Giant magnetocaloric effect in the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound

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The magnetocaloric properties of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound have been studied by x-ray diffraction, magnetic and heat capacity measurements. Powder x-ray diffraction measurement shows that the compound has a dominant phase of monoclinic $Gd_5Ge_2Si_2$-type structure and a small quantity of $Gd_5(Ge,Si)_3$-type phase at room temperature. At about 270 K, this compound shows a first order phase transition. The isothermal magnetic entropy change (ΔS_M) is calculated from the temperature and magnetic field dependences of the magnetization and the temperature dependence of MCE in terms of adiabatic temperature change (ΔT_{ad}) is calculated from the isothermal magnetic entropy change and the temperature variation in zero-field heat-capacity data. The maximum ΔS_M is -13.6 J·kg^{-1}·K^{-1} and maximum ΔT_{ad} is 13 K for the magnetic field change of 0–5 T. The Debye temperature (θ_D) of this compound is 149 K and the value of DOS at the Fermi level is 1.6 states/eV·atom from the low temperature zero-field heat-capacity data. A considerable isothermal magnetic entropy change and adiabatic temperature change under a field change of 0–5 T jointly make the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound an attractive candidate for a magnetic refrigerant.

Keywords: magnetic properties, magnetocaloric effect, isothermal magnetic entropy change, adiabatic temperature change

PACC: 7540C, 7530C

1. Introduction

Since the discovery of the giant magnetocaloric effect (GMCE) in the $Gd_5Ge_2Si_2$ compound in 1997,[1] many papers have been devoted to the magnetocaloric effect and room temperature magnetic refrigeration till now. Magnetic refrigeration is a method to generate cold temperatures using the magnetocaloric effect (MCE), which is the characteristic of some materials to heat up when they are magnetized and cool down when removed from the magnetic field.

Conventional vapour compression refrigeration uses CFC (chlorofluorocarbons), HCFC (hydrochlorofluorocarbons) or HFC (hydroflourocarbons) as a refrigerant. These gases can cause ozone depletion or global warming. Unlike conventional vapour compression refrigeration, magnetic refrigeration is an environmentally friendly technique since it is harmless to mankind and the environment. The greatest advantage of magnetic refrigeration is that it does not use a compressor, which requires a large amount of electricity and produces noise and vibration.[2]

The giant magnetocaloric effect in the $Gd_5Ge_2Si_2$ compound makes this compound a promising material to use for near room temperature magnetic refrigeration applications.[3] A martensiticlike, displacive structural transition from an orthorhombic to a monoclinic phase (at about 276 K) occurs simultaneously with the ferromagnetic to paramagnetic transition (at about 299 K) with increasing temperature, and the reverse transformations are observed with decreasing temperature. In addition to temperature, the same magnetostructural transition is triggered by a magnetic field when it is applied above the zero magnetic field. The $Gd_5(Ge_xSi_{1-x})_4$ family of compounds have been found to display a variety of interesting physical behaviours, such as giant magnetoresistance (GMR),[4–8] the giant magnetostrictive effect (GMSE)[5–9] and the giant magnetocaloric effect (GMCE).[1] This combination of properties makes the $Gd_5(Ge_xSi_{1-x})_4$ series of compounds a potential candidate in magneto-electrical, magneto-mechanical devices and also in magnetic refrigeration.

Alloying the parent $Gd_5Ge_2Si_2$ compound with 3d or p elements has been studied in detail.[6–10] It has been shown that in the crystal structure of $Gd_5Ge_2Si_2$, Si and Ge form a sublattice, in which both elements occupy any given position with equal probability. Substituting 3d or p elements in the parent $Gd_5Ge_2Si_2$ compound shifts the maximum in the maximum isothermal magnetic entropy change ΔS_M

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to higher temperatures and changes the monoclinic-orthorhombic structural transition temperature at the same time.

According to the established phase diagrams for both magnetic structure and crystal structure, $Gd_5Ge_{2.05}Si_{1.95}$, which exhibits a maximum magnetic entropy change value at round 262 K, is very similar to $Gd_5Ge_2Si_2$. The materials around this composition are among the most promising for magnetic refrigeration. The interest is due to the prospects of development of magnetic materials with operating temperatures close to 300 K. So lots of workers have studied $Gd_5Ge_{2.05}Si_{1.95}$ and obtained a target with ordering temperatures close to 300 K; the alloying of $Gd_5Ge_{2.05}Si_{1.95}$ is most popular method for tuning the suitable values of MCE. The substitution of a small amount of Sn in $Gd_5Ge_{2.05}Si_{1.95}$ significantly enhances its MCE as well as increasing its Curie temperature (T_C); it also leads to increase in hysteresis loss due to its field induced monoclinic to orthorhombic phase transformation.[11] The introduction of oxygen atoms into $Gd_5Ge_{2.05}Si_{1.95}$ can also increase its T_C, but significantly decreases or destroys the giant MCE due to the casualty of the first order nature of the magnetic/structure phase transition.[12]

In this work, we attempt to improve the magnetocaloric properties of the $Gd_5Ge_{2.05}Si_{1.95}$ compound with a doped small amount of indium. The structure and magnetocaloric effect of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound are investigated by powder x-ray diffraction, magnetic measurements and heat capacity measurement.

2. Experimental

The $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound is prepared by the arc-melting method in an argon atmosphere under normal pressure on a water-cooled copper hearth by using pure elements (Gd 99.8 wt.%, Ge 99.999 wt.%, Si 99.999 wt.% and In 99.99 wt.%) purchased from commercial sources. During melting, the compound is homogenized by turning over and remelting 6 times. To assure homogeneity, the melted compound is annealed at 1173 K for one week in an evacuated quartz tube. The heat treatment is done under argon atmosphere and the compound is quenched in ice-water.

The composition of the arc-melted alloy is determined by energy dispersive x-ray analysis-EDX using a Zeiss EVO 40 scanning electron microscope. The crystal structure of the compound is proved by room-temperature x-ray diffraction using Cu Kα radiation. The magnetic measurements are carried out in a physical property measurement system (PPMS, Quantum Design) in a magnetic field up to 5 T at temperatures between 5 and 325 K. The heat capacity measurement is also made using PPMS under zero magnetic field between 4 and 320 K.

3. Results and discussion

3.1. Structural properties

For microstructural studies the normal secondary electron and the contrast of the microstructure in the BSE micrograph have been carried out in order to determine the microchemistry of phases. Figure 1(a) and (b) reveal that the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound contains a major phase and a different type of minor phase.

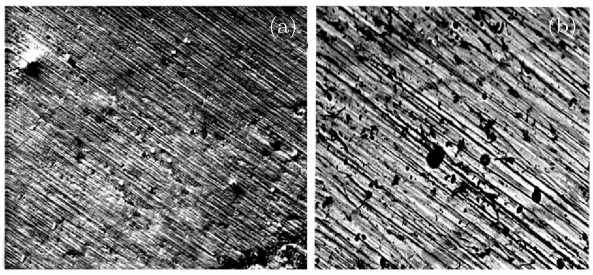


Fig. 1. SEM (a) secondary and (b) back scattered electron images of $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ alloy.

The microstructures of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound are characterized by the dominant matrix $Gd_5Ge_2Si_2$-type phase (5:2:2, matrix) along with a small piece of the phase $Gd_5(Ge,Si)_3$-type (5:3, matrix) from mapping analysis. In order to identify the characteristics of the elements among the various phases, the compositions of the alloys are determined by energy dispersive x-ray photoluminescence analysis (EDX) and summarized in Table 1. It can be seen that the estimated compositions of the alloys are reasonably close to the conceived nominal compositions.

Table 1. Compositions of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound determined by EDX analysis.

at.% Gd	at.% Ge	at.% Si	at.% In	phase type
55.39	22.62	21.27	0.72	$Gd_5Ge_2Si_2$-type
63.32	30.24	10.43	1.01	$Gd_5(GeSi)_3$-type

The powder x-ray diffraction result is given in Fig. 2 for $20^\circ \leq 2\theta \leq 70^\circ$. Figure 2 shows that the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound contains a dominant quantity of $Gd_5Ge_2Si_2$-type monoclinic structure and small quantity of Gd_5Ge_3-type. The phase composition of $R_5(Ge_xSi_{1-x})_4$ systems depend on the initial purity of the rare-earth element.[2] The $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound was prepared using commercial grade Gd and contained one other phase like the Gd_5Ge_3-type. The unit cell parameters of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound crystallized in the $Gd_5Ge_2Si_2$-type monoclinic structure are $a = 7.5804(1)$ Å, $b = 14.7970(2)$ Å, $c = 7.7648(2)$ Å, $\gamma = 93.17(1)^\circ$ and $V = 870.96(3)$ Å^3.

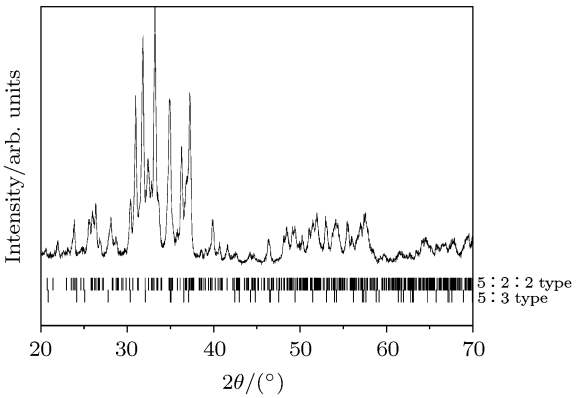


Fig. 2. The room temperature x-ray powder diffraction pattern of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound.

3.2. Magnetic properties

Figure 3 shows the temperature dependence of the magnetization between 5 and 320 K in an applied field of 50 Oe (1 Oe=79.5775 A/m) and a field-cooled (FC) sequence. The $M(T)$ curve indicates that the

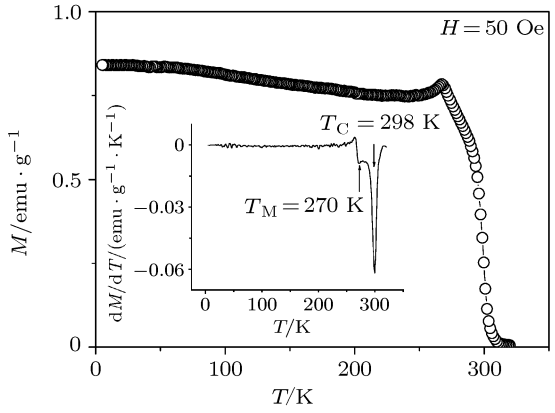


Fig. 3. The temperature dependence of the magnetization of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound in an applied field of 50 Oe in a field-cooled (FC) sequence.

$Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound is ferromagnetic below the Curie temperature. The Curie temperature $T_C = 298$ K is determined from the dM/dT curve (as seen in Fig. 3). Furthermore, in the dM/dT curve, the anomaly around $T_M = 270$ K should be related to the structural transition that is shown in the inset of Fig. 3.

Figure 4(a) displays the magnetization isotherms of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound between 250 and 315 K with temperature steps of 5 K. The field of sweeping rate is slow enough to ensure that the data are recorded in an isothermal process. The shape of the magnetization isotherms between 270 and 300 K supports the existence of a magnetic field induced structural transition.

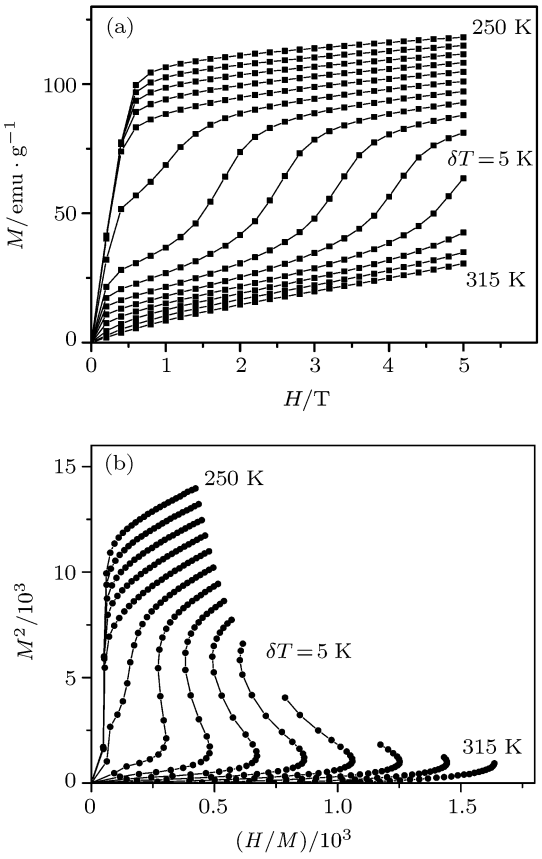


Fig. 4. (a) Isothermal magnetization curves of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound measured around transition temperature. (b) The Arrot plots of this compound.

The Arrot plots (M^2 versus H/M) of the compound are shown in Fig. 4(b) in order to determine the type of the magnetic transition. The negative slopes (S shaped) of the Arrot plots are normally associated with first order phase transition.[13] Since the negative slopes of the Arrot plots are observed above transition temperature, this supports the first order phase transition occurring in the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$

compound.[11,12]

3.3. Magnetocaloric properties

The magnetocaloric effect is represented by adiabatic temperature change ($\Delta T_{\rm ad}$) or isothermal magnetic entropy change ($\Delta S_{\rm M}$), which are functions of temperature (T) and magnetic field change (ΔH). The magnetic entropy change and adiabatic temperature change can be measured directly or can be calculated indirectly from the experimentally measured magnetization and heat capacity. Indirect techniques allow us calculate both $\Delta T_{\rm ad}(T)$ and $\Delta S_{\rm M}(T)$ from the experimentally measured heat capacity and magnetic field dependent magnetization measurements.[14,15]

We have estimated $\Delta S_{\rm M}(T)$ since the application of a magnetic field (H) was evaluated by treating the temperature and field dependent magnetization curves with the numerical approximation to the equation

$$\Delta S_{\rm M} = \int_{T_1}^{T_2} \left(\frac{\partial M}{\partial T}\right)_H {\rm d}H, \qquad (1)$$

where the partial derivations are replaced by a finite difference (see Fig. 5).

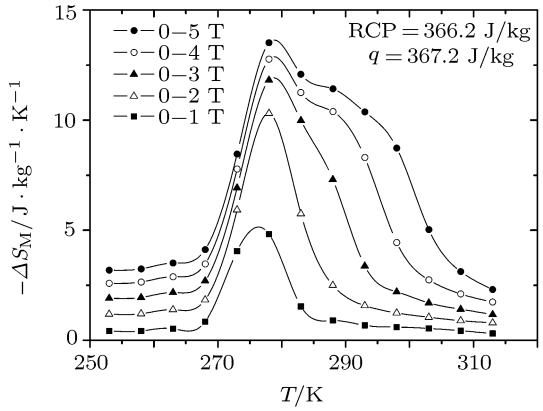


Fig. 5. The magnetic entropy change of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound as a function of temperature and magnetic field.

$M(H)$ curves are measured at discrete intervals of magnetic field and temperature (as seen in Fig. 4). $\Delta S_{\rm M}(T)$ is calculated by evaluating the integral in the equation with a numerical method.[14,15] The calculated $\Delta S_{\rm M}(T)$ is plotted as a function of temperature and magnetic field in Fig. 6. The maximum value of $\Delta S_{\rm M}(T)$ is -13.6 J·kg^{-1}·K^{-1} at 278 K in a magnetic field change of 5 T. This value is greater than that reported earlier.[9] In Ref. [9], the authors found that the maximum value of $\Delta S_{\rm M}(T)$ was -9.8 J·kg^{-1}·K^{-1} in a magnetic field change of 5 T at 276 K and $\Delta S_{\rm M}(T)$ decreased with increasing Ga.

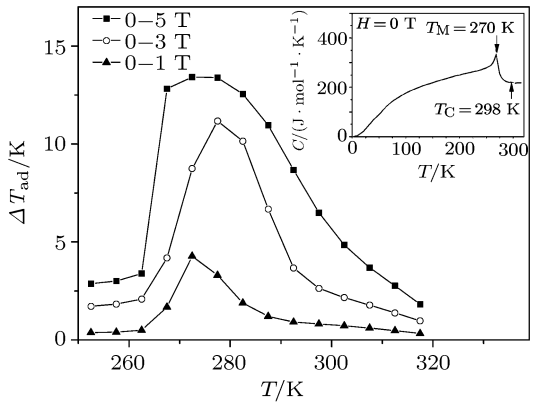


Fig. 6. The temperature dependence of $\Delta T_{\rm ad}$ in the magnetic field change of 1, 3, and 5 T. The inset shows the heat capacity measurement of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound in zero magnetic field.

The refrigerant capacity q is given by:

$$q = \int_{T_1}^{T_2} \Delta S_M(T){\rm d}T. \qquad (2)$$

Here, T_1 and T_2 are the temperatures of cold and hot sinks, respectively. q is a measure of how much heat can be transferred between cold and hot sinks in an ideal refrigeration cycle. The other parameter for the characterization of magnetocaloric properties is the relative cooling power RCP. This is determined as a product of the peak value of the magnetic entropy change $\Delta S_{\rm M}(T)_{\rm max}$ and the full width at half maximum of $\Delta S_{\rm M}(T)$[16] and is written as:

$${\rm RCP} = -(\Delta S_{\rm M})_{\rm max}\delta T_{\rm FWHM}. \qquad (3)$$

According to Eqs. (2) and (3), the q and RCP values for the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound are calculated to be 367.2 J·kg^{-1} and 366.2 J·kg^{-1}, respectively.

Percharsky and Gschneidner[17] showed that the $\Delta T_{\rm ad}(T)$ was estimated from the equation:

$$\Delta T_{\rm ad}(T)_H = [T(S)_H - T(S)_0]_S. \qquad (4)$$

For the estimation of $\Delta T_{\rm ad}(T)$, it is necessary to treat the entropy (S) as a function of T in zero magnetic field. The zero magnetic field S is calculated from the zero magnetic field heat capacity measurement.[17–19] To calculate $\Delta T_{\rm ad}(T)$, we measured the heat capacity in zero magnetic field between 4–320 K (see the inset of Fig. 6). According to the results of Ref. [17], the value of $\Delta T_{\rm ad}(T)$ is correctly calculated using the combined heat-capacity

and magnetization data and Eq. (4). We have estimated the $\Delta T_{\rm ad}(T)$ using the Eq. (4) and the results of heat capacity measurement in conjunction with the $\Delta S_{\rm M}(T)$ values calculated from magnetization data for the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound (as seen in Fig. 5).

The peak at $T_{\rm M} = 270$ K corresponds to the martensitic-like structural phase transition. At 298 K, the second small peak corresponds to the Curie temperature. Figure 6 shows the temperature dependence of $\Delta T_{\rm ad}(T)$ for the magnetic field change of 1, 3, 5 T applied from Eq. (4). The maximum $\Delta T_{\rm ad}$ value is about 4 K, 11 K and 13 K for the magnetic field change of 1, 3, 5 T, respectively. For the $Gd_5Si_2Ge_2$ compound with high purity Gd, the maximum $\Delta T_{\rm ad}$ value is about 15 K for the magnetic field change of 5 T.[2] For the Gd element, this value is about 12 K in Ref. [2]. As shown in Fig. 7, the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound is a good candidate for magnetic refrigeration. The heat capacity in zero magnetic field between 4–70 K is shown in Fig. 8. At low temperatures, the temperature change of the specific heat capacity is only defined as the sum of the lattice and electronic contributions,

$$C(T) = C_{\rm e}(T) + C_l(T) = \gamma T + \beta T^3, \qquad (5)$$

where γ and β are the coefficients. This gave us the opportunity to find the density of state (DOS) at the Fermi level $N(E_{\rm F})$ and Debye temperature ($\Theta_{\rm D}$) using the experimental results of γ and β that,

$$\gamma = \frac{1}{3} k_{\rm B}^2 \pi^2 N(E_{\rm F}), \qquad (6)$$

$$\beta = \frac{12\pi^4 k_{\rm B}}{5(\Theta_{\rm D})^3}, \qquad (7)$$

where $k_{\rm B}$ is the Boltzmann constant. We found that the Debye temperature ($\Theta_{\rm D}$) of this compound is 149 K (inset in Fig. 8). The experimental value of DOS at the Fermi level is found to be 1.6 states/(eV·atom). According to Paudyal *et al.*,[21] the value of $Gd_5Ge_2Si_2$ of DOS at the Fermi level is 1.8 states/(eV·atom). The experimental value of DOS at the Fermi level for our alloy is in good agreement with that of the previous result.[21]

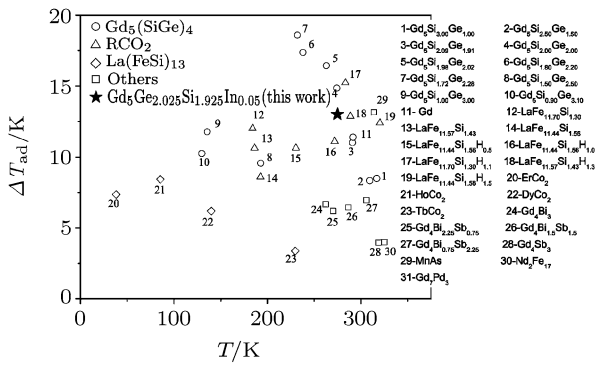


Fig. 7. The $\Delta T_{\rm ad}$ values of selected intermetallic compounds [Ref. [20], and references therein] and the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound in the magnetic field change of 0–5 T.

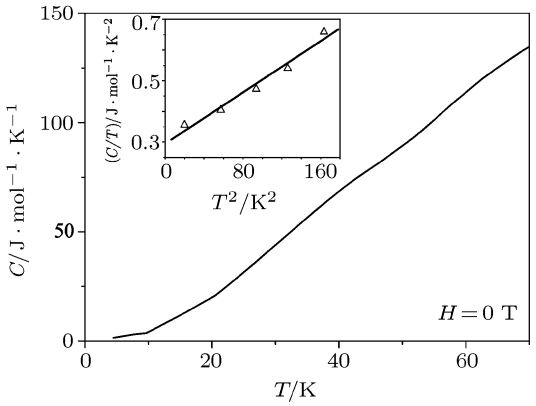


Fig. 8. The temperature dependence of $\Delta T_{\rm ad}$ in the magnetic field change of 1, 3, and 5 T.

4. Conclusion

In this work, we report experimental results on structural and magnetocaloric characteristics of the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound. This compound crystallizes in $Gd_5Ge_2Si_2$-type monoclinic structure at room temperature. The x-ray diffraction pattern shows that there is a small quantity of $Gd_5(GeSi)_3$-type phase.

The maximum value of isothermal $\Delta S_{\rm M}$ is -13.6 J·kg^{-1}·K^{-1} and the maximum $\Delta T_{\rm ad}$ value is about 13 K at 278 K in a magnetic field change of 5 T. The maximum value of isothermal ΔS_M of $Gd_5Ge_2Si_2$ and $Gd_5Ge_{2.05}Si_{1.95}$ are about -18.7 and -22 J·kg^{-1}·K^{-1} at the magnetic field change of 5 T, respectively.[2,17] These values are larger than that of $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ but another parameter of MCE, the $\Delta T_{\rm ad}$ value of our sample, is comparable with those of $Gd_5Ge_2Si_2$, $Gd_5Ge_{2.05}Si_{1.95}$ and the Ref. [20] alloys. The q and RCP values for the $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound are about 367.2 J·kg^{-1} and 366.2 J·kg^{-1} under a field change of 0–5 T, respectively, and these values are also better than those of $Gd_5Ge_2Si_2$. The $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ compound should be a good candidate for magnetic refrigeration due to these results.

In this work, we also report the results of the heat capacity measurement in zero magnetic field for understanding the thermal behaviour of $Gd_5Ge_{2.025}Si_{1.925}In_{0.05}$ at low temperature. From the heat capacity measurement in zero magnetic field at low temperature, it is found that the Debye temperature of this compound is 149 K and the value of DOS at the Fermi level is 1.6 states/(eV·atom).

Acknowledgments

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References

[1] Warburg E 1881 *Ann. Phys.* **13** 141
[2] Pecharsky V K and Gschneidner Jr K A 1997 *Phys. Rev. Lett.* **78** 4494
[3] Pecharsky V K and Gschneidner Jr K A 1997 *Appl. Phys. Lett.* **70** 3299
[4] Pecharsky V K and Gschneidner Jr K A 1997 *J. Magn. Magn. Mater.* **167** L179
[5] Pecharsky A O, Pecharsky V K and Gschneidner Jr K A 2000 *J. Alloys Comp.* **338** 126
[6] Pecharsky V K and Gschneidner Jr K A 1997 *J. Alloys Comp.* **260** 98
[7] Pecharsky V K, Pecharsky A O and Gschneidner Jr K A 2002 *J. Alloys Comp.* **344** 362
[8] Pecharsky A O, Pecharsky V K and Gschneidner Jr K A 2003 *J. Appl. Phys.* **93** 4722
[9] Aksoy S, Yucel A, Elerman Y, Krenke T, Acet M, Moya X and Manosa L 2008 *J. Alloys Comp.* **460** 94
[10] Zhung Y H, Li J Q, Huang W D, Sun W A and Ao W Q 2006 *J. Alloys Comp.* **421** 49
[11] Li J Q, Sun W A, Jian Y X, Zhung Y H, Huang W D and Liang J K 2006 *J. Appl. Phys.* **100** 073904
[12] Wu W, Tsokol A O, Gschneidner Jr K A and Sampaio J A 2005 *J. Alloys Comp.* **403** 118
[13] Yadin Y and Goldschmidt 1985 *Phys. Rev.* B **32** 264
[14] Yücel A, Elerman Y and Aksoy S 2006 *J. Alloys and Compounds* **420** 182
[15] Gschneidner Jr K A and Pecharsky V K 1999 *J. Appl. Phys.* **85** 5365
[16] Pecharsky V K and Gschneidner Jr K A In: Wesrbrook J H and Fleisher R L (Eds.) 2002 *Intermetallic Compounds Principles and Practice* vol. 3: (Chichester, UK: Progress, Wiley and Sons)
[17] Pecharsky V K and Gschneidner Jr K A 1999 *J. Appl. Phys.* **86** 565
[18] Sharma V K, Chattopadhyay M K, Kumar Ravi, Ganguli Tapas, Tiwari Pragya and Roy S B 2007 *J. Phys.: Condens. Matter* **19** 496207
[19] Dong Q Y, Shen B G, Chen J, Shen J, Wang F, Zhang H F and Sun J R 2009 *J. Appl. Phys.* **105** 053908
[20] Gschneidner Jr K A, Pecharsky Jr V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479
[21] Paudyal D, Percharsky V K, Gschneidner Jr K A and Harmon N 2006 *Phys. Rev.* B **73** 144406