Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K

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A giant magnetocaloric effect (ΔS_{mag}) has been discovered in the $Gd_5(Si_xGe_{1-x})_4$ pseudobinary alloys, where $x \leqslant 0.5$. For the temperature range between ~50 and ~280 K it exceeds the reversible (with respect to alternating magnetic field) ΔS_{mag} for any known magnetic refrigerant material at the corresponding Curie temperature by a factor of 2–10. The two most striking features of this alloy system are: (1) the first order phase transformation, which brings about the large ΔS_{mag} in $Gd_5(Si_xGe_{1-x})_4$, is reversible with respect to alternating magnetic field, i.e., the giant magnetocaloric effect can be utilized in an active magnetic regenerator magnetic refrigerator; and (2) the ordering temperature is tunable from ~30 to ~276 K by adjusting the Si:Ge ratio without losing the giant magnetic entropy change. © *1997 American Institute of Physics.* [S0003-6951(97)01624-0]

During a systematic study of rare earth containing intermetallic compounds which order magnetically between 250 and 310 K for use in a magnetic refrigerator to cool below room temperature, we discovered the existence of a giant magnetocaloric effect in the $Gd_5(Si_xGe_{1-x})_4$ alloys, where $x \leqslant 0.5$. As far as we are aware, the reversible magnetic field induced magnetic entropy changes are the largest ever observed experimentally in a magnetic refrigerant material by about a factor of 2 or more. This letter reports the results obtained to date.

A total of 12 $Gd_5(Si_xGe_{1-x})_4$ samples with x ranging from 0 to 1 were prepared by arc melting of the pure constituents in an argon atmosphere under normal pressure. No other phases (optical metallography and x-ray powder diffraction) were found in any of the as-cast alloys and, therefore, no heat treatment was performed. There are three extended solid solution regions in the system (see Fig. 1). Up to 50 at. % Ge is soluble in Gd_5Si_4 and up to 20 at .% Si is soluble in Gd_5Ge_4. The $Gd_5(Si_xGe_{1-x})_4$ phase ($0.24 \leqslant x \leqslant 0.5$) has a monoclinic crystal structure derivative from the parent Sm_5Ge_4 type. The details on the crystallography in this system are being published elsewhere.

The heat capacity in magnetic fields of 0, 2, 5, 7.5, and 10 T from ~3 to 350 K was measured using an automated heat pulse calorimeter with an accuracy better than 1%.[1] The ac and dc magnetic susceptibility and dc magnetization from ~4.2 to 325 K in bias dc magnetic fields from 0 to 5.5 T were measured using the Lake Shore ac/dc magnetometer, model No. 7225. The magnetocaloric properties were evaluated from the dc magnetization using the Maxwell relation, and from the zero and magnetic field heat capacity.[2]

The zero magnetic field phase diagram in pseudobinary system Gd_5Si_4–Gd_5Ge_4 as a function of Si- concentration is shown in Fig. 1. The Gd_5Si_4-based solid solution has a simple ferromagnetic ground state, and the Curie temperature is gradually lowered with increasing concentration of Ge from ~335 to ~295 K, which is in good agreement with an earlier study.[3] When the Si content reaches the first critical concentration ($x = 0.5$) the parent orthorhombic Gd_5Si_4 structure undergoes a monoclinic distortion and the intermetallide is no longer a simple ferromagnet. Initially it orders ferromagnetically to form an ordered magnetic structure (I) with a low net magnetic moment and then upon further cooling a first order phase transition from ferromagnet (I) to ferromagnet (II) occurs. Both Curie temperatures decrease rapidly with decreasing Si content until a second critical concentration is reached and a second crystal structure change occurs. At $x \leqslant 0.24$ the distorted monoclinic structure again becomes orthorhombic, and this crystallographic transition changes the higher temperature ground state to a ferrimagnet and nearly freezes the Néel temperature, while the Curie temperature continues to decrease proportionally as the amount of Si decreases in the alloy. The ferrimagnetic to ferromagnetic transition is also a first order phase transition. These differences between the three regions are maintained in magnetic fields of up to 10 T.

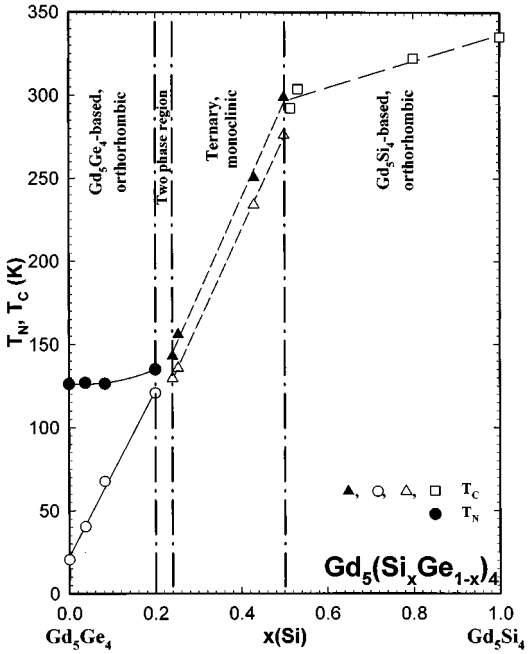

FIG. 1. The phase diagram of the Gd_5Si_4–Gd_5Ge_4 pseudobinary system at zero magnetic field. The solid and the dashed lines show magnetic phase boundaries, and the dot–dashed lines show crystallographic phase boundaries. T_C and T_N are the Curie and the Néel temperatures, respectively.

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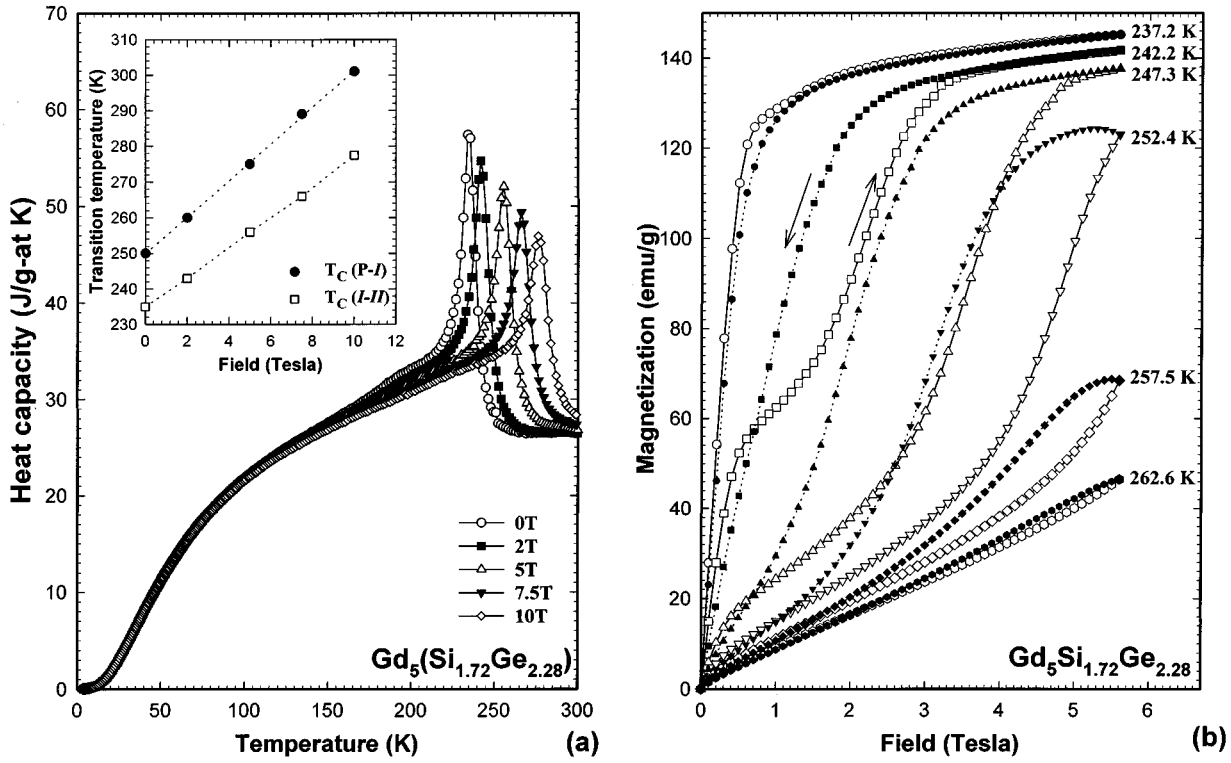

FIG. 2. The (a) heat capacity and (b) magnetization of $Gd_5(Si_xGe_{1-x})_4$, where $x=0.43$ as a function of temperature and magnetic field. The inset of (a) shows the influence of the magnetic field on the Curie temperatures: T_C(P-I) is the paramagnetic to ferromagnetic (I) and T_C(I-II) is the ferromagnetic (I) to ferromagnetic (II) transition temperature.

Figure 2 shows the heat capacity and magnetization as functions of temperature and magnetic field for one exemplary alloy. The heat capacity of the orthorhombic alloys with $x \leqslant 0.2$ in all magnetic fields maintains two anomalies: the high temperature paramagnetic/ferrimagnetic and low temperature ferrimagnetic/ferromagnetic transitions. The bulk of the magnetic entropy is associated with the ferrimagnetic/ferromagnetic transition. The magnetization isotherms near the Curie temperature confirm that the lower temperature transition is ferromagnetic. At this point it is difficult to determine whether the high temperature phase is truly antiferromagnetic or ferrimagnetic, but the fact that this phase has two eightfold and one fourfold inequivalent Gd atoms favors the ferrimagnetic structure. The dc magnetization behavior also favors ferrimagnetism. Differential scanning calorimetry near the low temperature transitions show thermal hysteresis (on warming they occur at 2–3 K higher than on cooling) and a latent heat (the entropy of transformation averages ~ 12 J/g atoms Gd K) for all of the studied alloys with $x \leqslant 0.5$. Combined with partial magnetic hysteresis [Fig. 2(b)] this shows that the transitions are first order, although the onsets (on heating) in the heat capacity [Fig. 2(a)] may suggest a second order, but this broadening could also be due to some inhomogeneities in the Si:Ge ratio throughout the sample.

The heat capacity and magnetization of $Gd_5(Si_{1.72}Ge_{2.28})$, which are shown in Fig. 2, are typical for the monoclinic ternary alloys. The behavior is quite similar to that discussed in the previous paragraph except that the higher temperature transition is not paramagnetic/ ferrimagnetic, but rather paramagnetic/ferromagnetic. Therefore, upon cooling, the alloys undergo a transition from paramagnet to ferromagnet (I), and then from ferromagnet (I) to ferromagnet (II). The inset of Fig. 2(a) indicates that both transitions are shifted towards higher temperatures by an increasing magnetic field (as determined from magnetic susceptibility, magnetization, and magnetic heat capacity data) which is consistent with ferromagnetic order for both magnetic phases. Another feature which is worth noting is the behavior of magnetization just after the field is reversed—the magnetization of $Gd_5(Si_{1.72}Ge_{2.28})$ actually rises when the field is lowered from its highest value of 5.6 T [Fig. 2(b), 252.4 K, and 257.5 K isotherms]. It is quite reasonable to assume that the magnetocaloric effect is so large at this temperature and field, that the sample temperature is significantly lowered when the field is reduced and thus the actual magnetization value is for a temperature slightly lower than that indicated in the figure.

Another interesting feature is seen in the heat capacity peaks as the magnetic field increases from 0 to 10 T. For the monoclinic phases the peak height decreases in a monotonic fashion [Fig. 2(a)], while for the Ge-rich orthorhombic alloys there is an initial decrease (0–2 T) and then a monotonic increase for $H>2$ T. This is due to the fact that for a ferromagnet the entropy is spread out to higher temperatures with increasing field, but for an ferrimagnet the entropy is shifted to lower temperatures, provided that the magnetic field does not destroy the ferrimagnetic order. In the case of the Ge-rich orthorhombic alloys this entropy is shifted towards the lower transition (Curie) temperature which has the effect of increasing entropy at the lower ordering temperature and thus enhancing the heat capacity peak.

The lower temperature magnetic ordering transition in the $Gd_5(Si_xGe_{1-x})_4$ alloys with $x \leqslant 0.5$ is first order. Even

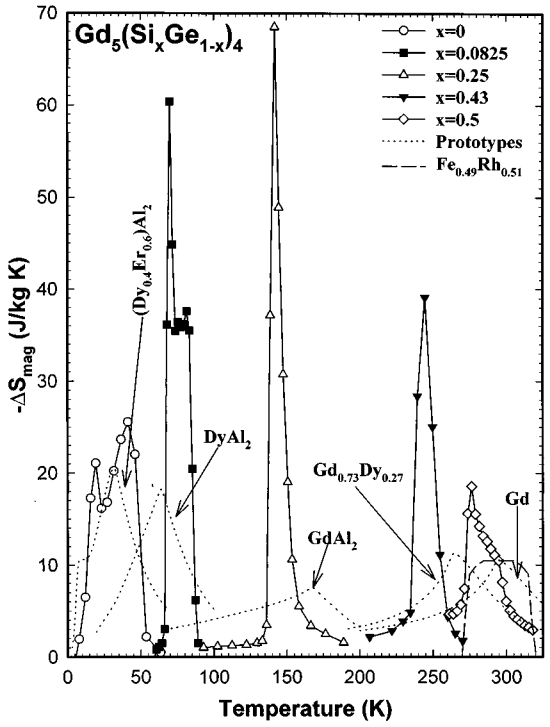

FIG. 3. The magnetic entropy change (ΔS_{mag}) of $Gd_5(Si_xGe_{1-x})_4$ alloys in the vicinity of the first order phase transition as determined from magnetization data for a magnetic field change from 0 to 5 T. Also shown in dotted lines are the ΔS_{mag} values for the best prototype magnetic regenerator alloys: $(Dy_{0.4}Er_{0.6})Al_2$ and $DyAl_2$ (Ref. 4); Gd (Ref. 5), $GdAl_2$ and $Gd_{0.73}Dy_{0.27}$ (our unpublished data). The irreversible ΔS_{mag} in $Fe_{0.49}Rh_{0.51}$ (Ref. 7) is shown for comparison.

though the transition is partially hysteretic, which is a specific feature of any first order phase transition, the magnetic structure changes back to ferrimagnetic [or ferromagnetic (I) depending on the alloy composition], the remnant magnetization for all of the alloys reduces to zero when the magnetic field is removed. The magnetocaloric effect (Fig. 3), expressed in terms of the magnetic entropy change, ΔS_{mag}, achieves the largest values ever reported in the literature for any magnetic solid. Except for the lowest temperature alloy, the ΔS_{mag} is as much as 2–10 times larger than that of the best known materials with a *reversible* (with regard to a changing magnetic field) magnetic phase transition compared at their respective temperatures.

It should be noted that a giant magnetocaloric effect near the first order antiferromagnetic↔ferromagnetic transition in $Fe_{0.49}Rh_{0.51}$ has been observed.[6,7] But this material has no practical use for two important reasons:

(1) Rh is prohibitively expensive ($120 000/kg which compares to $120/kg for Gd) and
(2) the transition (and the magnetocaloric effect) is irreversible in an alternating magnetic field and it eventually disappears after a few cycles.[6,7]

A study of the magnetocaloric effect near the antiferromagnetic↔ferromagnetic transition in $(Hf_{0.83}Ta_{0.17})Fe_{2+x}$ revealed that it is fairly small and typical or lower than that in common ferromagnets, although the authors claim that at $x=-0.02$ there is a possibility for the existence of a giant magnetic entropy change.[8] No data on the reversibility of the effect in $(Hf_{0.83}Ta_{0.17})Fe_{2+x}$ are given.[8]

A sharp (a 3 to 3.5-fold) reduction of the ΔS_{mag} is observed in $Gd_5(Si_xGe_{1-x})_4$ alloys on the opposite side of the phase boundary between the intermediate solid solution region and the Gd_5Si_4 solid solution phase, i.e., $x \cong 0.5$. This reduction in ΔS_{mag} is due to the fact that the Gd_5Si_4-based orthorhombic solid solution alloys ($x>0.5$) exhibit a second order paramagnetic/ferromagnetic transition, while the monoclinic phase ($x \leqslant 0.5$) undergoes a first order magnetic transition. This offers additional evidence that the first order nature of the phase transition creates conditions for the existence of a giant magnetocaloric effect.

This research has lead to the discovery of a new class of solid magnetic materials with a temperature and magnetic field dependent reversible first order magnetic phase transition which is accompanied by a giant magnetic entropy change. The magnetocaloric effect for a first order phase transition in $Gd_5(Si_xGe_{1-x})_4$, when $0 \leqslant x \leqslant 0.5$ is different from that for a second order one, as noted in the previous paragraph. This difference is similar to the difference between the constant temperature cooling by an evaporating liquid versus the cooling by a simple gas expansion, because both the first order magnetic phase transition and liquid evaporation utilize the enthalpy of transformation (evaporation) to increase their entropies at a constant temperature, while the second order magnetic phase transition and gas expansion does not. The evaporation of a liquid at its boiling point (constant temperature cooling) is much more effective, since a much larger entropy change is involved during evaporation as compared to that involved in just a gas expansion, although the temperature span is significantly smaller in the case of a boiling liquid than for a gas expansion process. Therefore, we believe that the experimental results reported in this letter bring the active magnetic regenerator magnetic refrigeration technology much closer to reality than here-to-fore, and that the $Gd_5(Si_{1-x}Ge_x)_4$ materials offer a long awaited breakthrough by bringing forth working bodies which should prove that magnetic refrigeration is a feasible, much more compact, CFC-free, and an energy saving technology.

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[1] V. K. Pecharsky, J. O. Moorman, and K. A. Gschneidner (unpublished).
[2] V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Cryogen. Eng. **42**, 423 (1997).
[3] F. Holtzberg, R. J. Gambino, and T. R. McGuire, J. Phys. Chem. Solids **28**, 2283 (1967).
[4] K. A. Gschneidner, Jr., V. K. Pecharsky, and S. K. Malik, Adv. Cryogen. Eng. **42**, 475 (1997).
[5] S. M. Benford and G. V. Brown, J. Appl. Phys. **52**, 2110 (1981); B. K. Ponomarev, J. Magn. Magn. Mater. **61**, 129 (1986).
[6] M. P. Annaorazov, K. A. Asatryan, G. Myalikgulyev, S. A. Nikitin, A. M. Tishin, and L. A. Tyurin, Cryogenics **32**, 867 (1992).
[7] M. P. Annaorazov, S. A. Nikitin, A. L. Tyurin, K. A. Asatryan, and A. Kh. Dovletov, J. Appl. Phys. **79**, 1689 (1996).
[8] J. F. Herbst, C. D. Fuerst, and R. D. McMichael, J. Appl. Phys. **79**, 5998 (1996).