Structural and magnetothermal properties of the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system

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The crystallographic and magnetic properties of the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ pseudobinary system were studied by x-ray powder diffraction at room temperature, and the heat capacity, magnetization, and electrical resistivity in the temperature interval 5–320 K in applied dc magnetic fields between 0 and 100 kOe. The $\text{Gd}_5\text{Sb}_{2.1}\text{Ge}_{1.9}$ compound adopts the $\text{Tm}_5\text{Sb}_2\text{Si}_2$ -type structure (space group *Cmca*) and orders magnetically via a second order ferromagnetic-paramagnetic transition at 200 K, whereas the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ compounds with $x=0.7$ and $x=1$ crystallize in the Sm_5Ge_4 -type structure (space group *Pnma*) and exhibit first order phase transformations at 45 and 37 K, respectively, and therefore, the giant magnetocaloric effect. The heat capacity and electrical resistivity measurements of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ indicate a second order antiferromagnetic transition at 60 K in fields 20 kOe and lower. © 2006 American Institute of Physics. [DOI: [10.1063/1.2150811](https://doi.org/10.1063/1.2150811)]

The magnetic properties of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, where R is a lanthanide metal, have been extensively studied since 1997 after Pecharsky and Gschneidner¹ discovered the giant magnetocaloric effect in the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound. Due to a coupled magnetostructural first-order phase transition in this and other $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds, a number of intriguing magnetic properties, such as the giant magnetostriction² and the giant magnetoresistance³ have been observed in addition to the giant magnetocaloric effect. The crystal structures of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds consist of $\frac{2}{x}[\text{Gd}_5\text{T}_4]$ slabs, where T is a statistical mixture of Ge and Si. Specific T - T dimers between the slabs can be reversibly broken or reformed by changing temperature, concentration (x) and/or by applying pressure or magnetic field, leading to magnetostructural transitions. Recent studies of the $\text{Gd}_5(\text{Ge}_x\text{Ga}_{1-x})_4$ system⁴ showed a sequence of structures changing with x , that mimic the martensitic transition observed in $\text{Gd}_5\text{Si}_2\text{Ge}_2$.⁵ The authors of Ref. 4 suggested that lack of one electron in the outer shell of Ga (3 valence electrons for Ga instead of 4 for Si) drives the change of the crystallography in the $\text{Gd}_5(\text{Ge}_x\text{Ga}_{1-x})_4$ system via a gradual reduction of the valence electron concentration. Therefore, it is natural to examine how a shift of the valence electron concentration in the opposite direction by substituting pentavalent antimony for tetravalent Si or Ge affects the crystallography and physical properties of the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ compounds.

A crystallographic study of several $R_5\text{Sb}_2(\text{Si},\text{Ge})_2$ compounds,⁶ showed the existence of a previously unknown

structure, called the $\text{Tm}_5\text{Sb}_2\text{Si}_2$ -type structure. The latter is closely related to the Sm_5Ge_4 type, but has a higher symmetry (space group is *Cmca* instead of *Pnma*). The authors⁶ reported several compounds with heavy rare-earth metals, however, they did not observe the $\text{Gd}_5\text{Sb}_2\text{Ge}_2$ compound.

The starting materials for synthesis of $\text{Gd}_5(\text{Sb}_x\text{Ge}_{1-x})_4$ samples were pieces of Gd (99.86 at. % or 99.99 wt %) prepared by the Materials Preparation Center of the Ames Laboratory, and Sb (99.99 wt %) and Ge (99.99 wt %) purchased from Meldform Metals (United Kingdom). Four samples weighting ~ 5 g each of the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ alloys with $x=0.5, 1, 2$, and 3 stoichiometry were prepared by arc melting the elements on a copper hearth in an argon atmosphere. Because of low boiling temperature of antimony (1860 K), we used $\sim 5\%$ excess of this metal to make up for evaporation to maintain the necessary stoichiometries. The alloy buttons were remelted four times to minimize inhomogeneities. The x-ray powder diffraction studies were performed on an automated Scintag powder diffractometer using $\text{Cu } K\alpha$ radiation; the crystal structures were refined using Rietveld technique. The magnetization and electrical resistivity data were measured using a Lake Shore magnetometer, model 7225. Magnetic measurements were carried out in the temperature interval from 4.5 to 300 K in applied magnetic fields up to 56 kOe. Electrical resistivity was measured by a standard four-probe technique in the temperature interval 5–350 K in applied magnetic fields up to 40 kOe. The heat capacity in magnetic fields up to 100 kOe was measured between ~ 2 and 350 K in a semiadiabatic heat pulse calorimeter, which has been described elsewhere.⁷

The room temperature x-ray data indicate that when x

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TABLE I. The crystallographic properties of alloys in the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system. Data for $x=0$ are taken from Ref. 10.

x	a (Å)	b (Å)	c (Å)	Interslab d_{T-T} (Å)	Structure type
0	7.697(5)	14.83(1)	7.785(6)	3.71	Sm_5Ge_4
0.7 ^a	7.786(6)	14.89(1)	7.844(6)	3.77	Sm_5Ge_4
1 ^a	7.865(9)	14.97(2)	7.901(9)	3.82	Sm_5Ge_4
2.1 ^a	15.17(1)	7.968(8)	7.982(9)	4.22	$\text{Tm}_5\text{Sb}_2\text{Si}_2$
2.7 ^a	15.28(1)	8.049(9)	8.072(9)	4.27	$\text{Tm}_5\text{Sb}_2\text{Si}_2$

^aAs determined from the Rietveld analysis.

≥ 2 , $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ adopts the $\text{Tm}_5\text{Sb}_2\text{Si}_2$ -type structure. When $x < 2$, $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ has the orthorhombic Sm_5Ge_4 -type structure, same as the binary Gd_5Ge_4 . The lattice parameters are listed in Table I. According to the results of the Rietveld refinement, the actual compositions of the $\text{Gd}_5\text{Sb}_{0.5}\text{Ge}_{3.5}$, $\text{Gd}_5\text{Sb}_2\text{Ge}_2$, and $\text{Gd}_5\text{Sb}_3\text{Ge}$ and alloys were $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$, $\text{Gd}_5\text{Sb}_{2.1}\text{Ge}_{1.9}$, and $\text{Gd}_5\text{Sb}_{2.7}\text{Ge}_{1.3}$, respectively. Based on the results obtained for the latter compound, it is quite likely that the largest amount of Sb soluble in Gd_5Ge_4 is $x=2.7$.

The magnetization, electronic transport, and heat capacity of the three compositions with $x=0.7$, 1, and 2.1 were measured. The $\text{Gd}_5\text{Sb}_{2.1}\text{Ge}_{1.9}$ compound exhibits a second order ferromagnetic-paramagnetic (FM-PM) transition at 200 K, whereas $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ with $x=0.7$ and $x=1$ undergo first order phase transformations at 45 and 37 K, respectively.

Selected magnetization isotherms of Gd_5SbGe_3 , shown in Fig. 1, are similar to those observed for $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$. Although there are no distinct steps of the magnetization on the isotherms, the presence of hysteresis points to a first order nature of the phase transformation that occurs between 45 and 67 K in magnetic fields below 50 kOe. The magnetization results have been confirmed by heat capacity that shows a sharp first-order phase transition peak moving to higher temperatures with increasing magnetic field, which is also similar to the behavior observed in $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$, see

below. A small anomaly observed at 100 K on the $M(T)$ dependencies (not shown) can be interpreted as the Néel point and the first order phase transition at 45 K most likely is of ferromagnetic-antiferromagnetic (FM-AFM) type. It follows from the noticeable FM component observed in low magnetic fields at temperatures as high as 94 K (see Fig. 1) that the AFM structure of this compound may be quite complex. The maximum isothermal magnetic entropy change (ΔS_M), calculated from the heat capacity data for Gd_5SbGe_3 , is -23.5 J/kg K at $T=53$ K for a 50 kOe magnetic field change, which is somewhat less than the $\Delta S_M=-37$ J/kg K exhibited by $\text{Gd}_5\text{Si}_{0.33}\text{Ge}_{3.67}$ for a 50 kOe magnetic field change at 70 K (Ref. 8), but the former still maintains all the characteristics of the giant magnetocaloric effect.

The temperature dependencies of magnetization of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ from 4 to 250 K in magnetic fields of 1, 10, and 20 kOe are presented in Fig. 2. The curves exhibit a sharp step of the magnetization at 37 K in a 1 kOe magnetic field, which shifts to higher temperatures with increasing magnetic field ($T=55$ K in a 20 kOe magnetic field). The step in the magnetization corresponds to a first-order magnetic phase transition that is also confirmed by the heat capacity data (Fig. 3). There are also anomalies at ~ 60 and ~ 150 K that can barely be seen in the 1 and 10 kOe curves (inset, Fig. 2). The anomaly at ~ 150 K may be due to the magnetic ordering of an impurity phase, whose concentration was too low to be detected by x-ray powder diffraction. The

FIG. 1. (Color online) The magnetization isotherms of Gd_5SbGe_3 in the temperature interval 29–94 K in the range of magnetic fields up to 50 kOe. Closed symbols correspond to data points collected on increasing magnetic field, whereas opened symbols correspond to decreasing magnetic field.

FIG. 2. (Color online) Temperature dependencies of the magnetization of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ measured in 1, 10, and 20 kOe magnetic fields. The inset shows the rate of change of the magnetization with temperature as a function of temperature. The arrows in the inset indicate observed anomalies.

FIG. 3. (Color online) Temperature dependencies of the heat capacity of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ in magnetic fields up to 100 kOe. The inset shows the details of the second order transition around 60 K.

heat capacity data only show the presence of a second order transformation at $T=60$ K in magnetic fields below 20 kOe (see inset in Fig. 3) and no anomaly at 150 K, which is consistent with a small amount of an impurity phase. To clarify the nature of the transformation at $T=60$ K, the electrical resistivity measurements were carried out (see Fig. 4). There is a step-like behavior at the first order phase transition and a broad maximum at 60 K that relates to the second order phase transition observed in the heat capacity data. The anomaly at 60 K can be interpreted as a Néel point corresponding to AFM-PM transition. The maximum isothermal magnetic entropy change (-27 J/kg K) for $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$, calculated from the heat capacity, is observed at 70 K for a 70 kOe magnetic field change. The corresponding value estimated from $M(H)$ data using Clausius-Clapeyron equation for the same magnetic field change is -25 J/kg K.

FIG. 4. (Color online) Temperature dependencies of the electrical resistivity of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ in applied magnetic fields up to 40 kOe.

We believe that similar to Gd_5Ge_4 , where AFM-FM transition is coupled to a martensitic-like structural change,⁹ the same happens in both $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ and Gd_5SbGe_3 . The nature of the structural transition in the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system, however, remains open and needs to be studied using x-ray diffraction measurements at low temperatures and in applied magnetic fields. At this point we only know that at room temperature the crystal structure is similar to that of the Gd_5Ge_4 compound, i.e., there are no $T-T$ dimers between the ${}^{2/3}[\text{Gd}_5\text{T}_4]$ slabs. Similar to $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, one can assume that temperature and/or magnetic field restore some or all of the $T-T$ dimers, causing a structural transition simultaneously with the ferromagnetic ordering. With this assumption and recalling that at room temperature for $x \geq 2$ the $T-T$ interslab distances (d_{T-T}) in $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ are much longer than for $x < 2$ (see Table I), one may explain the absence of a first-order transition when $x \geq 2$ by the inability of the system to restore $T-T$ bonding like in Gd_5Ge_4 . One can also notice that a 60 K antiferromagnetic transition for $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ is magnetic field independent and it disappears in fields above ~ 20 kOe, where it merges with a structural transformation. In other words, the AFM-PM transition is found only in the high temperature (low field) Sm_5Ge_4 -type phase.

In summary, the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system exhibits interesting structural and magnetic properties along with a high value of the isothermal magnetic entropy change. Compared to the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system exhibits narrower hysteresis during the first order transformation and the samples with antimony are less brittle. Detailed measurements of a single crystal of $\text{Gd}_5\text{Sb}_{0.7}\text{Ge}_{3.3}$ are planned in the near future.

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