



The Magnetocaloric Properties of Gd₅Si₄ Alloy Prepared by the New Method

Z. Momeni Larimi, A. Amirabadizadeh, A. Yazdani, H. Arabi

Magnetism and Superconducting Research Laboratory, Department of Physics, Faculty of Science,
University of Birjand, Birjand, Iran

momeni@birjand.ac.ir; z_momenilarimi@yahoo.com

Magnetism and Superconducting Research Laboratory, Department of Physics, Faculty of Science,
University of Birjand, Birjand, Iran

aamirabadizade@birjand.ac.ir

Tarbiat Modares University, Tehran, Iran

Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad

ABSTRACT

We report on a new method for preparation the magnetocaloric alloy Gd₅Si₄. By mechanical alloying under argon atmosphere and then melting sample by arc furnace, we produced the Gd₅Si₄ alloy. The structure and magnetothermal properties of the alloy have been investigated with the help of powder X-ray diffraction and magnetization measurements. This compound crystallized in the orthorhombic structure with space group *pnma*. In X-ray powder diffraction pattern, a minor orthorhombic GdSi₂ phase was observed as a second phase. For this compound, the second order phase transition was observed. The maximum isothermal magnetic entropy change of the Gd₅Si₄ compound at 348K was found to be -10 J/(kg K) in an applied field of 0.5T.

Keywords

Gd₅Si₄ alloy, Magnetocaloric effect, Isothermal magnetic entropy change, Second order phase transition



Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Physics

Vol 4, No.3

japeditor@gmail.com

www.cirjap.com



1. INTRODUCTION

The magnetocaloric effect (MCE) is the phenomenon of release or absorption of heat by a magnetic material due to a magnetic field change [1]. This effect can be quantified either in terms of isothermal magnetic entropy change (ΔS_M), or adiabatic temperature change (ΔT_{ad}). Magnetic refrigeration based on MCE has attracted ample attention because it has the potential to reduce the global energy consumption, and eliminate or minimize the use of ozone depleting alloys, greenhouse gases, and precarious chemicals [2].

Since the discovery of the giant magnetocaloric effect (GMCE) in intermetallic $Gd_5Si_2Ge_2$ alloys by Pecharsky and Gschneidner (1997) [4], the $Gd_5(Si_xGe_{1-x})_4$ alloys have received tremendous attention. The maximum magnetic entropy change near the transition temperature in these alloys is due to their large effective magnetic moment and minimal crystal field effects, which makes these materials a preferred candidate for room temperature magnetic refrigeration [5].

The crystal structures of $Gd_5(Si_xGe_{1-x})_4$ compounds consist of $\frac{2}{\infty}[Gd_5T_4]$ slabs, where T is a statistical mixture of Ge and Si. Specific T-T dimmers between the slabs can be reversibly broken or reformed by changing concentration (x), temperature and/or by applying magnetic field or pressure, leading to magnetostructural transitions [6].

The Gd silicide crystallizes in the Sm_5Ge_4 -type orthorhombic structure with space group *pnma*, orders ferromagnetically at a higher Curie temperature $T_c=336$ K than that of Gd pure metal ($T_c=294$ K), and has a second order ferromagnetic to paramagnetic transition near T_c [7]. This compound is used for the cooling of microelectronic chips [8] and introduced as a candidate for hyperthermia treatment of cancer [9]. In recent years Gd silicide nanoparticles because of biocompatibility and high magnetization value has considered as one of the best candidates for self-controlled hyperthermia applications [10].

Most of the research activity to date was focused on the $Gd_5Si_2Ge_2$ with substitutional doping different atoms [5]. The Magnetocaloric properties of the Gd_5Si_4 system have been studied to a much lesser extent. Also to our knowledge, The usual method which is mostly reported for the synthesis of the current alloys limited to arc melting method. For this reason, we employed for the first time mechanical alloying under argon atmosphere followed to arc melting to synthesize the Gd_5Si_4 alloy. We discussed its structural and magnetic properties using X-ray powder diffraction and magnetic measurements. We determined the entropy changes near the transition temperature using magnetization data.

2. EXPERIMENTAL

Sample Preparation:The starting materials for synthesis of Gd_5Si_4 sample were Gd powder (99%, Aldrich) and Si powder (99+%, ACROS). The metal powders were handled in an Ar-filled dry box. The stoichiometric amounts of the element powders are weighed to an accuracy of approximately 0.01 mg and mixed in hardened steel vials with hardened steel balls (about 10 mm in diameter) using a F5 planetary ball miller under argon atmosphere. The milling was performed for 20 h with balls to powder ratio 14:1 at a speed of 240 rpm. The milled powder was pressed into 10-mm pellets under a load of 10 metric tons and then arc-melted on a water cooled copper hearth in an argon atmosphere. Each sample was re-melted three times and after each re-melting the sample was turned over to ensure their homogeneity. The as-cast alloy was annealed at 1373 K for 3h in argon atmosphere with subsequent quenching in cold water. The weight losses after arc-melting were negligible.

The sample was characterized by powder X-ray diffraction experiment at room temperature. Magnetization measurement on this sample was carried out in the temperature range of 323-480 K using vibrating sample magnetometer (Lakeshore 7400). Several magnetizations vs. field isotherms were measured in the vicinity of magnetic transition temperature in fields up to 0.5 T and were used to calculate the magnetic entropy associated with the transition.

3. RESULTS AND DISCUSSTION

3.1. Structural Properties

Fig. 1 shows the powder X-ray diffraction pattern of as-milled powder after 20 h milling. Except the weak peak at $\sim 32^\circ$ which is characteristic for Gd_5Si_4 , the as-milled sample is a mixture of free Gd and Si phases. The respective positions of the peaks were identified in accordance with the JCPDS standard data. Fig. 2 represents XRD pattern of the annealed alloy. As can be seen the free Gd and Si phases disappeared. It reveals along with Gd_5Si_4 , $GdSi_2$ and $GdSi$ start to appear. But the Gd_5Si_4 -type orthorhombic structure has been detected as the major/ phase. The remaining two phases could be considered as minor phases corresponding to $GdSi_2$ and $GdSi$ compounds.

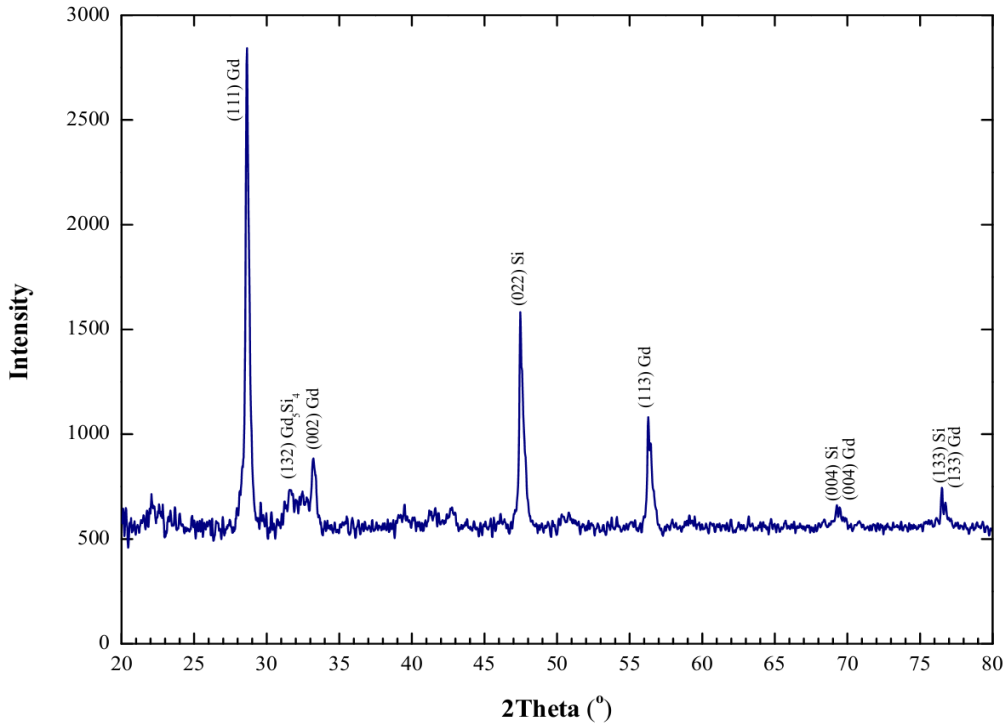


Figure 1: the XRD results of powder as milled at 240 rpm for 20 h milling.

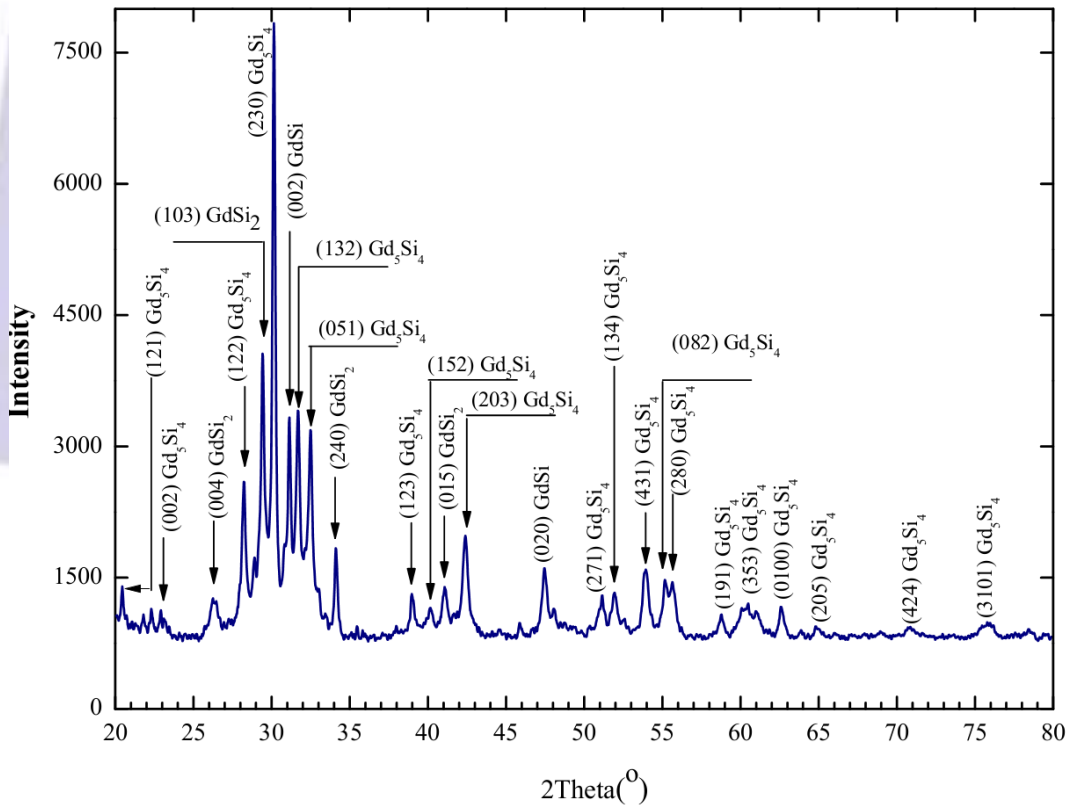


Figure 2: the powder XRD pattern of Gd_5Si_4 alloy

3. 2. Magnetic Properties

The temperature dependence of the magnetization- $M(T)$ of prepared sample from 300K to 760 K in magnetic field of 0.5 T is presented in Fig. 3. This figure shows obviously how most of the alloys contain two distinct Curie temperatures. The Curie temperature was determined as the minima in the first derivative of the M - T (dM/dT) curve, and the result is shown in the inset of Fig. 3. The first drop of M - T curve at 340 K corresponds to the second order transition for Gd_5Si_4 -type ($T_c=340$ K) which is in very good agreement with previous experimental results [8]. The next drop near 725 K is due to the presence of impurity $GdSi_2$ -type structure [18].

Fig. 4 displays the magnetization isotherms of the Gd_5Si_4 compound between 323 and 383 K with the temperature steps of 10 K.

3. 3. Magnetocaloric Properties

The magnetocaloric effect was evaluated from the isothermal magnetic entropy change (ΔS_M) that can be calculated around the Curie temperature using the Maxwell's equation [19].

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

For magnetization measured at discrete field and temperature intervals, the magnetic entropy change defined in Eq. (1) can be approximated by Eq. (2) [20],

$$\Delta S_M(T, H) = \frac{1}{\Delta T} \left[\int_0^H M(T+\Delta T, H) dH - \int_0^H M(T, H) dH \right] \quad (2)$$

The calculated ΔS_M from Eq. (2) is plotted as a function of temperature in Fig. 5. Since magnetic moments are spontaneously oriented at the Curie temperature, application of the magnetic field can lead to the higher magnetization at this region, thus this shape of the ($-\Delta S_M$ - T) curve is expected. As seen in Fig. 5, the magnetic entropy change as a function of temperature has the typical λ -shape of systems undergoing a second order transition. The maximum value of ΔS_M follows the Curie temperature and has the value of almost -10 J/kg K. This value of magnetic entropy change demonstrates the presence of a conventional magnetocaloric effect and suggests the absence of a first order magneto-structural transition. Our results show an increment in ΔS_M as compared to earlier experimental works which synthesized this alloy by arc melting technique[8]. This may be due to the presence of $GdSi_2$ phase, appeared in this method.

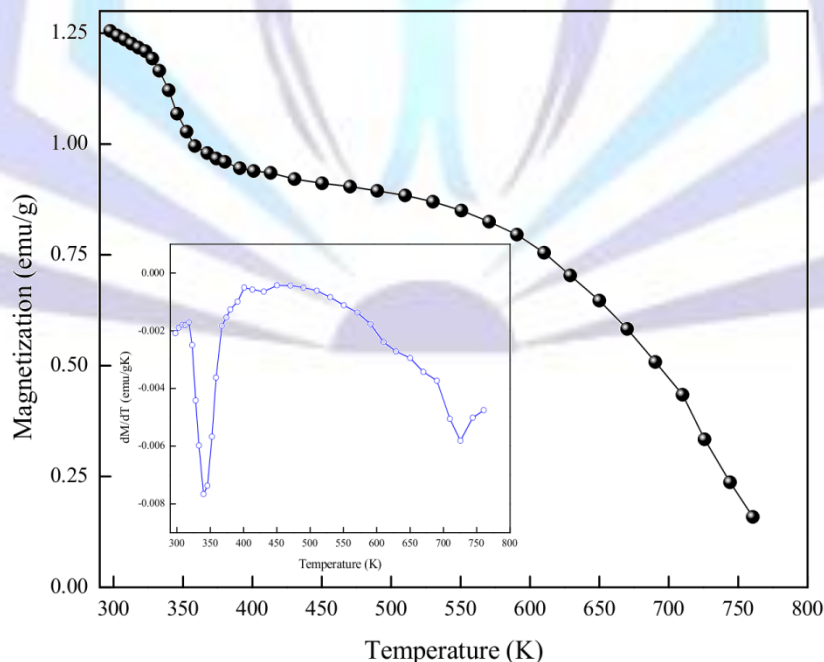


Figure 3: Temperature dependency of the magnetization of Gd_5Si_4 alloy measured in an applied field of 0.5T.

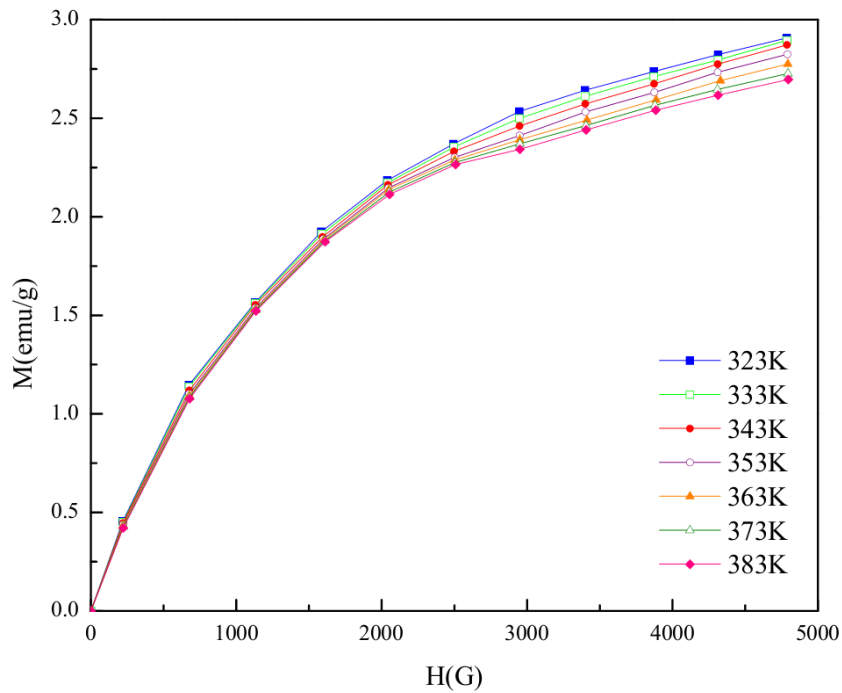


Figure 4: The magnetization vs. field (M vs. H) measurements around the Curie temperature for Gd_5Si_4 .

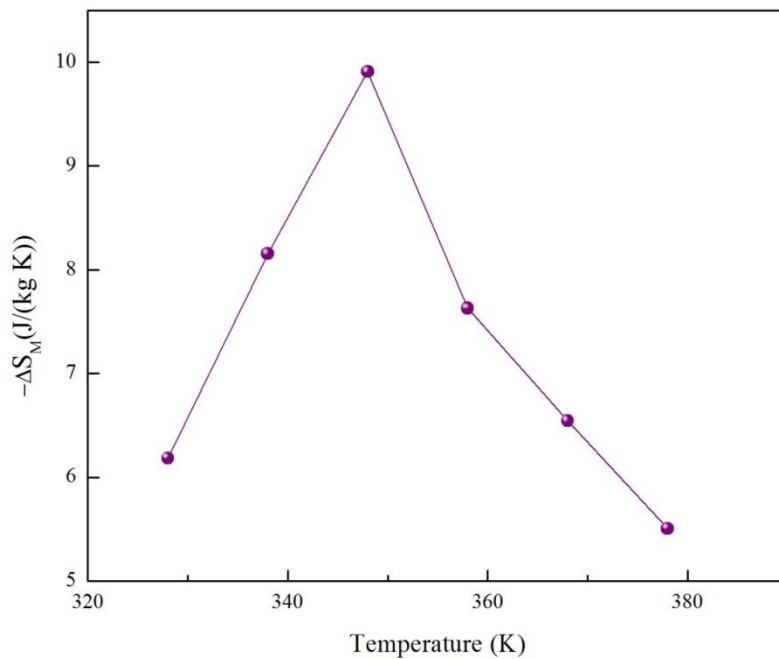


Figure 5: Magnetic entropy change for Gd_5Si_4 as a function of temperature for $\Delta H=0-0.5$ T.

4. CONCLUSION

We reported experimental results on structural and magnetocaloric characteristics of the Gd_5Si_4 compound which were successfully prepared by mechanical alloying under argon atmosphere followed to arc melting technique. The Gd_5Si_4 -type



orthorhombic structure has been detected as the major phase. Moreover, the minor phases corresponding to GdSi_2 and GdSi compounds have been observed in X-ray diffraction pattern of this compound. This sample shows two magnetic transitions, which correspond to the Gd_5Si_4 and GdSi_2 phases. The measured Curie temperature for Gd_5Si_4 is 340K. The MCE in terms of the magnetic entropy change, ΔS_M , reaches the maximum of -10J/kg K around the Curie temperature. Our results display the maximum ΔS_M value which is higher than that observed in other experimental works.

ACKNOWLEDGMENTS

We appreciate the help of Mr. Mardani (Birjand University) and Ms. Bazayr (Iran Technology and Entrepreneurial Company (KEFA)) for their cooperation in measuring VSM curve and XRD spectra of the samples.

REFERENCES

- [1] Tishin, A. M. and Spichkin, Y. I. 2003. The magnetocaloric effect and its applications. Institute of Physics Publishing. Bristol and Philadelphia.
- [2] Pecharsky, V. K., Holm, A. P., Gschneidner Jr., K. A. and Rink, R. Massive magnetic-field-induced structural transformation in Gd_5Ge_4 and the nature of the giant magnetocaloric effect. *Phy. Rev. Lett.* 91 (Nov. 2003), 197204/1-197204/4.
- [3] Li, J. Q., Sun, W. A. and Jian, Y. X. The giant magnetocaloric effect of enhanced by Sn doping. *J. Appl. Phys.* 100 (July 2006), 073904/1-073904/5.
- [4] Pecharsky, V. K. and Gschneidner Jr., K. A. Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$. *Phys. Rev. Lett.* 78 (June 1997), 4494-4497.
- [5] Yüzüak, E., Dincer, I., Elerman, Y. Effects of manganese doping on magnetocaloric effect in Ge-rich $\text{Gd}_5\text{Ge}_{2.05}\text{Si}_{1.95}$ alloy, *J. Rare Earths.* 30 (Mar. 2012), 217-221.
- [6] Chernyshov, A. S., Mudryk, Ya. S., Pecharsky, V. K. and Gschneidner Jr., K. A. Structural and magnetothermal properties of the $\text{Gd}_5\text{Sb}_x\text{Ge}_{4-x}$ system. *J. Appl. Phys.* 99 (Apr. 2006), 08Q102/1- 08Q102/3.
- [7] Altounian, Z. and Liu, X. B. Magnetovolume effect and magnetic transition in Gd_5Si_4 . *J. Appl. Phys.* 101 (Apr. 2007), 09D507/1-09D507/3.
- [8] Belo, J. H., Pereira, A. M., Magen, C., Morellon, L., Ibarra, M. R., Algarabel, P. A. and Araujo, J. P. Critical magnetic behavior of magnetocaloric materials with the Gd_5Si_4 -type structure. *J. Appl. Phys.* 113 (Apr. 2013), 133909/1-133909/5.
- [9] Ahmad, S. N., Akin, Y. and Shaheen, S. A., $\text{Gd}_5(\text{Si}, \text{Ge})_4$ and Gd_2C compounds: Candidates for hyperthermia treatment of cancer. *J. Appl. Phys.* 97 (May 2005), 10Q902/1-10Q902/3.
- [10] Tarasenko, N. V., Nedelko, M. I. and Nevar, A. A. Electrical discharge assisted synthesis of gadolinium silicide nanoparticles in liquid. *Nanosci. Nanotechnol. Lett.* 4 (Mar. 2012), 333-337.
- [11] Zhuang, Y.H., Li, J.Q., Huang, W.D., Sun, W.A. and Ao, W.Q. Giant magnetocaloric effect enhanced by Pb-doping in $\text{Gd}_5\text{Ge}_2\text{Si}_2$ compound. *J. Alloys Compd.* 421 (Sept. 2006), 49-53.
- [12] Yuzuak, E., Dincer, I. and Elerman, Y. Giant magnetocaloric effect in the $\text{Gd}_5\text{Ge}_{2.025}\text{Si}_{1.925}\text{In}_{0.05}$ compound. *Chin. Phys. B.* 19 (Mar. 2010), 037502/1-037502/6.
- [13] Franco, V., Conde, A., Provenzano, V. and Shull, R. D. Scaling analysis of the magnetocaloric effect in $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{X}_{0.1}$ ($X = \text{Al}, \text{Cu}, \text{Ga}, \text{Mn}, \text{Fe}, \text{Co}$). *J. Magn. Mater.* 322 (Jan. 2010), 218-223.
- [14] Zhang, T., Chen, Y., Tang, Y., Du, H., Ren, T. and Tu, M. The phase formation and thermal hysteresis of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ with the addition of transition elements (Mn, Fe, Co, Ni). *J. Alloys Compd.* 433 (May 2007), 18-21.
- [15] Shull, R. D., Provenzano, V., Shapiro, A. J., Fu, A., Lufaso, M. W., Karapetrova, J., Kletetschka, G. and Mikula, V. The effects of small metal additions (Co, Cu, Ga, Mn, Al, Bi, Sn) on the magnetocaloric properties of the $\text{Gd}_5\text{Ge}_2\text{Si}_2$ alloy. *J. Appl. Phys.* 99 (Apr. 2006), 08K908/1-08K908/3.
- [16] Shimotomai, S. and Ido, H. Magnetocaloric effect in $\text{Gd}_{5-x}\text{Dy}_x\text{Si}_4$ compounds. *J. Appl. Phys.* 99 (Apr. 2006), 08Q109/1-08Q109/3.
- [17] Elbicki, J. M., Zhang, L. Y., Obermyer, R. T., Wallace, W. E. and Sankar, S. G. Magnetic studies of $(\text{Gd}_{1-x}\text{M}_x)_5\text{Si}_4$ alloys ($M = \text{La}$ or Y). *J. Appl. Phys.* 69 (Apr. 1991), 5571-5573.
- [18] Sekizawa, K. and Yasukochi, K. Antiferromagnetism of disilicide of heavy rare earth metals. *J. Phys. Soc. Jpn.* 21 (Feb. 1966), 274-278.
- [19] Hashimoto, T., Numasawa, T., Shino, M. and Okada, T. Magnetic refrigeration in the temperature range from 10 K to room temperature: the ferromagnetic refrigerants. *Cryogenics.* 21 (Nov. 1981), 647-653.
- [20] Foldeaki, M., Chahine, R. and Bose, T. K. Magnetic measurements: A powerful tool in magnetic refrigerator design. *J. Appl. Phys.* 77 (Apr. 1995), 3528-3537.