ELSEVIER

Journal of Alloys and Compounds 303–304 (2000) 214–222

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The nonpareil $R_5(Si_xGe_{1-x})_4$ phases

K.A. Gschneidner Jr.[a,b,*], V.K. Pecharsky[a,b], A.O. Pecharsky[a], V.V. Ivtchenko[a], E.M. Levin[a]

[a] Ames Laboratory, Iowa State University, 255 Spedding, Ames, IA 50011-3020, USA
[b] Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-3114, USA

Abstract

The $R_5(Si_xGe_{1-x})_4$ materials have been known for over 30 years, but only in the last few years has their uniqueness become evident. Their exotic behaviors include a simultaneous first-order crystallographic–magnetic phase transition, the giant magnetocaloric effect, enhanced Curie temperature due to the existence of (Si,Ge)–(Si,Ge) bond pairs, and the absence of the magnetic contribution to the heat capacity below 10 K of ferrimagnetic Nd_5Ge_4, which orders at 55 K. These behaviors were observed in our studies of the phase relationships, crystallography, and the electrical, magnetic and thermal properties of the pseudo-binary 5:4 compounds with R=La, Nd, Gd, Dy and Lu.

Keywords: Rare earth–silicide–germanides; Magnetocaloric effect; Magnetic properties; Crystal structures; Electronic specific heat constant; Debye temperature

1. Introduction

The first R_5Si_4 or R_5Ge_4 phases were discovered by Smith et al. [1] in 1966. They reported that the R_5Si_4 (R=Tb, Er and Y) and R_5Ge_4 (R=Nd, Sm, Gd, Tb, Er and Y) phases have the Sm_5Ge_4 orthorhombic structure [2] and that Nd_5Si_4 has a tetragonal structure. Later they [3] reported that R_5Si_4 phases with R=La, Ce, Pr and Nd have the tetragonal Zr_5Si_4-type structure, and those with R=Sm, Gd, Tb, Dy, Er and Y crystallize in the Sm_5Ge_4-type structure, and that R_5Ge_4 (R=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y) compounds are also isostructural with Sm_5Ge_4-type structure. This was also confirmed by Holtzberg et al. [4] for the 5:4 silicides and germanides for R=Gd, Tb, Dy, Ho and Er. Furthermore, a study of some $Gd_5(Si_xGe_{1-x})_4$ alloys by these authors [4] indicated the existence of an intermediate phase for $0.24 \leq x \leq 0.5$ with an undetermined crystal structure. Thirty years later Pecharsky and Gschneidner [5] showed that this phase has a monoclinic structure at room temperature and is closely related to the Sm_5Ge_4-type structure. Furthermore, these authors found that Sm_5Ge_4 phase exists from $0.5 \leq x \leq 1.0$ and $0 \leq x \leq 0.2$ in the Gd_5Si_4–Gd_5Ge_4 pseudo-binary system. These results are summarized in Fig. 1, along with some new results obtained by us for the $R_5(Si_xGe_{1-x})_4$ systems for R=La, Nd, Dy and Lu.

In addition, literature data suggests that Nd_5Si_4 may be polymorphic (or perhaps one phase may be stabilized by impurities): Al-Shahery and McColm [6] and Raman [7] suggest that this compound has the orthorhombic Sm_5Ge_4-type structure, while Smith et al. [3], Eremenko et al. [8], and Mokra et al. [9] claim Nd_5Si_4 has the tetragonal Zr_5Si_4-type structure. Our results indicate that Nd_5Si_4 crystallizes in the Zr_5Si_4-type structure, but when doped with Ge, i.e. $Nd_5(Si_3Ge)$, this material is isostructural with Sm_5Ge_4 (see Fig. 1).

Only a little information exists on the physical properties of the R_5Si_4 and R_5Ge_4 alloys. The magnetic properties of the binary R_5Si_4 and R_5Ge_4 phases for R=Gd, Tb, Dy, Ho and Er and a few ternary compositions in the $Gd_5(Si_xGe_{1-x})_4$ system were investigated by Holtzberg et al. [4]. They found that the R_5Si_4 compounds are ferromagnetic with Curie temperatures ranging from 336 K for Gd_5Si_4 to 25 K for Er_5Si_4, while the R_5Ge_4 phases are antiferromagnetic with the Néel temperatures

---

*Corresponding author. Tel.: +1-515-294-7931; fax: +1-515-294-9579.

E-mail address: cagey@ameslab.gov (K.A. Gschneidner Jr.)

0925-8388/00/$ – see front matter
PII: S0925-8388(00)00747-7

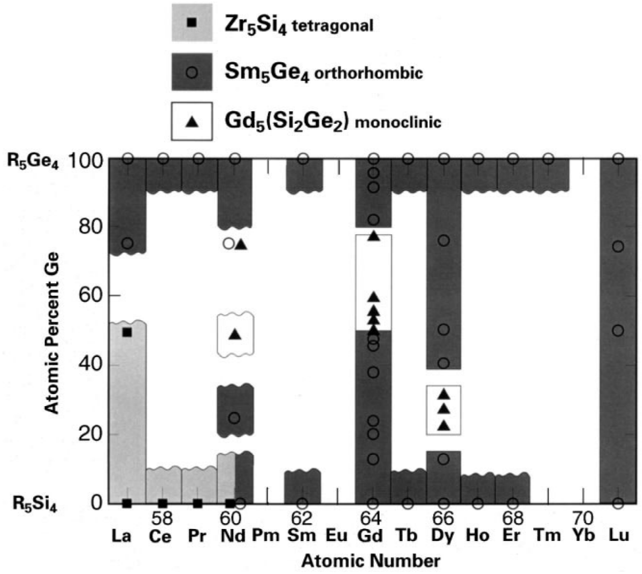

Fig. 1. The existence diagram for the R_5Si_4–R_5Ge_4 pseudo-binary alloys. To date only the pseudo-binary systems of La, Nd, Gd, Dy and Lu have been studied.

ranging from 47 K for Gd_5Ge_4 to 7 K for Er_5Ge_4. For the $Gd_5(Si_xGe_{1-x})_4$ alloys, Ge substitution for Si slowly lowers the Curie temperature from 336 K to ~300 K at the 50% substitution level [i.e. $Gd_5(Si_2Ge_2)$]. At the Ge-rich end, things are more complicated: the high temperature antiferromagnetic phase transforms to a ferromagnetic phase, but both the Néel and Curie temperatures drop rapidly (especially the former) as the Si content is decreased.

The high Curie temperature of Gd_5Si_4 was quite attractive to us in connection with our work on near-room temperature magnetic refrigeration, because it is about 40 K higher than that of pure Gd. This is important for two reasons. First, part of our goal is to find better magnetocaloric materials than Gd. Second, for some magnetic cooling applications the heat rejection temperature (hot heat exchanger) is well above room temperature and one needs a material(s) with a Curie temperature higher than that of Gd (294 K) for efficient operation. With this in mind we studied the magnetic and thermal properties of the $Gd_5(Si_xGe_{1-x})_4$ alloys from $x=0$ to $x=1$. Basically we confirmed the results of Holtzberg et al. [4] for the Si-rich alloys ($x>0.5$), and partially confirmed those for the Ge-rich alloys ($x\leq0.2$) [10]. But to our amazement, when we measured the properties for the intermediate monoclinic phase, we discovered that these alloys (for $0.24\leq x\leq0.5$) have significantly larger magnetocaloric effects, 50 to 200% better than any known material, when compared at their respective Curie temperatures [10,11]. This behavior is called the 'giant magnetocaloric effect.' Alloying studies showed that most alloying agents when substituted for (Si+Ge) destroy the giant magnetocaloric effect, a few will raise the ordering temperature (Al, Fe, Co and Ni), but only Ga preserves the giant magnetocaloric effect while raising the Curie temperature from ~276 to ~285 K [12]. Additional data on these alloys will be found in references [13–15]. Below we will briefly summarize some of the new developments we have made on the $Gd_5(Si_xGe_{1-x})_4$ alloys and the $R_5(Si_xGe_{1-x})_4$ systems for R=La, Nd, Dy and Lu.

2. New knowledge on the Gd_5Si_4–Gd_5Ge_4 system

The initial heat capacity and magnetic measurements on $Gd_5(Si_2Ge_2)$ indicated that there were two magnetic transitions in this phase: one a paramagnetic to ferromagnetic (I) second-order transition upon cooling at 299 K and a second ferromagnetic (I) to ferromagnetic (II) first-order transition at 276 K [11]. There was also some evidence for two transitions in the intermediate monoclinic phase alloys between $x=0.24$ and $x=0.5$, although the evidence was quite weak for the upper transition in the alloys [10], except for $x=0.5$ [$Gd_5(Si_2Ge_2)$] where it is quite clear [11]. More recently Morellon et al. [16,17] reported only a single transition in $Gd_5(Si_{1.8}Ge_{2.2})$, and that the ferromagnetic ordering is accompanied by a crystallographic transition. This led to a re-examination of our original data and additional measurements. The double transitions in the $Gd_5(Si_2Ge_2)$ alloy are due to the fact that this alloy was a two phase sample consisting of the orthorhombic Gd_5Si_4-based terminal solid solution alloy with a magnetic-ordering temperature of 299 K, and the monoclinic intermediate phase with a 276-K ordering temperature.

Electric resistance measurements of $Gd_5(Si_2Ge_2)$ in zero magnetic field [18] indicate a single transition which starts upon cooling at ~259 K and at ~272 K upon warming, see Fig. 2. The existence of hysteresis is a characteristic of a first-order phase transition. In the presence of an applied field of 4 T the first-order transition is shifted upward by ~20 K, see Fig. 2, which is consistent with the heat capacity results [11], and the hysteresis is still about 13 K.

A X-ray diffraction study of single crystal $Gd_5(Si_2Ge_2)$ at 163, 243 and 292 K shows that the high temperature paramagnetic monoclinic phase transforms to the low temperature ferromagnetic orthorhombic phase between 243 and 292 K [19]. This is quite interesting since the low temperature phase has a higher symmetry than the high temperature, which is the opposite of what is normally observed for other polymorphic systems. Furthermore, the low temperature phase has the same basic structure as that of the two-end members, i.e. Gd_5Si_4 and Gd_5Ge_4. There are, however, considerable differences in some of the

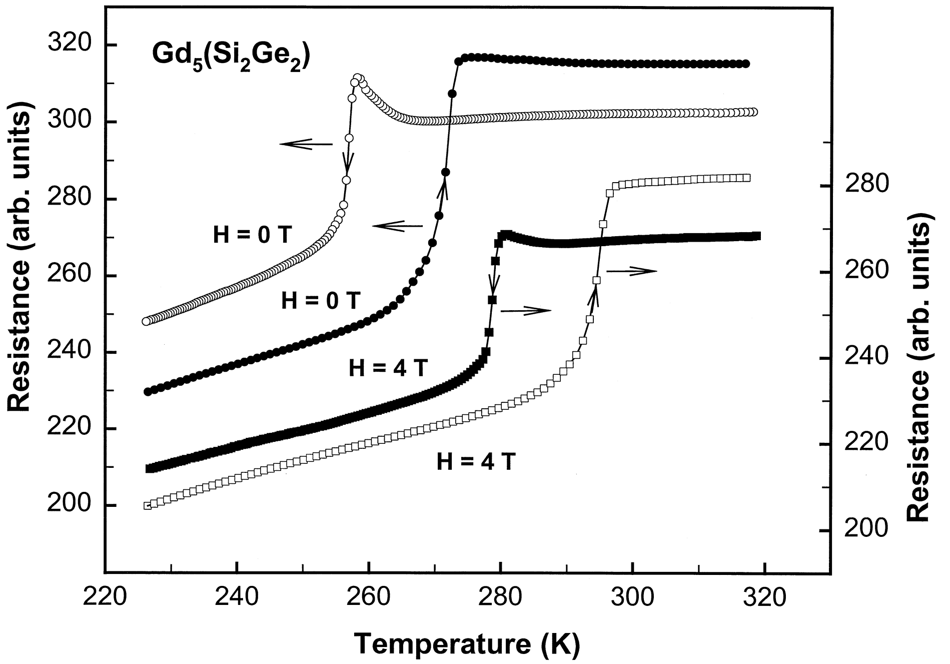

Fig. 2. Temperature dependence of the electrical resistance of $Gd_5(Si_2Ge_2)$ on cooling and heating in zero and 4-T magnetic fields (H).

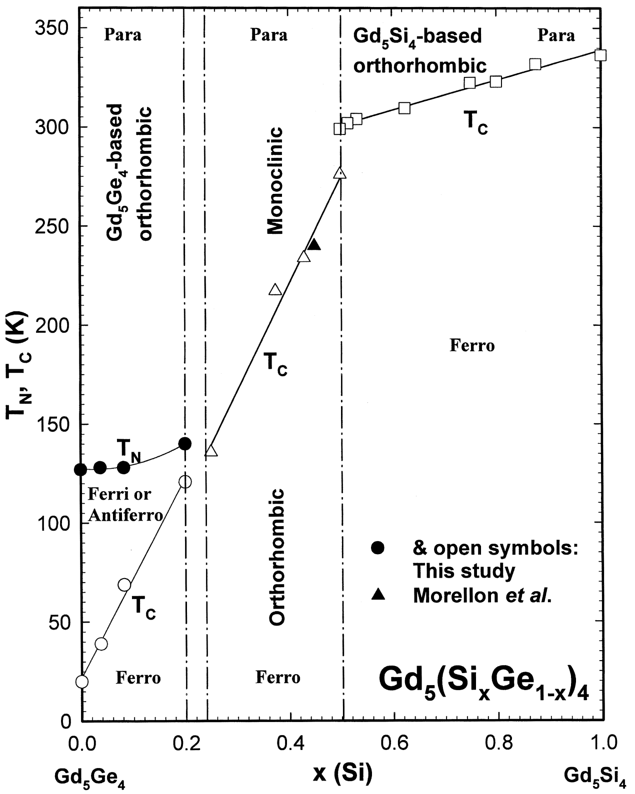

Fig. 3. Magnetic phase diagram of $Gd_5(Si_xGe_{1-x})_4$. The transition temperature for $x=0.45$ was taken from Morellon et al. [16,17]. The abbreviations in the figure have the following meanings: para= paramagnetic, ferro=ferromagnetic, ferri=ferrimagnetic, and antiferro= antiferromagnetic.

(Si,Ge)–(Si,Ge) bond pairs in the three phases. While all three structures are built from essentially the same infinite $[Ge_5X_4]$ slabs, no (Si,Ge)–(Si,Ge) bond pairs exist between the slabs in Gd_5Ge_4 (the true Sm_5Ge_4 structure), four sets of Si–Si bond pairs per unit cell are found in Gd_5Si_4, and only two sets of (Si,Ge)–(Si,Ge) bond pairs exist in the monoclinic $Gd_5(Si_2Ge_2)$ phase [5,19].

Additional magnetic and heat capacity measurements on the silicon-rich $Gd_5(Si_xGe_{1-x})_4$, $x>0.5$ have been made to characterize the magnetocaloric properties of these materials. Although the magnetocaloric properties are somewhat lower than that of Gd, they are still the largest known for materials which order magnetically between 300 and 340 K, and thus will be useful materials for magnetic refrigeration/heat pump applications.

Based on the above noted results, we have revised the magnetic phase diagram of the Gd_5Si_4–Gd_5Ge_4 pseudobinary system, as shown in Fig. 3. The Gd_5Ge_4 terminal solid solution region ($0\leq x\leq 0.2$) is the least understood. The lowest temperature phase ($T<T_C$) appears to be ferromagnetic, while the region between T_N and T_C may be ferrimagnetic or antiferromagnetic. Furthermore, we do not know if there is a crystallographic phase transition associated with the magnetic transition at T_C.

3. Other $R_5(Si_xGe_{1-x})_4$ systems

We have expanded our studies of some of the other lanthanide $R_5(Si_xGe_{1-x})_4$ alloy systems to (1) obtain a baseline of the non-magnetic behaviors of these alloy systems, and (2) to see if the unique properties of the monoclinic $Gd_5(Si_xGe_{1-x})_4$ phase also exists for other lanthanides.

3.1. Lanthanum and lutetium $R_5(Si_xGe_{1-x})_4$ systems

X-ray diffraction studies confirm the reported crystal structures for the binary R_5Si_4 and R_5Ge_4 phases for R=La and Lu, i.e. the tetragonal Zr_5Si_4-type for La_4Si_4 and the orthorhombic Sm_5Ge_4-type for La_5Ge_4, Lu_5Si_4 and Lu_5Ge_4 (see Fig. 1). Intermediate compositions between the respective end members shows that the Zr_5Si_4-type structure extends from pure La_5Si_4 to a composition between $La_5(Si_2Ge_2)$ and $La_5(SiGe_3)$, and the Sm_5Ge_4-type structure extends from at least $La_5(SiGe_3)$ to the pure binary La_5Ge_4, see Fig. 1. In the case of Lu_5Si_4–Lu_5Ge_4 pseudo-binary system all of the alloys examined have the orthorhombic Sm_5Ge_4-type structure.

The heat capacities of the R_5Si_4, $R_5(Si_2Ge_2)$, $R_5(SiGe_3)$ and R_5Ge_4 for R=La and Lu have been measured from 3.5 to 350 K. These data can be used to estimate the electronic and lattice contributions to the heat capacities of the magnetic lanthanide phases by taking the appropriate pro-rated heat capacities of the corresponding La and Lu phases to mimic the particular R element, e.g. 50% of La_5Si_4+50% of Lu_5Si_4 will give the estimated electronic and lattice heat capacities of Gd_5Si_4. Subtracting this value will then yield the purely magnetic contribution to the heat capacity of Gd_5Si_4. The magnetic heat capacities of the various alloys will be reported on in a future paper. Fitting the low temperature, <10 K, heat capacity to the standard linear C/T vs. T^2 plot yields the electronic specific heat constant, γ, from the intercept at $T^2=0$, and the Debye temperature, θ_D, from the slope of this straight line plot. The γ values for the four $La_5(Si,Ge)_4$ alloys are essentially constant with $\gamma=3.0\pm0.5$ mJ/mol $La_{0.55}(Si,Ge)_{0.45}$ K^2, and similarly for the four $Lu_5(Si,Ge)_4$ phases with $\gamma=1.2\pm0.3$ mJ/mol $Lu_{0.55}(Si,Ge)_{0.45}$ K^2. On a per gram-atom R basis, the γ values are 5.4 ± 0.9 and 2.2 ± 0.5 mJ/g-at R K^2, respectively, which are on the low side of being typical for a rare earth-based material. The θ_D values vary in a systematic manner as might be expected from the atomic masses and atomic volumes of the constituent atoms. The value of θ_D decreases from Si-rich phase to the Ge-rich phase, i.e. from 239 ± 27 for La_5Si_4 to 198 ± 10 K for La_5Ge_4, and from 262 ± 30 for Lu_5Si_4 to 215 ± 4 K for Lu_5Ge_4, and increases when La is replaced by Lu in the corresponding phases.

The magnetic susceptibility of La_5Ge_4 is quite small, $(0.34\pm0.02)\times10^{-6}$ emu/g Oe $[(67\pm4)\times10^{-6}$ emu/g-at. La Oe], and it is essentially constant from 5 to 300 K, i.e. it behaves as a Pauli paramagnet. The value of magnetic susceptibility is about what one would expect from the value of electronic specific heat constant, i.e. 74×10^{-6} emu/g-at. La Oe.

3.2. $Nd_5(Si_xGe_{1-x})_4$ system

X-ray analysis of the $Nd_5(Si_xGe_{1-x})_4$ alloys show that the binary alloys Nd_5Si_4 and Nd_5Ge_4 have the tetragonal Zr_5Si_4-type structure and the orthorhombic Sm_5Ge_4-type structure, respectively. However, when 25% of the Si is replaced by Ge, i.e. $Nd_5(Si_3Ge)$ this composition has the orthorhombic Sm_5Ge_4-type structure. This is consistent with literature, where both structures (tetragonal and orthorhombic) have been reported for Nd_5Si_4, and a small amount of an impurity (Ge, or other element) could stabilize the orthorhombic phase. Further additions of Ge, i.e. $Nd_5(Si_2Ge_2)$ stabilizes the monoclinic $Gd_5(Si_2Ge_2)$-type structure. At the $Nd_5(SiGe_3)$ composition both phases (the monoclinic and orthorhombic) co-exist. These results are summarized in Fig. 1.

Table 1
Magnetic properties of some $Nd_5(Si_xGe_{1-x})_4$ alloys[a]

Composition	Structure	T_C		θ_p (K)	p_{eff} (μ_B)	$-\Delta S_m$ (J/kg K)
		M^b (K)	χ_{ac} (K)			
Nd_5Si_4	Tetra.	71	–	74.0	3.39	8.3
$Nd_5(Si_3Ge)$	Ortho.	124	122	122.6	3.15	6.4
$Nd_5(Si_2Ge_2)$	Monocl.	65	64	61.6	4.27	5.6
$Nd_5(SiGe_3)$	Two phase	52, 61	–	58.1	3.41	4.1, 4.2
Nd_5Ge_4	Ortho.	55[c]	53 ± 1[d]	52.1	3.55	6.4

[a] Ferrimagnetic Curie temperature (T_C), paramagnetic Curie temperature (θ_p), effective magnetic moment per Nd atom (p_{eff}), and magnetocaloric effect at T_C ($-\Delta S_m$).

[b] From magnetization measurements.

[c] T_C=55 K from heat capacity measurements.

[d] Average value from measurements made on two different apparati.

The magnetization and dc magnetic susceptibility were measured on all five of the $Nd_5(Si_xGe_{1-x})_4$ alloys from 4.2 to 325 K. The results are summarized in Table 1. All of the compounds obey the Curie–Weiss law from slightly above their Curie temperatures (T_c) to 325 K, and the effective moments are in good agreement with the theoretical value for a Nd^{3+} ion (3.62 μ_B). The paramagnetic Curie temperatures are in excellent agreement with the ferrimagnetic ordering temperatures as obtained from magnetization isotherms (M) and ac magnetic susceptibility (χ_{ac}). The magnetocaloric effect ($-\Delta S_m$) is small, about half of that of $DyAl_2$ [20]. But these values are not unreasonable if one considers that the theoretical magnetic entropy of Nd is ~17% smaller than that of Dy, and also if these alloys are ferrimagnets. Neutron-scattering measurements confirm that Nd_5Ge_4 has a canted ferrimagnetic structure [21]. As seen in Table 1 the magnetization measurements confirm the existence of two phases, with one phase ordering at 52 K and the other at 61 K for $Nd_5(SiGe_3)$.

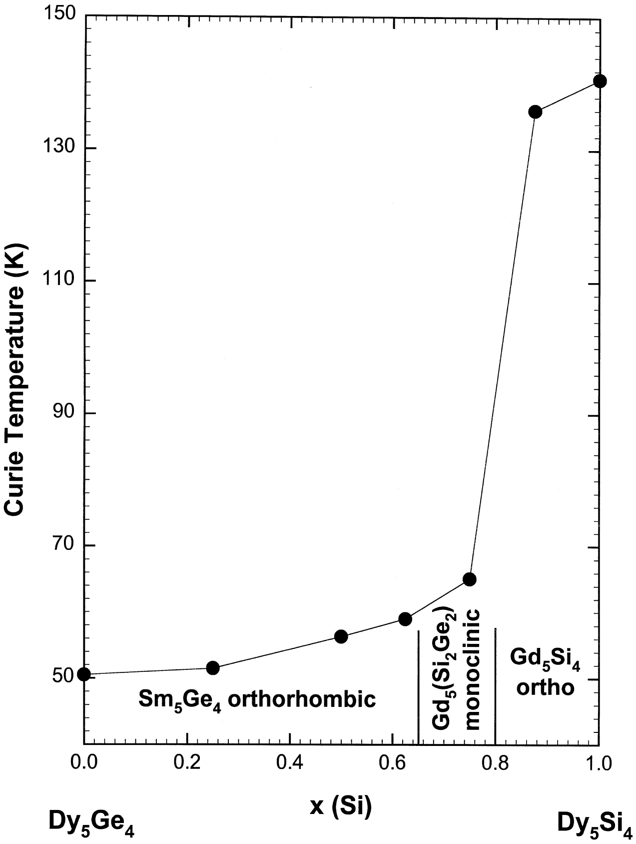

Fig. 5. Curie or Neel temperatures of the $Dy_5(Si_xGe_{1-x})_4$ alloys.

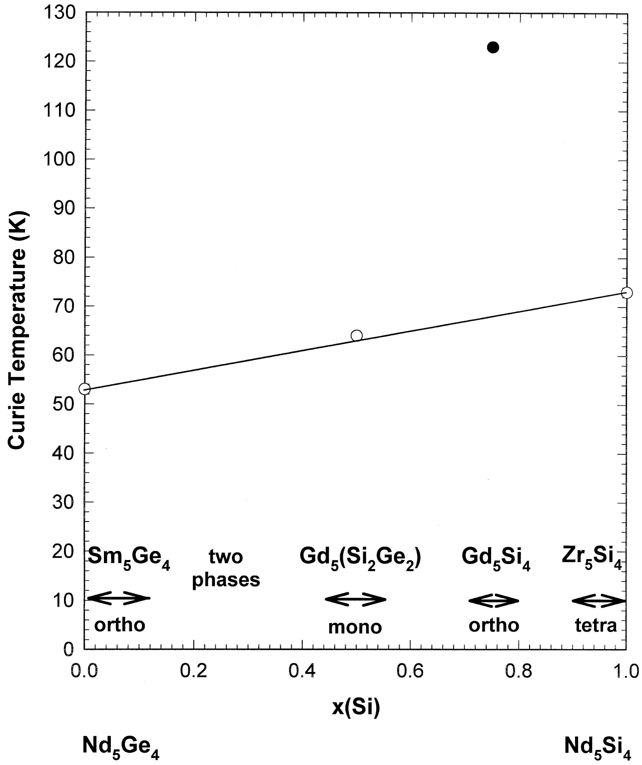

Fig. 4. Curie temperatures of the $Nd_5(Si_xGe_{1-x})_4$ alloys.

Three unusual features have been observed in these alloys. The first is that the Curie temperature of the $Nd_5(Si_3Ge)$ (orthorhombic Gd_5Si_4-type) phase is about 50 K higher than those of the other compositions which lie fairly close to a straight line connecting the T_C values of Nd_5Si_4 and Nd_5Ge_4 (see Fig. 4). This high value is consistent with what is observed in the $Gd_5(Si_xGe_{1-x})_4$ [5,10,11] and $Dy_5(Si_xGe_{1-x})_4$ [22] systems. In all of the systems the compositions which have significantly higher Curie temperatures are always associated with the phases that have all four (Si,Ge)–(Si,Ge) bond pairs per unit cell, i.e. the orthorhombic Gd_5Si_4-type structure. Those compositions which have only two (Si,Ge)–(Si,Ge) bond pairs [the monoclinic $Gd_5(Si_2Ge_2)$-type structure] or no (Si,Ge)–(Si,Ge) bond pairs [the orthorhombic Gd_5Ge_4-type structure] order magnetically at much lower temperatures, see Figs. 3 and 5, and also below. The influence of the (Si,Ge)–(Si,Ge) bond pairs on the magnetic-ordering temperature is truly unique. Apparently the electrons from the broken covalent-like (Si,Ge)–(Si,Ge) pairs become part of the metallic conduction band and these additional electrons modify (reduce the strength of) the RKKY interaction, which is responsible for the nature of the magnetic ordering, and thus lower the magnetic ordering temperatures for the monoclinic, orthorhombic Sm_5Ge_4-type and tetragonal phases.

The second is that the magnetocaloric effect observed in the monoclinic phase $Nd_5(Si_2Ge_2)$ is typical of that of a second order magnetic transition, it does not seem to have the characteristics of a first order magnetic phase transition, like that in $Gd_5(Si_2Ge_2)$ [11], or in $Dy_5(Si_3Ge)$ [22,

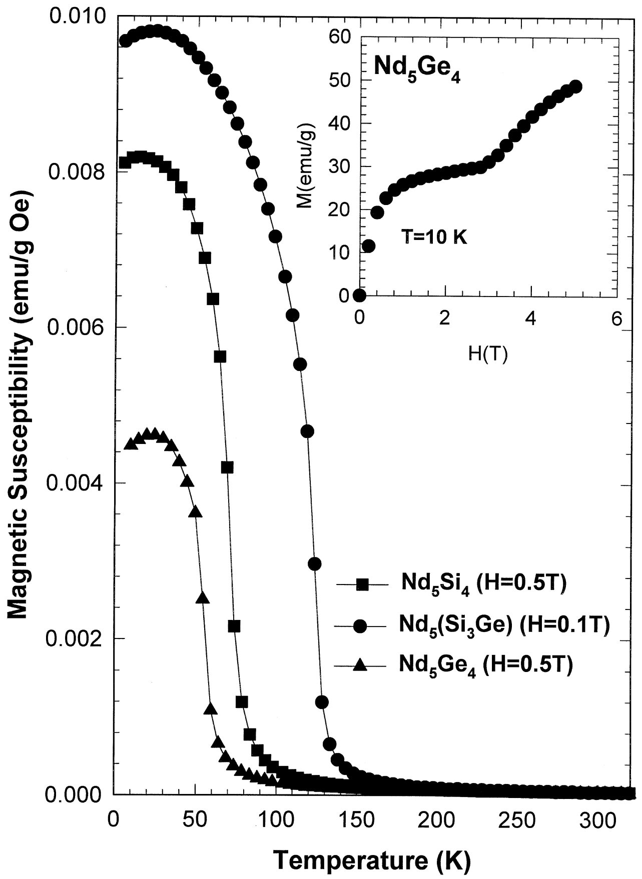

Fig. 6. Dc magnetic susceptibility vs. temperature for Nd_5Si_4, $Nd_5(Si_3Ge)$ and Nd_5Ge_4. The inset shows the 10-K magnetization isotherm.

and also see below], which gives rise to the giant magnetocaloric effect. Additional studies are being planned to confirm the absence of the first-order transition in $Nd_5(Si_2Ge_2)$.

The third is the unusual behavior of dc magnetic susceptibility (measured at the plateau of the magnetization isotherms) below the Curie temperature for Nd_5Ge_4 (55 K) relative to the other compositions of the $Nd_5(Si_xGe_{1-x})_4$ pseudo-binary, see Fig. 6. The magnetic susceptibility is considerably smaller than those of other alloys (only two of which are shown in Fig. 6). This may be related to the canted ferrimagnetic structure in Nd_5Ge_4 [21]. Furthermore, as shown in the inset Nd_5Ge_4 exhibits a metamagnetic transition at ~3 T at 10 K.

The absence of a strong magnetic moment in Nd_5Ge_4 at ~4 K, is also consistent with the heat capacity results on this phase. The low-temperature heat capacity exhibits the typical non-magnetic C/T vs. T^2 behavior below 10 K with no evidence for a magnetic contribution to the heat capacity. The resultant electronic specific heat constant and Debye temperature are $\gamma=2.6\pm1.5$ mJ/mol $Nd_{0.55}Ge_{0.45}$ K^2 and $\theta_D=199\pm14$ K. These values are almost identical with the γ and θ_D values for La_5Ge_4.

3.3. $Dy_5(Si_xGe_{1-x})_4$ system

The $Dy_5(Si_xGe_{1-x})_4$ system [22] is the second most studied R_5Si_4–R_5Ge_4 pseudo-binary system, after that of Gd_5Si_4–Ge_5Ge_4. The $Dy_5(Si_xGe_{1-x})_4$ system is quite similar to that of the $Gd_5(Si_xGe_{1-x})_4$ alloys, see Fig. 1, except the various phase regions are shifted closer to the Dy_5Si_4-end. The magnetic ordering temperatures follow a similar pattern in both systems, compare Figs. 3 and 5, except the ordering temperatures are much lower for the $Dy_5(Si_xGe_{1-x})_4$ system, which is consistent with the deGennes factor, $J(J+1)(g-1)^2$, of the specific lanthanide ion.

To date the heat capacity as a function of temperature in various applied magnetic fields has been measured on only one alloy in the $Dy_5(Si_xGe_{1-x})_4$ system — that of $Dy_5(Si_{3.5}Ge_{0.5})$. The resultant magnetocaloric effect — the magnetic entropy change ($-\Delta S_m$) and the adiabatic temperature rise (ΔT_{ad}) — are shown in Figs. 7a and 7b, respectively. These values are compared with $Gd_5(SiGe_3)$ which orders at about the same temperature. It is evident that both $-\Delta S_m$ and ΔT_{ad} are significantly (approximately by a factor of 2) smaller in the $Dy_5(Si_{3.5}Ge_{0.5})$ compound. The comparison, however, is not too meaningful since the Dy alloy undergoes a second-order magnetic transition at ~132 K while the Gd material undergoes a first-order magnetic transition at ~140 K which gives rise to the giant magnetocaloric effect. A more meaningful comparison would be between compositions both of which exhibit a first order magnetic transition and have approximately the same magnetic ordering temperature. Such a comparison is shown in Fig. 8, where the $-\Delta S_m$ values are compared for $Dy_5(Si_3Ge)$ and $Gd_5(Si_{0.33}Ge_{3.67})$, which order at ~66 and ~70 K, respectively. In this case the peak magnetocaloric effect of $Dy_5(Si_3Ge)$ is only 28% less than that of $Gd_5(Si_{0.33}Ge_{3.67})$, compared to 55% in the case of $Dy_5(Si_{3.5}Ge_{0.5})$ vs. $Gd_5(SiGe_3)$ (see Fig. 7a). The low value for $Dy_5(Si_3Ge)$ compound is disappointing because theoretical magnetic entropy for a Dy^{3+} ion is ~33% larger than that of a Gd^{3+} ion. However, there appears to be some sort of magnetic ordering occurring at ~15 K, which is evident as magnetocaloric peak at this low temperature, see Figs. 7 and 8. This second ordering would utilize some of the magnetic entropy and thus there would be less available at the higher ordering temperature resulting in the lower magnetocaloric effects seen in the two $Dy_5(Si_xGe_{1-x})_4$ alloys. More information about the structural, magnetic and thermal properties of the $Dy_5(Si_xGe_{1-x})_4$ alloys can be found in Ref. [22].

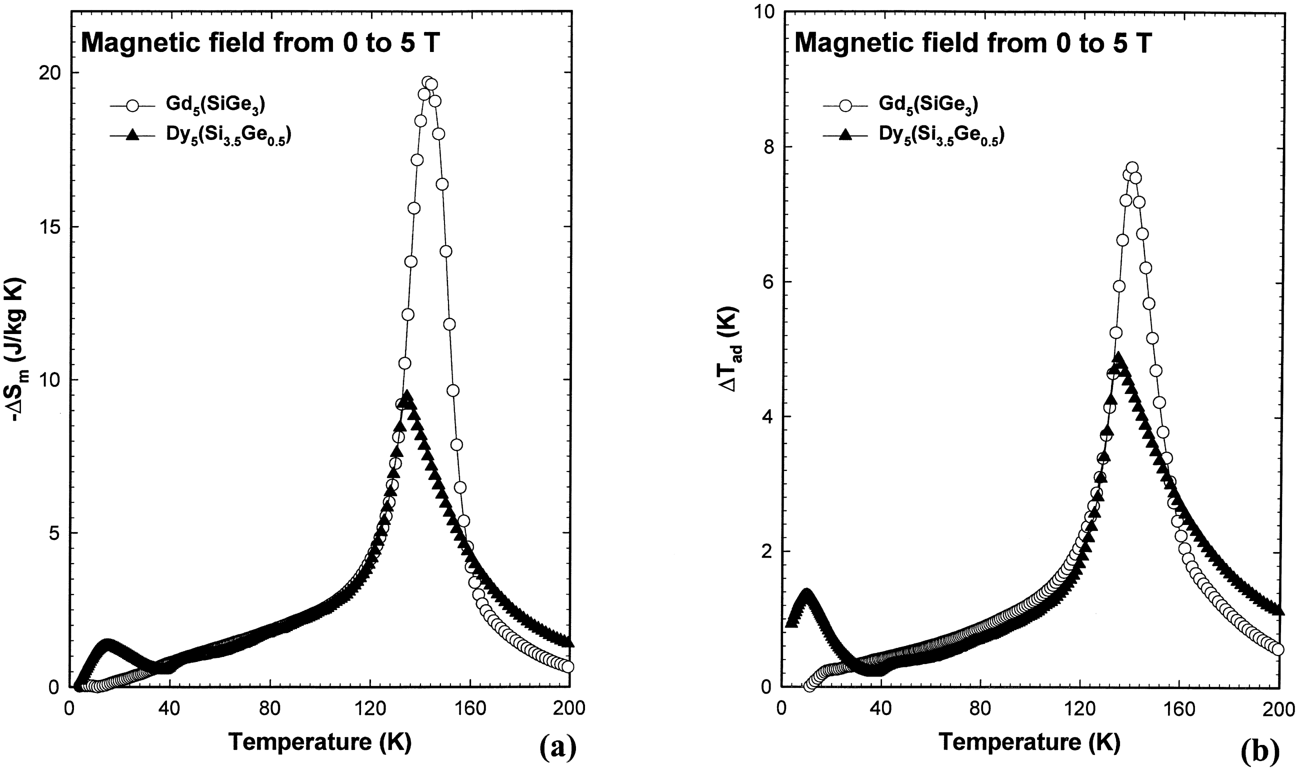

Fig. 7. The magnetocaloric effect vs. temperature of $Dy_5(Si_{3.5}Ge_{0.5})$ and $Gd_5(SiGe_3)$ as obtained from heat capacity measurements: (a) the magnetic entropy change, and (b) the adiabatic temperature rise.

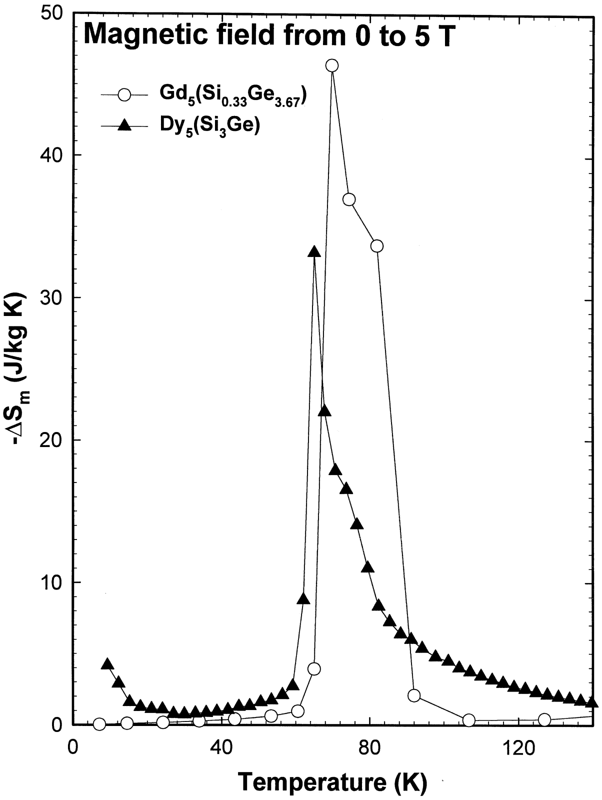

Fig. 8. The magnetocaloric effect vs. temperature of $Dy_5(Si_3Ge)$ and $Gd_5(Si_{0.33}Ge_{3.67})$ as obtained from magnetization measurements.

4. Magnetic refrigeration

4.1. Proof-of-principle apparatus

In the past three years we (the Ames Laboratory/Astronautics Corporation of America) have demonstrated that magnetic refrigeration is a viable competitive technology to gas compression refrigeration for near room temperature applications such as air conditioning, refrigerators/freezers [23–26]. We have designed, constructed and operated a near-room temperature proof-of-principle laboratory apparatus, which operated at magnetic fields between 1.5 and 5 T [24]. We have achieved (1) a record cooling power of 600 watts, which is 100 times larger than any other near-room temperature refrigerator; (2) a coefficient of performance, COP (the cooling power divided by the work input) of 16, which compares to about 2.5 for a typical vapor cycle apparatus; (3) a maximum efficiency of 60% of Carnot; (4) a maximum temperature span (the temperature difference between the cold and hot heat exchangers) of 38°C; and (5) a record longevity, it operated over an 18-month period for more than 1500 h, maintenance free, which is several orders of magnitude longer operating time compared to previous magnetic refrigerators which operated for a few hours or a day or two at the most. The cooling power of the Ames Laboratory/Astronautics refrigerator was provided by 3 kg of a commercial grade of 0.3-mm diameter Gd spheres. The proof-of-principle refrigerator is located at Astronautics' Technology Center in Madison, WI, USA.

4.2. $R_5(Si_xGe_{1-x})_4$ magnetic refrigerants

The $Gd_5(Si_2Ge_2)$ alloy, which has a magnetocaloric effect (ΔT_{ad}) which is 30% larger than that of Gd with a magnetic ordering temperature ~20 K below that of Gd [11], has considerable promise as the next generation magnetic refrigerant. The improvement over existing prototype magnetic refrigerants is even better as the operating temperature is reduced below 0°C (273 K) because the $Gd_5(Si_xGe_{1-x})_4$ alloys with $x<0.5$ have magnetocaloric effects up to 200% larger than any known material at the corresponding Curie temperatures [10]. These new materials have opened the door to new possible applications here-to-fore thought to be outside of the realm of practicability. These include home refrigeration and air conditioning, automotive and aircraft climate control, since one can use a permanent magnet to generate the necessary field instead of a superconducting magnet.

The $Gd_5(Si_xGe_{1-x})_4$ for $x>0.5$ also have a role to play in magnetic refrigeration especially when the extracted heat needs to be rejected in high ambient temperatures, i.e. >35°C (308 K). The $Gd_5(Si_xGe_{1-x})_4$ alloys with $0.5<x\leq 1.0$ have the highest known magnetocaloric effect between 27 and 62°C (300 and 335 K). These alloys would also be useful materials for low level heat pumps.

There are, however, a number of technical problems which need to be solved. These include an inexpensive method for preparing large quantities (>10 kg), and fabrication of the material into useful forms (such as spheres, sheets, wires, etc.).

5. Summary

The $R_5(Si_xGe_{1-x})_4$ phases are unique and a number of unusual interesting, and exciting behavior/properties have been observed, which have not been found in any other lanthanide compound series. The giant magnetocaloric effect due to first-order crystallographic–magnetic transformation which give rise to the giant magnetocaloric effect for the $R_5(Si_xGe_{1-x})_4$ phases which form the monoclinic $Gd_5(Si_2Ge_2)$-type structure at room temperature. Furthermore, this giant magnetocaloric effect may find commercial applications for refrigeration and other cooling applications. The development of a significantly enhanced Curie temperature due to covalent bonding of (Si,Ge)–(Si,Ge) bond pairs in alloys which crystallize in the orthorhombic Gd_5Si_4-type structure. The third unusual behavior is the anomalous electronic and magnetic behaviors of Nd_5Ge_4 at low temperature. Finally, the magnetocaloric effect in Si-rich $Gd_5(Si_xGe_{1-x})_4$ alloys ($x>0.5$) is the largest known such effect for materials which order between 300 and 340 K.

It is quite likely that other surprises are in store for us as we expand our studies to other lanthanide $R_5(Si_xGe_{1-x})_4$ phases since to date we have only tapped into this scientifically rich series of pseudo-binary systems, especially with respect to their crystallographic, magnetic and thermal behaviors.

Acknowledgements

The Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract No. W-7405-ENG-82. This work was supported by the Materials Sciences Division of the Office of Basic Energy Sciences.

References

[1] G.S. Smith, A.G. Tharp, Q. Johnson, Nature 210 (1966) 1148.

[2] G.S. Smith, Q. Johnson, A.G. Tharp, Acta Crystallogr. 22 (1967) 269.

[3] G.S. Smith, A.G. Tharp, Q. Johnson, Acta Crystallogr. 22 (1967) 940.

[4] F. Holtzberg, R.J. Gambino, R.T. McQuire, J. Phys. Chem. Solids 28 (1967) 2283.

[5] V.K. Pecharsky, K.A. Gschneidner Jr., J. Alloys Comp. 260 (1997) 98.

[6] G.Y.M. Al-Shahery, I.J. McColm, J. Less-Common Met. 98 (1984) L5.

[7] A. Raman, Trans. Indian Inst. Metals 21 (1968) 5.

[8] V.N. Eremenko, K.A. Meleshevich, Yu.I. Buyanov, I.M. Obushenko, Dopovidi Akad. Nauk Ukr. Ser. A Fiz. Mat. Tekh. Nauki 46 (11) (1984) 80.

[9] I.R. Mokra, O.I. Bodak, E.I. Gladyshevskij, Dopovidi Akad. Nauk Ukr., Ser. A Fiz. Mat. Tekh. Nauki 40 (1978) 1043.

[10] V.K. Pecharsky, K.A. Gschneidner Jr., Appl. Phys. Lett. 70 (1997) 3299.

[11] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.

[12] V.K. Pecharsky, K.A. Gschneidner Jr., J. Magn. Magn. Mater. 167 (1997) L179.

[13] V.K. Pecharsky, K.A. Gschneidner Jr., Adv. Cryog. Engin. 43 (1998) 1729.

[14] K.A. Gschneidner Jr., V.K. Pecharsky, J. Appl. Phys. 85 (1999) 5365.

[15] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Pecharsky, C.B. Zimm, Mater. Sci. Forum 315–317 (1999) 69.

[16] L. Morellon .Alg, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. García-Landa, Z. Arnold et al., Phys. Rev. B 58 (1998) 14721.

[17] L. Morellon, J. Stankiewicz, B. García-Landa, P.A. Algaragel, M.R. Ibarra, Appl. Phys. Lett. 73 (1998) 3462.

[18] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. B 60 (1999) 7993.
[19] W. Choe, V.K. Pecharsky, A.O. Pecharsky, K.A. Gschneidner Jr., V.G. Young Jr., G.J. Miller (in press).
[20] K.A. Gschneidner Jr., V.K. Pecharsky, S.K. Malik, Adv. Cryog. Engin. 42 (1997) 475.
[21] P. Schobinger-Papamantellos, A. Niggli, J. Phys. Chem. Solids 42 (1981) 583.
[22] V.V. Ivtchenko, V.K. Pecharsky, K.A. Gschneidner Jr., Adv. Cryog. Engin. (in press).
[23] K.A. Gschneidner Jr., V.K. Pecharsky, C.B. Zimm, Mater. Tech. 12 (1997) 145.
[24] C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner Jr., M. Osborne, I. Anderson, Adv. Cryog. Engin. 43 (1998) 1739.
[25] C. Zimm, A. Sternberg, V. Pecharsky, K. Gschneidner Jr., in: Proceedings of Appliance Manufacturer Conference and Expo., Nashville, TN, October 12–14, 1998.
[26] K.A. Gschneidner Jr., V.K. Pecharsky, C.B. Zimm, in: Proceedings of the 50th Annual International Appliance Technology Conference, International Appliance Technical Conference, Inc, Largo, FL, 1999, p. 144.