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Rare Earths and Magnetic Refrigeration

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Abstract: Magnetic refrigeration is a revolutionary, efficient, environmentally friendly cooling technology, which is on the threshold of commercialization. The magnetic rare earth materials are utilized as the magnetic refrigerants in most cooling devices, and for many cooling application the $Nd_2Fe_{14}B$ permanent magnets are employed as the source of the magnetic field. The status of the near room temperature magnetic cooling was reviewed.

Key words: magnetic refrigeration; magnetocaloric effect; gadolinium; $Gd_5(Si_{1-x}Ge_x)_4$; $La(Fe_{13-x}Si_x)H_y$; $Nd_2Fe_{14}B$ permanent magnets; active magnetic regenerator cycle; rare earths

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Modern cooling is almost entirely based on a compression/expansion refrigeration cycle. It is a high-energy demand industry with annual energy consumption measured in billions kWh. Over the years, all parts of a conventional refrigerator, i.e., compressors, heat exchangers, refrigerants, and packaging have been considerably improved by an extensive research and development effort, and partly by government edicts. This was made possible by a continuous dollar influx from both federal and industrial sources. Both achieved and anticipated improvements of this traditional technology, however, are incremental since modern refrigeration is already near its fundamental limit of energy efficiency, which is well below the maximum theoretical (Carnot) efficiency. Furthermore, the liquid chemicals used as refrigerants, eventually escape into the environment promoting ozone layer depletion and global warming and, therefore, conventional refrigeration ultimately promotes deleterious trends in the global climate. Other refrigerants, such as ammonia, are hazardous chemicals.

In 1997, a new, revolutionary, competitive, energy efficient, and environmentally friendly cooling technology emerged, i.e. magnetic refrigeration (MR). Two major events ushered in this new cooling technology: first, the unveiling of a proof-of-principle working magnetic refrigerator on February 20, 1997 at Madison, Wisconsin[1]; second, the discovery of the giant magnetocaloric effect in $Gd_5Si_2Ge_2$ and the related $Gd_5(Si_{1-x}Ge_x)_4$ alloys announced on June 9, 1997[2,3].

The February breakthrough was the successful testing of the Ames Laboratory, Iowa State University/Astronautics Corporation of America (AL, ISU/ACA) reciprocating proof-of-principle magnetic refrigerator. This machine operated in magnetic fields up to 50 kOe (5 T) provided by a superconducting magnet. It achieved a cooling power of 600 W with a coefficient

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of performance (COP) approaching 15, an efficiency reaching 60% of Carnot (a ~ 50% improvement over a typical vapor compression system), a temperature span of 38 K in magnetic fields of 5 T, and operated for over 1500 h without any mechanical or electrical problems.

The June breakthrough showed that there was at least one family of alloys, the $Gd_5(Si_{1-x}Ge_x)_4$ compounds, which may be considerably better refrigerants than the prototype Gd metal magnetic refrigerant because of the considerably larger magnetocaloric effect. This discovery not only brings magnetic refrigeration one step closer to commercialization, but also spawns explosive growth of related research, the results of which indicate that these unique materials display some extraordinary magnetic properties potentially useful in other energy-related applications. These unique properties include the colossal magnetostrictive and giant magnetoresistive behaviors[4], which can be used in energy conversion devices and data storage applications. Furthermore, the discovery of the giant magnetocaloric effect spurred a broad international interest in the magnetocaloric effect and lead to the discovery of four new families, members of which exhibit the giant magnetocaloric effect. These are $Mn(As_{1-x}Sb_x)$, $MnFe(P_{1-x}As_x)$, $La(Fe_{13-x}Si_x)H_y$, and $Ni_{\sim 55}Mn_{\sim 20}Ga_{25}$.

Between 1998 and 2006, following the footsteps of the Ames Laboratory and the Astronautics Corporation of America, 19 more magnetic refrigerators have been built and tested by scientists and engineers in Canada (1), China (7), Europe (4), Japan (5), and the USA (3), signaling the dawn of a new era of environmentally friendly, energy efficient and affordable magnetic cooling, refrigeration, and air conditioning. The most advanced magnetic cooling machine is the laboratory prototype, permanent magnet, rotating refrigerator built by the Astronautics Corporation of America in Madison, Wisconsin. It was publicly displayed at the Global Eight (G8) Energy Ministers Conference in Detroit, Michigan on May 1, 2002 and again at the Anniversary Celebration of the President's National Energy Policy at the US Department of Energy Headquarters in Washington, DC on May 17, 2002. More information about nine of these refrigerators and the references to the original papers will be found in a 2005 review by Gschneidner, et al.[5]

The interest in magnetic cooling is continuing to grow rapidly. This can be attested by the fact that in September 2005, the first international conference on magnetic refrigeration near room temperature was held in Montreux, Switzerland[6]. The next conference will be held in April 2007.

1 Magnetocaloric Effect

The magnetocaloric effect (MCE) is the response of a magnetic solid to the application (or removal) of a magnetic field, which is evident by a change in the temperature of the solid. For a ferromagnetic material near its magnetic ordering temperature (the Curie temperature [T_C]), when a magnetic field is applied, the unpaired $4f$ or $3d$ spins are aligned with the magnetic field, which decreases the entropy in the isothermal process or causes the sample to warm up in the adiabatic process. When the magnetic field is turned off, the spins randomize, thus increasing the entropy, or the material cools. A few materials, primarily antiferromagnetic compounds, may exhibit opposite behavior; they cool when a magnetic field is applied, and warm up when the field is removed.

The temperature change is called the adiabatic temperature change, ΔT_{ad}. The extensive parameter representing the MCE is the isothermal magnetic entropy change, ΔS_m. For Gd metal, $\Delta T_{ad} \cong 5.7$ K and $\Delta S_m \cong 5.5$ $J \cdot (kg \cdot K)^{-1}$ (~ 43 $mJ \cdot (cm^3 \cdot K)^{-1}$) for a magnetic field change of 20 kOe (2 T) as seen in Fig.1. Most magnetic solids undergo a second order magnetic transition when the solid orders magnetically, resulting in what has been called the conventional magnetocaloric effect.

A few magnetic materials, however, exhibit a significantly larger MCE, which is known as the giant magnetocaloric effect (GMCE). This occurs because the magnetic solid undergoes a coupled first order magnetic-structural transition. The ΔS_m for a GMCE material may be twice or more as large as the ordinary MCE of a substance that undergoes a second order transition. The extra entropy is because of the entropy difference between the two structures involved in the transition. However, since the GMCE materials undergo a first order transition, the very nature of this transition indicates that it often exhibits hysteresis and time dependence, and these may limit the usefulness of the GMCE materials in magnetic refrigeration. More details about the MCE can be found in Refs.[5, 7 ~ 11].

2 Magnetic Refrigeration

The basic principle of magnetic cooling is analogous to gas compression cooling. To achieve continuous refrigeration, the heat generated in the magnetic material when the magnetic field is increased must be rejected to the ambient. This is equivalent to the compression stage of a gas cycle refrigerator or air conditioner. During the demagnetization step, a thermal link is used to cool the load, which is equivalent to the gas expansion stage of a compressor. By continued repetition of these two steps, refrigeration is accomplished.

2.1 Regenerators

The performance of the magnetic cooling device can be considerably increased by simultaneously using the magnetic refrigerant as a regenerator. A regenerator is a thermal device that absorbs heat from a fluid heat transfer medium (a gas or liquid) as it passes through the regenerator thereby cooling the fluid. The cooled fluid absorbs heat from the item to be cooled, and on the reverse portion of the cycle, the fluid passes back over the regenerator material extracting heat to a hot heat exchanger, which rejects the heat to the ambient surroundings. In general, the higher the volumetric heat capacity of the regenerator material, the more efficient is the cooling device.

The regenerator is constructed of either a bed of tightly packed spheres (or irregularly shaped powders), or a set of closely spaced parallel thin plates (foils), or a wire mesh. The size of the spheres varies from 100 to 300 μm to provide effective heat transfer between the regenerator materials and the heat transfer fluid, and sufficient porosity to minimize the pressure drop across the bed of spheres. The plate (foil) thickness and wire mesh diameter are comparable to the sphere diameter for the same reasons.

2.2 Active magnetic regenerator cycle[5,12~14]

In the active magnetic regenerator (AMR) cycle, a porous bed of a magnetic refrigerant material acts as both the refrigerant (coolant) and the regenerator for the heat transfer fluid. Assume that the bed is at steady state with the hot heat exchanger at ~ 297 K and the cold heat exchanger at ~ 278 K (dashed line in Fig.2(a)). The first step in the AMR cycle is to apply a magnetic field to the refrigerant; each particle in the bed warms because of the MCE to form the final magnetized bed temperature profile (solid line in Fig.2(a)). The degree each particle warms is equal to ΔT_{ad} reduced by the effect of the heat capacity of the heat transfer fluid in the pores between the particles. The second step in the cycle is to push the ~ 278 K fluid through the bed from the cold end to the hot end. The bed is cooled by the fluid, thus lowering the temperature profile across the bed (the dashed line to the solid line in Fig.2(b)) and the fluid in turn is warmed by the bed, emerging at a temperature close to the temperature of the bed at the warm end. This temperature is higher than ~ 297 K, therefore, heat is removed from the fluid at the hot heat sink as the fluid flows through the hot heat exchanger. After the fluid flow is stopped, the magnetic field is removed (step three), and the bed is cooled by the MCE (the dashed line to the solid line in Fig.2(c)). The refrigeration cycle is completed by forcing the 297 K fluid to flow from the hot end to the cold end of the bed (the dashed line to the solid line in Fig.2(d)). The fluid is cooled by the bed, emerging at a temperature below ~ 278 K and removes heat from the cold sink as it passes through the cold heat exchanger.

The AMR cycle outlined above has several positive features useful for practical application in a magnetic cooling device. Firstly, the temperature span of a single stage can greatly exceed that of the MCE of the magnetic refrigerant because the MCE of each individual particle changes the entire temperature profile across the bed; Secondly, since the bed is a regenerator, heat need not be transferred between two separate solid assemblies, but rather between the solid particles in a single bed via the action of a fluid; and thirdly, the individual particles in the bed do not encounter the entire temperature span of the stage , and

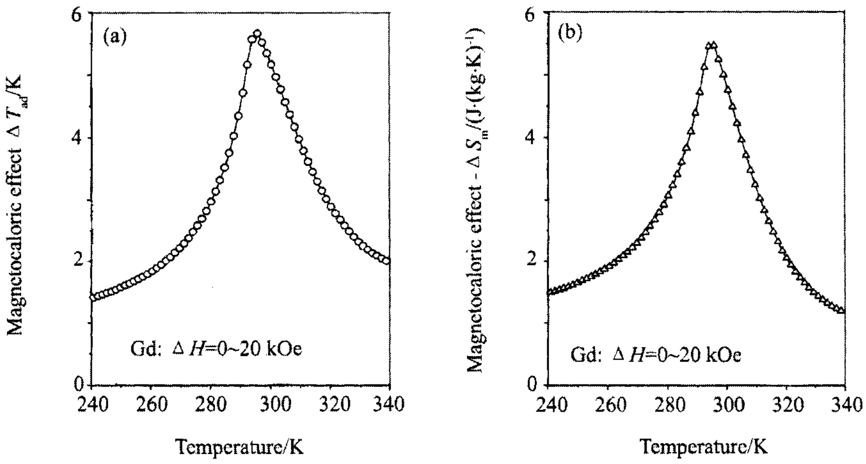

Fig.1 Magnetocaloric effect in Gd metal for a magnetic field change of 0 to 20 kOe (ΔT_{ad} is the adiabatic temperature change and ΔS_m is the isothermal magnetic entropy change)

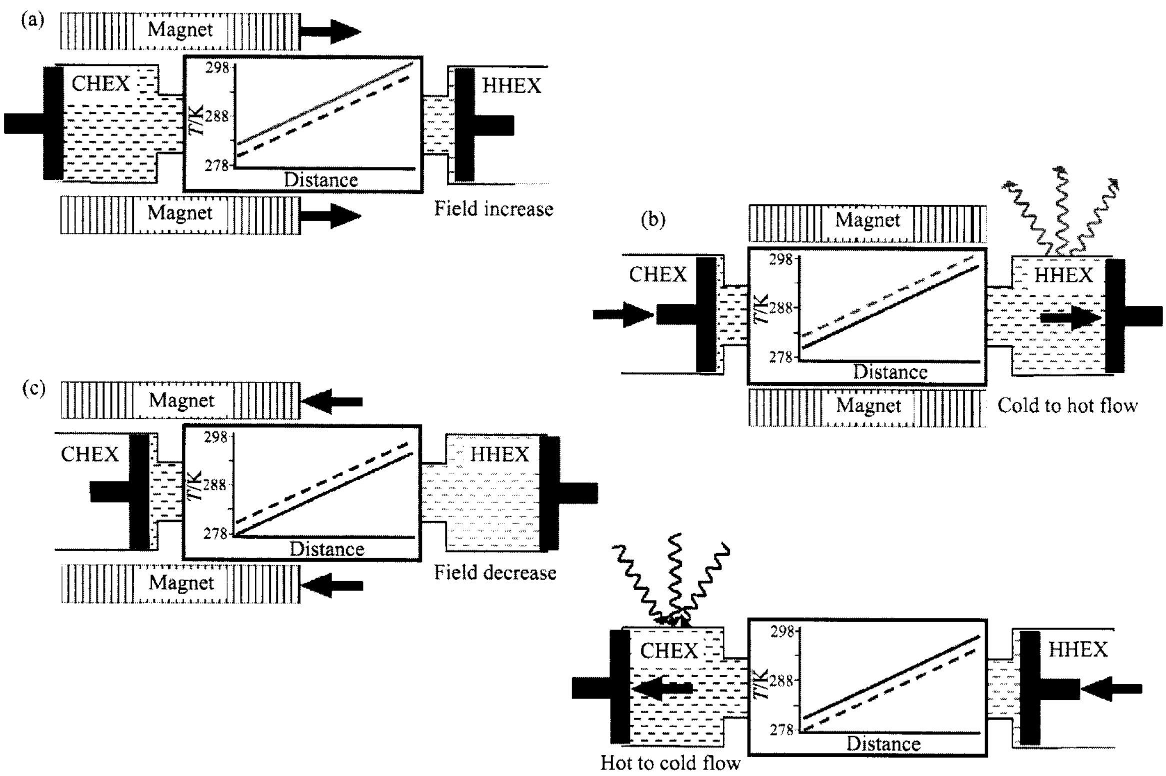

Fig.2 Active magnetic regenerator (AMR) cycle

(a) Magnetic field is applied to the magnetocaloric bed; (b) The cold fluid is passed over the bed; (c) The magnetic field is removed from the bed; (d) The hot fluid is passed over the bed. The dashed line represents the initial temperature profile across the bed prior to each step, whereas the solid line represents the final temperature after the step is completed. For clarity purposes, the magnet is not shown in (d). CHEX is the cold heat exchanger and HHEX is the hot heat exchanger. The magnetic refrigerator generally operates between 0.2 and 4 Hz

hence the bed may be made into layers, each containing a magnetic material with properties optimized for a particular temperature range.

2.3 Regenerator materials

Gadolinium metal is considered to be the prototype magnetic refrigerant material for near room temperature magnetic refrigerators. It is a good refrigerant; however, to make magnetic refrigeration even more efficient, it is important to have an array of materials with better MCE properties than Gd. Obviously, there are other ways to increase the efficiency, such as new and better thermodynamic cycles, improved engineering designs, increase in the number of AMR cycles per unit time, and better heat transfer fluids. Since the discovery of the GMCE in the $Gd_5(Si_{1-x}Ge_x)_4$ alloys[2,3], hundreds of magnetic materials with magnetic ordering temperatures ranging from 1 to 400 K have been reported in the literature[5, 15~18]. The other families of compounds/alloys that have at least one composition with a GMCE near room temperature include: the rare earth manganite, $(RE_{1-x}M_x)MnO_3$ where RE = a rare earth metal, and M = Ca, Sr, or Ba[5,15]; $Mn(As_{1-x}Sb_x)$ alloys[19]; $MnFe(P_{1-x}As)$ alloys[20]; the $Ni_{\sim 2}Mn_{\sim 1}Ge_{\sim 1}$ Heusler alloys[21]; $La(Fe_{13-x}Si_x)$ materials[22,23]; and $La(Fe_{13-x}Si_x)H_y$ alloys[23]. In most cases, the basis for claiming a GMCE is the large ΔS_m value, which is calculated from magnetization measurements. However, ΔT_{ad} is also an important parameter for the successful operation of a magnetic cooling machine. Most of these new materials have small ΔT_{ad} values for a given magnetic field change when compared to the Gd metal; the only exception is the $Gd_5(Si_{1-x}Ge_x)_4$ alloy for a 0 to 50 kOe field change, ΔT_{ad} is ~40% larger than that of Gd. However, for a 0 to 20 kOe field change, $La(Fe_{13-x}Si_x)H_y$ and $MnFe(P_{1-x}As_x)$ have ΔT_{ad} values that are comparable to that of Gd, as well as the $Gd_5(Si_{1-x}Ge_x)_4$ alloys.

There are, however, a few potential problems for the first order magnetic materials, which may limit their usefulness as magnetic regenerator materials-hysteresis[24], the temperature and magnetic field ranges over which the transformation occurs, and the time taken to achieve the full ΔT_{ad} value[5]. If the hysteresis is quite large, the original magnetic phase may not be fully recovered during a heating-cooling cycle, and thus on the next cycle, the full MCE is not obtained because part of the magnetic refrigerant has been already in the high magnetic field state. This problem can be tackled by correctly designing the AMR cycle and carefully layering the magnetocaloric bed with a range of materials of various T_Cs such that each particle along the bed has its optimum MCE at steady state.

If the magnetic-structural transformation occurs over a wide temperature range (2 to 10 K) and a wide magnetic field range (2 to 10 kOe), only part of the original magnetic phase may have transformed. The grain size and the sample purity probably play important roles on the width of the transformation, but this problem has not been studied in detail.

Recently, it has been pointed out[5] that there is a time dependence in the measurements of the ΔT_{ad}-the quicker the measurement, the smaller is the value of ΔT_{ad}. This can present a real problem in magnetic refrigeration because the cycle frequencies range from 0.2 to 4 Hz. This is only true for the first order magnetic-structural transitions, since there is a movement of atoms during the transition, volume change, and related strain, whereas there is no time dependence for the second order transformations because these involve only alignment (or disalignment) of the magnetic $4f$ or $3d$ electrons.

2.4 Evaluation of regenerator materials

There are a number of other important criteria for materials selection of a magnetic refrigerant for an operational magnetic cooling device in addition to having good to excellent ΔS_m and ΔT_{ad} values. These include the raw material cost, the preparation of tons per day quantities, the vapor pressure of the components, the fabrication costs to develop the material into a useful form for the regenerator, the refrigeration capacity (i.e., the amount of heat transferred per cycle), hysteresis, time dependence of ΔT_{ad}, environmental concerns, and corrosion. These have been discussed in details and the various highly touted magnetic refrigerant materials have been compared to the Gd metal.[5] As a whole, there is no material to date which is clearly better than Gd (and Gd doped with other rare earths). However, more research and development needs to be done to analyze whether some of the potentially adverse problems of other families of magnetic materials can be solved. Until then, Gd will be the material of choice as the magnetic refrigerant.

3 Magnetic Field Source

The strength of the magnetic field is important in the utilization of the MCE in magnetic cooling, since both ΔS_m and ΔT_{ad} are approximately proportional to the magnitude of the magnetic field change[5]. At low field, < 20 kOe, the two parameters vary almost linearly with the magnetic field; however, at fields > 20 kOe, the MCE change per unit magnetic field change becomes somewhat smaller as the field increases, i.e., the slope deviates from the linearity established at lower fields.

Owing to this dependence, the efficiency of magnetic cooling increases with the increasing field[5]. Thus a magnetic field as large as possible is required in the magnetic cooling device. However, there are some practical considerations that need to be taken into account. For example, a superconducting magnet can easily be designed to provide a magnetic field of 50 to 70 kOe (5 to 7 T) at a reasonably modest cost, but such a magnetic field source is impractical for household applications and most transportation methods.

The only practical magnetic field source for household and transportation applications is the high energy $Nd_2Fe_{14}B$ permanent magnet, which can deliver a magnetic field of 12 to 15 kOe for a reasonable gap size between the pole pieces to allow one to move the magnetic refrigerant material in and out of the magnetic field. Applications that would utilize the rare earth permanent magnets are: household refrigerator/freezers; household air conditioning; automotive, aircraft, small seafaring vessels for climate control (both heating and cooling, and humidity); portable coolers; active cooling of electronics; portable refrigerators (medical), etc.

The use of a superconducting magnet source is the only practical way for large scale applications, such as supermarket chillers; frozen food plants; building climate control (heating, cooling and humidity) such as office buildings, apartments, convention centers, meeting halls; and climate control for large seafaring vessels. As far as we know, no one has designed, built and tested a large scale cooling machine or even a prototype apparatus.

4 Impact on Rare Earth Markets

Magnetic refrigeration will have a tremendous impact on the rare earth markets as this technology grows and matures. It is believed that the first commercial units will be in the market within a few years. It is difficult to predict how rapidly this market will grow.

This will partly depend on the speed at which some of the impediments to commercialization are overcome as seen below.

The amount of magnetic refrigerants required will range from 0.01 to 100 kg per cooling device. The smaller quantity will be for small refrigerators and coolers noted above, whereas the larger kilogram quantities are required in the magnetic cooling machines for large scale applications.

For refrigerators that will use permanent magnets as the power source, it is believed that 0.5 to 100 kg of the $Nd_2Fe_{14}B$ alloy is required per refrigerator or cooling device.

Thus, magnetic refrigeration, even before it matures, will be the biggest rare earth market. This is especially true for the small scale units since both the magnetic refrigerant material and the permanent magnet will contain significant amounts of rare earth metals per cooling unit.

It is conceivable that in the forthcoming ten years, the high magnetic field source will be a superconducting magnet, which uses one of the high temperature ceramic superconductors, such as $YBa_2Cu_3O_7$. This occurence will be another big plus to the rare earth market. In addition, the use of the ceramic oxide superconductor is expected to reduce the operating costs when compared to the conventional liquid helium superconducting system in use today.

5 Obstacles to Commercialization

As noted above, at least 20 laboratory scale prototype magnetic refrigerators have been built and tested, but there are still a number of obstacles that need to be overcome for successful large scale commercialization[5]. The main obstacles are as follows, but are not listed in any priority.

Magnetic refrigerants, which have a second order magnetic transition, with better MCE properties than Gd will provide a big boost towards moving this technology to large scale production of magnetic cooling devices. This is especially true if the costs associated with forming the final regenerator material (spheres, wires, and foils) are not considerably more expensive than the costs to make Gd foils and/or spheres and/or wire mesh.

The production of large quantities of the magnetic refrigerant, tons per day, at a reasonable cost is critical. Most of the materials studied to date have been prepared only in small quantities, generally less than 25 g. To date, only one material, the $Gd_5(Si_{1-x}Ge_x)_4$ family of alloys, has been successfully produced on a kilogram scale[5].

Permanent magnets having higher magnetic strength and lower costs will benefit the commercialization. About one-third of the cost of a magnetic refrigerator is the magnet source. Improved magnetic field strength will lead to high efficiencies, and this will allow the engineer to reduce the size of the permanent magnet array for the same amount of cooling.

Engineering considerations must be examined closely to improve the efficiency. This can involve: the heat flow from the cold object to the hot heat exchangers; improving the heat exchangers; increasing the cycle frequency; and improved heat exchange fluids, etc.

The AMR thermodynamic cycle is considered to be the best cooling cycle today for magnetic cooling/heating, which can be possibly improved by making some modifications. New thermodynamic cycles, especially to take into account the MCE behaviors of the first order magnetic transitions, will be a big step forward to utilize their unique properties in a practical magnetic refrigerator.

The first order magnetic transformation materials have a large MCE (i.e., GMCE) due to the fact that in addition to normal magnetic entropy associated with magnetic ordering, there is a second contribution, the entropy associated with the structural change in materials that exhibit a magnetic-structural transformation. The magnitudes of the two entropies are comparable. There are several problems associated with such materials, one of which is the hysteresis inherently associated with first order transitions. It may be possible to reduce the hysteresis, but never eliminate it, by increasing the purity, modifying the grain size, and perhaps by alloying an appropriate impurity element. Also, as noted above, carefully packing regenerator beds with appropriate alloy compositions from the cold end to the hot end may circumvent problems arising due to hysteresis. Finally, there appears to be a time dependence associated with these first order transformations, on the order of minutes, to achieve the full MCE, especially ΔT_{ad}. This problem may be more critical than hysteresis if first order magnetic transition materials are to be used.

6 Conclusion

Commercial magnetic refrigeration/cooling units will be a reality in the near future; however, it is difficult to predict whether it will just be a niche market or a full-blown growth market 5 to 10 years from now. Either way, this technology will be an important market for the rare earth industry.

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