

Magnetic Refrigeration
A Chilling Attraction

*An Evaluation of Recent Materials
and Technological Developments*

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On a summer day, one may reach for a glass of cool water from one's refrigerator while sitting down inside one's cool home. While this setting seems simple enough to the common consumer, the engineer sees specifically engineered cooling systems allowing such climate control. A cooling system consists of a device or devices used to lower the temperature of a defined region in space through some cooling process. Currently, the most popular commercial cooling agent is the refrigerant. A refrigerant in its general sense is what makes a refrigerator cool foods, and it also makes air conditioners and other appliances perform their respective duties. A typical consumer-based refrigerator lowers temperatures by modulating a gas compression-expansion cycle, to cool a refrigerant fluid which has been warmed by the contents of the refrigerator (i.e. the food inside). Typical refrigerants used in refrigerators from the late 1800's through 1929 included ammonia, methyl chloride, and sulfur dioxide, all of which are toxic. To mitigate the risks associated with toxic refrigerants, a collaboration by Frigidaire, General Motors, and DuPont netted the development of Freon (or R12), a chlorofluorocarbon. Freon is a non-flammable and non-toxic, but ozone-depleting gas¹. Because of the damaging effects of Freon to the ozone layer, there has been much interest in targeting other refrigerants. The popular refrigerant R134a (called Suva by DuPont) is currently used in most refrigerators, but American and international laws are beginning to phase out this refrigerant as well. The future seems ripe for new refrigeration technology.

There has been much research done as of late by the group of Karl Gschneidner Jr., Vitalij Pecharsky, and David Jiles at Ames Laboratory, run by the Department of Energy, working in collaboration with the Astronautics Corporation of America. Their research has focused on the materials suitable for a magnetic refrigeration process and the

design of a suitable prototype. However with a drop off in funding from the Department of Energy, such efforts have been prolonged and have taken greater amounts of time than were initially expected.

There are two attractive reasons why magnetic refrigeration research continues. While a magnetic refrigerator would cost more than today's refrigerator at purchase, it could conserve over and above 20% more energy than current expansion-compression refrigerators, drastically reducing operating costs.¹⁰ The other attraction to magnetic refrigeration is the ecological impact a magnetic refrigerator would bring should it supplant current technologies. Not only would ozone-depleting refrigerant concerns be calmed, but the energy savings itself would lessen the strain our household appliances put on our environment.

The primary vehicle for magnetic refrigeration is the magnetocaloric effect (MCE), discovered by Warburg in 1881. Specifically, the MCE is "the response of a magnetic solid to a changing magnetic field which is evident as a change in its temperature" (Gschneidner)². When a magnetic field is applied to a magnetic material, the unpaired spins partially comprising the material's magnetic moment are aligned parallel to the magnetic field. This spin ordering lowers the entropy of the system since disorder has decreased. To compensate for the aligned spins, the atoms of the material begin to vibrate, perhaps in an attempt to randomize the spins and lower the entropy of the system again. In doing so, the temperature of the material increases. Conversely, outside the presence of a field, the spins can return to their more chaotic, higher entropy states, and one then observes a decrease in the material's temperature. The warming and

cooling process can be likened to a standard refrigerator which implements compressing and expanding gases for variations in heat exchange and surrounding temperature.

Bohigas quantifies the MCE through a definition of the entropy in a system as a function of temperature and magnetic field:

$$S = S_0 - \frac{M^2}{2\chi} - \frac{MB}{T} \quad (Eq. 1)$$

In Equation 1, B is the magnetic field, T is the temperature and M is the magnetization of the material in a given thermodynamic system. Bohigas notes, "This change in entropy is associated with the alignment of the spins on the system parallel to the magnetic field"³. One can derive this equation from the differential Helmholtz free energy of a system, which is to be minimized.

$$dF = -SdT - MdB \quad (Eq. 2)$$

Since there is no outside work (i.e. no volume change), $pdV = 0$. One can substitute the applied B field for $u \cdot H$. To find the change in entropy when the B field is changed (i.e. when a sample is rotated into the field of magnitude B and then out to B = 0), integrate over the B field to get Equation 1.

Magnetic refrigeration therefore operates by a changing magnetic field. As one is created, a warming effect is seen, and as one is dissipated, a cooling effect happens. The

MCE works only in the vicinity of a material's transition temperature. It reaches a maximum value at a material's Curie temperature, the temperature above which a ferromagnetic material becomes paramagnetic due to the noise generated by atomic vibrations. The range of temperatures about which a material experiences a substantial MCE and adiabatic temperature drop is typically +/- 20 C around the Curie temperature. Gadolinium has a Curie temperature of 20 C, near room temperature making it an excellent candidate for research in the area. Thus, Gd is a suitable magnetic material for refrigeration (though not for freezing) since it has a substantial MCE for temperature ranges roughly between 0 C and 40 C.⁴

The magnetic refrigeration process has been around for over seventy years to achieve near 0 K temperatures in small volumes by a process known most specifically as adiabatic demagnetization refrigeration. Magnetic refrigeration has long been considered one of the simplest ways to retrieve such low temperatures. However the application of focus in current research has shifted from cooling near 0 K to more practical uses, including consumer-based refrigerators. In the 1950's, several magnetic refrigerators operated at temperatures between 1 and 30 K. However, these were too inefficient to be used commercially and could only run for a couple of days⁵.

By 1976, a team of engineers had already built a refrigerator with working-temperature capability that spanned 80 C around room temperature, using Gd rotating plates and a 7 T magnetic field (description of full unit below) to "regenerate a column of a water-alcohol mixture" (Gschneidner)². This work allowed two scientists in 1982 to

find that a magnetic refrigerator could also be used as a regenerator, which greatly helped the innovation process along. This led to the development by Gschneidner et al. in the mid 1990s of the Active Magnetic Regenerator (AMR) magnetic refrigerator based on the application and removal of a magnetic field and on regeneration of a fluid in warm and cool states. In 1997, two key developments enhanced the feasibility for producing a magnetic refrigerator for commercial or industrial use. First, it was observed that the magnetic refrigerator could be a viable technology with the invention of the vapor cycle refrigeration unit. A vapor cycle unit is a refrigeration device which consists of a rotating table, (so-called Ericsson style rotation named after its inventor) which rotates the magnetic material in and out of a strong field to take advantage of the MCE. The Astronautics Corporation of America and Ames Laboratory built a unit using the Ericsson cycle system that had lasted 1500 hours as of mid 1998, and had run maintenance free.

Secondly, the discovery of the so-called "giant" MCE made previously considered implausible advancements possible. Some materials were observed to have unusually large magnetocaloric effects, and this discovery made it much more feasible to develop a machine at lower costs. It was observed first in Gd alloys, most notably $Gd_5(Si_2Ge_2)$, "due to a simultaneous magnetic and crystallographic first order transition. The adiabatic temperature rise for the material was 30% higher than that of just Gd and 200-600% higher than the previous refrigerant materials, $DyAl_2$, $GdAl_2$, and $Gd_{0.73}Dy_{0.27}$." (Gschneidner)². The magnetic entropy change approached a 100% increase over Gd. It

was, thus, discovered that $Gd_5(Si_2Ge_2)$ fared much better as a magnetic material for magnetic refrigeration than the previously considered materials. There was new-found hope for an efficient refrigerator using this technology.

There are several types of magnetocaloric effects as seen graphically in Figure 1. Each type is differentiated by how strongly the effect exists performs at varying temperatures. One can note that $(Dy_{0.5}Er_{0.5})Al_2$ experiences a second order paramagnetic to ferromagnetic transition at 40 K where the largest peak occurs. It is at this transition temperature that its highest MCE is observed. A second variety of MCE is shown by the enormous peak in $Gd_5(Si_{0.33}Ge_{3.67})$, due to its first order ferromagnetic to ferromagnetic transitions. This is an example of the giant MCE. Notice how much higher a value is obtained, albeit at a higher temperature. However, it is, overall, more energy efficient at

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the higher temperature since the MCE is much greater compared to the temperature. Finally, the plateau shaped MCE effect in $(\text{Gd}_{0.54}\text{Er}_{0.46})\text{NiAl}$ is due to three magnetic transitions in the material, and is suitable in some refrigerators. The best choice for an Ericsson cycle refrigerant would be a material with a good entropy profile and thus a suitable MCE profile. Since an ideal material's maximum MCE is useful for about ± 20 C, a material with table like MCE is an optimum choice for magnetic refrigeration.

The ultimate shape of the MCE peak is important in designing a thermodynamic cycle for a magnetic refrigeration system. "In an Ericsson cycle (where a plate rotates inside the magnetic field), the entropy change must be constant over the desired temperature range and one would choose a material which exhibits a table like MCE" (Gschneidner)². For an AMR's cycle, the optimal MCE would have a constant slope as temperature is increased. This is not represented in any of the plots and consequently, there are no present day alloys to satisfy this constraint. Gschneidner et al. are working on the materials science to solve this problem. One idea is to layer several different materials on top of each other with differing critical transition temperatures, forming a composite alloy, which could create a linear temperature rise as each material reaches its critical temperature. "In an attempt to circumvent the problem, several composite or multilayer systems have been studied, where ferromagnetic materials with varying Curie temperatures are layered according to their transition temperatures, thereby spanning a full temperature range" (Korte, Pecharsky)⁶. There is a way to predict what mass ratio of components is necessary to produce a constant magnetic entropy, based on the

experimentally determined entropy of each constituent. This technique allows one to find a suitable material composition which has a constant slope on a MCE vs. temperature plot.

In order for a working machine to be developed, materials had to be chosen that had good magnetocaloric effect and could withstand the process of cooling. Some materials used for refrigerants are taken from the gadolinium silicon germanium ternary system (Gd-Si-Ge), with stoichiometry $Gd_5(Si_xGe_{1-x})_4$. The Si rich alloys ($0.5 < x < 1.0$), are ferromagnets. The intermediate ternary solid solution phase $Gd_5(Si_xGe_{1-x})_4$ extends from $0.24 < x < 0.5$ and has a monoclinically distorted lattice, closely resembling samarium germanium (Sm_5Ge_4). The alloys in this phase region have two interesting features. By lowering the temperature they undergo a transition from one ferromagnet phase to a different ferromagnet phase. The bulk of the magnetic entropy is associated with this lower temperature phase transition which brings about a magnetocaloric effect, and can also be expressed in terms of the magnetic entropy change, S_{mag} , exceeding that of other lanthanide metals and alloys by up to seven times as much. The $Gd_5(Si_2Ge_2)$ alloy represents the most suited composition displaying the highest MCE and is durable enough to be used in a refrigerator.

Transition temperatures of the alloys formed by Gd, Tb, Dy, Ho, Er, Tm, and Lu show large MCE associated with transitions above 180 K. When decreasing transition temperatures prevail, the MCE rapidly falls apart⁷. Other materials being researched for use in magnetic refrigerators include amorphous alloys. The atomic structure of

amorphous alloys has some properties, such as higher resistivity and improved corrosion resistance, which aid the process of magnetic refrigeration. Some scientists feel that amorphous alloys may be able to fill the gaps between 100 and 200 K transition temperature applications. Amorphous materials such as $\text{Re}_{70}\text{Fe}_{30}$ ($\text{Re} = \text{Dy}, \text{Er}, \text{Ho}, \text{Tb}, \text{Gd}$) have a eutectic composition and provide a high concentration of rare-earth metal, which is necessary for the material to have a large MCE.

For low temperature applications between 1.5 and 20 K, paramagnetic salts like $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and $\text{Dy}_3\text{Al}_5\text{O}_{12}$ were tested at the outset of magnetic refrigeration research, but more recently ceramic perovskites have been found to be well-suited too. Such materials as $\text{La}_{0.65}\text{Ca}_{0.35}\text{Ti}_{1-x}\text{Mn}_x\text{O}_{3-z}$ and $\text{La}_{0.5+x+y}\text{Li}_{0.5-3y}\text{Ti}_{1-3x}\text{Mn}_{3x}\text{O}_{3-z}$ ($x < 0.16$ and $0.2 < y < 0.33$) have been shown to have good MCEs. The transition temperatures of these salts vary over great temperature ranges, some having the necessary MCE to be considered for use in magnetic refrigeration while others do not.³

A plot of adiabatic temperature rise as a function of operating temperature for $(\text{Gd}_{1-x}\text{Er}_x)\text{NiAl}$ of varying compositions is shown in Figure 2. Note the peaks resulting from this relationship which determine the MCE, thus determining the refrigeration ability of a system with each material. It appears that $(\text{Gd}_{0.2}\text{Er}_{0.8})\text{NiAl}$ has the largest giant MCE, but the most table-top like plot (similar to Figure 1) is $(\text{Gd}_{0.54}\text{Er}_{0.46})\text{NiAl}$ pointing to the fact that this material is a good selection for magnetic refrigeration. Note too that as x decreases (Gd composition increases) the peaks level off with a table top effect, but the adiabatic temperature change decreases. Ideally, a high peak and a table

top effect would be best, but realistically, one takes the best of both, and this is why $(\text{Gd}_{0.54}\text{Er}_{0.46})\text{NiAl}$ is currently being implemented in Ericsson cycle refrigerators.

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It is an important fact that the Gd materials used in the Ericsson style units must be of very high purity. However, by 1997, purifying such a material from commercial Gd had not yielded the same purity as Gd formed in research laboratories. In fact, the giant MCE had been reduced through processing procedures. It was found that the MCE was 2.5 times lower when commercial material was used to form the necessary magnetic material composition. The major impurities that are in commercial substances are carbon, nitrogen and oxygen.⁸ It is not yet known which impurity has the largest effect on the giant MCE.⁹ As we shall see later, recent developments at Ames Laboratory have afforded increased Gd purity processed from commercial sources.

The two most important features to materials used in magnetic refrigerators are the Curie temperature (or the magnetic transition that yields the largest MCE) and the magnetic entropy. The Curie temperatures of various lanthanide elements and their alloys have yielded MCEs across a broad range of temperatures between $\sim 0 - 300$ K.

There are still some gaps in this spectrum, meaning that cooling from room temperature to liquid helium temperatures will still requires materials research. Additionally, magnetic heating (the inverse process of magnetic refrigeration) would require investigating materials with transition temperatures above 300 K. Pure lanthanides would no longer be suitable, and iron alloys would be investigated. To this point, there has been little to no research in the area of magnetic heating.

Magnetic entropy of a material can be computed as follows (with units in parentheses)⁴:

$$S_{\text{mag}} = k_B \ln(2J + 1) \quad (\text{Eq. 3})$$

The lanthanides Gd, Tb, Dy, Ho, Er, and Tm have very high magnetic entropies (roughly 2 - 3 times as large as iron), and when these materials are considered along with their proper transition temperatures (Gd is the only element with a Curie temperature near room temperature) as well as cost/material (Ho is prohibitively expensive for a refrigerator), one finds that Gd and its alloys are good fits for magnetic refrigerators.

The process by which the Ames Laboratory/Astronautics Corporation of America magnetic refrigerator works is relatively simple. The refrigerant is of course solid in magnetic refrigerators, as opposed to liquid in commercial refrigerators, thus water, anti-freeze, and even some gases can provide heat transfer between the contents of the refrigerator and the refrigerant itself. The refrigerant chosen depends on the temperature

at which the machine is to be used. All other refrigerator components remain unchanged from current refrigeration technology.

A schematic of the unit built by Ames Laboratory and the Astronautics Corporation of America is shown in Figure 3.

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The magnetic field is generated by a solenoid made of niobium titanium (NbTi), a superconductor, which is placed in liquid helium. Gd is used as the cooling agent. There are two regenerator beds made of Gd that are alternately inserted into the field. Thus the relative movement of the refrigerant out of the field causes the lowering of the temperature. Each bed rotates through the magnetic field in one second. The first

regenerator bed inside the magnetic field experiences an increase in temperature as the one outside feels a decreasing temperature as it is outside the field. It will again be warmed by entering into the field. The heat is dissipated into passing water which carries the heat to a heat exchanger. This serves two purposes. The water cools the Gd so it can begin lowering its temperature quicker and it aids in the eventual cooling by the changing magnetic field. The whole process takes about 2 seconds. Another issue in the design of a magnetic refrigerator is efficiency. The Carnot efficiency compares the net work of a machine and the net heat it generates. For the lowest change in magnetic fields studied, from 0 to 1.5 Teslas, the efficiency was between 20% and 30%. Between 0 and 5 Teslas, the efficiency increased to 50%-60%, a substantial increase. In the Ames Laboratory experiments, the seals used for the refrigerator to insulate it were standard processed seals. With higher quality seals Gschneidner notes, better results would have been obtainable. The cooling power of the machine ranges between 200W and 600W, which at this point is a great beginning for building a refrigerator that will eventually have much better cooling power than refrigerators of today.

Another big advantage of magnetic refrigeration is the environmental impact it has. There are no toxic fluids involved in the current units under development. There is also less wasted energy and greater efficiency. All of this comes at a higher cost, however, but with continued research, magnetic refrigeration could become the next big advance in refrigeration technology.

Since the first prototype in Figure 3. was introduced, Gschneidner et al. have developed a rotary-designed magnetic refrigerator. It was even presented at the G-8 world conference in 2001. Its design is similar to the initial prototype in Figure 3, with the main difference in structure being the use of a rotary head to circulate the Gd metal into and out of a small gap in a $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet. The new model had a refrigerator and freezer component to resemble current consumer refrigerators. The rotary element rotates material into and out of the field at a rate of 0.25 revolutions/second under a field of 15 kOe. Table 1 summarizes the performance of the new refrigerator.

Table 1: Model results for rotary magnetic refrigerator/freezer.¹¹

Stage/Property	Freezer	Refrigerator	Total
Cold side temp., C (F)	-12 (10)	-1 (30)	-12 (10)
Hot side temp., C (F)	-1 (30)	32 (90)	32 (90)
Fluid	Ethylene Glycol 40%	Water	N/A
Pump work rate, Watt	1.3	6.4	7.7
Cooling power, Watt	40.0	127.0	120.0
Heat rejection, Watt	47.0	160.0	160.0
Electric power required, Watt	6.7	32.7	39.4
COP	6.0	3.85	3.0
Efficiency, % Carnot	51.4	49.0	N/A

The refrigerator has a measured coefficient of performance (COP) of 3.85 while the freezer was 6.0 and the overall COP was 3.0. These numbers compare favorably with current refrigerators.

There has been work in improving the rotary refrigerator, specifically in generating larger magnetic fields. The technique is geometrical in nature, by manipulating the arrangement of an array of eight $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets such that the flux

density is extremely high in the air gap through which the rotary's plate rotates.

Additionally, Gschneidner et al. have recently discovered a technique for adequately purifying the refrigerant $Gd_5(Si_xGe_{1-x})_4$ from commercial grade sources. Not only does this lower the cost of materials production, but it allows a larger amount of material to be used in the refrigerator due to a greater ease of fabrication. Currently, research has been centered on fabricating small spheres (on the order of 150-300 microns) of $Gd_5(Si_xGe_{1-x})_4$. Once this has been studied, it appears that magnetic refrigeration will be much closer to its introduction into the real world.¹¹

While Gschneidner et al. have had a large footprint in magnetic refrigeration research, they are by no means alone. Two Japanese companies, Chubu Electric Power and Toshiba Corporation, have invested money into research into this area. Additionally, a Chinese firm has become the first to use $Gd_5(Si_xGe_{1-x})_4$, patented by Ames Laboratory, in a refrigerator. It has thus far proven to be a successful material in the application. A French team at the Laboratoire d'Electrotechnique de Grenoble have been doing similar work in magnetic refrigeration using rotary technology. Their material of choice has been Gd. A list of all known groups working in magnetic refrigeration is listed in Appendix A.

The future in magnetic refrigeration appears bright. Much research is being done in the field of the magnetocaloric effect in an attempt to find a suitable way to make an efficient machine. It is clear that more research is needed before a finished product appears for sale commercially. Materials such as Gd alloys and ceramic perovskites are

being used in much of the research and some have shown large MCEs. Relationships between magnetic entropy and temperature have been derived and studied to increase MCEs in some materials. The Ericsson style magnetic refrigerator was the first proof-of-principle prototype that showed magnetic refrigeration was plausible. The latest rotary model seems to have a future in research and potentially in commercialization.

Though the first prototype costs more and is less efficient than current refrigerators, the discovery of the giant MCE has further opened the prospects of the magnetic refrigerator as a viable device. As more research is done on the MCE and magnetic refrigerators, the future possibilities of efficient cooling will be limitless.

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