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Recent Developments in Magnetic Refrigeration

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Abstract

The large magnetocaloric effect (MCE) of Gd metal has enabled us to successfully test a near-room temperature proof-of-principle apparatus and to show that magnetic refrigeration (MR) is a viable and competitive technology with gas compression/expansion refrigeration. A search for new materials with improved magnetocaloric properties has led to the discovery of the giant MCE in $Gd_5(Si_xGe_{1-x})_4$ alloys. These intermetallic compounds should make MR even more efficient and will open the doors to new possibilities for MR. The future prospects of magnetic refrigeration as an important rare earth market are discussed.

1 Introduction

The MCE, which was discovered in 1881 [1], is the response of a magnetic substance to an applied magnetic field, which is observed as a change in its temperature. The MCE has been successfully utilized for about 70 years to achieve ultra low temperatures by employing a process known as adiabatic demagnetization [2]. This is accomplished by cooling a magnetic solid in a large magnetic field (H) to as low a temperature as possible by ordinary means, then thermally isolating the solid from its immediate surroundings and finally turning off the magnetic field. The sample will reach its minimum temperature when H=0. Since the 1950's a few continuously operating MR working at various temperatures from ~1 to ~300 K have been constructed and tested, but most were inefficient and at best ran for only a few days. [2]

The principle of a continuous MR using a ferromagnetic material is illustrated in Fig. 1. Initially the spins of the unpaired electrons are random in the absence of a magnetic field (Fig. 1a), but when a magnetic field is applied the spins align causing the sample to heat up (and the entropy to decrease because of increasing magnetic order in the system), Fig. 1b. The MCE heat is removed from the magnetic material by a heat transfer fluid (gas or liquid) and is rejected to the ambient. When the magnetic field is turned-off the spins randomize cooling the magnetic substance and heat is extracted from the system to be cooled using a heat transfer fluid (Fig. 1c) completing the cycle.

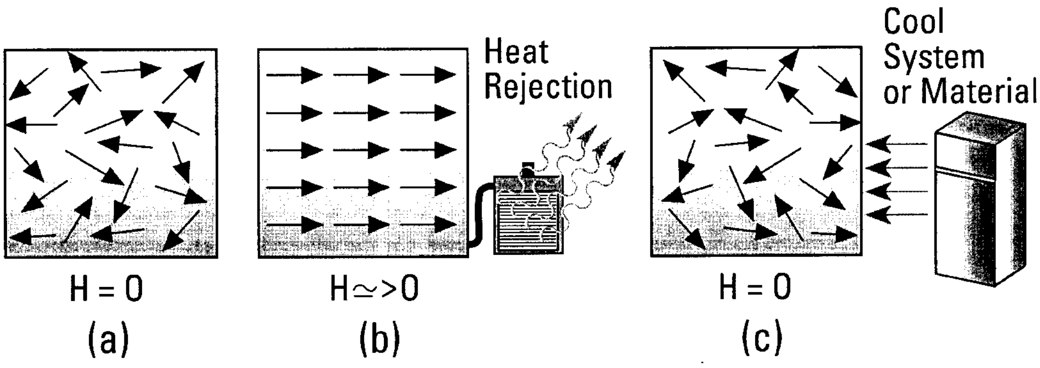

Figure 1: A schematic representation of how magnetic refrigeration works

Below we present a summary of our research during the past two years, which led to two major breakthroughs: (1) the demonstration that MR is a viable and competitive cooling technology with standard gas compression systems; and (2) the discovery of the giant magnetocaloric materials $Gd_5(Si_xGe_{1-x})_4$, which promises to improve the performance of MR and open the door to new applications.

2 Proof-of-Principle Magnetic Refrigerator [3]

A laboratory, reciprocating MR for near room temperature applications was designed, constructed and tested by Astronautics Corporation of America in collaboration with the Ames Laboratory. This demonstration unit began operation about December 1, 1996 and successfully ran for more than 1500 h over an 18 month period. Two magnetocaloric beds, each containing about 1.5 kg of Gd spheres, were moved in and out of a magnetic field such that as one bed moved into the solenoid the other was moving out so that the magnetic forces are essentially balanced. The magnetic field was supplied by a superconducting magnet and could be adjusted from 0 to 5 T. The minimum cycle time was 6 seconds (i.e. operating frequency was 0.17 Hz). The 93 at. % (99.7 wt. %) pure Gd was purchased from China and Gd spheres were prepared by the plasma-rotating electrode process. The heat transfer fluid is water, but if cooling below 273 K (0°C) is required automotive antifreeze can be added to the water to prevent ice formation. The notable achievements obtained with this demonstration unit running at 0.17 Hz, a magnetic field of 5 T and a flow rate of 4 l/min. are: (1) a cooling power of 600 watts (about 100 times greater than previous near room temperature MRs); (2) a COP (coefficient of performance, i.e. cooling power divided by input work) of 8 for a 10 K span (typical gas compression cycle refrigerators have COPs between 2 and 6); (3) a maximum efficiency of 60% of Carnot (seal friction was subtracted-off); and (4) a maximum temperature span of 38 K (the difference in the temperatures of the hot and cold heat exchangers). It should be noted that the maximum cooling power of 600 watts was achieved when the temperature span was only 5 K, while for the maximum temperatures span (38 K) the cooling power was ~120 watts. That is, one must sacrifice cooling power for a large temperature span or vice versa.

The strength of the magnetic field has a pronounced effect on the cooling power, COP, efficiency and temperature span — the larger the magnetic field the better the performance. For example, for H=1.5 T (a field which can be obtained using a high strength permanent magnet such as Nd-Fe-B), a flow rate of 4 l/min., and a frequency of 0.17 Hz the following maximum values were obtained: a cooling power of 180 watts, a COP of 6.5, a Carnot efficiency of 20% and a temperature span of 16 K.

Increasing the frequency of moving the magnetocaloric material in and out of the magnetic field improved the performance. However, the design of the demonstration unit limits the frequency to 0.17 Hz. Increasing the frequency by a factor of 10 should lead to significant improvements of the cooling power and COP of a MR as based on the performances of commercial cryocoolers which run at frequencies up to 30 Hz.

3 Giant Magnetocaloric Effect Materials [4-7]

As part of our study of the MCE in magnetic materials we investigated potential magnetic refrigerants for near room temperature applications. Of the ~12 candidate materials examined one was Gd_5Si_4, which was known to order ferromagnetically at 335 K [8]. In an effort to lower the T_c to between 270 and 300 K (the useful range for air conditioning and refrigerators/freezers) we substituted Ge for Si, since it was known that Ge would lower T_c [8]. But it was also known that pure Gd_5Ge_4 orders ferrimagnetically at ~40 K [8], which might complicate and diminish the MCE properties of Gd_5Si_4 when Ge was substituted for Si. Much to our surprise Ge not only lowered T_c as expected, but actually improved the MCE properties when the concentration of Ge was 50% or greater in the $Gd_5(Si_xGe_{1-x})_4$ system (i.e. $x \leq 0.5$). The T_cs for the $Gd_5(Si_xGe_{1-x})_4$ system for $0.4 \leq x \leq 1.0$ are shown in Fig. 2. For alloys with $0.5 \leq x \leq 1.0$ the materials exhibit a second order paramagnetic (P) to ferromagnetic (F) transition (upon cooling) with a slight decrease in T_c from 335 to 295 K. As seen in Fig. 2, when $x \leq 0.5$ the phases exhibit a simultaneous magnetic and crystallographic phase transition. This change in ordering has a pronounced effect on the MCE, (see below).

4 Heat Capacity

The H = 0 heat capacity of the $Gd_5(Si_xGe_{1-x})_4$ alloys from ~3.5 to ~350 K is shown in Fig. 3. It is seen that for the Si-rich alloys with $x > 0.5$ both T_c and the peak maximum decrease with decreasing x. Also the peak shape changes from the typical textbook λ-shape for x = 1.0 and 0.80, to a rounded peak at $x \cong 0.52$. But for alloys poor in Si ($x \leq 0.5$), the heat capacity peak is very sharp, has a large value, and on the high temperature side of the main peak there is a small bump; the sharp peak corresponds to the first order transition, while the small bump is most likely due to the presence of a small amount of a second phase.

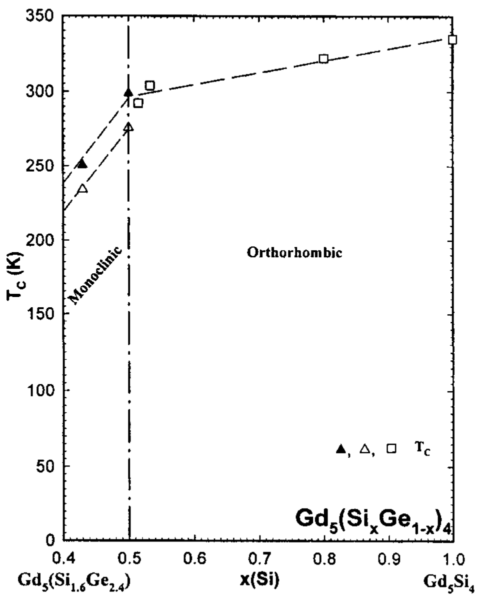

Figure 2: The magnetic ordering temperatures for the $Gd_5(Si_xGe_{1-x})_4$ alloys from x = 0.4 to x = 1.0

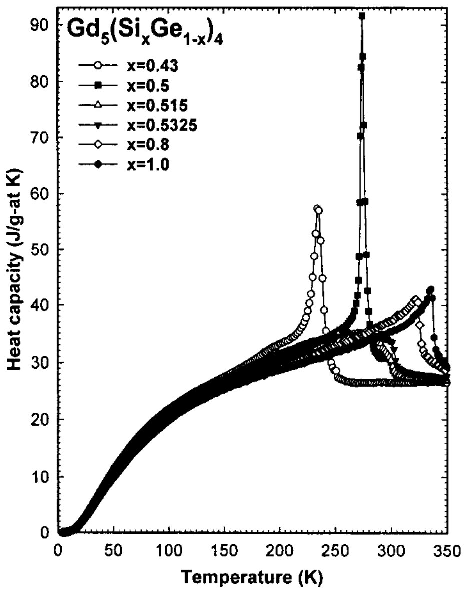

Figure 3: The zero magnetic field heat capacity for six $Gd_5(Si_xGe_{1-x})_4$ alloys.

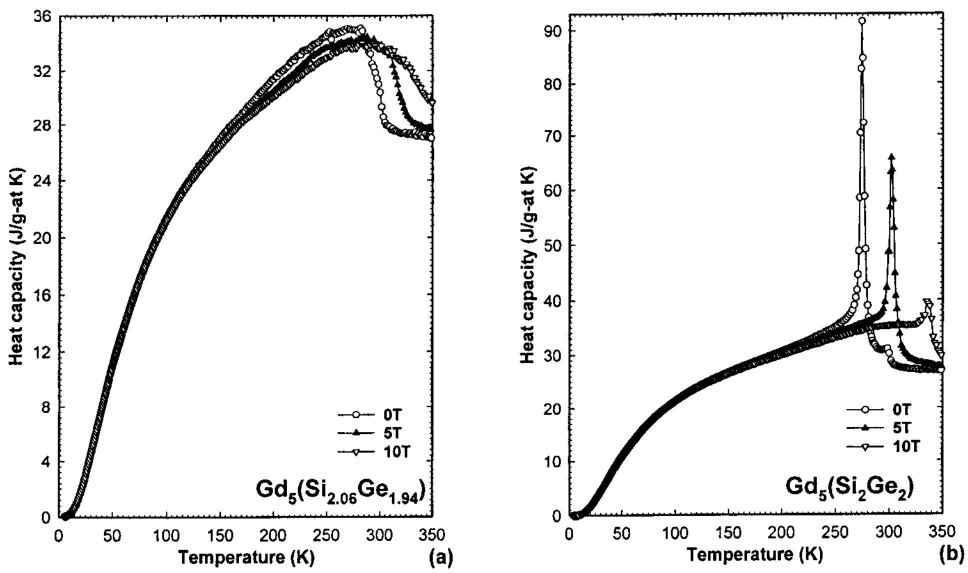

Figure 4: The heat capacity of $Gd_5(Si_{2.06}Ge_{1.94})$ [x = 0.515] and $Gd_5(Si_2Ge_2)$ [x = 0.50] from 3.5 to 350 K at magnetic fields of 0, 5 and 10 T

The magnetic field dependencies of the heat capacities of the alloys with x > 0.5 are quite similar, but differ significantly from those alloys where x ≤ 0.5, see Fig. 4. The heat capacity peak of $Gd_5(Si_{2.06}Ge_{1.94})$ shifts to higher temperatures and lower maximum values with increasing fields. This behaviour is typical of second order F to P (on heating) transformation. In contrast to this behaviour, for the $Gd_5(Si_2Ge_2)$ alloy the peaks retain their shape, the ordering temperatures increase and the peak values decrease with increasing magnetic field. This is an amazing change in the thermal properties with such a small change in concentration from x = 0.515 to x = 0.50.

The MCE, ΔS_{mag}, for the six alloys (x = 0.43 to x = 1.0) for a 0 to 5 T field change are shown in Fig. 5. These values were obtained from magnetization measurements [9] for x = 0.43, 0.50 and 0.515, while those for x = 0.5325, 0.8 and 1.0 were obtained from heat capacity measurements [9]. Again the large differences in behaviour between the alloys with x > 0.5, with those for x ≤ 0.5 is immediately obvious. The large MCE values for the x=0.43 and 0.50, which is significantly larger than has been observed here-to-fore for a *reversible* first order magnetic phase transition, led to the name of "giant magnetocaloric effect" for these materials.

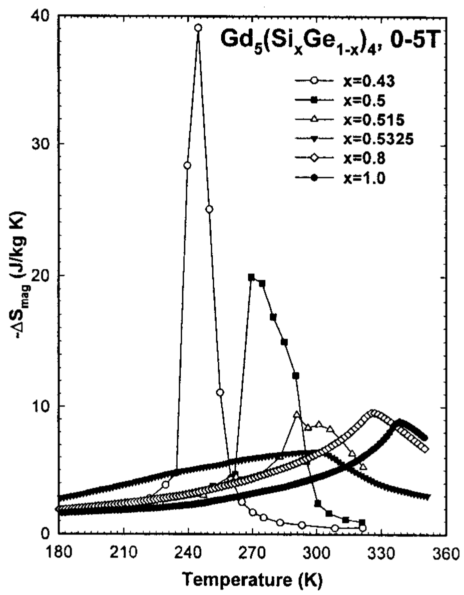

Figure 5: The magnetocaloric effect for six $Gd_5(Si_xGe_{1-x})_4$ alloys for a magnetic field change from 0 to 5 T

The abrupt change in properties at x ≅ 0.5 is thought to be due to a change in the chemical bonding in which one-half of the covalent $Si_2(Ge_2)$ bonds in the Gd_5Si_4 orthorhombic crystal structure are broken in the $Gd_5(Si_2Ge_2)$ monoclinic phase [7]. This change in the number $(Si,Ge)_2$ bonds would add a fraction of an electron to the conduction band, which in turn would affect the RKKY interactions between the Gd atoms, especially since there are 5 independent Gd sites in the monoclinic phase.

5 Refrigeration Capacity

The refrigeration capacity is an important parameter for evaluating the cooling (heating) power of magnetic refrigerants for use in a MR. The refrigerant capacity is defined as

$$q = \int_{T_1}^{T_2} \Delta S_{mag}(T)dT \tag{1}$$

where T_1 and T_2 are temperatures of the hot and cold sinks, respectively, and $\Delta S_{mag}(T)$ is the refrigerant's magnetic entropy change as a function of temperature (see above). This quantity (q) is a measure of how much heat can be transferred between the cold and hot sinks in one ideal refrigeration cycle. A comparison of some of the $Gd_5(Si_xGe_{1-x})_4$ alloys, including one in which a small amount of Ga is substituted for Si+Ge, with the best known refrigerants in the corresponding temperature ranges shows that the new materials have 25 to 70% more capacity than any known magnetic refrigerant (Fig. 6).

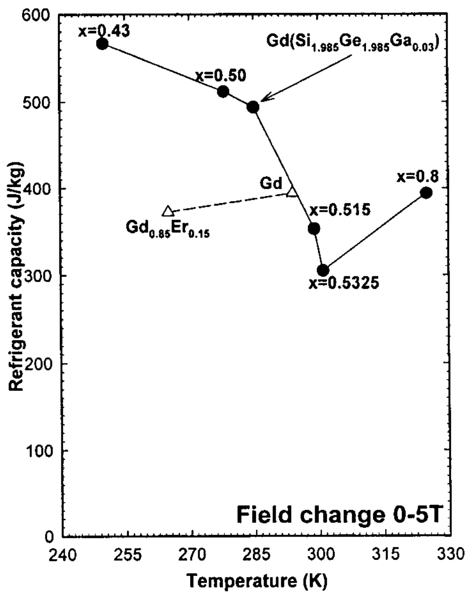

Figure 6: The refrigeration capacity of some $Gd_5(Si_xGe_{1-x})_4$ alloys and the best known prototype materials, $Gd_{0.85}Er_{0.15}$ and Gd, for a field change of 0 to 5 T, and a temperature span of 50K (±25 K of T_c). The results for Gd_5Si_4 are not included because of the lack of experimental data above 350 K, but the value is expected to be equal to or greater than for x = 0.8

6 Physical Properties of $Gd_5(Si_2Ge_2)$

Other than the crystal structure and the magnetic properties little else is known about the $Gd_5(Si_xGe_{1-x})_4$

alloys. Gd_5Ge_4 is reported to melt incongruently at 1690°C [10], while Gd_5Si_4 is thought to melt congruently at a temperature greater than 1650°C. These data suggest that the $Gd_5(Si_xGe_{1-x})_4$ alloys are quite refractory. This has been confirmed for $Gd_5(Si_2Ge_2)$ which melts at 1750±25°C.

The oxidation of $Gd_5(Si_2Ge_2)$ and $Gd_5(Si_{1.985}Ge_{1.985}Ga_{0.03})$ and corrosion resistances have been measured over a period of 5 months. Within experimental error of ±0.1 mg no measurable weight gain was observed in air at room temperature and at 123°C for both alloys. Furthermore, when powders of these 2 samples were placed in tap water, there was no evidence of a reaction.

7 Epilogue

The successful testing of the laboratory MR represents a major breakthrough for the commercialization of MR. The cooling power, efficiency and temperature span, show that MR is a viable and competitive technology for cooling. By the proper choice of magnetic refrigerants and MR design this technology can be used for refrigerator/freezers and air conditioning, and for the liquefaction of H_2, natural gas and propane. Furthermore, MR is scalable from watts to megawatts. The initial large scale applications are expected to be building climate control, refrigeration/frozen food processing plants and supermarket chillers.

Furthermore, MR is an environmentally friendly technology. It does not use ozone depleting chemicals, such as CFCs; or hazardous chemicals, such as NH_3; and greenhouse gases, such HCFCs and HFCs. And because of its expected energy efficiency, it should reduce the amount of energy consumed and in turn reduce the amount of CO_2 released helping to meet the Kyoto goals for reduced emission of greenhouse gases.

The discovery of the giant magnetocaloric materials is the second major breakthrough. The improved MCE properties and refrigeration capacity over prototype magnetic refrigerants, will not only lead to increased performance and efficiencies, but should open the door to application areas previously considered inaccessible to MR technology. These include automotive and aircraft climate control, home air conditioning and home refrigerator/freezers. In these applications the magnetic fields would be generated by permanent magnets instead of superconducting solenoids used in large scale applications. One of the earliest applications might be automotive climate control for electric vehicles because of legislative mandates for the production of zero emission vehicles. MR appears to be the best alternative climate control technology to replace gas compression/expansion air conditioners in these vehicles, since the latter uses large amounts of electrical energy and greatly reduces the range that the electrical vehicle can be driven between battery recharging.

Because of these advances, and also environmental and political factors, we expect that MR will become a major market for the rare earth industry in 5 to 10 years.

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