Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$

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An extremely large magnetic entropy change has been discovered in $Gd_5(Si_2Ge_2)$ when subjected to a change in the magnetic field. It exceeds the *reversible* (with respect to an alternating magnetic field) magnetocaloric effect in any known magnetic material by at least a factor of 2, and it is due to a first order [ferromagnetic (I) ↔ ferromagnetic (II)] phase transition at 276 K and its unique magnetic field dependence. [S0031-9007(97)03321-8]

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Currently, there is a great deal of interest in utilizing the magnetiocaloric effect as an alternate technology for refrigeration from the ambient temperature to the temperatures of hydrogen and helium liquefaction ($\sim 20-4.2$ K) replacing the common gas compression/expansion technology in use today. Refrigeration in the subroom temperature ($\sim 250-290$ K) range is of particular interest because of potential impact on energy savings and environmental concerns. Materials with the larger magnetocaloric effects are needed to improve the energy efficiency. In a study of the magnetic properties of Gd-based materials with Curie temperatures between 250 and 350 K, we have discovered an extraordinarily large magnetocaloric effect in $Gd_5(Si_2Ge_2)$. This letter describes the results obtained to date on this alloy.

Gd_5Si_4 orders ferromagnetically at 335 K [1]. The related phase Gd_5Ge_4, orders antiferromagnetically at much lower temperature [1]. As shown by Holtzberg *et al.* [1], when Ge substitutes for Si in $Gd_5(SiGe)_4$, the Curie temperature is lowered from 335 to ~295 K at the $Gd_5(Si_2Ge_2)$ composition. Further substitution of Ge for Si induces the appearance of a then unidentified intermediate phase and the beginning of a sharp decrease in the ordering temperature when the Si:Ge ratio is further reduced [1].

Our experimental studies confirm that the extended solid solution $Gd_5(Si_xGe_{1-x})_4$ exists for $1 \le x < 0.5$ and that the Curie temperature of Gd_5Si_4 is gradually lowered from 335 to ~300 K near the $Gd_5(Si_2Ge_2)$ composition which is in excellent agreement with the results reported by Holtzberg *et al.* [1]. At this composition, however, the parent (Sm_5Ge_4-type, [2]) orthorhombic structure of Gd_5Si_4 no longer exists, but undergoes a monoclinic distortion. According to single crystal and powder x-ray diffraction data $Gd_5(Si_2Ge_2)$ crystallizes in the space group $P2_1/a$ with the unit cell parameters $a = 7.5808(5), b = 14.802(1), c = 7.7799(5)$ Å, $\gamma = 93.190(4)°$. The phase purity of $Gd_5(Si_2Ge_2)$ has been confirmed by optical metallography. Gd atoms occupy five symmetrically inequivalent $4(e)$ sites, and Si and Ge also occupy the $4(e)$ sites of four inequivalent sublattices in a random fashion in the monoclinic structure. The structural investigation of $Gd_5(Si_2Ge_2)$ is being published elsewhere. The change from orthorhombic Sm_5Ge_4-type to a monoclinic $Gd_5(Si_2Ge_2)$-type structure brings about a fundamental difference in the magnetic behavior of the alloy. Initially, it orders ferromagnetically (299 K) and then upon further cooling it undergoes a first order phase transition from the high temperature ferromagnetic (I) to a second ferromagnetic structure (II) at 276 K; see Figs. 1 and 2. The temperatures of both phase transitions were estimated from the corresponding χ_{ac} anomalies in different dc fields (Fig. 2) and from the magnetization data (Fig. 3) showing that both magnetic phase transitions shift to higher temperatures with increasing field (see inset of Fig. 2), and therefore they are ferromagnetic in origin.

The magnetization isotherms of $Gd_5(Si_2Ge_2)$ between 272 and 309 K are shown in Fig. 3. The shape of the magnetization isotherms at $278 \le T \le 298.6$ K also

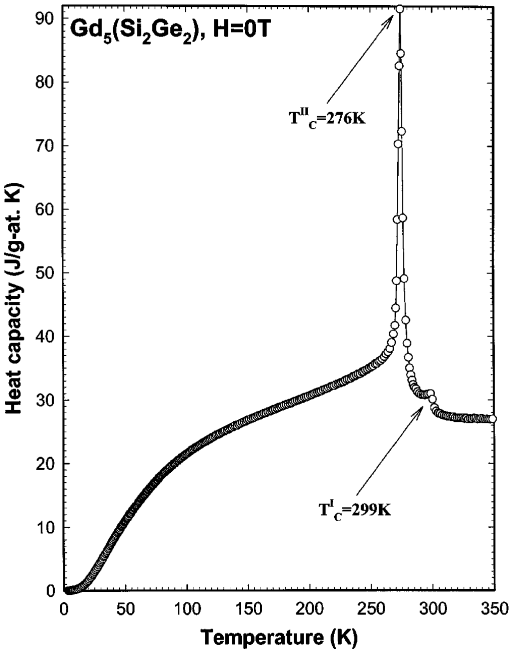

FIG. 1. The zero magnetic field heat capacity of $Gd_5(Si_2Ge_2)$ from 3.5 to 350 K. The arrows point to heat capacity anomalie due to a second order paramagnetic ↔ ferromagnetic (I) transformation at 299 K and a first order ferromagnetic (I) ↔ ferromagnetic (II) transition at 276 K.

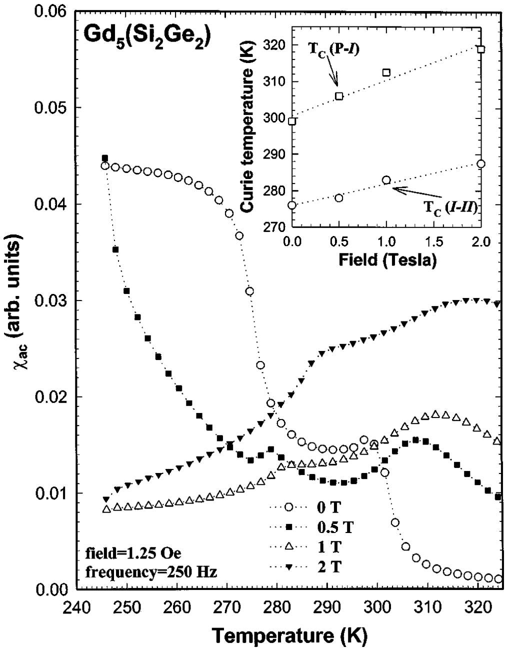

FIG. 2. The ac susceptibility of $Gd_5(Si_2Ge_2)$ from 240 to 325 K in bias dc magnetic fields. The inset shows the magnetic field dependence of the Curie temperatures of the two magnetic transformations: paramagnetic ↔ ferromagnetic (I) [*P*-*I*] and ferromagnetic (I) ↔ ferromagnetic (II) [I-II]. The errors in the temperatures in the inset are 1 to 2 K.

supports the existence of the two ferromagnetic transitions, and from the intercepts of the linear portion of the steps extrapolated to $H = 0$ ($\sigma_H = 0$), it appears that two of the five crystallographically inequivalent Gd sublattices order at 299 K and the remaining three order at 276 K. The hysteresis of the ferromagnetic (I) ↔ ferromagnetic (II) transition is limited to a small field range and, most importantly, does not extend to zero field where high magnetic field structure (II) changes back to low magnetic field structure (I) when the field is reduced to zero (Fig. 3). The magnetocaloric effect (ΔS_{mag}) can be determined from the magnetization *M* data utilizing the Maxwell relation

$$(\partial S_{\mathrm{mag}}/\partial H)_T = (\partial M/\partial T)_H ,$$

where *T* is the absolute temperature and *H* is the applied magnetic field. The magnetocaloric effect is shown in Fig. 4 for field changes of 0 to 2 T and 0 to 5 T. For comparison, the magnetocaloric effect of pure Gd metal is also shown, and it is evident that the magnetocaloric effect in $Gd_5(Si_2Ge_2)$ is about twice as large as that of Gd, when comparing the peak values, irrespective of their Curie temperatures. Not only are the ΔS_{mag} values much larger, but the breadth of the peaks is much narrower for $Gd_5(Si_2Ge_2)$ than that of Gd, thus concentrating the entropy change over a smaller temperature interval.

The magnetic field dependencies of the heat capacities of $Gd_5(Si_2Ge_2)$ and Gd are shown in Fig. 5(a) and 5(b), respectively. One notices a significant difference in the influence of the magnetic field on the heat capacity of the two materials. For $Gd_5(Si_2Ge_2)$ the low temperature heat capacity peak is quite sharp and it essentially retains the same shape while the peak height falls off and the peak temperature increases more-or-less in a linear fashion with increasing field. In contrast, for Gd the typical broad λ-like peak is reduced in height by low magnetic fields,

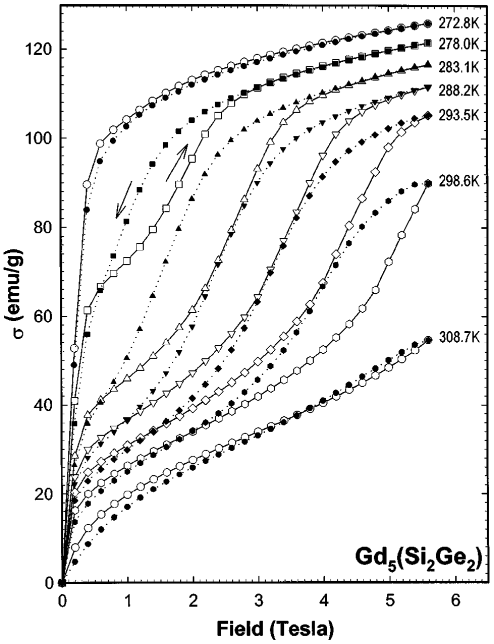

FIG. 3. The magnetization isotherms of $Gd_5(Si_2Ge_2)$ between 272 and 310 K measured on field increase (solid lines and open points) and field decrease (dotted lines and solid points).

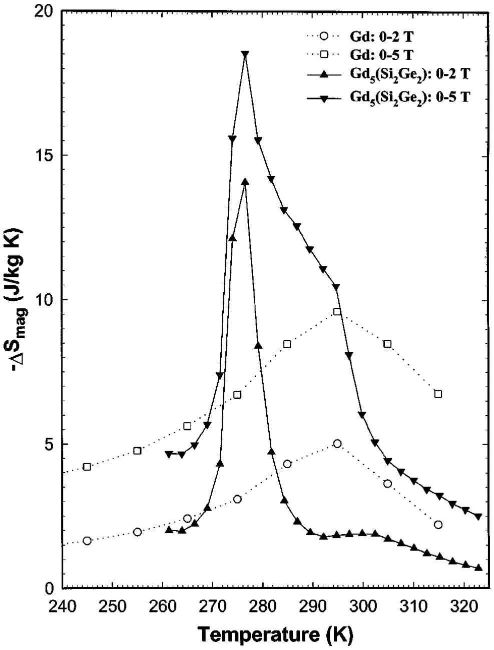

FIG. 4. Magnetic entropy change of the $Gd_5(Si_2Ge_2)$ between 240 and 325 K for a magnetic field change 0 to 2 and 0 to 5 T, respectively, compared to that of pure Gd as determined from magnetization measurements.

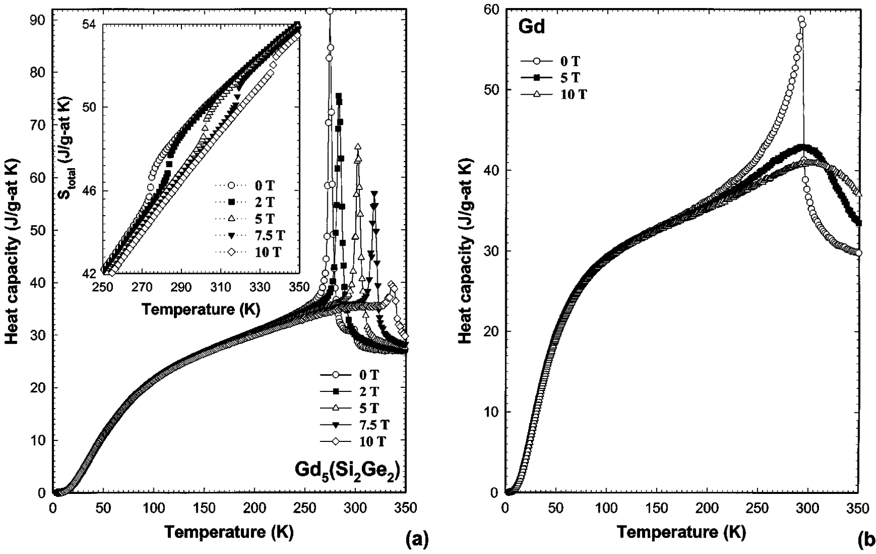

FIG. 5. The heat capacity of $Gd_5(Si_2Ge_2)$ as a function of temperature and magnetic field (a) in comparison with that of pure Gd (b). The inset in (a) shows total entropy of $Gd_5(Si_2Ge_2)$ as a function of temperature and magnetic field from 250 to 350 K as determined from the heat capacity.

becomes rounded off, and is spread out over a wide temperature with increasing field. This difference is due to the fact that for $Gd_5(Si_2Ge_2)$ the lower temperature and dominant magnetic ordering [ferromagnetic $(\mathrm{I}) \leftrightarrow$ ferromagnetic (II)] is a first order phase transformation, while for Gd it is a second order transformation. The field dependence of $Gd_5(Si_2Ge_2)$ entropy, which is shown in the inset of Fig. 5(a) indicates that the $S(T)$ discontinuity is shifted to higher temperature by increasing magnetic field and that the transition remains thermodynamically a first order phase transformation in magnetic fields as high as 7.5 T (and, maybe, even 10 T).

Finally, we show in Fig. 6, the magnetocaloric effect as the adiabatic temperature rise (ΔT_{ad}) as determined from the magnetization and heat capacity measurements as functions of temperature and magnetic field. The ΔT_{ad}, which is the isentropic difference between $S(B = 0, T)$ and $S(B_0, T)$ [see inset to Fig. 5(a)] can be determined entirely from the heat capacity. Here S is the total entropy which can be calculated as a function of temperature by numerical integration: $S(B_0, T) = \int_0^T \frac{C(B_0,T)}{T}\, dT$, where B_0 is the magnetic field at which heat capacity was experimentally measured. On the other hand, ΔT_{ad} can also be determined by using the zero magnetic field heat capacity to calculate the $S(B = 0, T)$ curve and then use the ΔS_{mag} from magnetization measurements to determine the $S(B_0, T)$ curve(s) for nonzero magnetic fields. Since the ΔS_{mag} calculated from magnetization data is the isothermal magnetic field induced magnetic entropy change (see the Maxwell relation, above), then $S(B_0, T)$ is obtained by subtracting off the corresponding $\Delta S_{\mathrm{mag}}(B_0, T)$ from $S(B = 0, T)$ isothermally. Once this is done, then again ΔT_{ad} represents the isentropic difference between $S(B = 0, T)$ and $S(B_0, T)$. It is important that both methods yield the same results, which insures that there is no unaccounted systematic errors, particularly when relying only on the heat capacity data [3].

The adiabatic temperature rise for $Gd_5(Si_2Ge_2)$ is quite sharp and extends over a narrow temperature range, just as the ΔS_{mag} (Fig. 4). The ΔT_{ad} values of $Gd_5(Si_2Ge_2)$ are larger than the corresponding ΔT_{ad} values for Gd by $\geq 30\%$, comparing the peak values, regardless of the temperature. The extremely large magnetic entropy change in $Gd_5(Si_2Ge_2)$ is consistent with thermodynamics, since it follows directly from the Maxwell

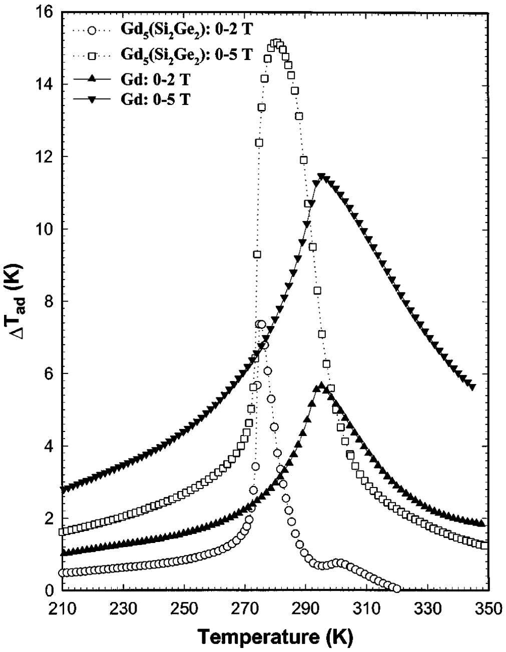

FIG. 6. The magnetocaloric effect in $Gd_5(Si_2Ge_2)$ from 210 to 350 K in comparison with that of pure Gd for magnetic field change from 0 to 2 and from 0 to 5 T.

relation $[(\partial S_{\mathrm{mag}})_T = (\partial M/\partial T)_H \times (\partial H)_T]$ that the largest ΔS_{mag} for the same magnetic field change, ΔH, is expected at the most abrupt change in the magnetization with temperature. This can be most easily achieved during order-order magnetic phase transitions compared to order-disorder ones, since the former reduces the effects of spin fluctuations and short range order in paramagnetic region and, therefore, produces greater $(\partial M/\partial T)_H$.

Although the majority of magnetocaloric effect studies were performed on ferromagnetic materials near their respective Curie temperature (i.e., paramagnetic to ferromagnetic transitions), the magnetocaloric properties in the vicinity of a first order phase transformation (generally involving an antiferromagnetic [or ferrimagnetic] phase and a ferromagnetic phase) have been reported for several pure lanthanides, Dy [4–6], Ho [7], Er [7–9], and the intermatallic compounds $HoCo_2$ [10,11], $NdMn_2Si_2$ [11], $Fe_{0.49}Rh_{0.51}$ [12,13], and $(Hf_{0.83}Ta_{0.17})Fe_{2+x}$ [14]. In all cases except $Fe_{0.49}Rh_{0.51}$ the observed magnetocaloric effect is much smaller than that of $Gd_5(Si_2Ge_2)$ and even those of typical ferromagnets (e.g., Gd). This can be understood if one recalls that molar magnetic entropy has a theoretical upper limit given as $S_{\mathrm{mag}} = R\ln(2J + 1)$ J/mol K, where R is a universal gas constant and J is total angular momentum. Hence, when a system has more than one successive magnetic ordering then the total available magnetic entropy must be divided between the two. As a result, the magnetocaloric effect should be larger at a transition which involves the larger portion of the available magnetic entropy. Generally, one would expect that the splitting of the total available magnetic entropy would decrease ΔS_{mag} near both of the two successive transformations. The reasons for the large magnetocaloric effect in $Gd_5(Si_2Ge_2)$ are (i) a small temperature difference between the two magnetic phase transitions (see Figs. 1, 2); (ii) an inequivalent distribution of the magnetic entropy between the first order and the second order transitions [see Figs. 1, 5(a) and inset in 5(a)] with bulk of the entropy being utilized in the first order one; and (iii) the fact that the transition thermodynamically remains a first order phase transformation with increasing magnetic field.

The reported giant magnetocaloric effect in $Fe_{0.49}Rh_{0.51}$ is of approximately the same order of magnitude as observed in $Gd_5(Si_2Ge_2)$. However, the low temperature phase of $Fe_{0.49}Rh_{0.51}$ is an antiferromagnet and the high temperature phase is a ferromagnet, which combined with a large thermal hysteresis ($\sim 10-12$ K) between the transition on warming and on cooling [12,13] and the probable large volume changes during the transition [13], causes the irreversibility of the magnetocaloric effect with regard to alternating magnetic field (i.e., it disappears after one cycle). According to differential scanning calorimetry studies, the width of the thermal hysteresis in $Gd_5(Si_2Ge_2)$ transition is much narrower, ~ 2 K. Furthermore, cycling of a magnetic field does not induce an irreversible change in the magnetic and magnetocaloric behaviors of $Gd_5(Si_2Ge_2)$.

The unique features of $Gd_5(Si_2Ge_2)$, as compared to a more typical ferromagnet, e.g., Gd, or the reported irreversible magnetocaloric effect in $Fe_{0.49}Rh_{0.51}$, which have been discussed above, account for the observed giant magnetocaloric effect. As shown in Figs. 4 and 6, a first order magnetic phase transition concentrates the entropy change and the adiabatic temperature rise, respectively, to much narrower temperature range compared to a second order magnetic phase transformation. Unlike $Fe_{0.49}Rh_{0.51}$, the magnetocaloric effect in $Gd_5(Si_2Ge_2)$ is reversible in alternating magnetic fields. This has a significant impact on the utilization of magnetic materials in magnetic refrigeration, since one can get substantially more cooling power from the magnetic materials near their Curie temperature if they undergo a first order transition. Thus, by the proper design of magnetic refrigerators, one can make use of this new unique behavior to improve the efficiencies of the magnetic refrigerator.

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[1] F. Holtzberg, R. J. Gambino, and T. R. McGuire, J. Phys. Chem. Solids **28**, 2283 (1967).

[2] G. S. Smith, Q. Johnson, and A. G. Tharp, Acta Crystallogr. **22**, 269 (1967).

[3] V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Cryog. Eng. **42A**, 423 (1996).

[4] A. C. Hudgins and A. S. Pavlovic, J. Appl. Phys. **36**, 3628 (1965).

[5] S. M. Benford, J. Appl. Phys. **50**, 1868 (1979).

[6] S. A. Nikitin, A. M. Tishin, and P. I. Leontiev, J. Magn. Magn. Mater. **92**, 405 (1991).

[7] S. A. Nikitin, A. S. Andreenko, A. M. Tishin, and A. M. Arkharov, Phys. Met. Metallogr. **60**, 56 (1985).

[8] C. B. Zimm, P. L. Kral, J. A. Barclay, G. F. Green, and W. G. Patton, in Proceedings of the 5th International Cryocooler Conference, Monterey, California, 1988 (Wright-Patterson Air Force Base, Dayton, Ohio, 1988), p. 49.

[9] C. B. Zimm, Adv. Cryog. Eng. **40**, 647 (1994).

[10] S. A. Nikitin and A. M. Tishin, Cryogenics **31**, 166 (1991).

[11] A. M. Tishin, J. Adv. Mater. **1**, 403 (1994).

[12] M. P. Annaorazov, K. A. Asatryan, G. Myalikgulyev, S. A. Nikitin, A. M. Tishin, and L. A. Tyurin, Cryogenics **32**, 867 (1992).

[13] M. P. Annaorazov, S. A. Nikitin, A. L. Tyurin, K. A. Asatryan, and A. Kh. Dovletov, J. Appl. Phys. **79**, 1689 (1996).

[14] J. F. Herbst, C. D. Fuerst, and R. D. McMichael, J. Appl. Phys. **79**, 5998 (1996).