Crystal structure and magnetic properties of $\text{GdSi}_{1.78}$, $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, $\text{GdGe}_{1.57}$, and GdSn_2 compounds

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Abstract:

Intermetallic compounds of Gd with Si, Ge, and Sn near 1:2 stoichiometry adopt several closely related crystal structures. We find that $\text{GdSi}_{1.78}$ and $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$ crystallize in the same $\text{GdSi}_{1.4}$ -type orthorhombic structure (space group *Imma*), while $\text{GdGe}_{1.57}$ and GdSn_2 adopt α - ThSi_2 -type tetragonal structure (space group *I4₁/amd*) and ZrSi_2 -type orthorhombic structure (space group *Cmcm*), respectively. All compounds order antiferromagnetically; their Néel temperatures are only weakly affected by the magnetic field of less than 50 kOe. Unusual features are observed including multiple phase transitions and thermomagnetic irreversibilities.

Keywords: rare earth intermetallics; magnetic properties; phase transition; antiferromagnetism; heat capacity.

I. INTRODUCTION

Intermetallic compounds formed by lanthanide metals with the elements of group 14 in the periodic system have been attracting continuous attention since 1960's when relatively pure lanthanides have become commercially available, and especially so after the discovery of giant magnetocaloric,^{1,2} magnetoresistance,^{3,4} and magnetostriction⁵ effects in Gd-rich $\text{Gd}_5\text{Si}_{4-x}\text{Ge}_x$ compounds. The latter adopt three different yet closely related structures at room temperature depending on composition (x), namely the Gd_5Si_4 -type, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type, and Sm_5Ge_4 -type structures.^{6,7,8} The magnetic and structural phase transitions that occur in the $\text{Gd}_5\text{Si}_{4-x}\text{Ge}_x$ compounds can be controlled by changing chemical composition, magnetic field, temperature, and/or applied pressure.^{1,2, 9, 10} Experimental and theoretical studies show that most of the interesting phenomena observed in $\text{Gd}_5\text{Si}_{4-x}\text{Ge}_x$ compounds are associated with field (temperature or pressure)-induced first-order structural transitions between paramagnetic (PM) monoclinic or antiferromagnetic (AFM) orthorhombic and ferromagnetic (FM) orthorhombic structures.¹¹

Gd-poor compounds, GdT_2 ($T=\text{Si, Ge, and Sn}$), in some aspects, are similar to the 5:4-type compounds, especially with respect to their polymorphism. It has been reported that the 1:2 compounds adopt several closely related crystal structures, including $\text{GdSi}_{1.4}$ -type and ZrSi_2 -type orthorhombic (space groups *Imma* or *Cmcm*),^{12,13,14,15,16,17} α - ThSi_2 -type tetragonal (space group *I4₁/amd*),^{18, 19, 20} and AlB_2 -type hexagonal structures (space group *P6/mmm*).²¹ Figure 1 shows the unit cells of three structures which will be discussed in this work. The bonds between Gd and the elements in group 14 are omitted. Earlier studies show that GdSi_2 has very low Schottky-barrier height suggesting potential

applications in infrared detectors.²² Nanowires, a highly anisotropic form of nanocrystals, have attracted considerable interest due to their unusual physical properties and potential applications in nanoscale devices and interconnections.²³ Growth of GdSi₂ nanowires on a silicon substrate, Si (100), has been reported.^{24,25,26,27} Yet even today, these Gd-based compounds are not well understood, and their fundamental properties should be further studied.

The 1:2-type rare earth compounds RT₂ (R=rare earth, T=group 14 element) show rich magnetism. At low temperature, light lanthanide compounds (such as CeGe₂, PrGe₂, NdGe₂, and PrSi₂) are ferromagnets, while heavy lanthanide compounds are antiferromagnets (the Néel temperatures, T_N , do not follow the de Gennes law) or Pauli paramagnets.^{12,16,19} In the past, basic magnetic properties of orthorhombic GdSi₂ and GdGe₂ were studied: they order AFM at 27 and 28 K, respectively.^{12,16} The effective magnetic moments of Gd in GdSi₂ and GdGe₂ are 7.81, and 8.1 μ_B/Gd^{3+} , respectively, which are close to 7.94 μ_B – theoretical value of the free ion. The high temperature x-ray diffraction (XRD) confirms that GdSi₂ undergoes a transformation from tetragonal to orthorhombic structure at ~818 K.¹⁴ First principles electronic structure calculations (performed without accounting for the interatomic $4f$ interactions and f - d hybridization) reveal that the AFM state of GdSi₂ is energetically more stable than the FM state in any of the three possible structures.²⁸ No detailed magnetic properties of GdSn₂ have been reported.

II. EXPERIMENT DETAILS

The Gd metal was prepared by the Materials Preparation Center of the Ames Laboratory and was 99.93 wt.% pure with respect to all other elements in the periodic

table.²⁹ The major impurities were O (0.018 wt.%), Yb (0.002 wt.%), Al (0.015 wt.%), C (0.017 wt.%), and N (0.012 wt.%). The purities of Si, Ge, and Sn were better than 99.99 wt.%. GdSi₂, GdSiGe, GdGe₂ and GdSn₂ samples with the stoichiometric 1:2 (R:T) compositions were prepared by arc melting pure elements under argon gas atmosphere on a water-cooled copper hearth. The GdGe₂ and GdSn₂ specimens were separately sealed in quartz tubes backfilled with pure helium gas, and then annealed at 1423 K for 21 days and 1073 K for 14 days, respectively. These two samples were quenched in ice-water mixture after annealing procedure. Crystal structures of phases presenting in the samples were determined from room-temperature x-ray powder diffraction (XRD) data collected using a PANalytical X'Pert Pro powder diffractometer employing monochromatic Cu $K\alpha_1$ radiation (wavelength of 1.54056 Å). The lattice parameters, phase concentrations, and other structural parameters were determined by performing Rietveld refinement using Rietica-LHPM.³⁰

Magnetization measurements were conducted by using the magnetic properties measurement system MPMS XL-7, Quantum Design, Inc. The measurements were performed in the temperature range of 5-40 K in applied dc magnetic fields up to 50 kOe. A homemade adiabatic heat-pulse calorimeter was used to conduct the heat-capacity measurements.³¹ The measurements were performed in the temperature range from ~2 to 50 K in zero magnetic field and in applied magnetic fields up to 50 kOe.

III. RESULTS AND DISCUSSIONS

A. Crystal structure

The observed and calculated room-temperature XRD patterns are displayed in Fig.2, and the structural parameters are summarized in Table 1. According to earlier reports,

GdSi₂ can crystallize in orthorhombic,^{12,13} tetragonal,^{18,19} and hexagonal structures.²¹ The as-prepared GdSi₂ and GdSiGe crystallize in the orthorhombic crystal structure (space group *Imma*), which is an orthorhombically distorted variant of the tetragonal α -ThSi₂-type structure. The Rietveld refinement results (Fig. 2(a), 2(b) and Table 1) show that these two samples contain about 7 wt.% of Si and Si-Ge phases, respectively. Both samples are nonstoichiometric compounds, and the actual ratio between Gd and Si (or Si-Ge) is 1:1.78, as determined from Rietveld refinement of site occupancies. The orthorhombic structure remains stable after 21 days heat treatment at 1423 K, but the concentrations of the impurity phases (pure Si or Si-Ge) somewhat increase.

For the GdGe₂ compound, previous studies indicate that it adopts the orthorhombic structure after annealing under vacuum.^{15, 16} Our sample adopts tetragonal α -ThSi₂-type structure (space group *I4₁/amd*) after annealing at 1423 K for 21 days, see Fig. 1(b) and 2(c). This sample also contains atomic defects with an accurate composition of GdGe_{1.57}. Annealing at lower temperature, e.g. 973 K, is insufficient to achieve the single phase. In addition to Ge (far less than 1 wt.%), our GdGe_{1.57} sample contains about 6 wt.% of Gd₃Ge₅ which adopts the face-centered Y₃Ge₅-type orthorhombic structure with space group *Fdd2*.^{32,33} The as-prepared GdSn₂ sample crystallizes in the orthorhombic structure (space group *Cmcm*). The results of Rietveld refinement of the heat-treated GdSn₂ are shown in Fig 2(d) and Table 1. This heat-treated GdSn₂ sample contains about 3 wt.% of Sn metal as a minor impurity. Compared with the as-cast sample, the heat treatment at 1073 K for 14 days is beneficial in reducing the concentration of Sn impurity. Unlike the nonstoichiometric GdSi_{1.78} and GdGe_{1.57} compounds, we note that GdSn₂ is a stoichiometric compound.

B. Magnetic properties

Although the phase volume monotonically increases in the series $\text{GdSi}_{1.78}$, $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, $\text{GdGe}_{1.57}$, and GdSn_2 , as expected, considering the difference in the atomic volumes of Si, Ge, and Sn, the magnetic properties exhibit a more complicated behavior. The magnetic measurements show that all four samples order antiferromagnetically. The temperature dependence of magnetization of $\text{GdSi}_{1.78}$, shown in Fig. 3, indicates AFM ordering below 25 K. The Néel temperature (T_N) of $\text{GdSi}_{1.78}$ is close to previous reports.^{12, 34} Besides the main AFM transition, two anomalies are observed below T_N ; they are marked as T' and T'' . Thermomagnetic irreversibility between zero-field-cooling (ZFC) and field-cooling (FC) measurements is observed between 14 K and $T'=20$ K in 1 kOe. The thermal hysteresis region shifts toward higher temperature at 50 kOe. In addition, the ZFC and FC curves in 50 kOe show a substantial thermal hysteresis down to the lowest measurement temperature and the ZFC curve shows an anomaly at $T''=8$ K. The $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$ sample crystallizes in the same structure as $\text{GdSi}_{1.78}$, but its T_N decreases to 22 K as a result of Ge substitution (Fig. 4). Weak thermal hysteresis is observed below 10 K in low fields, and the thermal hysteresis becomes more prominent with the increasing magnetic field. Similar to $\text{GdSi}_{1.78}$, an anomaly is also observed at $T''=7$ K.

Although the annealed $\text{GdGe}_{1.57}$ crystallizes in the tetragonal structure, which is different from $\text{GdSi}_{1.78}$ and $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, T_N of $\text{GdGe}_{1.57}$ further decreases to 18 K which is lower than the reported value of the orthorhombic GdGe_2 ($T_N=28$ K),¹⁶ see Fig. 5. The minor break of the slope at 25 K is possibly due to the impurity phase of Gd_3Ge_5 .³⁴ The thermal hysteresis behavior of the germanide is different from that of $\text{GdSi}_{1.78}$ and

Gd(Si_{0.684}Ge_{0.316})_{1.78}. The thermal hysteresis of GdGe_{1.57} compound begins at T_N in 1 kOe. With the increase of the magnetic field, the start point of thermal hysteresis drop below 15 K, and the hysteresis regions keep decreasing.

Compared with GdSi_{1.78} and Gd(Si_{0.684}Ge_{0.316})_{1.78}, GdSn₂ compound also adopts an orthorhombic structure, but it belongs to a different space group (*Cmcm*). T_N of GdSn₂ increases to 28 K (Fig. 6) which is higher than T_N of GdSi_{1.78}. Thermal hysteresis can be observed at the lowest temperatures, and it persists up to 50 kOe. Thermal hysteresis features in all four samples most likely suggest the existence of magnetic clustering which originate from the layered structure. Note that the extended 5d bands of Si, Ge, and Sn might offer a small FM component which also can lead to thermomagnetic irreversibility behaviors in all title samples.³⁵ In addition to the AFM ordering transition at T_N , another anomaly is observed at $T'=21$ K. T' of GdSn₂ does not obviously change with the applied magnetic field which is different from that in GdSi_{1.78}.

The effective magnetic moment p_{eff} of Gd in GdSi_{1.78} and GdSn₂ are 8.19 μ_B and 8.16 μ_B , respectively, which are larger than the theoretical value of 7.94 μ_B for free trivalent ion Gd³⁺, but are actually very close to the usually observed values. p_{eff} of GdGe_{1.57} is 7.98 μ_B which is almost the same as the theoretical value. p_{eff} of Gd(Si_{0.684}Ge_{0.316})_{1.78} is 7.69 μ_B which is lower than the expected value. It is well known that the 4f-4f exchange interactions in rare-earth elements are mediated by conduction electrons (*spd*). The 4f-4f exchange interactions spin split the conduction electrons (mainly the 5d electrons). The Si, Ge and Sn in GdSi_{1.78}, Gd(Si_{0.684}Ge_{0.316})_{1.78} and GdSn₂ would be hybridized in both spin directions by Gd atoms leading to strong 5d-p hybridization. Therefore, the deviation of magnetic moment to the theoretical value can

be quite possibly ascribed to strong $5d$ - p hybridization. In addition, the deviation also possibly originate from the spin density wave (SDW) state and magnetic polaron of extended $5d$ bands of Si, Ge, and Sn induced by localized $4f$ moments.^{35,36} The Néel temperature T_N decreases from 25 K (GdSi_{1.78}) to 22 K (Gd(Si_{0.684}Ge_{0.316})_{1.78}), to 18 K (GdGe_{1.57}), then increases to 28 K (GdSn₂). The paramagnetic Weiss temperature θ_p increases from -73 K (GdSi_{1.78}) to -54 K (Gd(Si_{0.684}Ge_{0.316})_{1.78}), to -39 K (GdGe_{1.57}), and then decreases to -69 K (GdSn₂). The changing tendency of T_N and the absolute value of θ_p match with each other very well. Usually, it is expected that T_N and $|\theta_p|$ should decrease with the expansion of unit cell volume, such as the cases of GdSi_{1.78}, Gd(Si_{0.684}Ge_{0.316})_{1.78}, and GdGe_{1.57}. However, T_N and $|\theta_p|$ of GdSn₂ anomaly increase.

C. Heat-capacities

We have performed heat-capacity measurements in order to further explore the observed magnetic phase transitions. Figure 7 show the heat-capacities, C_p , of all four samples measured as a function of temperature in zero and 50 kOe magnetic fields. The heat-capacity of GdSi_{1.78} only shows one peak at $T_N=25$ K, see Fig. 7(a). The heat-capacity behavior of Gd(Si_{0.684}Ge_{0.316})_{1.78} is similar with that of GdSi_{1.78} except that the peak shifts downward to 22 K, shown in Fig. 7(b). Figure 7(c) shows the heat-capacity of GdGe_{1.57}, and a small peak is observed at $T_N=18$ K. Another anomaly appears at 25 K due to the orthorhombic impurity phase. As for GdSn₂, two phase transitions are confirmed at 21 K and 28 K, respectively, as shown in Fig. 7(d). The positions of the two peaks correspond with T' and T_N in the temperature dependence magnetization, as shown in Fig. 6. Compared with the C_p curves in zero field, the heat-capacity peaks of all samples slightly yet clearly move to low temperatures and the height of these peaks goes down a

little in 50 kOe which might be signs of magnetic field induced phase transitions. It should be noted that anomalous increases are observed in C_p curves below around 15 K for all samples. This behavior might originate from the anomalous increase in the magnetic part of specific heat as a function of temperature while it is independent on the magnetic field less than 50 kOe.

IV. CONCLUSIONS

Although $\text{GdSi}_{1.78}$, $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, $\text{GdGe}_{1.57}$ and GdSn_2 compounds adopt different structures, all compounds are AFM ordering. Moreover, the unit cell volumes monotonically increase with the increase in atomic number, while T_N decreases from 25 K for $\text{GdSi}_{1.78}$ to 18 K for $\text{GdGe}_{1.57}$, then increase to 27 K for GdSn_2 . In addition to AFM transitions, two anomalies are observed in $\text{GdSi}_{1.78}$ in magnetic measurements, while these anomalies cannot be observed in C_p curves. GdSn_2 shows another magnetic phase transition below T_N confirmed by both magnetic and heat-capacity measurements. All compounds show the thermal hysteresis between ZFC and FC curves below T_N , but the thermal hysteresis in $\text{GdSi}_{1.78}$ and $\text{GdGe}_{1.57}$ are prominent in particular.

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Figure captions:

Figure 1. (Color online) Unit cells of three structures adopted by the title compounds. (a) The $\text{GdSi}_{1.78}$ and $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$ compounds adopt orthorhombic structure (space group *Imma*); (b) The $\text{GdGe}_{1.57}$ adopts the tetragonal structure (space group *I4₁/amd*), (c) The GdSn_2 adopts the orthorhombic structure (space group *Cmcm*). The coordinates of (a) and (b) are different. The large black spheres represent Gd atoms, and the small red and blue spheres represent Si, Ge, or Sn atoms. For convenience, only the covalent-like T-T bonds are shown.

Figure 2. (Color online) Observed and calculated powder x-ray diffraction patterns for (a) $\text{GdSi}_{1.78}$, (b) $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, (c) $\text{GdGe}_{1.57}$ and (d) GdSn_2 at room temperature. Data were analysed by Rietveld refinement technique using the program of Rietica-LHPM. The wavelength of Cu $K\alpha_1$ radiation used in the refinement is 1.54056 Å.

Figure 3. Temperature dependence of magnetization of $\text{GdSi}_{1.78}$ under different applied magnetic fields. Gray lines and black lines show the results of ZFC and FC, respectively. Dash lines indicate the positions of T' and T_N , respectively.

Figure 4. Temperature dependence of magnetization of $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$ under different applied magnetic fields. Gray lines and black lines show the results of ZFC and FC, respectively. Dash line indicates the position of T_N .

Figure 5. Temperature dependence of magnetization of $\text{GdGe}_{1.57}$ under different applied magnetic fields. Gray lines and black lines show the results of ZFC and FC, respectively. Dash line indicates the position of T_N .

Figure 6. Temperature dependence of magnetization of GdSn_2 under different applied magnetic fields. Gray lines and black lines show the results of ZFC and FC, respectively. Dash lines indicate the positions of T' and T_N , respectively.

Figure 7. Heat-capacity of (a) $\text{GdSi}_{1.78}$, (b) $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, (c) $\text{GdGe}_{1.57}$ and (d) GdSn_2 as a function of temperature and magnetic field. The gray lines show the results in zero magnetic field, and the black lines show the results in 50 kOe.

Table 1. Chemical formula, space group, lattice parameters, atomic positions and occupations of $\text{GdSi}_{1.78}$, $\text{Gd}(\text{Si}_{0.684}\text{Ge}_{0.316})_{1.78}$, $\text{GdGe}_{1.57}$ and GdSn_2 .

FIG. 1.

FIG.2

FIG. 3

FIG. 4

FIG.5

FIG. 6

FIG. 7

Table 1.

	Atom	Position	Symmetry	x/a	y/b	z/c	Occupancy
GdSi _{1.78}	Gd	4e	mm2	0	0.25	0.625	1.0
	Si1	4e	mm2	0	0.25	0.0488(6)	0.968(3)
	Si2	4e	mm2	0	0.25	0.2142(7)	0.812
S.G. <i>Imma</i>	a=4.0090(1) Å	b=4.0893(2) Å	c=13.4417(4) Å	v=220.36(1) Å ³	R _p =3.14	R _{wp} =3.96	χ ² =1.33
Gd(Si _{0.684} Ge _{0.316}) _{1.78}	Gd	4e	mm2	0	0.25	0.6224(3)	1.0
	Si1	4e	mm2	0	0.25	0.0515(5)	0.64(3)
	Si2	4e	mm2	0	0.25	0.2185(5)	0.577(3)
	Ge1	4e	mm2	0	0.25	0.0515(5)	0.25(3)
	Ge2	4e	mm2	0	0.25	0.2185(5)	0.313(3)
S.G. <i>Imma</i>	a=4.0583(1) Å	b=4.0922(1) Å	c=13.6539(4) Å	v=226.75(1) Å ³	R _p =3.60	R _{wp} =4.67	χ ² =1.70
GdGe _{1.57}	Gd	4a	-4m2	0	0.75	0.125	1.0
	Ge	8e	2mm	0	0.25	0.2936(2)	0.788(2)
S.G. <i>I4₁/amd</i>	a=4.1234(8) Å	b=4.1234(8) Å	c=13.7594(3) Å	v=233.94(8) Å ³	R _p =4.11	R _{wp} =5.33	χ ² =2.06
GdSn ₂	Gd	4c	m2m	0	0.0978(2)	0.25	1.0
	Sn1	4c	m2m	0	0.75	0.25	1.0
	Sn2	4c	m2m	0	0.4365(2)	0.25	1.0
S.G. <i>Cmcm</i>	a=4.4280(2) Å	b=16.4036(6) Å	c=4.3230(2) Å	v=314.00(2) Å ³	R _p =5.67	R _{wp} =7.35	χ ² =1.66