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Low hysteresis and large room temperature magnetocaloric effect of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08, 0.1$) alloys

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$Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08, 0.1$) alloys were prepared by arc melting followed by annealing at 1273 K for 96 h. Mixed monoclinic $Gd_5Si_2Ge_2$-type phase, orthorhombic Gd_5Si_4-type phase, and a small amount of Gd_5Si_3-type phase were obtained in these alloys. $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy undergoes a second-order transition (T_C) around 300 K, whereas $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ alloy exhibits two transitions including a first-order transition (${T_C}^{II}$) at ∼295 K and second-order transition (${T_C}^{I}$) 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 ($|\Delta S_M^{max}|$) of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys with $2x = 0.08$ and 0.1 are 4.4 and 5.0 J kg^{-1} K^{-1}, respectively, for 0–2 T, and are 8.0 and 9.1 J kg^{-1} K^{-1}, respectively, for 0–5 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 materials[2–7] have been investigated regarding to their applications in this new cooling technology. In particular, discovery of the giant magnetocaloric effect (GMCE) in the $Gd_5(Si_2Ge_2)$ and $Gd_5(Si_xGe_{1-x})_4$ ($0.24 \leq x \leq 0.5$) alloys[2,8] is a benchmark in the study of magnetic refrigerants near room temperature. However, $Gd_5(Si_2Ge_2)$ 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 $Gd_5Ge_2Si_2$ 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 $Gd_5Ge_2Si_2$ 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 $Gd_5Ge_{1.9}Si_2Fe_{0.1}$.[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 $Gd_5Si_{2-x}Ge_{2-x}Nb_{2x}$ alloys increased T_C to ∼295 K and enhanced the magnetocaloric effect as x increased to $x = 0.05$. The $\Delta S_M = -9.6$ J kg^{-1} K^{-1} for $\Delta H = 2$ T was obtained, which is ∼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, $Gd_5Si_{2.05}Ge_{1.95}$ 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$ 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-Kα 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08, 0.1$) alloys. Three types of phases, i.e., monoclinic $Gd_5Si_2Ge_2$-type phase, orthorhombic Gd_5Si_4-type phase, and hexagonal $Gd_5(Si,Ge)_3$-type phase, were observed. The XRD peaks at ∼26.2° and 37.9°

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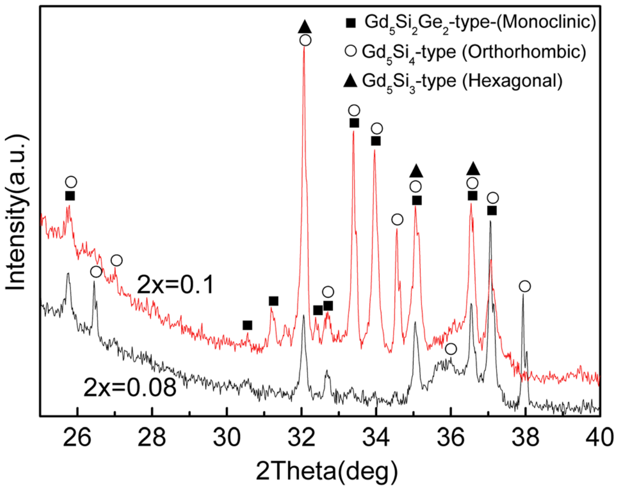

FIG. 1. The XRD patterns for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys at room temperature.

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 ∼31.2° and 32.4° correspond to the monoclinic $Gd_5Si_2Ge_2$-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 $Gd_5Si_2Ge_2$-type phase increases. The XRD peaks at ∼35.2° and ∼36.6° in Fig. 1 are related to the hexagonal $Gd_5(Si, Ge)_3$-type phase.

The temperature dependencies of magnetization for the $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 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 $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy indicates that it should undergo a second-order magnetic transition, and T_C is around 300 K. For $Gd_5Si_2Ge_{1.9}Ni_{0.1}$, two slopes are observed in M-T curves, indicating two magnetic transitions, 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.

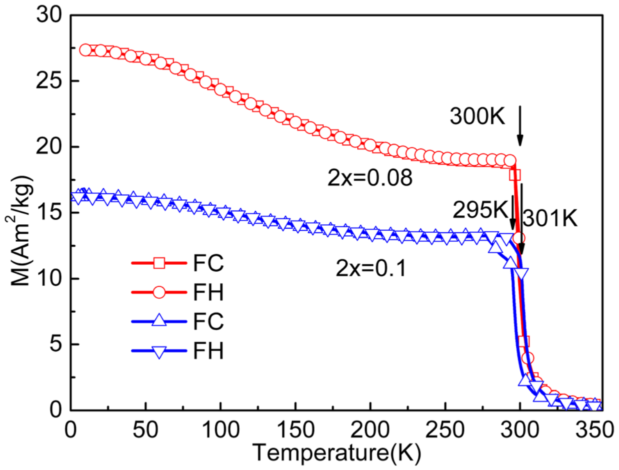

FIG. 2. Magnetization–temperature curves for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys measured in a magnetic field of 0.05 T.

Figure 3 displays the isothermal magnetization curves for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, and 0.1) alloys. The $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ alloy (Fig. 3(b)) has the typical magnetization characteristics of pure $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_{1.9}Ni_{0.1}$ 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 $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy (Fig. 3(a)),

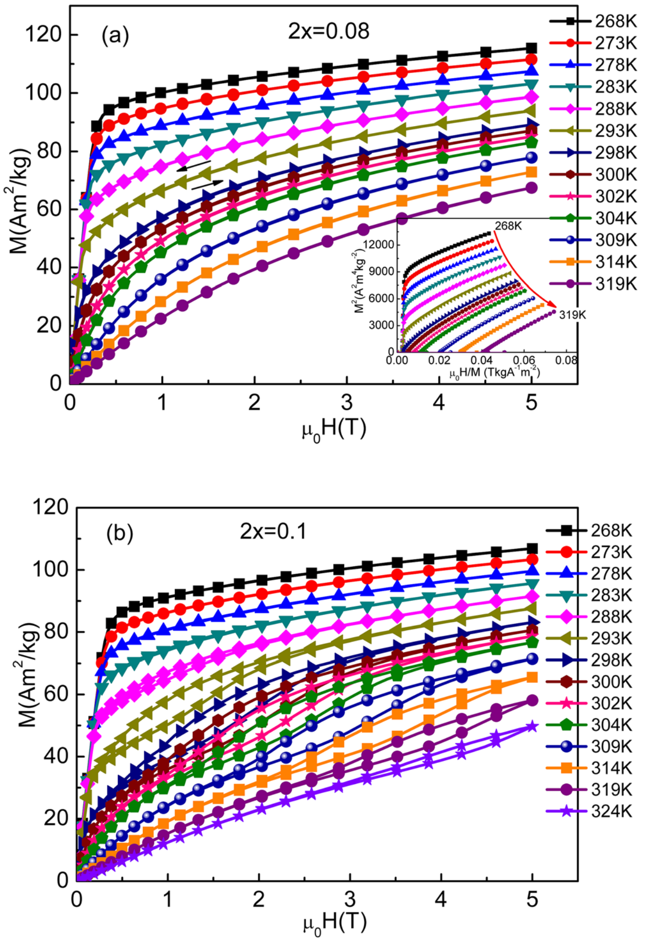

FIG. 3. Field dependencies of magnetization of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) compounds measured with increasing field and decreasing field in maximum fields up to 5 T. The inset of the lower right corner of Fig. 3(a) shows the Arrott plots of the $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ alloy.

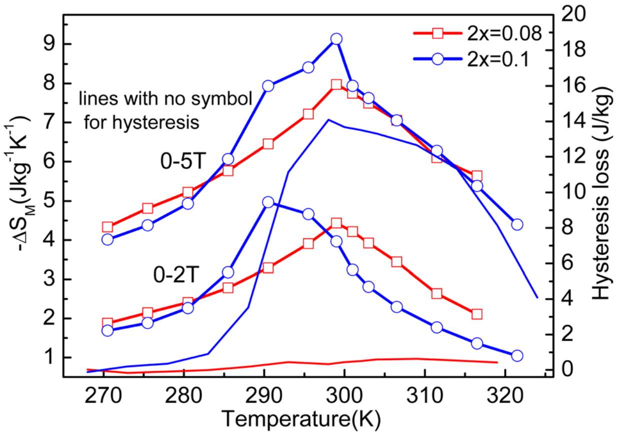

FIG. 4. Temperature dependencies of magnetic entropy change and hysteresis loss for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) compounds. Hysteresis loss is plotted for the magnetic-field change from 0 to 5 T.

however, has lost the two-step magnetic ordering and shows negligible hysteresis, and it performs as a typical ferromagnet. The Arrott plots of the $Gd_5Si_{2.01}Ge_{1.91}Ni_{0.08}$ 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys are presented in Fig. 4. The maximum magnetic entropy change ($|\Delta S_M^{max}|$) for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ with $2x = 0.08$ and 0.1 is 4.4 and 5.0 J kg^{-1} K^{-1}, respectively, for the applied-field change of 0 to 2 T. The $|\Delta S_M^{max}|$ is 8.0 and 9.1 J kg^{-1} K^{-1}, respectively, for 0 to 5 T. These values are comparable to that of pure Gd (5.1 J kg^{-1} K^{-1} at $\Delta\mu_0 H = 2.0$ T and 10.2 J kg^{-1} K^{-1} at $\Delta\mu_0 H = 5.0$ 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.1$) alloy is 288 J kg^{-1}, which is slightly smaller than that of $Gd_5Si_2Ge_2$ (305 J kg^{-1}, $\Delta\mu_0$ H = 5.0 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 $Gd_5Si_2Ge_2$ (average value is about 65 J/kg). The low hysteresis with relatively large magnetic entropy change for $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ ($2x = 0.08$, 0.1) alloys is favorable for the applications of magnetic refrigeration materials.

IV. CONCLUSIONS

Ni substituted $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ 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 ($|\Delta S_M^{max}|$) of $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys with $2x = 0.08$ and 0.1 is 4.4 and 5.0 J kg^{-1} K^{-1}, 8.0 and 9.1 J kg^{-1} 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 ~6–13 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 $Gd_5Si_{2.05-x}Ge_{1.95-x}Ni_{2x}$ alloys ($2x = 0.08$ and 0.1) be good candidates for magnetocaloric materials working at room temperature.

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