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Low hysteresis and large room temperature magnetocaloric effect of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08, 0.1$) alloys

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$\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08, 0.1$) alloys were prepared by arc melting followed by annealing at 1273 K for 96 h. Mixed monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type phase, orthorhombic Gd_5Si_4 -type phase, and a small amount of Gd_5Si_3 -type phase were obtained in these alloys. $\text{Gd}_5\text{Si}_{2.01}\text{Ge}_{1.91}\text{Ni}_{0.08}$ alloy undergoes a second-order transition (T_C) around 300 K, whereas $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Ni}_{0.1}$ alloy exhibits two transitions including a first-order transition (T_C^{I}) at ~ 295 K and second-order transition (T_C^{II}) at ~ 301 K. Ni substitution can effectively reduce the thermal hysteresis and magnetic hysteresis while maintaining large magnetic entropy change. The maximum magnetic entropy changes (ΔS_M^{max}) of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ alloys with $2x = 0.08$ and 0.1 are 4.4 and $5.0 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, for $0-2 \text{ T}$, and are 8.0 and $9.1 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, for $0-5 \text{ T}$. Low hysteresis performance and relatively large magnetic entropy change make these alloys favorable for magnetic refrigeration applications. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795434>]

I. INTRODUCTION

As an energy-saving, efficient and eco-friendly cooling technology, magnetic refrigeration is receiving more and more global attention.¹ Various materials²⁻⁷ have been investigated regarding to their applications in this new cooling technology. In particular, discovery of the giant magnetocaloric effect (GMCE) in the $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ and $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ ($0.24 \leq x \leq 0.5$) alloys^{2,8} is a benchmark in the study of magnetic refrigerants near room temperature. However, $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ exhibits large hysteretic loss in the temperature range between 270 and 300 K, which reduces its potential cooling efficiency.⁹ As reported earlier, a small amount (total of 0.33 at. %) of Fe, Co, Ni, or Cu substitution for Si and Ge in the $\text{Gd}_5\text{Ge}_2\text{Si}_2$ alloy have significant impact on the maximum value of the magnetic entropy change (ΔS_M) and the Curie temperature (T_C).¹⁰ Among the different 3d metal substitutions, Ni was the one providing the most promising results, as it increases the transition temperature and did not decrease much ΔS_M . Shull and his coworkers found that the addition of Cu, Ga, Mn, and Al completely eliminated the hysteresis loss presented in the undoped $\text{Gd}_5\text{Ge}_2\text{Si}_2$ alloy between 270 and 330 K, broadened the magnetic entropy change (ΔS_M) peak, and shifted its peak position from 275 to 305 K, similar to that observed earlier for $\text{Gd}_5\text{Ge}_{1.9}\text{Si}_{2.1}\text{Fe}_{0.1}$.^{11,12} However, in the case of doping the same amount of either Sn or Bi, a negligible effect on the magnetocaloric properties was evident.¹¹ Recent results show that partial substitution of Nb in $\text{Gd}_5\text{Si}_{2-x}\text{Ge}_{2-x}\text{Nb}_{2x}$ alloys increased

T_C to ~ 295 K and enhanced the magnetocaloric effect as x increased to $x = 0.05$. The $\Delta S_M = -9.6 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta H = 2 \text{ T}$ was obtained, which is $\sim 50\%$ higher than that of Nb-free alloy. And microstructure examination indicated that a low amount of detrimental Gd_5Si_3 phase was precipitated.¹³ As far as Ni doping is concerned, most previous work focused on the alloy with very low Ni concentrations, typically less than 0.03 at. %.¹⁰ In the present work, $\text{Gd}_5\text{Si}_{2.05}\text{Ge}_{1.95}$ based alloys doped with slightly higher Ni contents were prepared. Their hysteresis behavior, structure, and magnetocaloric properties were investigated.

II. EXPERIMENTS

The alloys with nominal composition of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08$ and 0.1) were prepared by arc melting the raw materials of Gd, Si, Ge, and Ni with purities higher than 99.95 wt. % under argon atmosphere. The ingots were re-melted several times to ensure the composition homogeneity. As-cast ingots were sealed in a quartz tube and annealed at 1273 K for 96 h and subsequently quenched in water. The structural characterization was performed by the X-ray diffractometer (XRD) with Cu-K α radiation. Magnetic measurements were carried out using a Quantum Design Physical Property Measurement System (model PPMS-9).

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for the $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08, 0.1$) alloys. Three types of phases, i.e., monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type phase, orthorhombic Gd_5Si_4 -type phase, and hexagonal $\text{Gd}_5(\text{Si,Ge})_3$ -type phase, were observed. The XRD peaks at $\sim 26.2^\circ$ and 37.9°

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FIG. 1. The XRD patterns for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x=0.08, 0.1$) alloys at room temperature.

corresponding to 5:4-type phase were present on the pattern of $2x=0.08$ sample, but absent on that of $2x=0.1$ sample. The XRD peaks at $\sim 31.2^\circ$ and 32.4° correspond to the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type phase. The result also indicates that the content of Ni-substitution has an effect on the formation of 5-2-2 phase. With increasing Ni content from ~ 0.89 ($2x=0.08$) to ~ 1.11 at. % ($2x=0.1$), the amount of orthorhombic Gd_5Si_4 -type phase decreases and the amount of monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type phase increases. The XRD peaks at $\sim 35.2^\circ$ and $\sim 36.6^\circ$ in Fig. 1 are related to the hexagonal $\text{Gd}_5(\text{Si, Ge})_3$ -type phase.

The temperature dependencies of magnetization for the $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x=0.08, 0.1$) alloys measured in an applied field of 0.05 T between 5 and 300 K under field cooling (FC) and field heating (FH) conditions are shown in Fig. 2. The T_C was defined as the temperature at the maximum of $|dM/dT|$ vs T plot based on FH curve. The lack of thermal hysteresis in $\text{Gd}_5\text{Si}_{2.01}\text{Ge}_{1.91}\text{Ni}_{0.08}$ alloy indicates that it should undergo a second-order magnetic transition, and T_C is around 300 K. For $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Ni}_{0.1}$, two slopes are observed in M - T curves, indicating two magnetic transitions,

FIG. 2. Magnetization-temperature curves for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x=0.08, 0.1$) alloys measured in a magnetic field of 0.05 T.

a first-order transition (T_C^{II}) at ~ 295 K and a second-order transition (T_C^{I}) at ~ 301 K. It is also found that the thermal hysteresis between FC and FH curves is negligible for $2x=0.08$ alloy, whereas that is ~ 6 – 13 K for $2x=0.1$. A similar behavior was observed for the magnetic hysteresis in the magnetic isotherms for the experimental alloys, as will be discussed later.

Figure 3 displays the isothermal magnetization curves for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x=0.08, 0.1$) alloys. The $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Ni}_{0.1}$ alloy (Fig. 3(b)) has the typical magnetization characteristics of pure $\text{Gd}_5\text{Si}_2\text{Ge}_2$ for the temperatures above T_C^{I} (~ 301 K). We can see a typical field induced transition from the PM to the field-induced ferromagnetic state. Combined with partial magnetic hysteresis with respect to a reversed magnetic field, this shows that the transitions are first order. The transition occurs at higher field values with increasing temperature in the range between 288 K and 324 K. As already stated, it has been hypothesized that this transition is the result of a field-induced first-order crystallographic phase change from the paramagnetic monoclinic phase to a ferromagnetic orthorhombic phase,¹⁴ which results in the peak of $(-\Delta S_M)$ for $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Ni}_{0.1}$ alloy shifting ~ 290 K at low field ($\Delta\mu_0 H = 2.0$ T) to ~ 300 K at high field ($\Delta\mu_0 H = 5.0$ T) (shown in Fig. 4). The $\text{Gd}_5\text{Si}_{2.01}\text{Ge}_{1.91}\text{Ni}_{0.08}$ alloy (Fig. 3(a)),

FIG. 3. Field dependencies of magnetization of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x=0.08, 0.1$) compounds measured with increasing field and decreasing field in maximum fields up to 5 T. The inset of the lower right corner of Fig. 3(a) shows the Arrott plots of the $\text{Gd}_5\text{Si}_{2.01}\text{Ge}_{1.91}\text{Ni}_{0.08}$ alloy.

FIG. 4. Temperature dependencies of magnetic entropy change and hysteresis loss for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08, 0.1$) compounds. Hysteresis loss is plotted for the magnetic-field change from 0 to 5 T.

however, has lost the two-step magnetic ordering and shows negligible hysteresis, and it performs as a typical ferromagnet. The Arrott plots of the $\text{Gd}_5\text{Si}_{2.01}\text{Ge}_{1.91}\text{Ni}_{0.08}$ alloy are displayed in the inset of Fig. 3(a). No inflection or negative slope is observed as an indication that FM-PM transition is of second-order.^{15,16}

The magnetic-entropy changes ($-\Delta S_M$) were calculated based on the magnetic isotherms in the vicinity of T_C using the Maxwell relation. The ($-\Delta S_M$) vs T plots of the $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ alloys are presented in Fig. 4. The maximum magnetic entropy change ($|\Delta S_M^{\text{max}}|$) for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ with $2x = 0.08$ and 0.1 is 4.4 and $5.0 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, for the applied-field change of 0 to 2 T . The $|\Delta S_M^{\text{max}}|$ is 8.0 and $9.1 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, for 0 to 5 T . These values are comparable to that of pure Gd ($5.1 \text{ J kg}^{-1} \text{ K}^{-1}$ at $\Delta\mu_0 H = 2.0 \text{ T}$ and $10.2 \text{ J kg}^{-1} \text{ K}^{-1}$ at $\Delta\mu_0 H = 5.0 \text{ T}$). Refrigerant capacity (RC) as another effective criterion for characterizing the refrigerant efficiency could be estimated by the method of Gschneidner.¹⁷ When the applied field changed from 0 to 2 T , RC values of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ with $2x = 0.08$ and 0.1 are 122 and 90 J kg^{-1} , respectively. The RC value under an applied field change of 5 T for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.1$) alloy is 288 J kg^{-1} , which is slightly smaller than that of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (305 J kg^{-1} , $\Delta\mu_0 H = 5.0 \text{ T}$).¹² One way to take into account the hysteresis loss of each alloy is to simply subtract it from the corresponding RC value.¹² From Fig. 4, the value of magnetic hysteresis loss for $2x = 0.08$ compound is calculated as less than 1 J/kg and the maximum magnetic hysteresis loss for $2x = 0.1$ alloy is about 14 J/kg . Both values are much smaller than that of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (average value is about 65 J/kg). The low hysteresis with relatively large magnetic entropy change for $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ ($2x = 0.08, 0.1$) alloys is favorable for the applications of magnetic refrigeration materials.

IV. CONCLUSIONS

Ni substituted $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ alloys ($2x = 0.08$ and 0.1) exhibit multiphase structure. The Curie temperature for second order transition of the alloys with $2x = 0.08$ and

0.1 is 300 and 301 K , respectively. An obvious first order transition is exhibited around 295 K for $2x = 0.1$ compound. The maximum of magnetic entropy change ($|\Delta S_M^{\text{max}}|$) of $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ alloys with $2x = 0.08$ and 0.1 is 4.4 and $5.0 \text{ J kg}^{-1} \text{ K}^{-1}$, 8.0 and $9.1 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, under an applied field changes from 0 to 2 T and 0 to 5 T , respectively. The thermal and magnetic hysteresis behaviors are negligible in $2x = 0.08$ alloy. Though thermal hysteresis is $\sim 6\text{--}13 \text{ K}$ for the alloy with $2x = 0.1$, the maximum magnetic hysteresis loss is only about 14 J/kg around transition temperature. This study extends the range of Ni doping in GdSiGeX , as well as focuses on compositions with Si:Ge ratios larger than one, which can be beneficial for magnetic refrigeration applications. Low hysteresis and large ΔS_M suggest that $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Ni}_{2x}$ alloys ($2x = 0.08$ and 0.1) be good candidates for magnetocaloric materials working at room temperature.

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- ¹Z. G. Zheng, H. Y. Yu, X. C. Zhong, D. C. Zeng, and Z. W. Liu, *Int. J. Refrig.* **32**, 78 (2009).
- ²V. K. Pecharsky and K. A. Gschneidner, Jr., *Appl. Phys. Lett.* **70**, 3299 (1997).
- ³H. Wada and Y. Tanabe, *Appl. Phys. Lett.* **79**, 3302 (2001).
- ⁴F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, *Appl. Phys. Lett.* **78**, 3675 (2001).
- ⁵O. Tegus, E. Brück et al., *Nature* **415**, 150 (2002).
- ⁶X. C. Zhong, P. F. Tang, Z. W. Liu, D. C. Zeng, Z. G. Zheng, H. Y. Yu, W. Q. Qiu, and M. Zou, *J. Alloys Compd.* **509**, 6889 (2011).
- ⁷V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, *Annu. Rev. Mater. Res.* **42**, 305 (2012).
- ⁸V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- ⁹A. Giguere, M. Foldeaki, B. Ravi Gopal, R. Chahine, T. K. Bose, A. Frydman, and J. A. Barclay, *Phys. Rev. Lett.* **83**, 2262 (1999).
- ¹⁰V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **167**, L179 (1997).
- ¹¹R. D. Shull, V. Provenzano, A. J. Shapiro, A. Fu, M. W. Lufaso, J. Karapetrova, G. Kletetschka, and V. Mikula, *J. Appl. Phys.* **99**, 08K908 (2006).
- ¹²V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature* **429**, 853 (2004).
- ¹³K. Prabakar, D. M. Raj Kumar, M. Manivel Raja, M. Palit, and V. Chandrasekaran, *Mater. Sci. Eng., B* **172**, 294 (2010).
- ¹⁴W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, Jr., V. G. Young, Jr., and G. J. Miller, *Phys. Rev. Lett.* **84**, 4617 (2000).
- ¹⁵Z. G. Zheng, X. C. Zhong, K. P. Su, H. Y. Yu, Z. W. Liu, and D. C. Zeng, *Sci. China-Phys. Mech. Astron.* **54**, 1267 (2011).
- ¹⁶Y. K. Fang, C. H. Lai, C. C. Hsieh, X. G. Zhao, H. W. Chang, W. C. Chang, and W. Li, *J. Appl. Phys.* **107**, 09A901 (2010).
- ¹⁷K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, and C. B. Zimm, *Mater. Sci. Forum* **315–317**, 69 (1999).