Magnetic, caloric and crystallographic properties of $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys

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ABBREVIATIONS

A – Amperes

Å – Angstrom

ac – alternating current

AFM – antiferromagnetic / antiferromagnet

CSD – crystal structure determination

C – Celsius (was Centigrade)

cm – centimeter

DIC – differential interference contrast

DTA – diffraction thermal analysis

dc – direct current

DiaM – diamagnetic / diamagnet

emf – electromotive force

emu – electromagnetic unit

FerriM – ferrimagnetic / ferrimagnet

FM – ferromagnetic / ferromagnet

g - gram

GMR – giant magnetoresistance

Hz – Hertz

IEEE – Institute of Electrical and Electronic Engineers

J – Joule

K – Kelvin

m – meter

MCE – magnetocaloric effect

MFA – mean-field approximation

mol – mole (short for molecule)

Oe – Oersted

PM – paramagnetic / paramagnet

psi – pounds per square inch

RMS – root mean square

RKKY – Ruderman – Kittel – Kasuya – Yosida

T – Tesla

W – Watts

wt – weight

SYMBOLS

δA	– infinitesimal amount of work
δA_M	– infinitesimal amount of magnetization work
C	– Curie constant
C_e	– electronic heat capacity
C_L	– lattice heat capacity
C_M	– magnetic heat capacity
C_p	– heat capacity at constant pressure
C'_p	– extrapolated value of heat capacity
σC_p	– heat capacity error
$\sigma C'_p$	– extrapolated value of heat capacity error
C_{total}	– total heat capacity
C_V	– heat capacity at constant volume
D	– demagnetization factor
E_{in}	– input signal to the inductors
E_{out}	– output signal to the inductors
f	– frequency of <i>ac</i> field
g_J	– Lande splitting factor
$\vec{H}$	– external magnetic field
$d\vec{H}$	– change of magnetic field
$\vec{H}_o$	– static magnetic field
$\vec{H}_B$	– magnetic field in the material
H_{cr}	– critical field
k_B	– Boltzmann's constant
$\vec{M}$	– magnetization

$\vec{m}$ – magnetic moment

$\vec{M}_o$ – equilibrium value of the magnetization in the static field

N – number atoms in the crystal, or demagnetization factor

P – pressure

δQ – infinitesimal amount of heat

R – gas constant

σS – entropy error

ΔS_m – magnetic entropy change

S_{total} – total entropy

σS_{total} – total entropy error

t – time

$\sigma \Delta T$ – adiabatic temperature change error

dT or ΔT – temperature change

T_B – boiling temperature

T_C – Curie temperature

T_D – Debye temperature

T_M – melting temperature

T_{min} – minimal temperature

dU – internal energy change

V – volume

α – calibration coefficient for ac susceptibility measurements

χ'_{ac} – real part of ac susceptibility

χ''_{ac} – imaginary part of ac susceptibility

χ_d – differential magnetic susceptibility

χ_{dc} – magnetic susceptibility

γ – electronic specific heat constant

φ – phase angle

μ_B – Bohr magneton

v – voltage

θ_P – PM Curie temperature

ω – Angular frequency

1. INTRODUCTION

A study of a series of $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys using *dc* and *ac* magnetic susceptibility, magnetization, heat capacity, and x-ray powder diffraction techniques revealed that the variation of the magnetic properties and crystal structures with composition is similar to that observed in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, except that the magnetic ordering temperatures are lower. The magnetic phase transition temperatures vary from $\sim 46\text{K}$ (Dy_5Ge_4) to $\sim 137\text{K}$ (Dy_5Si_4). The intermediate ternary phase $\text{Dy}_5\text{Si}_3\text{Ge}$ undergoes a first order magnetic phase transition at $\sim 65\text{K}$. The value of magnetic entropy change for this composition is quite large (-34J/kgK for magnetic field change from 0 to 50kOe), compared to the values for the two end members (-7 J/kgK for Dy_5Ge_4 and -12.5J/kgK for Dy_5Si_4). The magnetization and *ac* susceptibility measurements showed that alloys with monoclinic crystal structure have a non-collinear ordering of the magnetic moments at low temperatures. The alloy $\text{Dy}_5\text{Si}_3\text{Ge}$ appears to exhibit a FM phase transition below the Curie temperature at 65K . Also a series of critical fields are observed at low temperature during magnetization vs magnetic field measurements in all of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys regardless type of crystal structure. The $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys, where $0.67 \leq x \leq 1$, may be useful magnetic refrigerant materials in the ~ 50 to $\sim 160\text{K}$ temperature range.

2. BACKGROUND AND LITERATURE REVIEW

2.1 Thermodynamic and magnetic properties

2.1.1 Magnetocaloric Effect

The magnetocaloric effect, MCE, is the temperature change dT of a magnetic material under adiabatic change of the magnetic field $d\vec{H}$. This effect first was observed by Warburg late in the 19th century [1]. When we change the field $d\vec{H}$, the performed magnetization work δA_M is:

$$\delta A_M = \vec{M} d\vec{H},$$

where $\vec{M}$ is the magnetization.

The first law of thermodynamics defines the relationship between the work performed on (or by) the system, the amount of heat transfer to (or from) the system, and the change internal energy of the system:

$$\delta A = \delta Q - dU,$$

where δQ is amount of heat transfer to the magnetic material (under adiabatic conditions $\delta Q = 0$), dU is the internal energy change of the magnetic material. Thus, if $\delta Q = 0$, the work performed by the internal energy change only is:

$$\delta A = dU,$$

In case, when the internal energy is dependent on temperature, this effect produces a temperature change in the magnetic material.

From the general principles of thermodynamics the following expression can be written for the infinitesimal gain in MCE [2]:

$$dT = -\frac{T(\partial\vec{M}(\vec{H}, T)/\partial T)_{\vec{H}}}{C(\vec{H}, T)} d\vec{H}$$

Theoretically, maximum MCE value dT for a field change $d\vec{H}$ is reached when the maximum heat capacity value in this field is shifted with respect to a large value of $\partial\vec{M}/\partial T$

for the corresponding field and temperature changes. The thermodynamic approach is the simplest way to understand magnetocaloric effect.

Two other approaches commonly used are Landau's theory of second-order phase transitions and Weiss' mean-field approximation. Both these techniques describe the behavior of a number of magnetic quantities. However, they are inapplicable in the vicinity of the magnetic phase transition due to the critical fluctuation effects.

The experimental value of the MCE most often is determined by direct measurements or by calculation from the measured magnetization or heat capacity, both as a function of temperature and magnetic field. From direct method, we can only obtain the adiabatic temperature change vs magnetic field change. From indirect experiment measurements, we can calculate both adiabatic temperature change and the magnetic entropy change from experimental heat capacity data, and only the magnetic entropy change from experimental magnetization data [3, 4].

Technologically, the interest in MCE results from the possibility of employing materials with large dT values in magnetic refrigeration. For instance, the Ames Laboratory (Iowa State University) and Astronautics Corporation of America have been collaborating for years to develop an advanced industrial prototype of magnetic refrigerator operating at room temperature [5].

In some PM materials the MCE is used to produce super low temperatures using the so-called adiabatic demagnetization method.

The above reasons and some other applications have given a push to the study of new materials with large MCE, such as nanocomposites [6], amorphous alloys [7], intermetallic compounds [8], and perovskite-type oxides [9-10].

2.1.2 Heat Capacity

The heat capacity of the system can be expressed as the ratio of the heat added to or taken from the system due to the resultant change in the temperature of the system either at constant volume, C_V , or at constant pressure, C_P :

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

$$C_P = \left(\frac{\delta Q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$$

The total heat capacity of a magnetic material usually is described by three contributions in the form:

$$C_{total} = C_L + C_e + C_M,$$

where C_L is the lattice heat capacity under constant pressure. For temperatures substantially lower than the Debye temperature (T_D) C_L is quite big [11]:

$$C_L = \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3,$$

where $\pi \approx 3.1416$, N is the number of atoms, k_B is the Boltzmann's constant, T_D is the Debye temperature.

C_e is the electronic heat capacity under constant pressure [2], and is given by:

$$C_e = \gamma T,$$

where γ is the electronic specific heat constant.

The magnetic heat capacity, $C_M(\vec{H}, T)$, of a ferromagnet in the vicinity of its Curie temperature T_C is given by [12]:

$$C_M(\vec{H}, T) = -\frac{T}{dT} 1.07 R \left(\frac{g_J \mu_B \vec{M} \vec{H}}{k_B T_C} \right)^{2/3}$$

For this study, the heat capacity were collected under constant pressure,

$C_P \cong \left(\frac{\Delta Q}{\Delta T}\right)_P$, where ΔQ is the amount of heat introduced into the calorimeter during a heat pulse, ΔT is the resulting temperature rise of a sample, and the index P shows that the measurements were performed at a constant pressure [13].

2.1.3 Magnetization

The magnetization, $\vec{M}$ usually is defined as the magnetic moment, $\vec{m}$, per unit volume, V , induced by any external magnetic field.

$$\vec{M} = \frac{\vec{m}}{V}$$

The magnetization of the material depends upon external magnetic field $\vec{H}$, the magnetic properties of the material, its shape and orientation in the external magnetic field. The relationship between magnetic field in the material $\vec{H}_B$ and external magnetic field $\vec{H}$ can be expressed as:

$$\vec{H}_B = \vec{H} - N\vec{M}$$

where N is demagnetization factor. In isotropic materials the direction of $\vec{M}$ is the same as the direction of $\vec{H}$. In the anisotropic materials the $\vec{M}$ and $\vec{H}$ directions are usually different.

2.1.4 dc and ac Susceptibility

dc susceptibility:

The *dc* magnetic susceptibility (χ_{dc}) is a value, which characterizes the relationship between magnetization of the magnetic material with magnetic field applied upon a material. In static magnetic field, we can describe χ as following [14]:

$$\chi_{dc} = \frac{\vec{M}}{\vec{H}}$$

Both positive and negative values of the magnetic susceptibility have been observed. Diamagnetic materials have negative values of magnetic susceptibility, whereas in paramagnets, PM and FM the magnetic susceptibility is positive. DiaM and PM have small values ($\sim 10^{-4} - 10^{-6}$) of χ_{dc} , whereas in a FM it can reach 1 to 1000. Also in a FM the dependence between $\vec{H}$ and χ_{dc} is stronger and more complicated than in a DiaM or PM. Therefore, in some cases it is better to introduce the differential magnetic susceptibility:

$$\chi_d = \frac{d\vec{M}}{d\vec{H}}$$

This susceptibility characterizes the magnetization at each point of the magnetization curve.

For a normal PM (substances, which contain permanent magnetic dipoles) the susceptibility obeys the Curie law:

$$\chi_{dc} = \frac{C}{T},$$

where C is the Curie constant.

Experiments showed that most PM materials do not obey the Curie's law, instead they have susceptibilities that can be fitted only to the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta_p},$$

where θ_p is a paramagnetic Curie temperature.

ac susceptibility

In an alternating magnetic field,

$$\vec{H}(t) = \vec{H} + \vec{H}_1 \cos \omega t,$$

the magnetization may be represented by:

$$\vec{M}(t) = \vec{M}_0 + \vec{M}_1 \cos \omega t \cos \varphi + \vec{M}_1 \sin \omega t \sin \varphi,$$

where $\vec{H}$ is a static field, $\vec{M}_0$ is the equilibrium value of the magnetization in a static field, φ is the phase angle by which the magnetization lags the field. Therefore:

$$\chi'_{ac} = \frac{\vec{M}_1 \cos \varphi}{\vec{H}_1},$$

and

$$\chi''_{ac} = \frac{\vec{M}_1 \sin \varphi}{\vec{H}_1}$$

the imaginary part of the ac susceptibility, so that

$$\chi''_{ac} / \chi'_{ac} = \tan \varphi.$$

Therefore,

$$\vec{M}(t) = \chi_{dc} \vec{H} + \chi'_{ac} \vec{H}_1 \cos \omega t + \chi''_{ac} \vec{H}_1 \sin \omega t$$

Both χ'_{ac} and χ''_{ac} depend on the frequency, ω , and magnitude of the static field, $\vec{H}$. χ'_{ac} is called the high frequency susceptibility and the variation of χ'_{ac} with ω is called the PM dispersion. χ''_{ac} is proportional to the energy absorbed by the substance from the high frequency field.

Kramers and Kronig [15, 16] had shown that χ'_{ac} and χ''_{ac} are not independent of each other and related by the following equations:

$$\chi'_{ac}(\omega_0) = \frac{2}{\pi} \int_0^\infty \frac{\omega \chi''_{ac}(\omega) d\omega}{\omega^2 - \omega_0^2} + \chi'_{ac}(\infty)$$

and

$$\chi''_{ac}(\omega_0) = -\frac{2}{\pi} \int_0^\infty \frac{\omega_0 \chi'_{ac}(\omega) d\omega}{\omega^2 - \omega_0^2}$$

2.2 Previous Work on $R_5(\text{Si}_x\text{Ge}_{1-x})_4$

The first studies on the $R_5\text{Si}_4$ or $R_5\text{Ge}_4$ phases were performed by Smith et al. [17]. They investigated thirteen rare earth germanides and eleven rare earth silicides of 5:4 stoichiometry. They found that the Tb_5Si_4 , Er_5Si_4 , Y_5Si_4 , Nd_5Ge_4 , Sm_5Ge_4 , Gd_5Ge_4 , Tb_5Ge_4 , Er_5Ge_4 , and Y_5Ge_4 phases have the Sm_5Ge_4 orthorhombic crystal structure and that Nd_5Si_4 has a tetragonal structure [18]. They determined that most of the lanthanide phases have either the Zr_5Si_4 or Sm_5Ge_4 type structures. One year later Holtzberg et al. [19] confirmed the $R_5\text{Si}_4$ and $R_5\text{Ge}_4$ crystal structures, and reported the magnetic properties for these alloys, include the intermediate $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ phase. Thirty years later an intensive study of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys was started at the Ames Laboratory due to the discovery of the giant MCE observed by Pecharsky and Gschneidner in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys [20].

2.2.1 $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$

Smith et al. [17, 18] first reported lattice parameters and unit cell volumes for Dy_5Si_4 and Dy_5Ge_4 , see Table 2.2.1. Both of these alloys had the Sm_5Ge_4 -type orthorhombic crystal structure.

Table 2.2.1 Lattice parameters and unit cell volume of Dy_5Si_4 and Dy_5Ge_4 alloys [18]

	a , (Å)	b , (Å)	c , (Å)	V , (Å ³)
Dy_5Si_4	7.58	14.54	7.65	843
Dy_5Ge_4	7.36	14.48	7.65	815

Year later Holtzberg et al. [19] confirmed previously the published results. Furthermore, from magnetic measurements they determined that Dy_5Si_4 has a FM phase transition near 140K and Dy_5Ge_4 has an AFM phase transition with Néel temperature around 40K. The magnetic data obtained by Holtzberg et al. for Dy_5Si_4 and Dy_5Ge_4 are presented in the Table 2.2.2.

Table 2.2.2 Magnetic Properties of Dy₅Si₄ and Dy₅Ge₄

	θ_p , K	T_C , K	T_N , K	$\sigma_{4.2at25kOe}$, emu/g	σ_{th} , emu/g	C_M , cm ³ -K	C_{Mth} , cm ³ -K
Dy ₅ Si ₄	133	140		213	301	13.34	14.17
Dy ₅ Ge ₄	43		40	50	253	13.87	14.17

In Table 2.2.2 θ_p is the PM Curie temperature; T_C is the Curie temperature; T_N is the Neel temperature; $\sigma_{4.2at25kOe}$ is the measured magnetic moment at 4.2K and 25kOe; σ_{th} is the theoretical saturation moment; C_M is the molar Curie constant; and C_{Mth} is the theoretical molar Curie constant.

Fifteen years later the magnetic susceptibility of Dy₅Ge₄ between 300K and 1800K was reported by Batalin et al. [21]. They calculated the PM Curie temperature and magnetic effective moment for the germanide.

The electrical resistivity (ρ) of Dy₅Si₄ in the temperature range from 4.2K to 360K was reported by Serdyuk et al. [22]. They found that the functions $\rho(T)$ display distinct kinks at temperatures corresponding to the FM $\leftrightarrow$ PM transitions. They also studied the heat capacity of the silicide, using a low-temperature adiabatic calorimeter. From an analysis of the $C_p(T)$ data above, T_C they estimated the Debye temperature θ_D . Using the Debye formula [23] they calculated the heat capacity, $C_p(T)$, in the vicinity of magnetic phase transition with Curie temperature, T_C .

In 1994, Eremenko et al. [24] using microstructural, X-ray and DTA analyses studied the structure and phase composition of the cast and annealed alloys of dysprosium with silicon. This was the first time the phase diagram for the dysprosium-silicon system was reported.

2.2.2 Gd₅(Si_xGe_{1-x})₄

The first crystallographic studies were done by Smith et al. [17, 18]. A year later the structure was confirmed by Holtzberg et al. [19]. Furthermore, Holtzberg et al. stated that an incomplete solid solubility in the system Gd₅Si₄ – Gd₅Ge₄ indicates that these alloys are not

isostructural. From magnetic measurements they showed that the silicide is FM with relatively high ordering temperature (~ 336 K), and that the germanide is AFM with ordering temperature (~ 94 K). However, the replacement of a small amount of Ge by Si in Gd_5Ge_4 produces a solid solution, which is FM at low temperatures and has intermediate transitions to AFM before becoming PM.

An extensive study of the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloy system was started at Ames Laboratory in 1996 by Pecharsky and Gschneidner due to the discovery of the giant magnetic entropy change in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloy when subjected to a change in the magnetic field [20]. This effect (MCE or magnetic entropy change) exceeded the reversible (with respect to an alternating magnetic field) MCE in any known magnetic material. They also found [25] that as Ge is substituted for Si in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ the Curie temperature is lowered and the giant MCE effect even become larger.

Pecharsky and Gschneidner reported [26] that the formation of the monoclinic phase at $0.24 \leq x \leq 0.5$ is due to the large difference in bonding characteristics of Si and Ge in Gd_5Si_4 - Gd_5Ge_4 pseudobinary system. For the composition $\text{Gd}_5\text{Si}_2\text{Ge}_2$ the lattice parameters of the monoclinic structure (space group $P112_1/a$) are $a = 7.5808 \text{ \AA}$, $b = 14.802 \text{ \AA}$, $c = 7.7799 \text{ \AA}$, $\gamma = 93.19^\circ$ [26]. Furthermore, it was found that Gd_5Si_4 and Gd_5Ge_4 have significant difference in the atomic arrangement. Large shifts of all the atoms occur along the shortest crystallographic direction and the covalently bonded $(\text{Si,Ge})_2$ pairs break upon transition from Gd_5Si_4 to Gd_5Ge_4 .

The same authors also studied the effect of small amounts (~ 0.33 at.%) of Ga additions substituting for the non-magnetic Si and Ge in the compound $\text{Gd}_5\text{Si}_2\text{Ge}_2$. It was observed that the Curie temperature rose from 276K to 285K with MCE value staying the same. However, larger quantities of Ga led to a significant reduction in the MCE, even though the Curie temperature continued to rise [27]. Many 3d-metal (Fe, Co, Ni, Cu) and p-element (C, Al) additions reduced the MCE in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ due to the changes in the thermodynamic nature of the magnetic phase transformations. In general, alloying additions rise the Curie temperature of the parent $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloy.

The studies of the magnetic and electrical properties of the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds were reported in the following papers [28-34].

Various studies of the *dc* magnetization and *dc/ac* magnetic susceptibility of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})$ were also completed [35,36]. The spontaneous generation of voltage has been observed during the first-order magnetic-martensitic phase transition in this alloy system. The thermoelectric power was considered to be the major contributor to this effect.

Structural, electronic, and magnetic changes, which occur in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, bring about extreme changes of some properties, such as the MCE, magnetostriction, and magnetoresistance.

2.2.3 Previous work on $R_5(\text{Si}_x\text{Ge}_{1-x})_4$, where *R* is rare earth other than Dy and Gd

A limited number of research papers have been published on the $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ phases with lanthanide metals other than Gd. The crystal structures of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys at room temperature are presented in the Table 2.2.5.

Table 2.2.3 Crystal structure at room temperature of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ [39]

Element	Crystal structure type	Composition interval
La	Sm_5Ge_4 -orthorhombic	$0 \leq x \leq 0.33$
	Zr_5Si_4 -tetragonal	$0.48 \leq x \leq 1$
Ce, Pr	Sm_5Ge_4 -orthorhombic	$x=0$
	Zr_5Si_4 -tetragonal	$x=1$
Nd	Sm_5Ge_4 -orthorhombic	$0 \leq x \leq 0.18$
	Sm_5Ge_4 -orthorhombic/ $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -monoclinic	$0.18 \leq x \leq 0.55$
	$\text{Gd}_5\text{Si}_2\text{Ge}_2$ -monoclinic	$0.55 \leq x \leq 0.61$
	Zr_5Si_4 -tetragonal/ Sm_5Ge_4 - orthorhombic	$0.85 \leq x \leq 1$
Sm	Sm_5Ge_4 -orthorhombic	$x=0, x=1$
Gd	Sm_5Ge_4 -orthorhombic	$0 \leq x \leq 0.2$
	$\text{Gd}_5\text{Si}_2\text{Ge}_2$ -monoclinic	$0.22 \leq x \leq 0.51$
	Gd_5Si_4 -orthorhombic	$0.52 \leq x \leq 1$

Tb	Sm ₅ Ge ₄ -orthorhombic	$0 \leq x \leq 0.27$
	Gd ₅ Si ₂ Ge ₂ -monoclinic	$0.45 \leq x \leq 0.56$
	Gd ₅ Si ₄ -orthorhombic	$0.75 \leq x \leq 1$
Dy	Sm ₅ Ge ₄ -orthorhombic	$0 \leq x \leq 0.625$
	Gd ₅ Si ₂ Ge ₂ -monoclinic	$0.675 \leq x \leq 0.775$
	Gd ₅ Si ₄ -orthorhombic	$0.825 \leq x \leq 1$
Ho	Sm ₅ Ge ₄ -orthorhombic	$x=0$
	Gd ₅ Si ₄ -orthorhombic	$x=1$
Er	Sm ₅ Ge ₄ -orthorhombic	$0 \leq x \leq 0.81$
	Gd ₅ Si ₂ Ge ₂ -monoclinic	$0.83 \leq x \leq 0.91$
	Gd ₅ Si ₂ Ge ₂ -monoclinic/ Gd ₅ Si ₄ -orthorhombic	$0.92 \leq x \leq 1$
Tm	Sm ₅ Ge ₄ -orthorhombic	$x=0$
Lu	Sm ₅ Ge ₄ -orthorhombic	$0 \leq x \leq 1$
Y	Sm ₅ Ge ₄ -orthorhombic	$0 \leq x \leq 0.81$
	Gd ₅ Si ₂ Ge ₂ -monoclinic	$0.83 \leq x \leq 1$

La₅(Si_xGe_{1-x})₄ and Lu₅(Si_xGe_{1-x})₄

The heat capacities of the La₅(Si_xGe_{1-x})₄ and Lu₅(Si_xGe_{1-x})₄ can be used to estimate the electronic and lattice contributions for other lanthanides [37]. Therefore, the pure magnetic contribution to the heat capacity can be estimated for different rare earth elements. The electronic specific heat constant, γ , and the Debye temperature, θ_D , were calculated for these intermetallic compounds [37].

Nd₅(Si_xGe_{1-x})₄

In 1974, the phase diagram of the Nd-Ge system was reported as based on the microstructural, DTA, differential dilatometric, and X-ray phase analysis [38]. The formation of Nd₅Si₄ was studied using auger electron spectroscopy, X-ray diffraction, and Rutherford backscattering spectrometry [39]. The magnetization and *dc* magnetic susceptibility were

reported for $\text{Nd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys with $x=0, 0.25, 0.5, 0.75, 1$ compositions [37]. The MCE observed in the monoclinic phase $\text{Nd}_5\text{Si}_2\text{Ge}_2$ does not have first order phase transition, as found in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ or in $\text{Dy}_5\text{Si}_3\text{Ge}$ monoclinic alloys. It undergoes second order phase transition. The electronic specific heat constant, $\gamma = 2.6 \pm 1.5 \text{ mJ/mol}$, and the Debye temperature, $\theta_D = 199 \pm 14 \text{ K}$ were also given [37].

$\text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4$

Physical properties of Tb_5Si_4 were reported for the first time in early eighties [22,41]. The heat capacity, magnetization, susceptibility and electric resistance of Tb_5Si_4 were studied in terms of the RKKY and the molecular-field theories. The PM Curie temperature, the Curie-Weiss constant, and the molecular-field constant were determined [40]. From measurements of the electrical resistance and susceptibility, the effective mass of electrons, the s-f interaction constant, the Debye temperature, and the Fermi energy were established. The phase diagrams of the Tb-Ge and Tb-Si systems were reported in the papers [41] and [42], respectively.

More recent investigations [43] of the properties of $\text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system showed that the alloys with monoclinic ($\text{P}112_1/\text{a}$) crystal structure ($x=0.4, 0.5, 0.6$) have a first-order phase transition to orthorhombic (Pnma) canted-FM structure. The strong coupling between crystallographic and magnetic degrees of freedom in the $\text{Tb}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds was experimentally observed [43]. The ΔS_m values of the alloys with monoclinic phase structure are more than twice as large as then the values of the two end members (Tb_5Si_4 and Tb_5Ge_4) [44, 45].

$\text{Pr}_5(\text{Si}_x\text{Ge}_{1-x})_4, \text{Ho}_5(\text{Si}_x\text{Ge}_{1-x})_4, \text{Er}_5(\text{Si}_x\text{Ge}_{1-x})_4, \text{Tm}_5(\text{Si}_x\text{Ge}_{1-x})_4$ and $\text{Y}_5(\text{Si}_x\text{Ge}_{1-x})_4$

Only a limited amount of well-established experimented data exist for the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ phases for $\text{R} = \text{Pr, Ho, Er, Tm, and Y}$; these includes phase diagrams, and magnetic, electronic, and thermodynamic properties. [46-57].

2.3 Magnetocaloric Refrigeration

2.3.1 History

Magnetic cooling technique was first proposed by P. Debye [58] in 1926 for reaching temperatures below the boiling point of liquid helium. It was achieved by Giauque and Mac Dougall [59] in 1933 by cooling down to 0.25 K. In 1976, G.V. Brown [60] demonstrated a regenerative magnetic refrigerator operating near room temperature with a 50 K span. The efficiency of this refrigerator was low for two reasons: 1) the temperature gradient had to be maintained in a liquid with constant mixing; and 2) the cycle time of charging and discharging the magnet was too long. Currently work on near room temperature magnetic refrigeration is being conducted at the Astronautics Corporation of America in Wisconsin in conjunction with the Ames Laboratory [61]. Other magnetic refrigerator also being constructed and tested at the University of Victoria in Canada. The research on the magnetic refrigerant materials proceeds at the Ames Laboratory, the University of Quebec in Canada, and NIST (Gathersburg, MD) [62].

2.3.2 Basic principles

The MCE is the response of a solid to an applied magnetic field by changing the temperature of the material. This effect can be observed in any magnetic material. The maximum temperature change occurs near the magnetic ordering temperature. In a FM material the magnetic moments of the atoms are aligned upon the application of a magnetic field and as result the temperature rises. The material is cooled down when the magnetic moments become randomly oriented after removing the magnetic field. This process similar to the warming and the cooling of a gas in compression and expansion gaseous refrigerators. The refrigerant in magnetic refrigerators is a solid in a form of spheres. A low hazard fluid, e.g. water, antifreeze, or an inert gas provides the heat transfer. The demonstration of an operating magnetic refrigerator by the Astronautic corp. / Ames Laboratory team showed that it is possible to obtain cooling powers of 600W at 60% Carnot efficiencies with a large coefficient of performance near room temperature in magnetic fields $\leq 50\text{kOe}$ [63]. The

discovery of giant MCE in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ series of alloys most likely will increase the performance of such refrigerator [26].

One of the biggest obstacle to the development of magnetic refrigerators is the cost of the superconducting or the permanent magnet. Therefore for now, commercial uses would be limited to large-scale operations only. However, if the MCE can be sufficiently enhanced, the device may be able to run efficiently enough with the weaker field generated by a permanent magnet. Then small size refrigerators will be used in wide range applications.

3. EXPERIMENTAL TECHNIQUES AND SAMPLES

3.1 Samples

3.1.1 Preparation of the $Dy_5(Si_xGe_{1-x})_4$ alloys from the initial components (Dy, Si, Ge)

A total of 11 alloys with the $Dy_5(Si_xGe_{1-x})_4$ stoichiometry (where $0 \leq x \leq 1$) were prepared. The samples were obtained using an electric – arc-melting furnace with a water-cooled copper hearth in an argon atmosphere. The initial materials used pure components of Dy, Ge, and Si. The dysprosium was prepared and analyzed for impurities by the Materials Preparation Center (Ames Laboratory). The chemical analysis of the metal was found to be 99.9 at.% (99.99 wt.%) pure with the major impurities shown in the Table 3.1.1. The silicon and germanium were purchased from CERAC. The purity of these semiconductors was claimed as 99.99+ wt.%.

Table 3.1.1 Chemical analysis of the Dy-metal used in this study

Element	O	C	F	N	Fe
at. % x 10^{-4}	602	189	111	45	6
wt. % x 10^{-4}	59	14	13	4	2

Total weight of each arc-melted alloy was in the range between 7 and 12 grams (see Table 3.1.2). All alloys were arc-melted 6-7 times. Each time the alloy was turned over.

Because of the high melting point of the $Dy_5(Si_xGe_{1-x})_4$ and high vapor pressure of Dy some vaporization of Dy metal was observed during arc-melting. The losses of dysprosium were confirmed on X-ray diffraction. In order to compensate for the losses of the material, an excess of 1.1% – 1.5% Dy was added in each alloy before arc-melting, see Table 3.1.2

Table 3.1.2 Weights and weight changes of arc-melted $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys

Compound	m_{aftmelt} , (g) ^a	+Dy, (%)	wt. loss of Dy, (g)	wt. loss of Dy, (%)
Dy_5Si_4	8.2252	1.5	0.11	1.34
$\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$	7.6407	1.5	0.12	1.49
$\text{Dy}_5\text{Si}_{3.3}\text{Ge}_{0.7}$	10.5446	1.3	0.12	1.22
$\text{Dy}_5\text{Si}_{3.1}\text{Ge}_{0.9}$	10.8965	1.2	0.12	1.07
$\text{Dy}_5\text{Si}_3\text{Ge}$	10.6959	1.3	0.13	1.17
$\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$	13.4233	1.1	0.15	1.09
$\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$	11.9916	1.3	0.12	0.99
$\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$	9.1485	1.5	0.1	1.08
$\text{Dy}_5\text{Si}_2\text{Ge}_2$	9.912	1.5	0.13	1.32
Dy_5SiGe_3	8.5265	1.5	0.15	2.2
Dy_5Ge_4	9.4317	1.5	0.12	1.26

^awhere m_{aftmelt} is the mass of the sample after arc melting.

As seen in Table 3.1.2, after arc-melting the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ samples contained about a 1% excess Dy.

The samples were quite brittle and easily ground to powder. The most brittle samples were Ge - based solid solutions with the orthorhombic crystal structure.

Several alloys, which were prepared first and showed extra x-ray diffraction peaks due to the presence of second phases, were subjected to heat treatment at about 1000°C. Unfortunately, this procedure did not significantly improve their phase compositions. Therefore, the alloys, which were used in this study, were not heat-treated, and were selected for their phase purity on the basis of X-ray powder diffraction and optical metallographic analyses.

3.1.2 Samples preparation for magnetic and heat capacity measurements

For the magnetic measurements (i.e. *ac/dc* susceptibilities and *dc* magnetization) the mass of the samples weighed between 0.15g and 0.2g. Long and thin rectangular shapes of

the samples were intended to reduce the demagnetization factor. However this was achieved in less than 50% of the cases. Many of the measurements were performed on specimens which have an arbitrary shape.

The specimens for the heat capacity measurements were cut into a rectangular parallelepiped. The sizes of the samples were: length 8-11 mm, width 6-8 mm, and height 2-3 mm, and the weights varied from 0.8g to 1.8g.

3.1.3 Optical metallographic analysis

Optical *metallographic* analyses were used to analyze the microstructure and phase purity of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys.

First images of the microstructure of the alloy were obtained by using an ordinary optical microscope. Unfortunately, the distinctions between grains, different phases and impurities were not evident. On these micrographs, it was possible to observe only severe microcracks in the bulk material were observed in these micrographs. Therefore, the Differential Interference Contrast (DIC) illumination method was used. This microscopic technique uses a beam-splitting double-quartz prism, which is placed ahead of the objective, together with a polarizer and analyzer in the 90° crossed positions. The two light beams are made to coincide at the focal plane of the objective, revealing height differences as variations in color. The prism can be moved, shifting the interference image through the range of Newtonian colors. By using this technique we observed grains, grain boundaries, cracks, imperfections, etc.

A 100X DIC optical micrograph of Dy_5Ge_4 alloy is shown on the Figure 3.1.1. We can observe many imperfections as well as a number of cracks. These cracks make the specimen very fragile and difficult to measure such physical properties as the heat capacity, magnetization, and *ac/dc* susceptibility. During heat capacity measurements the bulk polycrystal specimen breaks into pieces during 3K to 350K thermocycling and/or application of strong magnetic fields above 20 kOe. This behavior is very typical for all Ge-rich alloys with orthorhombic crystal structure. Therefore, all $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys within the composition range $0 \leq x \leq 0.622$ have similar microstructures, i.e. large number of cracks. Several examples for different alloy composition are shown in Figure 3.1.2 and Figure 3.1.3.

The micrograph for the $\text{Dy}_5\text{Si}_3\text{Ge}$ alloy with the monoclinic crystal structure is shown in Figure 3.1.4. Even though the number of microcracks are less, the alloys with $0.675 \leq x \leq 0.775$, the samples still have a lot of hollow areas. Therefore, these specimens also easily fell apart during thermocycling and/or application of magnetic field.

The least fragile samples among of all the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys were silicon rich samples within the composition range vary from 0.822 to 1. Two of them are shown on Figure 3.1.5 and Figure 3.1.6. Even though it was easier to carry out measurements on these materials, which have the Gd_5Si_4 -type orthorhombic crystal structure, they still broke into pieces several times during heat capacity measurements.

Figure 3.1.1 100X DIC illumination optical micrograph of the Dy_5Ge_4 as cast alloy

Figure 3.1.2 100X DIC illumination optical micrograph of the Dy_5SiGe_3 as cast alloy

Figure 3.1.3 100X DIC illumination optical micrograph of the Dy₅Si₂Ge₂ as cast alloy

Figure 3.1.4 100X DIC illumination optical micrograph of the Dy₅Si₃Ge as cast alloy

Figure 3.1.5 100X DIC illumination optical micrograph of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ as cast alloy

Figure 3.1.6 100X DIC illumination optical micrograph of the Dy_5Si_4 as cast alloy

3.2 X-ray Diffraction

The collected X-ray powder diffraction data were used to determine the crystal structures, space group symmetry, lattice parameters (a , b , c , and γ), unit cell volume, density, the number of atoms, atomic coordinates, and positions of the atoms in the unit cell of the investigated alloys. The X-ray diffraction data were collected using an automated Scintag powder diffractometer using Cu-K α radiation with a graphite monochromator attached to the detector. All scans were made in the two-theta angular range of 20 to 90 degrees. The powder samples for the x-ray measurements were prepared by grinding several polycrystals into a powder using a mortar and pestle. After grinding the powder was evenly distributed over a greased quartz slide. The slide was attached to the diffractometer's sample holder parallel to the horizontal surface. The diffraction data were analyzed using the CSD crystallographic software [64].

3.3 Magnetic Measurements

Most of the magnetic measurements were performed on a LakeShore Model 7225 *ac* susceptometer / *dc* magnetometer. Only few measurements were done on an Oxford Instruments MagLab 2000. For the most part, the data collected on the Oxford magnetometer were used to check the data obtained on the LakeShore magnetometer.

3.3.1 LakeShore Model 7225 *ac* susceptometer / *dc* magnetometer specifications [65]

- 1) Temperature Range: from 4.2K to 325K
- 2) *ac/dc* Magnetic Field (Primary Coil):
  - + Range: 4-digit selectable from 0.1Am^{-1} (0.00125Oe) to 1600Am^{-1} (20Oe) RMS, both *ac* and *dc*
  - + Frequency: 1Hz to 1kHz, 1Hz step; 1kHz to 10kHz, 10Hz steps
- 3) *ac* susceptibility sensitivity: to $2 \times 10^{-8}\text{emu}$ in terms of equivalent magnetic moment
- 4) *dc* moment sensitivity: $9 \times 10^{-5}\text{emu}$
- 5) 56kOe superconducting Magnet:
  - + Field Range: $\pm 56,000\text{gauss}$ ($\pm 56\text{kOe}$)
  - + Field Resolution: $< 1.0\text{gauss}$, -56,000 to +56,000gauss (-56kOe to + 56kOe)
  - + Remnant Field: 15gauss ($< 0.5\text{gauss}$ after demagnetization cycle) (15kOe)
- 6) Helium Capacity: 60liters
- 7) Static Boil-Off: 0.45liter/hour (nominal static boil-off)
- 8) A disposable nylon sample holder screws to a nylon rod at the end of the 0.25inch stainless steel sample rod. The stainless steel insert attaches to a stepping motor at the top of the cryostat. Nylon sample holder can hold up to 3.6mm x 13mm sample, including powder and bulk samples.
- 9) Data acquisition/control and analysis software: ACS7000 *ac* susceptibility software and DCM7000 *dc* moment software control the temperature of the sample, *ac/dc* magnetic fields, and stepping motor

Figure 3.3.1 Model 7225 *ac* susceptometer / *dc* magnetometer block diagram [65]

3.3.2 Oxford Instruments MagLab 2000 specifications [66]

- 1) Two inserts for different temperature ranges: a) from 2K to 400K, b) from 300K to 900K
- 2) A superconducting magnet with maximum field of 90kOe
- 3) Two cryogenic jackets: a) with liquid helium around a superconducting magnet, b) with liquid nitrogen for overall shielding
- 4) Two sample rods for different temperature ranges; it is positioned by the motor drive unit
- 5) A PC automatic software Object Bench version 3.7, which controls the temperature, *ac/dc* magnetic fields, and motor drive unit

The basic physical and engineering principles of *ac/dc* susceptibility and *dc* magnetization measurements are the same for both of these apparatuses.

3.3.3 *ac* susceptibility measurements

For *ac* susceptibility measurements, the principle of operation involves applying a small alternating magnetic field on the sample. It is achieved by driving an *ac* current through a primary coil. Two secondary coils, which located inside the primary coil, are balanced so the coils produces identical signals when there is no sample present in either coil. Therefore, the subtraction of the signals of two coils gives us zero. When the magnetic material is placed into one of the coils the resulting induced voltage in the coil is effected. This voltage (v) is directly proportional to the magnetic susceptibility of the sample. Therefore, when the voltage signals are subtracted the resultant is no longer zero. The measured voltage and magnetic susceptibility have following relationship [65]:

$$v = (1/\alpha) V f H \chi,$$

where v is the measured RMS voltage, α is the calibration coefficient, V is the sample volume, f is the frequency of *ac* field, H is the RMS magnetic field, and χ is the volume susceptibility of sample.

Therefore, the sample susceptibility is given by:

$$\chi = \alpha v / (V f H).$$

An improved accuracy of the magnetic susceptibility can be achieved by correcting for the demagnetization effect. This phenomenon is caused by the shape of the material due to the differences between the internal magnetic field in the sample and the applied magnetic field. The true internal magnetic susceptibility is given by the following relationship [65]:

$$\chi_{\text{int}} = \chi / (1 - D\chi),$$

where D is the demagnetization factor and χ is measured susceptibility.

The complex susceptibility with real and imaginary components arises from the phase difference (φ) between the input signal (E_{in}) and the reference signal (E_{out}) [65]:

$$E_{\text{out}} = E_{\text{in}} \cos \varphi$$

The phase angle φ has two contributions: 1) the circuit itself (in the case of ideal inductors there is a 90° phase shift in the circuit), and 2) the signal due to the sample. Therefore, the real χ' and the imaginary χ'' internal susceptibilities are interdependent on both the real and imaginary measured susceptibilities and have a form:

$$\chi'_{\text{int}} = \frac{\chi'(1 - D\chi') - D\chi''^2}{(1 - D\chi')^2 + D^2\chi''^2},$$

$$\chi''_{\text{int}} = \frac{\chi''}{(1 - D\chi')^2 + D^2\chi''^2}.$$

The *dc* magnetic moment measurements is done by utilizing an extraction technique. A sample is moved through a pair of pickup coils at a given moment (dt), which induces a voltage (v). This voltage proportional to the moment (m) with a calibration factor α . It has a form:

$$m = -\alpha \int v dt,$$

where

$$v = \frac{\partial \varphi}{\partial t},$$

and therefore,

$$m = \alpha \varphi,$$

where m is the magnetic moment, α is the calibration coefficient, dt is the time interval, and φ is rate of flux change.

It is difficult to estimate the accuracy of magnetic measurements, because the manufacturer provided no such data. However, measurements of standards (such as Pt) show that the accuracy of the magnetometer is better than 1%. From magnetization data, using the Maxwell relation the isothermal magnetic entropy change ($\Delta S_m(T)$) as a function of temperature was calculated:

$$\Delta S_m(T) = \int_0^{H_0} \left(\frac{\partial M}{\partial T} \right)_H dH.$$

3.4 Heat Capacity Measurements

The heat capacity from ~3.5K to 350K in zero magnetic field and in magnetic fields of 20, 50, 75, and 100kOe was measured by using an automatic small sample calorimeter [13]. The basic components of the calorimeter are:

- 1) an insert with low temperature liquid helium pot, which allows to cool the sample holder to be cooled to about ~3K,
- 2) 120kOe superconducting magnet with a cryostat,
- 3) current sources and voltage measuring devices,
- 4) a high speed vacuum pumping system (vacuum down to 10^{-7} Torr), and
- 5) an IBM-PC to run the collecting data automatic program.

One of the most sensitive and difficult part to build and to repair in the automatic small sample calorimeter is the copper sample holder. It is made from a low-oxygen pure copper (99.99+wt%Cu). It has a clamp-like holder design, where the sample is tightly held to a round copper plate using a copper screw. The intermediate layer between the sample and the plate is a mixture of 50:50 (by volume) Apiezon-N grease and fine silver powder. It is used to improve the thermal conductivity between sample and sample holder. A temperature sensor (CERNOX) is placed in a small copper clamp and glued there with GE7031 varnish. Such a design provides better thermal contact. A heater (a thin film strain gauge) is attached to the sample holder using a silver epoxy, providing as best contact between these two surfaces as possible. The sample holder is connected to a helium pot by an alligator clamp, which gives a reliable thermal contact. When the alligator clamp is open the sample has contact only with four thin bad thermoconducting ($\varnothing$ 0.15mm) nylon threads, which hold the sample holder tight in the design position.

Heat capacity during the experiment can be expressed in the form:

$$C_P \cong \left(\frac{\Delta Q}{\Delta T} \right)_P,$$

where ΔQ is the amount of heat introduced into the sample holder and sample during a heat pulse, ΔT is the resulting temperature rise, and P is the constant pressure index.

The accuracy of heat capacity data was $\sim 1\text{-}2\%$ (typically it is less than 1%) due to the large number of cracks in the samples. The total entropy, $S_{total}(T, H_i)$, was calculated using the measured heat capacity data, $C_p(T, H_i)$, by the formula [67]:

$$S_{total}(T, H_i) = \int_0^T \frac{C_p(T, H_i)}{T} dT + S_0(H_i),$$

where $S_0(H_i)$ was defined as equal to 0 (i.e. field independent), and H_i is a fixed magnetic field, i.e. $\mu_0 H = 0, 20, 50, 75$, or 100 kOe.

Numerical integration was started at a selected low temperature, T_{min} , for all fields to minimize the effect of a varying experimented starting temperature (i.e. the lowest experimental data point which varies from min to max). Therefore:

$$S_{total}(T, H_i) = \int_0^{T_{min}} \frac{C_p(T, H_i)}{T} dT + \int_{T_{min}}^T \frac{C_p(T, H_i)}{T} dT$$

Where $C_p(T, H_i)$ is the extrapolated value of heat capacity from $T = T_{min}$ to $T = 0K$.

The errors in temperature measurements were assumed to be negligibly small compared to the errors in heat capacity $\sigma C_p(T, H_i)$. Therefore the errors in total entropy, $\sigma S_{total}(T, H_i)$, can be expressed as [67]:

$$\sigma S_{total}(T, H_i) = \int_0^{T_{min}} \frac{\sigma C_p(T, H_i)}{T} dT + \int_{T_{min}}^T \frac{\sigma C_p(T, H_i)}{T} dT$$

The magnetic entropy change $\Delta S_m(T)$ was calculated as the difference between two isotherms. The adiabatic temperature rise $\Delta T(T)$ was calculated as the difference between $S_{total}(T, 0)$ and $S_{total}(T, H_i)$. The errors $\sigma \Delta S_m$ and $\sigma \Delta T$ are [68]:

$$\sigma \Delta S_{mag}(T) = \sigma S(T, 0) + \sigma S(T, H_i)$$

and

$$\sigma \Delta T(T) = \frac{\sigma S(T, 0)}{\left(\frac{dS(T, 0)}{dT}\right)} + \frac{\sigma S(T, H_i)}{\left(\frac{dS(T, H_i)}{dT}\right)}$$

4. DATA ANALYSIS AND RESULTS

4.1 Crystal Structure

To date three different crystal structures have been determined in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloy system [31, 69]. Dy_5Ge_4 , Dy_5SiGe_3 , $\text{Dy}_5\text{Si}_2\text{Ge}_2$, and $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$ alloys have the Sm_5Ge_4 -type orthorhombic crystal structure. $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$, $\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$, $\text{Dy}_5\text{Si}_3\text{Ge}$, and $\text{Dy}_5\text{Si}_{3.1}\text{Ge}_{0.9}$ alloys have $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type monoclinic structure. $\text{Dy}_5\text{Si}_{3.3}\text{Ge}_{0.7}$, $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$, and Dy_5Si_4 have the orthorhombic Gd_5Si_4 -type crystal arrangement. The observed, calculated and difference between the observed and calculated crystal structures of Dy_5Si_4 , $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$, $\text{Dy}_5\text{Si}_3\text{Ge}$, $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$, $\text{Dy}_5\text{Si}_2\text{Ge}_2$, Dy_5SiGe_3 , and Dy_5Ge_4 diffraction patterns are shown in Figures 4.1.1 – 4.1.7, respectively. The calculated intensity values were determined by using a full profile least-squares refinement [64]. All positional parameters and the overall thermal displacement parameters were refined.

Figure 4.1.1 The observed and calculated X-ray powder diffraction data profiles and their difference of the Dy_5Si_4 as cast alloy

Figure 4.1.2 The observed and calculated X-ray powder diffraction data profiles and their difference of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ as cast alloy

Figure 4.1.3 The observed and calculated X-ray powder diffraction data profiles and their difference of the $\text{Dy}_5\text{Si}_3\text{Ge}$ as cast alloy

Figure 4.1.4 The observed and calculated X-ray powder diffraction data profiles and their difference of the $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$ as cast alloy

Figure 4.1.5 The observed and calculated X-ray powder diffraction data profiles and their difference of the $\text{Dy}_5\text{Si}_2\text{Ge}_2$ as cast alloy

Figure 4.1.6 The observed and calculated X-ray powder diffraction data profiles and their difference of the Dy_5SiGe_3 as cast alloy

Figure 4.1.7 The observed and calculated X-ray powder diffraction data profiles and their difference of the Dy_5Ge_4 as cast alloy

Figure 4.1.1 and Figure 4.1.2 are typical X-ray diffraction patterns for the orthorhombic Gd_5Si_4 -type crystal structure. This phase exists in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys for $0.822 \leq x \leq 1$ composition range.

In Figure 4.1.3 is shown X-ray powder diffraction of a typical monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type crystal structure formed in $\text{Dy}_5\text{Si}_3\text{Ge}$ compound. Calculated and observed intensity vs angle 2θ match well with each other. No significant extra peaks were found in the X-ray patterns.

The full profile least – squares analysis shows that the structure of $\text{Dy}_5\text{Si}_3\text{Ge}$ differs from the other crystal structures of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloy system. When we tried to use the lattice and atomic parameters of either the Si or the Ge orthorhombic crystal systems as a starting model for the full profile least squares refinement for the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$, it was unsuccessful. The answer showed clearly that the crystal structure of this intermetallic compound is quite different from orthorhombic Sm_5Ge_4 type. Therefore, the initial crystallographic data and structure refinement parameters were taken from the reported by Pecharsky and Gschneidner [26] for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloy with the monoclinic crystal structure with the $\text{P}112_1/\text{a}$ phase group. This space group is a subgroup of Pnma , where the glide plane n and the mirror plane m are absent. Even though both Gd_5Si_4 and Gd_5Ge_4 alloys crystallize in the Pnma space group, the intermediate group of alloys have the monoclinic $\text{P}112_1/\text{a}$ crystal structure. Both the orthorhombic (Pnma) and monoclinic ($\text{P}112_1/\text{a}$) types of diagrams are considered to be quite complex and difficult to identify.

Figures 4.1.4 – 4.1.7 show the X-ray diffraction diagrams for the orthorhombic Sm_5Ge_4 -type crystal structure. The calculated and measured X-ray diffraction profiles show that the phase purity of the specimens is within acceptable limits. There are no extra peaks with large intensity values in the observed X-ray profiles.

The samples of the Dy_5Si_4 , $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$, $\text{Dy}_5\text{Si}_{3.3}\text{Ge}_{0.7}$, $\text{Dy}_5\text{Si}_{3.1}\text{Ge}_{0.9}$, $\text{Dy}_5\text{Si}_3\text{Ge}$, $\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$, $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$, $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$, $\text{Dy}_5\text{Si}_2\text{Ge}_2$, Dy_5SiGe_3 , and Dy_5Ge_4 compounds were considered to be single-phase pattern with an admixture of other phases being less than 3%. Some deviations in intensity of peaks between observed and calculated profiles are probably due to the texture of the powders.

Figure 4.1.8 Comparison of the Dy_5Si_4 , $\text{Dy}_5\text{Si}_3\text{Ge}$, and Dy_5Ge_4 X-ray powder diffraction patterns

Comparison of X-ray data for the different crystal structures in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system (i.e. Dy_5Si_4 , $\text{Dy}_5\text{Si}_3\text{Ge}$, and Dy_5Ge_4) are shown in Figure 4.1.8. The presentation of crystallographic data of the orthorhombic Gd_5Si_4 -type, the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type, and the orthorhombic Sm_5Ge_4 -type crystal structures gives us the distinctions between these three structures. A full profile Rietveld analysis [70] of the experimental X-ray data was performed on the samples used in this study and the results are given in Table 4.1.1. The initial lattice and atomic parameters for Dy_5Si_4 and Dy_5Ge_4 were taken from Smith et al. [18]. The lattice parameters (a , b , c , and γ), unit cell volume (V), density (ρ) and number of atoms in the unit cell were calculated for all seven compounds. The X-ray diffraction measurements were taken using $\text{Cu } \alpha_1$ radiation with wavelength $1.5406\text{\AA}$. The 2θ range and the number of free parameters presented in the table were utilized for the full profile least – square refinement. The results are in good agreement with previous work presented in Table 2.2.1 [18,19].

Table 4.1.1 Crystallography data after refinement of Dy₅Si₄, Dy₅Si_{3.5}Ge_{0.5}, Dy₅Si₃Ge, Dy₅Si_{2.5}Ge_{1.5}, Dy₅Si₂Ge₂, Dy₅SiGe₃ and Dy₅Ge₄ as cast alloys

Compounds/Parameters			Dy ₅ Si ₄	Dy ₅ Si _{3.5} Ge _{0.5}	Dy ₅ Si ₃ Ge	Dy ₅ Si _{2.5} Ge _{1.5}	Dy ₅ Si ₂ Ge ₂	Dy ₅ SiGe ₃	Dy ₅ Ge ₄
Space group			<i>Pnma</i>	<i>Pnma</i>	<i>P112₁/a</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)			7.3800	7.395	7.4630	7.5383	7.5525	7.5796	7.6072
<i>b</i> (Å)			14.536	14.559	7.6569	14.591	14.599	14.622	14.643
<i>c</i> (Å)			7.6603	7.675	14.580	7.6358	7.6384	7.6565	7.6788
γ (°)			90	90	93.060	90	90	90	90
<i>V</i> (Å ³)			821.8	826.3	832.0	839.9	842.2	848.6	855.4
ρ (g/cm ³)			7.475	7.613	7.739	7.841	7.995	8.284	8.563
Number of atoms in the unit cell			36.0	36.0	36.0	36.0	36.0	36.0	36.0
Wavelength, $\lambda K\alpha_1$ (Å)			1.5406	1.5406	1.5406	1.5406	1.5406	1.5406	1.5406
2θ range			20-90°	20-90°	20-90°	20-90°	20-90°	20-90°	20-90°
Free parameters (including profile)			22	22	37	22	22	22	22
Contents	Dy	# in the unit cell	20.00	20.00	20.00	20.00	20.00	20.00	20.00
		Atomic %	55.56	55.56	55.56	55.56	55.56	55.56	55.56
		Weight %	87.85	85.79	83.82	81.94	80.14	76.77	73.67
	Si	# in the unit cell	16.00	14.00	12.00	10.00	8.00	4.00	–
		Atomic %	44.44	38.89	33.33	27.78	22.22	11.11	–
		Weight %	12.15	10.38	8.69	7.08	5.54	2.65	–
	Ge	# in the unit cell	–	2.00	4.00	6.00	8.00	12.00	16.00
		Atomic %	–	5.56	11.11	16.67	22.22	33.33	44.44
		Weight %	–	3.83	7.49	10.98	14.32	20.58	26.33

The atomic positions in the polycrystals Dy₅Si₄, Dy₅Si₃Ge, Dy₅Si₂Ge₂, Dy₅Si_{2.5}Ge_{1.5}, Dy₅SiGe₃, Dy₅Si_{3.5}Ge_{0.5}, and Dy₅Ge₄ were calculated and are listed in Table 4.1.2. The sites that the Dy and Si (Ge) atoms occupy in these alloys are given in this table. In the two orthorhombic structures there are three different coordinating polyhedra for Dy atoms in the unit cell and three for the Si (Ge) atoms. In the monoclinic crystal structure there are 5 different sites in the unit cell for the Dy and 4 for the Si (Ge) atoms. The increase of the different coordinating polyhedra with decrease of symmetry of crystal is typical.

In Table 4.1.2 it is seen that the constraint positional parameter $y = \frac{1}{4}$ in orthorhombic crystal structure becomes a free parameter in the monoclinic system. This is due to the losses of the glide plane n and the mirror plane m during the phase transformation from the orthorhombic to the monoclinic crystal structure.

Table 4.1.2 Atomic coordinates of Dy₅Si₄, Dy₅Si_{3.5}Ge_{0.5}, Dy₅Si₃Ge, Dy₅Si_{2.5}Ge_{1.5}, Dy₅Si₂Ge₂, Dy₅SiGe₃, and Dy₅Ge₄ as cast alloys

Atom/Position	x/a	y/b	z/c	N
Dy ₅ Si ₄				
Dy1	.3424(10)	¼	.0137(10)	4
Dy2	.0278(6)	.0984(3)	.1747(7)	8
Dy3	.3225(6)	.8784(4)	.1897(7)	8
Si1	.223(3)	¼	.364(4)	4
Si2	.061(5)	¼	.929(5)	4
Si3	.141(3)	.9354(13)	.508(3)	8
Dy ₅ (Si _{3.5} Ge _{0.5})				
Dy1	.331(2)	¼	.013(2)	4
Dy2	.0153(12)	.0960(5)	.1790(14)	8
Dy3	.3248(10)	.8769(5)	.1862(12)	8
0.875 Si1 + 0.125 Ge1	.231(3)	¼	.360(3)	4
0.875 Si2 + 0.125 Ge2	.041(7)	¼	.916(7)	4
0.875 Si3 + 0.125 Ge3	.147(5)	.929(2)	.508(5)	8
Dy ₅ (Si ₃ Ge)				
Dy1	.3136(13)	.0035(13)	.2537(6)	4
Dy2	.9899(13)	.184(2)	.0994(7)	4
Dy3	.0126(13)	.176(2)	.4056(6)	4
Dy4	.3634(14)	.1741(15)	.8809(7)	4
Dy5	.3385(14)	.1749(14)	.6226(7)	4
0.750 Si1 + 0.250 Ge1	.209(4)	.342(4)	.256(2)	4
0.750 Si2 + 0.250 Ge2	.948(5)	.909(5)	.272(3)	4
0.750 Si3 + 0.250 Ge3	.218(5)	.492(5)	.962(2)	4
0.750 Si4 + 0.250 Ge4	.165(4)	.464(4)	.564(2)	4
Dy ₅ (Si _{2.5} Ge _{1.5})				
Dy1	.283(2)	¼	.001(2)	4
Dy2	.9916(12)	.0979(6)	.1839(14)	8
Dy3	.3697(11)	.8818(5)	.1712(12)	8
0.625 Si1 + 0.375 Ge1	.165(5)	¼	.371(5)	4
0.625 Si2 + 0.375 Ge2	.913(9)	¼	.914(10)	4
0.625 Si3 + 0.375 Ge3	.182(3)	.9486(14)	.484(3)	8
Dy ₅ (Si ₂ Ge ₂)				
Dy1	.286(2)	¼	.002(2)	4
Dy2	.9842(10)	.0976(5)	.1830(12)	8
Dy3	.3764(10)	.8821(4)	.1673(10)	8
0.625 Si1 + 0.375 Ge1	.168(3)	¼	.363(4)	4
0.625 Si2 + 0.375 Ge2	.916(6)	¼	.902(6)	4
0.625 Si3 + 0.375 Ge3	.206(3)	.9516(11)	.475(2)	8

Dy ₅ (SiGe ₃)				
Dy1	.2866(14)	¼	.9962(14)	4
Dy2	.9789(9)	.0977(5)	.1817(10)	8
Dy3	.3781(9)	.8835(4)	.1640(9)	8
0.250 Si1 + 0.750 Ge1	.169(3)	¼	.361(3)	4
0.250 Si2 + 0.750 Ge2	.915(3)	¼	.897(3)	4
0.250 Si3 + 0.750 Ge3	.216(2)	.9533(8)	.474(2)	8
Dy ₅ Ge ₄				
Dy1	.2898(11)	¼	.9993(11)	4
Dy2	.9751(7)	.0999(4)	.1818(9)	8
Dy3	.3783(7)	.8829(4)	.1619(8)	8
Ge1	.171(2)	¼	.356(2)	4
Ge2	.918(2)	¼	.893(2)	4
Ge3	.2202(15)	.9536(7)	.4764(15)	8

In Table 4.1.1 it is evident that even though the volume, positions of the atoms, and the shape of the unit cell remain about the same for the monoclinic Dy₅Si₃Ge phase compared to the orthorhombic Dy₅Si₄ and Dy₅Ge₄ structures to one of the angles of the unit cell is 93°, compared to 90° for the other structure.

Figure 4.1.9 Lattice parameters vs composition change in the as cast Dy₅(Si_xGe_{1-x})₄ system

Figure 4.1.10 Unit cell volume vs composition change in the as cast Dy₅(Si_xGe_{1-x})₄ system

The phase relations of the Dy₅(Si_xGe_{1-x})₄ pseudobinary system were established from 11 arc-melted compositions. The lattice parameters and the unit cell volume as a function of Si concentration are shown in Figures 4.1.9 and 4.1.10, respectively. It is seen that the orthorhombic crystal structures have the ranges between $0 \leq x \leq 0.622$ and $0.822 \leq x \leq 1$. The lattice parameters change more rapidly when concentration of Si lies in the interval $0.622 \leq x \leq 0.822$, where alloys with the monoclinic crystal structure form. The exact values of compositions of Dy₅(Si_xGe_{1-x})₄ at which the crystal structure change from orthorhombic to monoclinic and back to orthorhombic were not determined due to the difficulty of preparing pure phases of these alloys. During arc-melting vaporization of Dy-metal was observed, which shift the designed stoichiometry of the alloy.

The dependencies of lattice parameters and volume unit cell change with composition follow a linear behavior, except for the transition from orthorhombic (I) to monoclinic, and monoclinic to orthorhombic (II) crystal structures. At these phase boundaries the biggest change in the unit cell occurs along the axis *a*. From Figure 4.1.10 we can see, that the

overall unit cell volume is increased by $\sim 4.1\%$ with a composition change from $x=1$ (Dy_5Si_4) to $x=0$ (Dy_5Ge_4).

The positions of the atoms in the unit cell of the Dy_5Si_4 , $\text{Dy}_5\text{Si}_3\text{Ge}$, and Dy_5Ge_4 structure are shown in Table 4.1.3. Three independent atomic coordinates were found for Dy (Dy1, Dy2, Dy3), and 3 were found for Si – Ge (Si-Ge1, Si-Ge2, Si-Ge3) for these alloys with the orthorhombic crystal structure. When the monoclinic system occurs each of the three 8-fold sites from the parent orthorhombic structure are split into pairs of independent 4-fold sites with the first 4-fold site maintaining the same positional parameters as in parent orthorhombic structure. For Dy it means that 8Dy2 and 8Dy3 were split into 4Dy2_a, and 4Dy2_b, 4Dy3_a and 4Dy3_b (The meaning of the symbols are presented in Table 4.1.3). The Si – Ge atoms change from 8Si-Ge3 to 4Si-Ge3_a and 4Si-Ge3_b. The abbreviations *x, *y, *z are presented in Table 4.1.3 as atomic coordinates for $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys with the monoclinic crystal structure. It helped to express the differences, which were mention above. The symbols *y $\rightarrow$ *z and *z $\rightarrow$ *y in Table 4.1.3 represent the switch of the y axis to the z axis and the z axis to the y axis when we calculated positions of the atoms in the unit cell for the alloys with monoclinic crystal structure.

Table 4.1.3 Positions of the atoms in the unit cell of compounds Dy₅Si₄, Dy₅Si₃Ge, and Dy₅Ge₄ as cast alloys

Atom	Coordinates			Dy ₅ Si ₄			Dy ₅ Si ₃ Ge*			Dy ₅ Ge ₄		
	x(*x)	y(*y→*z)	z(*z→*y)	x	y	z	*x	*y	*z	x	y	z
Dy1	x	y	z	.3424	¼	.0137	.3136	.0035	.2537	.2898	¼	.9993
Dy1	1-x	½+y (1-y)	1-z	.6576	¾	.8863	.6864	.9965	.7463	.7102	¾	.0007
Dy1	½+x	y	½-z	.8424	¼	.4863	.8136	.4965	.2537	.2102	¾	.5007
Dy1	½-x	½+y (1-y)	½+z	.1576	¾	.5137	.1864	.5035	.7463	.7898	¼	.4993
Dy2 _a	x	y	z	.0278	.0984	.1747	.9899	.184	.0994	.9751	.0999	.1818
Dy2 _a	x (x-½)	½-y (y)	z (½-z)	.0278	.4016	.1747	.4899	.316	.0994	.9751	.4001	.1818
Dy2 _a	½+x (½-x)	½-y (1-y)	½-z (½+z)	.5278	.4016	.3253	.6101	.684	.9006	.4751	.4001	.3182
Dy2 _a	½+x (1-x)	y (1-y)	½-z (1-z)	.5278	.0984	.3253	.0101	.816	.9006	.4751	.0999	.3182
Dy2 _b	½-x (x)	½+y (y)	½+z (z)	.4722	.5984	.6747	.0126	.176	.4056	.5249	.5999	.6818
Dy2 _b	½-x (½+x)	1-y (y)	½+z (½-z)	.4722	.9016	.6747	.5126	.324	.4056	.5249	.9001	.6818
Dy2 _b	1-x (½-x)	1-y	1-z (½+z)	.9722	.9016	.8253	.4874	.676	.5944	.0249	.9001	.8182
Dy2 _b	1-x	½+y (1-y)	1-z	.9722	.5984	.8253	.9874	.824	.5944	.0249	.5999	.8182
Dy3 _a	x	y	z	.3225	.8784	.1897	.3634	.1741	.8809	.3783	.6171	.1619
Dy3 _a	x (½+x)	½+y (y)	z (½-z)	.3225	.6216	.1897	.8634	.3259	.8809	.3783	.8829	.1619
Dy3 _a	½+x (½-x)	½+y (1-y)	½-z (½+z)	.8225	.6216	.3103	.1366	.6741	.1191	.8783	.6171	.3381
Dy3 _a	½+x (1-x)	y (1-y)	½-z (1-z)	.8225	.8784	.3103	.6366	.8259	.1191	.8783	.8829	.3381
Dy3 _b	½-x (x)	y-½ (y)	½+z (z)	.1775	.3784	.6897	.3385	.1749	.6226	.1217	.3829	.6619
Dy3 _b	½-x (½+x)	1-y (y)	½+z (½-z)	.1775	.1216	.6897	.8385	.3251	.6226	.1217	.1171	.6619
Dy3 _b	1-x (½-x)	1-y	1-z (½+z)	.6775	.1216	.8103	.1615	.6749	.3774	.6217	.1171	.8381
Dy3 _b	1-x	y-½ (1-y)	1-z	.6775	.3784	.8103	.6615	.8251	.3774	.6217	.3829	.8381
Si-Ge1	x (½+x)	y	½-z	.723	¼	.136	.709	.158	.256	.671	¼	.144
Si-Ge1	½+x (x)	y	z	.223	¼	.364	.209	.342	.256	.171	¼	.356
Si-Ge1	1-x	½+y (1-y)	1-z	.777	¾	.636	.791	.658	.744	.829	¾	.644
Si-Ge1	½-x	½+y (1-y)	½+z	.277	¾	.864	.291	.842	.744	.329	¾	.856
Si-Ge2	1-x	½+y (1-y)	1-z	.061	¾	.071	.052	.091	.728	.082	¾	.107
Si-Ge2	½-x	½+y (1-y)	z-½	.561	¾	.429	.552	.409	.728	.582	¾	.393
Si-Ge2	x-½	y	½-z	.439	¼	.571	.448	.591	.272	.418	¼	.607
Si-Ge2	x	y	z	.939	¼	.929	.948	.909	.272	.918	¼	.893
Si-Ge3 _a	½+x	½-y (y)	½-z	.643	.541	.992	.718	.008	.962	.7202	.9536	.0136
Si-Ge3 _a	½+x (x)	y	½-z (z)	.643	.959	.992	.218	.492	.962	.7202	.5464	.0136
Si-Ge3 _a	x (1-x)	y (1-y)	z (1-z)	.143	.959	.508	.782	.508	.038	.2202	.5464	.4764
Si-Ge3 _a	x (½-x)	½-y (1-y)	z (½+z)	.143	.541	.508	.282	.992	.038	.2202	.9536	.4764
Si-Ge3 _b	1-x (½+x)	1-y (y)	1-z (½-z)	.857	.041	.492	.665	.036	.564	.7798	.0464	.5236
Si-Ge3 _b	1-x (x)	y-½ (y)	1-z (z)	.857	.459	.492	.165	.464	.564	.7798	.4546	.5236
Si-Ge3 _b	½-x (1-x)	y-½ (1-y)	z-½ (1-z)	.357	.459	.008	.835	.536	.436	.2798	.4546	.9864
Si-Ge3 _b	½-x	1-y	z-½ (½+z)	.357	.041	.008	.335	.964	.436	.2798	.0464	.9864

The projections of the crystal structures of Dy_5Si_4 , $\text{Dy}_5\text{Si}_3\text{Ge}$, and Dy_5Ge_4 along the c – axes are shown in Figures 4.1.11, 4.1.12, and 4.1.13, respectively. There are total of 36 atoms in the unit cell. The Si (Ge) atoms are shown as solid circles and the Dy atoms are drawn as open circles. The size of the circles varies with the value of z ($0 \leq z \leq 1$). The larger circles have a larger value of the z coordinate. In Figure 4.1.12 a small distortion of $\sim 3^\circ$ of the unit cell is observed. A large shift along crystallographic axis (especially along axis x) is observed when comparing Dy_5Si_4 to Dy_5Ge_4 .

Figure 4.1.11 The z -axis projection of the crystal structure of Dy_5Si_4

Figure 4.1.12 The z-axis projection of the crystal structure of $\text{Dy}_5\text{Si}_3\text{Ge}$

Figure 4.1.13 The z-axis projection of the crystal structure of Dy_5Ge_4

4.2 Magnetic Properties

4.2.1 *dc* magnetic susceptibility measurements

The *dc* magnetic susceptibility have been measured for nine $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys. These data allowed us to determine an approximate temperatures of the magnetic phase transition for each alloy. The paramagnetic Curie temperature (θ_p) can be estimated from the intercept for $1/\chi = 0$ from a Curie-Weiss plot of $1/\chi$ vs T in different *dc* magnetic fields. Based on the calculated paramagnetic Curie temperatures the magnetic phase transition region can be investigated in detail using other techniques.

The inverse *dc* magnetic susceptibility vs temperature of the alloys with the Gd_5Si_4 -type orthorhombic crystal structure in 10, 20, 30, 40, and 50kOe *dc* magnetic fields are shown in Figure 4.2.1 and Figure 4.2.2. Based on these two data sets the paramagnetic Curie temperatures for the Dy_5Si_4 and $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ were calculated and found equal to $\theta_p \cong 130$ K

Figure 4.2.1 The inverse *dc* magnetic susceptibility vs temperature for Dy_5Si_4 as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.2 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

and $\theta_p \cong 125$ K, respectively. Therefore, the paramagnetic Curie temperature is decreased with an increasing amount of Ge.

The inverse *dc* magnetic susceptibility vs temperature of the alloys with the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type monoclinic crystal structure in 10, 20, 30, 40, and 50kOe *dc* magnetic fields are shown in Figures 4.2.3, 4.2.4, and 4.2.5. Based on these three sets of data the paramagnetic Curie temperatures for the $\text{Dy}_5\text{Si}_3\text{Ge}$, $\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$, and $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$ alloys were calculated and found equal to $\theta_p \cong 65$ K, $\theta_p \cong 62$ K, and $\theta_p \cong 58$ K, respectively.

The inverse *dc* magnetic susceptibility vs temperature of the alloys with Sm_5Ge_4 -type orthorhombic crystal structure in 10, 20, 30, 40, and 50kOe *dc* magnetic fields are shown in Figures 4.2.6, 4.2.7, 4.2.8, and 4.2.9. Using an interpolation technique for the data presented on these graphs, the paramagnetic Curie temperatures for the $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$, $\text{Dy}_5\text{Si}_2\text{Ge}_2$, Dy_5SiGe_3 , and Dy_5Ge_4 alloys were calculated and found equal to $\theta_p \cong 55$ K, $\theta_p \cong 45$ K, $\theta_p \cong 40$ K, and $\theta_p \cong 35$ K, respectively.

Figure 4.2.3 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_3\text{Ge}$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.4 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.5 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.6 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.7 The inverse *dc* magnetic susceptibility vs temperature for $\text{Dy}_5\text{Si}_2\text{Ge}_2$ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.8 The inverse *dc* magnetic susceptibility vs temperature for Dy_5SiGe_3 as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

Figure 4.2.9 The inverse *dc* magnetic susceptibility vs temperature for Dy₅Ge₄ as cast alloy in 10, 20, 30, 40, and 50kOe *dc* magnetic fields

The *dc* magnetic susceptibility for all measured alloys obey linear behavior in the PM region (i.e. for the temperatures above the temperature of magnetic phase transition). The paramagnetic Curie temperatures (θ_p) for the Dy₅Si₄, Dy₅Si_{3.5}Ge_{0.5}, Dy₅Si₃Ge, Dy₅Si_{2.9}Ge_{1.1}, Dy₅Si_{2.7}Ge_{1.3}, Dy₅Si_{2.5}Ge_{1.5}, Dy₅Si₂Ge₂, Dy₅SiGe₃, Dy₅Ge₄ alloys are presented in the Table 4.2.1. The anomalies at low temperature for the Dy₅Si₂Ge₂, Dy₅SiGe₃, and Dy₅Ge₄ suggests that a FerriM or an AFM structure occurs in these magnetic materials.

Table 4.2.1 The paramagnetic Curie temperature of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys

Compound	Our result (θ_p)	Literature data (θ_p) [19]
Dy_5Si_4	130K	133K
$\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$	125K	—
$\text{Dy}_5\text{Si}_3\text{Ge}$	65K	—
$\text{Dy}_5\text{Si}_{2.9}\text{Ge}_{1.1}$	62K	—
$\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$	58K	—
$\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$	55K	—
$\text{Dy}_5\text{Si}_2\text{Ge}_2$	45K	—
Dy_5SiGe_3	40K	—
Dy_5Ge_4	35K	43K

4.2.2 *ac* susceptibility measurements

The 2Oe *ac* field, 125Hz frequency real and imaginary components of the susceptibility vs temperature dependencies in 0kOe applied *dc* magnetic field for Dy₅Si₄ alloy, which form the Gd₅Si₄ orthorhombic structure, are shown in Figure 4.2.10. The sample was demagnetized each time at the beginning of *ac* susceptibility measurements. The data were collected under heating and cooling conditions. The temperature range was varied from ~5K to ~325K. The thermocycling allowed us better understand the physical properties below magnetic phase transition temperature of the alloy. Plots with large and open symbols represent on the graph measurements with decreasing temperature. Plots with small and solid symbols represent the measurements with increasing temperature. As seen there is no change in χ'_{ac} and χ''_{ac} data upon cooling and heating the sample during measurements. The *ac* susceptibility maximum peaks were observed in the region of magnetic phase transformation for Dy₅Si₄ alloy. The temperature of the maxima was determined as 137K.

The 2Oe *ac* field, 125Hz frequency real and imaginary susceptibility vs temperature dependencies in an 1kOe applied *dc* magnetic field for Dy₅Si₄ alloy are shown in Figure 4.2.11. The sample was demagnetized each time at the beginning of *ac* susceptibility measurements. The data were collected under heating and cooling conditions. The temperature range was varied from ~5K to ~325K. The thermocycling did not effect the magnetic properties of the sample. Plots with large and open symbols represent the measurements with decreasing temperature. Plots with small and solid symbols represent the measurements with increasing temperature. The *ac* susceptibility maximum peaks were observed in the region of magnetic phase transition for this alloy.

A comparison of the real and imaginary components of the 2Oe *ac* field with 125Hz frequency *ac* susceptibility 0kOe and 1kOe applied *dc* magnetic fields is shown in Figure 4.2.12. The maxima of the real and imaginary components of the *ac* susceptibility in the 1kOe *dc* magnetic field is shifted to lower temperatures and have a smaller value then in the 0kOe *dc* magnetic field.

Figure 4.2.10 Real and imaginary components of *ac* susceptibility in 0kOe *dc* field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy_5Si_4

Figure 4.2.11 Real and imaginary components of *ac* susceptibility in 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy_5Si_4

Figure 4.2.12 Comparison of *ac* susceptibility in 0kOe and 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy₅Si₄

The 20e *ac* field at 125Hz frequency real and imaginary susceptibility vs temperature dependencies in a 0kOe applied *dc* magnetic field for Dy₅Si_{3.5}Ge_{0.5} alloy, which has the orthorhombic Gd₅Si₄-type structure, are shown in Figure 4.2.13. The sample was demagnetized each time at the beginning of *ac* susceptibility measurements. The data were collected in the temperature interval from ~5K to ~200K under heating. The shape of the curves in Figure 4.2.13 are similar to the shape of *ac* susceptibility vs temperature plots for Dy₅Si₄ alloy, but the relative values of the χ'_{ac} and χ''_{ac} are more than twice as small. The maximum peak, 133K, of the real component *ac* susceptibility was observed in the region of magnetic phase transition for this alloy.

The real and imaginary components of the *ac* susceptibility vs temperature for the $\text{Dy}_5\text{Si}_3\text{Ge}$ alloy are shown in Figure 4.2.14. The measurements were performed in a 0kOe applied *dc* magnetic field, using a 20e alternating current field at 125Hz frequency, and under heating and cooling conditions. The sample was demagnetized each time at the beginning of the *ac* susceptibility measurements. Temperature range was varied from ~5K to ~200K. Plots with large and open symbols represent measurements with decreasing temperature, while those with small and solid symbols represent measurements with increasing temperature. Both values of the real and imaginary *ac* susceptibility components of the heating curves are visibly smaller then those taken on the cooling. The real part of *ac* susceptibility during cooling is broadening in the temperature interval from ~57K to ~65K, indicating a small temperature hysteresis. The maximum peak of the real component *ac* susceptibility was determined to the 75K.

Figure 4.2.13 Real and imaginary components of *ac* susceptibility in 0kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$

The 20e *ac* field at 125Hz frequency real and imaginary components of *ac* susceptibility vs temperature dependencies in 1kOe applied *dc* magnetic field for the Dy₅Si₃Ge alloy, which has the monoclinic Gd₅Si₂Ge₂-type structure, are shown in Figure 4.2.15. The sample was demagnetized each time at the beginning of *ac* susceptibility measurements. The data were collected under heating and cooling conditions. The temperature range was varied from ~5K to ~120K. Curves with large and open symbols represent measurements with decreasing temperature. Plots with small and solid symbols represent measurements with increasing temperature. The broadening of the maximum with increasing magnetic field from 0kOe to 1kOe was observed for the Dy₅Si₃Ge alloy. Therefore, the value of the temperature hysteresis increases with the application of magnetic field.

Figure 4.2.14 Real and imaginary components of *ac* susceptibility in 0kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy₅Si₃Ge

Figure 4.2.15 Real and imaginary components of *ac* susceptibility in 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy₅Si₃Ge

A comparison of the real and imaginary *ac* susceptibility vs temperature dependencies in 0kOe and 1kOe *dc* magnetic fields during heating for the Dy₅Si₃Ge alloy is shown in Figure 4.2.16. The measurements were done in 20e *ac* field with frequency 125Hz. The application of magnetic field significantly decreases the value of the maximum for both the real and imaginary components of *ac* susceptibility (see Figure 4.2.16).

Figure 4.2.16 Comparison of *ac* susceptibility in 0kOe and 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy₅Si₃Ge

Comparison of the real component *ac* susceptibility vs temperature in 20e and 50e *ac* fields at 125Hz frequency for Dy₅Si₃Ge alloy are shown in Figure 4.2.17. An increase of the *ac* field provides an increase of the real part of the *ac* susceptibility, by ~2.5 times. However, the broadening and shifting of the maximum was not observed with the increase of the *ac* field.

The real and imaginary parts of *ac* susceptibilities vs temperature dependencies for Dy₅Si_{2.5}Ge_{1.5}, Dy₅Si₂Ge₂, and Dy₅SiGe₃ alloys with the Sm₅Ge₄-type orthorhombic crystal structure are shown in Figure 4.2.18, Figure 4.2.19, and Figure 4.2.20, respectively. The measurements were done in a 0kOe applied *dc* magnetic field, 20e *ac* field with frequency 125Hz, upon heating from ~5K to ~120K. The specimens were demagnetized each time at the beginning of *ac* susceptibility measurements. The relative values of *ac* susceptibility for the germanium-rich compounds are much smaller than for the silicon-rich compounds and alloys with monoclinic crystal structure. The relative *ac* susceptibility value gradually decreases with increasing amount of Ge in the alloys.

Figure 4.2.17 Comparison of *ac* susceptibility in 20e and 50e *ac* field at 125Hz frequency, 0kOe *dc* field during heating and cooling for Dy₅Si₃Ge

Figure 4.2.18 Real and imaginary component of *ac* susceptibility in 0kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating for $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$

Figure 4.2.19 Real and imaginary component of *ac* susceptibility in 0kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating for $\text{Dy}_5\text{Si}_2\text{Ge}_2$

Figure 4.2.20 Real and imaginary component of *ac* susceptibility in 0kOe *dc* magnetic field, 2Oe *ac* field at 125Hz frequency during heating for Dy₅SiGe₃

The real and imaginary components of *ac* susceptibility for Dy₅Ge₄ in a 2Oe *ac* field with frequency 125Hz under heating and cooling conditions in 0kOe and 1kOe applied *dc* magnetic fields are shown in Figures 4.2.21 and 4.2.22 respectively. The sample were demagnetized each time at the beginning of *ac* susceptibility measurements. It was found from the collected data that the behavior of this alloy does not depend on thermocycling (i.e. heating or cooling). The temperature range of the measurements varied from ~5K to ~100K. Curves with the large and open symbols represent measurements taken with decreasing of temperature, while the small and solid symbols were measured on heating.

A comparison of the real and imaginary components of the *ac* susceptibility vs temperature of Dy₅Ge₄ alloy in 0kOe and 1kOe applied *dc* magnetic fields is shown in Figure 4.2.23. The real part of *ac* susceptibility in 1 kOe applied *dc* magnetic field is more than three times smaller then the real part of *ac* susceptibility in 0kOe *dc* magnetic field. The imaginary

part of ac susceptibility in both dc magnetic fields almost lie on a perfect straight line with values close to zero and have essentially the same value in the temperature interval from 5K to 100K.

Based on the information presented in Figures 4.2.10 to 4.2.23 we make the following conclusions; that (1) the temperature hysteresis in 0kOe and 1kOe applied dc magnetic fields was observed only in alloys with monoclinic crystal structure. The small temperature hysteresis in Dy_5Si_3Ge under a 0kOe applied dc magnetic field is increased with application of a 1kOe dc magnetic field. (2) The silicides and germanides do not showed any signs of temperature a hysteresis. (3) The compounds with the monoclinic crystal structure become non-collinear magnetic materials below magnetic phase transition temperature. The applied dc field has tendency to freeze the magnetic moments in the samples with monoclinic crystal structure, such as Dy_5Si_3Ge .

Figure 4.2.21 Real and imaginary components of ac susceptibility in 0kOe dc magnetic field, 20e ac field at 125Hz frequency during heating and cooling for Dy_5Ge_4

Figure 4.2.22 Real and imaginary components of *ac* susceptibility in 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy_5Ge_4

Figure 4.2.23 Comparison of *ac* susceptibility in 0kOe and 1kOe *dc* magnetic field, 20e *ac* field at 125Hz frequency during heating and cooling for Dy_5Ge_4

4.2.3 Magnetization vs temperature measurements

The magnetization vs temperature dependencies for the alloys Dy_5Ge_4 , $\text{Dy}_5\text{Si}_3\text{Ge}$, and Dy_5Si_4 are shown in Figure 4.2.24. Measurements were performed under an applied magnetic field of 1 kOe during heating and cooling. Curves with large and open symbols were taken on cooling, and those with small and solid symbols on heating.

The Dy_5Ge_4 and Dy_5Si_4 magnetization vs temperature curves do not exhibit a temperature hysteresis. The magnetization vs temperature curves for the Dy_5Si_4 alloy show typical ferromagnetic behavior. The type of magnetic phase transition of Dy_5Ge_4 does not appear to be obvious, but it is clearly not FM. Referring to the literature data, this alloy was reported to have an AFM structure below critical temperature. The positive value of paramagnetic Curie point and the shape of the *ac* susceptibility no temperature curves do not support the statement that it is an AFM transition. At the same time, the value of magnetization is small and linear relationship of magnetic moment vs magnetic field exists at 5K. More in-depth investigations need to make for the germanides using other magnetic measurement techniques. For now, we can only state that this structure appears to have non-collinear spin interactions. It is difficult, if not impossible, to determine exact magnetic structures of these compounds without neutron diffraction measurements.

Due to the freezing of the magnetic moments with the application of a *dc* magnetic field a significant effect was observed in the magnetization vs temperature during heating and cooling of the $\text{Dy}_5\text{Si}_3\text{Ge}$ alloy (see Figure 4.2.24). This and the *ac* susceptibility data for this compound suggest that the ordering may be FM with some coercivity below magnetic phase transition. Such behavior probably occurs as a result of the pinning of domain walls motion by lattice defects.

Figure 4.2.24 The magnetization vs temperature for Dy_5Ge_4 (orthorhombic-I), $\text{Dy}_5\text{Si}_3\text{Ge}$ (monoclinic), and Dy_5Si_4 (orthorhombic-II) alloys in 1kOe applied *dc* magnetic field

For these measurements all samples were cooled down to 5K in zero *dc* field, and when 5K was reached the 1kOe *dc* field was turned on. Therefore, the samples were demagnetized before each measurements.

4.2.4 Magnetization vs *dc* magnetic field measurements

The dependencies of magnetization vs *dc* magnetic field for the alloys Dy_5Si_4 and $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ with the Gd_5Si_4 -type orthorhombic crystal structure are shown in Figure 4.2.25 and Figure 4.2.26, respectively. The magnetization for these alloys has almost reached saturation at the low temperatures ($\sim 5\text{K}$) and in high magnetic fields ($\sim 56\text{kOe}$). It still can increase and reach bigger value. The difference between the measured maximum value at 56kOe and the saturation magnetization is much smaller in Dy_5Si_4 than in germanium-rich alloys and alloys with the monoclinic crystal structure. The curves exhibit a linear behavior at temperatures above magnetic phase transition, i.e. in the PM region.

The *dc* magnetization vs the *dc* magnetic field curves for the $\text{Dy}_5\text{Si}_3\text{Ge}$ alloy with the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type monoclinic crystal structure are shown in Figure 4.2.27. The curves exhibit a linear behavior in the PM region.

Figure 4.2.25 Magnetization vs *dc* magnetic field dependencies for Dy_5Si_4

Figure 4.2.26 Magnetization vs *dc* magnetic field dependencies for $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$

Figure 4.2.27 Magnetization vs *dc* magnetic field dependencies for $\text{Dy}_5\text{Si}_3\text{Ge}$

Figure 4.2.28 Magnetization vs *dc* magnetic field dependencies for $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$

The magnetization curves vs *dc* magnetic field for $\text{Dy}_5\text{Si}_{2.7}\text{Ge}_{1.3}$, $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$, $\text{Dy}_5\text{Si}_2\text{Ge}_2$, Dy_5SiGe_3 , and Dy_5Ge_4 which have Sm_5Ge_4 -type orthorhombic crystal structure, are presented in Figures 4.2.28, 4.2.29, 4.2.30, 4.2.31, and 4.2.32, respectively. In all of these graphs, above magnetic phase transition temperature (i.e. in PM region) the magnetization shows a linear behavior. It is also seen that the magnetization is far from saturation at 56kOe at low temperatures.

The magnetization vs magnetic field data also allow one to calculate the magnetic entropy change (magnetocaloric effect) for these alloys.

Figure 4.2.29 Magnetization vs *dc* magnetic field dependencies for $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$

Figure 4.2.30 Magnetization vs *dc* magnetic field dependencies for $\text{Dy}_5\text{Si}_2\text{Ge}_2$

Figure 4.2.31 Magnetization vs *dc* magnetic field dependencies for Dy_5SiGe_3

Figure 4.2.32 Magnetization vs *dc* magnetic field dependencies for Dy_5Ge_4

It is characteristic for all of the compounds of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ series to exhibit metamagnetic transitions at $\sim 5\text{K}$. In Figures 4.2.25 – 4.2.32 it is obvious to see several “step-like” transitions with the application of external magnetic field at low temperatures for the first time, i.e. after the sample have been zero field cooled to 5K. Furthermore, hysteresis was observed in the magnetization vs magnetic field curves in all of the compounds of low temperature. The maximum hysteresis was measured in $\text{Dy}_5\text{Si}_3\text{Ge}$ with the monoclinic crystal structure.

The magnetization curves vs temperature and the values of critical fields for 7 alloys at 5K are shown in Figure 4.2.33 and Table 4.2.2. The critical fields (H_{cr}) of the metamagnetic transitions are very distinct. An increase in the number of critical fields and a decrease in value of magnetization with an increase in the germanium content in the alloy are evident. The value of first critical field also strongly depends upon the composition. For example, $H_{cr}(\text{Dy}_5\text{Si}_4) \approx 4\text{kOe}$ and $H_{cr}(\text{Dy}_5\text{Si}_2\text{Ge}_2) \approx 20\text{kOe}$. The “step like” transitions, in our opinion, are transformations of a non-collinear magnetic structures, which occur by

Figure 4.2.33 First magnetization vs *dc* magnetic field measurements at $\sim 5\text{K}$ after PM state of $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys

exchange interactions with positive and negative values and magnetocrystalline anisotropy. More experiments have to be done to finalize our conclusions about this phenomenon.

Table 4.2.2 The estimated critical fields at 5K of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys

alloy	Dy_5Ge_4	Dy_5SiGe_3	$\text{Dy}_5\text{Si}_2\text{Ge}_2$	$\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$	$\text{Dy}_5\text{Si}_3\text{Ge}$	$\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$	Dy_5Si_4
1	25kOe	25kOe	21kOe	9kOe	7kOe	7kOe	5kOe
2			25kOe	17kOe	11kOe	11kOe	7kOe
3			29kOe	23kOe			
4				29kOe			

4.2.5 Magnetic entropy change calculations

The magnetic entropy change ($-\Delta S_m$) as a function of temperature for the Dy_5Si_4 and $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ with Gd_5Si_4 -type orthorhombic crystal structure for the changes in magnetic field of $\Delta H = 10, 20, 30, 40$, and 50kOe are shown in Figure 4.2.34 and Figure 4.2.35. The magnetic entropy change was calculated from the magnetization vs temperature data presented in Figures 4.2.25 and 4.2.26. The maximum values of $-\Delta S_m$ for the Dy_5Si_4 alloy

were determined at $T \cong 141\text{K}$ and found equal to: $-\Delta S_m(\Delta H = 10\text{kOe}) \cong 3.7 \text{ J/kg} \cdot \text{K}$,

$-\Delta S_m(\Delta H = 20\text{kOe}) \cong 6.4 \text{ J/kg} \cdot \text{K}$, $-\Delta S_m(\Delta H = 30\text{kOe}) \cong 8.7 \text{ J/kg} \cdot \text{K}$,

$-\Delta S_m(\Delta H = 40\text{kOe}) \cong 10.8 \text{ J/kg} \cdot \text{K}$, $-\Delta S_m(\Delta H = 50\text{kOe}) \cong 12.6 \text{ J/kg} \cdot \text{K}$. The maximum

values of $-\Delta S_m$ for the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy were determined at $T \cong 136\text{K}$ and found equal

to: $-\Delta S_m(\Delta H = 10\text{kOe}) \cong 3 \text{ J/kg} \cdot \text{K}$, $-\Delta S_m(\Delta H = 20\text{kOe}) \cong 5.6 \text{ J/kg} \cdot \text{K}$,

$-\Delta S_m(\Delta H = 30\text{kOe}) \cong 7.7 \text{ J/kg} \cdot \text{K}$, $-\Delta S_m(\Delta H = 40\text{kOe}) \cong 9.6 \text{ J/kg} \cdot \text{K}$,

$-\Delta S_m(\Delta H = 50\text{kOe}) \cong 11.3 \text{ J/kg} \cdot \text{K}$.

Figure 4.2.34 The magnetic entropy change vs temperature of Dy_5Si_4 calculated from magnetization data for various magnetic field changes

Figure 4.2.35 The magnetic entropy change vs temperature of $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ calculated from magnetization data for various magnetic field changes

Figure 4.2.36 The magnetic entropy change vs temperature of Dy₅Si₃Ge calculated from magnetization data for various magnetic field changes

The typical caret-like shape of magnetic entropy change for the Dy₅Si₄ alloy confirms that the magnetic structure of this alloy is FM below ~141K. Two other prepared alloys [Dy₅Si_{3.5}Ge_{0.5} and Dy₅Si_{3.3}Ge_{0.7}], which belong to this phase region show a similar magnetic entropy change behavior.

The magnetic entropy change as a function of temperature for the Dy₅Si₃Ge alloy with the monoclinic crystal structure for the changes in magnetic field of $\Delta H = 10, 20, 30, 40,$ and 50kOe are shown in Figure 4.2.36. It was calculated from the data presented in Figure 4.2.27. The maximum values of $-\Delta S_m$ for the Dy₅Si₃Ge alloy were determined at

$T \cong 65\text{K}$ and found equal to: $-\Delta S_m (\Delta H = 10\text{kOe}) \cong 10.7 \text{ J/kg} \cdot \text{K}$,

$$\begin{aligned}
-\Delta S_m(\Delta H = 20kOe) &\cong 26 \text{ J/kg} \cdot K, \quad -\Delta S_m(\Delta H = 30kOe) \cong 31.5 \text{ J/kg} \cdot K, \\
-\Delta S_m(\Delta H = 40kOe) &\cong 34.3 \text{ J/kg} \cdot K, \quad -\Delta S_m(\Delta H = 50kOe) \cong 36.4 \text{ J/kg} \cdot K.
\end{aligned}$$

The alloys, which belong to the monoclinic phase region apparently undergo a first order phase transition similar to what is observed in corresponding $Gd_5(Si_xGe_{1-x})_4$ monoclinic phase. This first order phase transition brings about a quite narrow but much larger MCE compared to that of the second order phase transition in Dy_5Si_4 . It is seen in Figure 4.2.35 for the Dy_5Si_3Ge composition that the $-\Delta S_m$ peak value exceeds that of Dy_5Si_4 by $\sim 300\%$, which justifies its classification as a giant magnetocaloric effect. It is difficult to determine whether the mechanism of the giant magnetocaloric effect in Dy_5Si_3Ge is similar to or different from that observed in the $Gd_5Si_2Ge_2$ material. More studies, including low-temperature crystallography, are required to verify if magnetic ordering here is accompanied by a change of the material's crystal structure.

The magnetic entropy change as a function of temperature for the $Dy_5Si_{2.5}Ge_{1.5}$, $Dy_5Si_2Ge_2$, Dy_5SiGe_3 , and Dy_5Ge_4 alloys with the orthorhombic Sm_5Ge_4 -type crystal structure for the changes in magnetic field of $\Delta H = 10, 20, 30, 40$, and $50kOe$ are shown in Figures 4.2.37, 4.2.38, 4.2.39, and 4.2.40, respectively. The $-\Delta S_m$ values were calculated from the data presented in Figures 4.2.29, 4.2.30, 4.2.31, and 4.2.32.

A negative maximum of $-\Delta S_m = -0.14 \text{ J/kg} \cdot K$ for the $Dy_5Si_{2.5}Ge_{1.5}$ alloy (Figure 4.2.37) was found at $T \cong 51K$ in $\Delta H = 10kOe$, which then broadens, increases in magnitude towards positive value, and shifts towards lower temperature for a larger magnetic field change. The positive maximum values of $-\Delta S_m$ for the $Dy_5Si_{2.5}Ge_{1.5}$ alloy were determined at $T \cong 59K$ and found equal to: $-\Delta S_m(\Delta H = 10kOe) \cong 0.6 \text{ J/kg} \cdot K$,

$$\begin{aligned}
-\Delta S_m(\Delta H = 20kOe) &\cong 1.9 \text{ J/kg} \cdot K, \quad -\Delta S_m(\Delta H = 30kOe) \cong 3.5 \text{ J/kg} \cdot K, \\
-\Delta S_m(\Delta H = 40kOe) &\cong 5.3 \text{ J/kg} \cdot K, \quad -\Delta S_m(\Delta H = 50kOe) \cong 7.1 \text{ J/kg} \cdot K.
\end{aligned}$$

A negative maximum of $-\Delta S_m = -0.73 \text{ J/kg} \cdot \text{K}$ for the $\text{Dy}_5\text{Si}_2\text{Ge}_2$ alloy (Figure 4.2.38) was found at $T \cong 51\text{K}$ in $\Delta H = 10\text{kOe}$, which then broadens, increases in magnitude (i.e. becomes more negative) at $\Delta H = 20\text{kOe}$, and for larger magnetic field changes shifts towards lower temperature. The positive maximum values of $-\Delta S_m$ for the $\text{Dy}_5\text{Si}_2\text{Ge}_2$ alloy were observed at $T \cong 56\text{K}$ and found equal to: $-\Delta S_m(\Delta H = 10\text{kOe}) \cong 0.5 \text{ J/kg} \cdot \text{K}$,

$$-\Delta S_m(\Delta H = 20\text{kOe}) \cong 1.7 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 30\text{kOe}) \cong 3.5 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 40\text{kOe}) \cong 5.5 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 50\text{kOe}) \cong 7.4 \text{ J/kg} \cdot \text{K}.$$

The negative maximum of $-\Delta S_m = -0.56 \text{ J/kg} \cdot \text{K}$ for the Dy_5SiGe_3 alloy (Figure 4.2.39) was found at $T \cong 47\text{K}$ in $\Delta H = 10\text{kOe}$, which then broadens, become more negative, and shifts towards lower temperatures for larger magnetic field changes. The positive maximum values of $-\Delta S_m$ for the Dy_5SiGe_3 alloy were observed at $T \cong 52\text{K}$ and found

$$\text{equal to: } -\Delta S_m(\Delta H = 10\text{kOe}) \cong 0.4 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 20\text{kOe}) \cong 1.4 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 30\text{kOe}) \cong 2.9 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 40\text{kOe}) \cong 4.6 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 50\text{kOe}) \cong 6.4 \text{ J/kg} \cdot \text{K}.$$

The negative maximum of $-\Delta S_m = -0.97 \text{ J/kg} \cdot \text{K}$ for the Dy_5Ge_4 alloy (Figure 4.2.40) were found at $T \cong 45\text{K}$ in $\Delta H = 10\text{kOe}$, which then broadens, become more negative, and shifts towards lower temperatures, for larger magnetic field changes. The positive maximum values of $-\Delta S_m$ for the Dy_5Ge_4 alloy were determined at $T \cong 50\text{K}$ and

$$\text{found equal to: } -\Delta S_m(\Delta H = 10\text{kOe}) \cong 0.3 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 20\text{kOe}) \cong 1.3 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 30\text{kOe}) \cong 2.9 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 40\text{kOe}) \cong 4.9 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 50\text{kOe}) \cong 6.9 \text{ J/kg} \cdot \text{K}.$$

Figure 4.2.37 The magnetic entropy change vs temperature of $\text{Dy}_5\text{Si}_{2.5}\text{Ge}_{1.5}$ calculated from magnetization data for various magnetic field changes

Figure 4.2.38 The magnetic entropy change vs temperature of $\text{Dy}_5\text{Si}_2\text{Ge}_2$ calculated from magnetization data for various magnetic field changes

Figure 4.2.39 The magnetic entropy change vs temperature of Dy_5SiGe_3 calculated from magnetization data for various magnetic field changes

Figure 4.2.40 The magnetic entropy change vs temperature of Dy_5Ge_4 calculated from magnetization data for various magnetic field changes

The alloys from the Dy_5Ge_4 -based solid solution region display an unusual magnetocaloric behavior (see Figures 4.2.37 – 4.2.40). For example, for the Dy_5Ge_4 alloy, at the lowest temperatures, a negative $-\Delta S_m$ peak exist for all magnetic field changes between 0kOe and 50kOe. For the lowest magnetic field change (from 0kOe to 10kOe), a negative $-\Delta S_m$ peak of -1 J/kgK is observed at ~45K, which then broadens, increases in magnitude (i.e. become more negative), and shifts towards lower temperature for larger magnetic field changes. The positive $-\Delta S_m$ peak occurs at ~50K and continuously increases in a magnitude as the magnetic field change rises. Such behavior, i.e. the existence of a negative and a positive MCE peaks, indicates that there is a considerable degree of FerriM or AFM in the magnetic structure of this material. Similar behaviors were reported for some heavy lanthanides and their intermetallic compounds [71-73].

In Figure 4.2.41 we summarized the results of $-\Delta S_m$ for seven different compositions in the Dy_5Si_4 - Dy_5Ge_4 system for magnetic field change from 0 to 50kOe. As seen the MCE behavior is distinctly different for the different phase regions, but it is qualitatively similar for the alloys belonging to the same phase region.

The magnetic phase transition temperature vs Si concentration (solid circles) along with magnetic entropy change at transition temperature vs Si concentration (open circles) are shown in Figure 4.2.42. Similar to the behavior for the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, the Curie temperature gradually decreases in the Dy_5Si_4 -based alloys with the Gd_5Si_4 -type orthorhombic crystal structure, O(II). In Dy_5Ge_4 -based alloys with Sm_5Ge_4 -type orthorhombic crystal structure, O(I), the transition temperature also decreases at a slow rate in relation to composition, which is quite different from behavior in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system [25]. The magnetic properties, e.g. the magnetic entropy change, of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys are different for the alloys from the different crystal structure regions. For the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system the orthorhombic regions have the maximums values of the magnetic entropy change which are smaller than those for the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys. The $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys with monoclinic crystal structure the magnetic entropy change is comparable with those for the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys and the shape of the maximum is similar for both of these systems.

Figure 4.2.41 The magnetic entropy change calculated from magnetization of different alloys from the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system for a magnetic field change from 0kOe to 50kOe

Table 4.2.3 The magnetic phase transition temperature in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system

Compound	Magnetic ordering temperature		Phase region
	from $-\Delta S_m$	from χ_{ac}	
Dy_5Si_4	141K	137K	Dy_5Si_4
$\text{Dy}_5(\text{Si}_{3.5}\text{Ge}_{0.5})$	136K	133K	Dy_5Si_4 -based solid solution
$\text{Dy}_5(\text{Si}_3\text{Ge})$	65K	75K	monoclinic phase
$\text{Dy}_5(\text{Si}_{2.5}\text{Ge}_{1.5})$	51K, 59K	72K	Dy_5Ge_4 -based solid solution
$\text{Dy}_5(\text{Si}_2\text{Ge}_2)$	52K, 56K	56K	Dy_5Ge_4 -based solid solution
$\text{Dy}_5(\text{SiGe}_3)$	47K, 52K	50K	Dy_5Ge_4 -based solid solution
Dy_5Ge_4	45K, 50K	46K	Dy_5Ge_4

Table 4.2.3 lists magnetic ordering temperature determined from the MCE behavior and from the *ac* magnetic susceptibility measurements in 2Oe *ac* field with 125Hz frequency. The two different transition temperatures apparent from the magnetocaloric effect in the Dy₅Ge₄-based solid solution region are indistinguishable from the *ac* magnetic susceptibility data, due to a small temperature differences between them.

Figure 4.2.42 The magnetic phase transition temperature vs Si concentration and magnetic entropy change at critical temperatures diagrams of the Dy₅(Si_xGe_{1-x})₄ alloy estimated from magnetic entropy change

4.3 Caloric Properties

Even though heat capacity were measured on most of the prepared alloys the collected data were accepted as valid for only three of the samples; Dy_5Ge_4 , $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$, Dy_5Si_4 . Reasonable values of $-\Delta S_m$ and ΔT were possible only for the last two samples. The problems in collecting heat capacity data were due to the fact that 1) the samples were very brittle, especially alloys with the Sm_5Ge_4 -type orthorhombic crystal structure and with the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type monoclinic crystal structure. A large number of microcracks were observed in these samples. Typical heat capacity data for the specimens with such imperfections are shown in Figure 4.3.1. Data plotted with small solid circles represents the heat capacity of the sample in a bulk form. Even though the first order magnetic phase transition can be observed, the individual points are quite scattered from the fitted smoothed line (much more than is normally observed for a good quality sample). This phenomenon is

Figure 4.3.1 The heat capacity of the $\text{Dy}_5\text{Si}_3\text{Ge}$ in a form of bulk material (solid small circles) and a compacted mixture of powder of this alloy and Ag (open large circles) from $\sim 3.5\text{K}$ to 350K in zero dc magnetic field

due to the cracks and imperfections found in the sample. The second curve in Figure 4.3.1 shows the heat capacity of a mixture of $\text{Dy}_5\text{Si}_3\text{Ge}$ and pure Ag-metal powders compacted into a tablet under high pressure. However, the first order phase transition, which observed in the bulk alloy shows here as a second order lambda-like peak. Therefore, these samples can not be measured using a mixture of the alloy and Ag powders. 2) A second problem of not having satisfactory quality heat capacity data for the $\text{Dy}_5\text{Si}_4\text{-Dy}_5\text{Ge}_4$ pseudobinary system arises from a large magnetostriction effect observed in these alloys. Even though, direct measurements of magnetostriction were not performed on the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys, indirect signs provide a basis for this conclusion. The first sign of this effect is that the sample broke into several pieces, usually when a strong magnetic field (above 50kOe) was applied on the heat capacity sample. This was typically observed on the Ge-rich alloys. Therefore, when some parts of the alloy fell off the sample holder, the total heat capacity became quite small (see Figure 4.3.2). On the graph the solid small circles represent the heat capacity data for the Dy_5Ge_4 alloy in 0kOe magnetic field and the open large circles show the heat capacity data in a 75kOe magnetic field when there was almost no sample left in the sample holder. As a result, the value of heat capacity on the plot is much smaller over the entire all temperature interval and the magnetic heat capacity at the ordering temperature was not observed.

Another good example of this phenomenon is shown in Figure 4.3.3. The solid small circles represent the heat capacity data for the Dy_5Si_4 alloy in 0kOe magnetic field. The open large circles represent the heat capacity data for the Dy_5Si_4 alloy in a 75kOe magnetic field, when several pieces fell off of the sample holder during the measurements.

Figure 4.3.2 The heat capacity of the Dy_5Ge_4 alloy from $\sim 3.5\text{K}$ to 350K in 0kOe and 75kOe *dc* magnetic fields

Figure 4.3.3 The heat capacity of the Dy_5Si_4 alloy from $\sim 3.5\text{K}$ to 350K in 0kOe and 75kOe *dc* magnetic fields

The heat capacity vs temperature from $\sim 3.5\text{K}$ to $\sim 350\text{K}$ in 0, 20, and 50kOe *dc* magnetic fields of the Dy_5Ge_4 alloy are shown in Figure 4.3.4. The distinct feature of this alloy's heat capacity is the presence of a λ -type anomaly in the 35K-50K temperature region with a shape that corresponding to a second order magnetic phase transition. The decrease of heat capacity peak value with increase the value of magnetic field is another indicator that the transition has second order nature. The heat capacity data points are quite scattered and therefore it was not possible to calculate the magnetic entropy change and adiabatic temperature change.

Figure 4.3.4 The heat capacity of the Dy_5Ge_4 alloy from $\sim 3.5\text{K}$ to 350K in 0, 20, and 50kOe *dc* magnetic fields

The measured heat capacities vs temperature in 0, 20, 50, 75, and 100kOe *dc* magnetic fields of $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ are shown in Figure 4.3.5. The values of the heat capacity maximum decreased at $\sim 132\text{K}$ with application of *dc* magnetic field. The heat capacity maximum completely disappeared when 100kOe *dc* magnetic field was applied. The shape and the behavior of the heat capacity maxima are characteristic of a second order magnetic phase transition. The *dc* magnetic fields shifted the temperature of the heat capacity maximum towards higher temperatures while broadening it, which is characteristic for ferromagnets. Based on these heat capacity measurements the magnetic entropy change and adiabatic temperature change were calculated for the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy. First, the total entropy (S_{total}) as a function of temperature were determined at each of the different magnetic fields including $H = 0\text{ kOe}$. From S_{total} vs T , the magnetic entropy change (ΔS_m vs T) and adiabatic temperature change (ΔT vs T) were evaluated and are presented in Figures 4.3.6 and 4.3.7, respectively. The peaks on both plots occurs at the Curie temperature of this alloy ($\sim 134\text{K}$). The values of ΔS_m are large, but much less than for intermediate alloys with monoclinic crystal structure in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system.

Figure 4.3.5 The heat capacity of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy from $\sim 3.5\text{K}$ to 350K in 0, 20, 50, 75, and 100 kOe *dc* magnetic fields

Figure 4.3.6 Magnetic entropy change of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy from $\sim 3.5\text{K}$ to 350K for *dc* magnetic field changes up to 100 kOe as determined from heat capacity measurements

The maxima of magnetic entropy change for the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy as shown in Figure 4.3.6 have the following values depending on applied magnetic fields:

$$-\Delta S_m(\Delta H = 20\text{kOe}) \cong 3.9 \text{ J/kg} \cdot \text{K}, \quad -\Delta S_m(\Delta H = 50\text{kOe}) \cong 10 \text{ J/kg} \cdot \text{K},$$

$$-\Delta S_m(\Delta H = 75\text{kOe}) \cong 13.5 \text{ J/kg} \cdot \text{K}, \quad \text{and} \quad -\Delta S_m(\Delta H = 100\text{kOe}) \cong 17.4 \text{ J/kg} \cdot \text{K}.$$

The maxima of adiabatic temperature change for the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy as shown in Figure 4.3.7 have the following values depending on applied magnetic fields:

$$\Delta T(\Delta H = 20\text{kOe}) \cong 2.3\text{K}, \quad \Delta T(\Delta H = 50\text{kOe}) \cong 4.9\text{K}, \quad \Delta T(\Delta H = 75\text{kOe}) \cong 6.7\text{K}, \quad \text{and}$$

$$\Delta T(\Delta H = 100\text{kOe}) \cong 8.8\text{K}.$$

It is also important to note that $-\Delta S_m$ and ΔT in the temperature interval from 0K and 50K exhibit a non-monotonic behavior. The origin of this anomaly is not obvious.

Figure 4.3.7 Adiabatic temperature change of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy from 3.5K to 350K for *dc* magnetic field changes of 0-20, 0-50, 0-75, and 0-100kOe as determined from heat capacity measurements

Figure 4.3.8 The heat capacity of the Dy_5Si_4 alloy from $\sim 3.5\text{K}$ to 350K in 0, 20, and 50kOe *dc* magnetic fields

The 0, 20, and 50kOe *dc* magnetic fields heat capacity of the Dy_5Si_4 alloy are shown in Figure 4.3.8. The value and the shape of the heat capacity peak is almost identical to the value and the shape of the heat capacity for $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloy. Both alloys have the Gd_5Si_4 -type orthorhombic crystal structure. The temperature of the heat capacity maximum observed at 137K. It is a second order magnetic phase transition with the characteristic λ -shape curve in vicinity of the Curie temperature. The data are only slightly scattered from the fitted smoothed heat capacity. Therefore, it is possible to calculate the magnetic entropy change and adiabatic temperature change for this alloy. Increasing the magnetic field broadens and shifts the heat capacity maximum of Dy_5Si_4 alloy towards higher temperatures. This behavior is typical for FM materials.

Figure 4.3.9 Magnetic entropy change of the Dy₅Si₄ alloy from ~3.5K to 350K for *dc* magnetic field changes of 0-20kOe and 0-50kOe as determined from heat capacity measurements

The magnetic entropy change in 20kOe and 50kOe *dc* magnetic fields are shown in Figure 4.3.9. The curves are typical for the alloys with a composition in the $0.822 \leq x \leq 1$ range. There is a non-monotonic temperature interval from ~3.5K to ~20K for the 50kOe field change. The maximum ΔS_m value at 140K is equal to 5.5J/kgK in *dc* magnetic field 20kOe, and 11.9J/kgK in *dc* magnetic field 50kOe.

The adiabatic temperature change of Dy₅Si₄ in 20kOe and 50kOe magnetic fields are shown in Figure 4.3.10. The maximum value of ΔT at 140K is equal to 2.7K in *dc* magnetic field 20kOe and 6K in *dc* magnetic field 50kOe. The non-monotonic behavior from 4K to 20K is shown on the graph. A small negative value of magnetocaloric effect from 224K to 350K in 20kOe *dc* magnetic field is evident in Figure 4.3.10, but considering the experimental error this may not be real.

Figure 4.3.10 Adiabatic temperature change of the Dy₅Si₄ alloy from 3.5K to 350K for *dc* magnetic fields changes of 0-20kOe and 0-50kOe as determined from heat capacity measurements

The comparison of magnetic entropy change calculated from the magnetization and heat capacity data of Dy₅Si₄ and Dy₅Si_{3.5}Ge_{0.5} in 50kOe magnetic field are shown in Figure 4.3.11 and 4.3.12. The temperatures of the $-\Delta S_m$ maximums calculated from the magnetization and heat capacity data are in a good agreement for both types experiments and equal to: 141K (Dy₅Si₄) and 136K (Dy₅Si_{3.5}Ge_{0.5}) respectively. The values of $-\Delta S_m$ calculated from different experiments for both these alloys are lying within an error range.

Figure 4.3.11 The magnetic entropy change calculated from magnetization and heat capacity data of the Dy_5Si_4 alloys for a magnetic field change from 0 to 50kOe

Figure 4.3.12 The magnetic entropy change calculated from magnetization and heat capacity data of the $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ alloys for a magnetic field change from 0 to 50kOe

5. CONCLUSIONS

Polycrystals of the intermetallic compound of the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, where $x = 0, 0.25, 0.5, 0.625, 0.675, 0.725, 0.75, 0.775, 0.825, 0.875$, and 1 , have been prepared by electric-arc-melting on water-cooled copper hearth in an argon atmosphere.

A study of phase relationships and crystallography in the pseudobinary system $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ using X-ray powder diffraction data and optical metallography was completed. It revealed that silicides in the composition range from 0.825 to 1 crystallize in the Gd_5Si_4 -type crystal structure: germanides in the composition range from 0 to 0.625 crystallize in the Sm_5Ge_4 -type structure, and alloys with intermediate composition range from 0.675 to 0.775 crystallize in the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure.

The $-\Delta S_m$ values were determined from magnetization measurements for 7 alloys. The alloys with a monoclinic crystal structure which belong to an intermediate phase region have large MCE value, which exceeds those observed in the other two phase regions by 300 to 500%.

The nature of the observed magnetic and structural transformations in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system seems to be similar with those reported for the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system. However, the interval and concentration range of three different phase regions in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system are different from that observed in Gd-based alloys.

A non-collinear ordering of magnetic moments at low temperature was observed for the alloys with monoclinic crystal structure. The $\text{Dy}_5\text{Si}_3\text{Ge}$ alloy exhibited FM phase transition below Curie temperature.

A series of magnetic transitions were observed at low temperature in the $\text{Dy}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys. The number of transitions increased and the magnetization decreased with increasing germanium content in the alloys.

The $-\Delta S_m$ and $-\Delta T$ values were calculated from heat capacity data for $\text{Dy}_5\text{Si}_{3.5}\text{Ge}_{0.5}$ and Dy_5Si_4 alloys only, due to the fragile nature of the germanides-rich samples.

Based on the MCE values, the alloys from the orthorhombic Dy_5Si_4 -based solid solution and the intermediate monoclinic phase regions may be useful magnetic refrigerant materials in the temperature range $\sim 50\text{K}$ to -160K .

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