and $\mu_{eff/Gd} = 8.48\,\mu_B$ for $Gd_5Ni_{0.96}Sb_{2.04}$ and $\Theta_p = 182$ K and $\mu_{eff/Gd} = 9.61\,\mu_B$ $Gd_5Ni_{0.71}Bi_{2.29}$. The calculated magnetic moment for Gd in $Gd_5Ni_{0.96}Sb_{2.04}$ is similar to those observed in orthorhombic and hexagonal Gd_5Bi_3, thus suggesting that magnetic contribution of Ni atoms is small. Even if assumed otherwise, the Ni contribution would be insufficient to yield large magnetic moments observed in $Gd_5Ni_{0.96}Sb_{2.04}$ and especially in $Gd_5Ni_{0.71}Bi_{2.29}$. It is also difficult to say whether the Ni presence influences the Gd moment since the phases with the same structure have to be compared. However only two Gd-containing phases, Gd_5Bi_3 and $Gd_5Ni_{0.71}Bi_{2.29}$, with the same Yb_5Sb_3-type structure are known, and thus no general conclusions can be drawn.

Magnetic moments larger than $\mu_{eff} = g[J(J+1)]^{1/2}\mu_B = 7.94\,\mu_B$ expected for a free Gd^{3+} ion are found not only in Gd_5Bi_3, Gd_5Sb_3 and their Ni derivatives, but also in other Gd-containing phases: e.g. 8.32 μ_B in $Gd_4Pd_{10}In_{21}$ [16]. Even elemental Gd shows a ~9% increase for its measured magnetic moment [17]. Generally, increase in $\mu_{eff/Gd}$ is attributed to the polarization of conduction electrons, predominantly the Gd 5*d* ones, through the 4*f*–5*d* exchange interactions [18,19].

Magnetocaloric effect in terms of entropy change, ΔS, for the Ni-substituted materials was evaluated from the magnetization data (Fig. 3) using the Maxwell relationships [3]:

$$\left(\frac{\partial S(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H,$$

which after the integration yields $\Delta S(T)_{\Delta H} = \int_{H_1}^{H_2}(\partial M(T,H)/\partial T)_{H,P}\,dH$. In practice, a numerical integration is performed using the following formula:

$$\Delta S(T)_{\Delta H} = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i}\delta H,$$

where δH is a magnetic field step and M_i and M_{i+1} are the

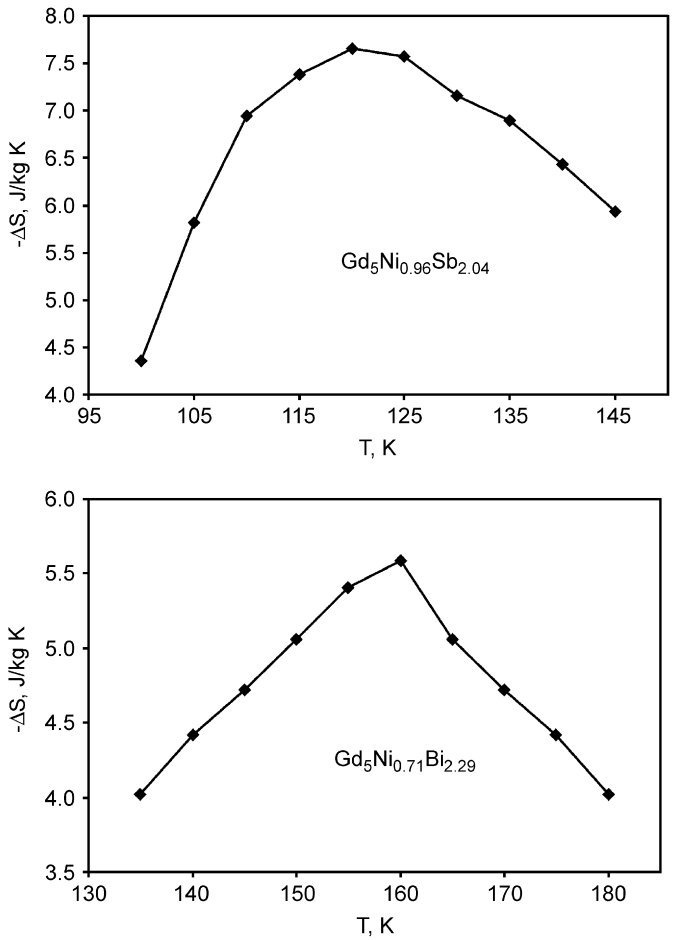

Fig. 6. Entropy change for $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ as a function of temperature for $\Delta H = 0$–50,000 Oe.

Table 4
Magnetic parameters for Gd_5Sb_3, Gd_5Bi_3, $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$

Compound	Space group	Magnetic behavior	T_C (K)	$\mu_{eff/Gd}$, μ_B)	θ_p (K)	$-\Delta S$ (J/kg K)	Ref.
Gd_5Sb_3	$P6_3/mcm$	Ferromagnetic	187	10.9	266.8		[8]
$Gd_5Ni_{0.96}Sb_{2.04}$	*Pnma*	Ferromagnetic	115	8.48	161	7.7[a]	This work
Gd_5Bi_3	$P6_3/mcm$	Ferromagnetic	112	8.57	137		This work
Gd_5Bi_3	*Pnma*	Ferromagnetic	110	8.43	120		[6]
$Gd_5Ni_{0.71}Bi_{2.29}$	*Pnma*	Ferromagnetic	162	9.61	182	5.6[a]	This work

[a] ΔS is the maximum entropy change for a magnetic field change $\Delta H = 0$–50,000 Oe.

values of magnetization at temperatures T_i and T_{i+1}, respectively. The magnetic entropy change, ΔS, for $\Delta H = 0$–50,000 Oe is plotted in Fig. 6. As expected, ΔS peaks around the Curie temperatures and has the maximum value of -7.7 J/kg K for $Gd_5Ni_{0.96}Sb_{2.04}$ and -5.6 J/kg K for $Gd_5Ni_{0.71}Bi_{2.29}$. While these values of ΔS are substantial, they are smaller (by absolute values) than -9.8 J/kg K measured for pure gadolinium or -18.5 J/kg K found for $Gd_5Si_2Ge_2$ [1].

4. Conclusion

The two binaries Gd_5Sb_3 and Gd_5Bi_3 exhibit different structural behavior with temperature. Gd_5Bi_3 adopts two polymorphs: a LT Mn_5Si_3-type one below 800 °C and a HT orthorhombic Yb_5Sb_3-type one at 1350 °C. In contrast, Gd_5Sb_3 crystallizes only with a hexagonal Mn_5Si_3-type structure and is not found to undergo any structural transition up to 1350 °C. Ni substitution leads to the formation of the orthorhombic structure for $Gd_5Ni_{0.96}Sb_{2.04}$ and stabilizes the orthorhombic bismuthide $Gd_5Ni_{0.71}Bi_{2.29}$ to lower temperatures.

The magnetic behavior of orthorhombic $Gd_5Ni_{0.96}Sb_{2.04}$ and $Gd_5Ni_{0.71}Bi_{2.29}$ is similar as both phases order ferromagnetically at low temperatures. Hexagonal Gd_5Bi_3 shows a more complex magnetic behavior as the ferromagnetic ordering is followed by spin reorientation.

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