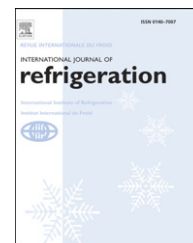


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## Review

# Thirty years of near room temperature magnetic cooling: Where we are today and future prospects

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## ABSTRACT

The seminal study by Brown in 1976 showed that it was possible to use the magnetocaloric effect to produce a substantial cooling effect near room temperature. About 15 years later Green et al. built a device which actually cooled a load other than the magnetocaloric material itself and the heat exchange fluid. The major breakthrough, however, occurred in 1997 when the Ames Laboratory/Astronautics proof-of-principle refrigerator showed that magnetic refrigeration was competitive with conventional gas compression cooling. Since then, over 25 magnetic cooling units have been built and tested throughout the world. The current status of near room temperature magnetic cooling is reviewed, including a discussion of the major problems facing commercialization and potential solutions thereof. The future outlook for this revolutionary technology is discussed.

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# Trente ans de froid magnétique proche de la température ambiante : Situation actuelle et perspectives

Mots clés : Réfrigérateur magnétique ; Enquête ; Technologie ; Historique

## 1. Introduction

The interest in magnetic refrigeration as a new solid state cooling technology competitive with the conventional vapor compression approach has grown considerably over the past 10 years coinciding with rising international concerns about global warming due to an ever increasing energy consumption.

As pointed out by Coulomb (2007) in his introductory talk at the Second International Conference on Magnetic Refrigeration at Room Temperature (Thermag II), 15% of the total worldwide energy consumption involves the use of refrigeration (air conditioning, refrigeration, freezing, chilling, etc.). In addition, he noted that the International Institute of Refrigeration is taking an active role in helping to develop magnetic refrigeration

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which has the potential to lower energy consumption by 20–30% over conventional vapor compression technology.

The potential of magnetic cooling has not gone unnoticed by fundamental sciences as well. As shown in Fig. 1, the number of published papers per annum on the magnetocaloric effect has grown at an exponential rate in the past 10 years. We have estimated, based on the number of papers published in the first three quarters of 2007, that on the average a paper on the magnetocaloric effect appears in print every working day (5 days per week).

Yet in spite of this large number of publications, magnetic cooling technology is in its earliest stages: an initial infinitesimally slow growth in the first 50 years after the discovery of the effect from 1881 to 1930, to a slightly greater growth rate in the ensuing 45 years (1930–1975). In the following 30 years (1975–to date), the growth rate has been increasing more rapidly perhaps signaling the initial stages of an exponential increase. But it still has a way to go before it will reach its maximum growth rate – this is to be realized in the future, hopefully most of us will be around to witness this growth of magnetic cooling to a mature technology. The following pages are a brief description of the developments that have occurred since 1975, and the paper concludes with a discussion of the present situation regarding near room temperature magnetic cooling.

## 2. Developments before 1997

Although the roots of magnetic cooling can be traced back to Warburg's discovery of the magnetocaloric effect in 1881, the true beginning of near room temperature cooling has its origin in the seminal paper by Brown (1976). Between 1881 and 1976 a number of important papers were published on magnetic cooling, but since most were concerned with cooling below 20 K, and since these papers have been discussed in

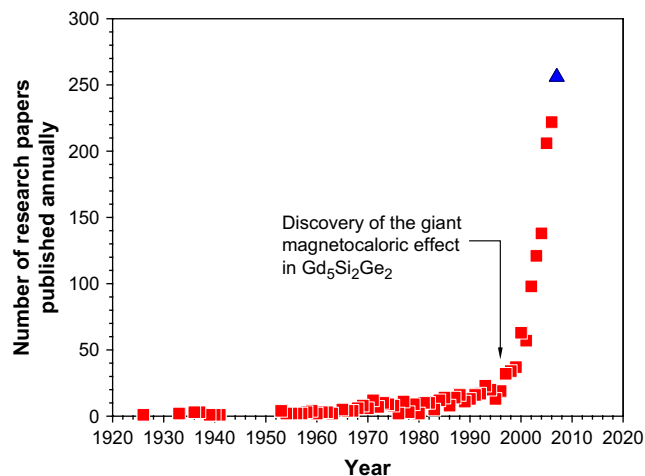


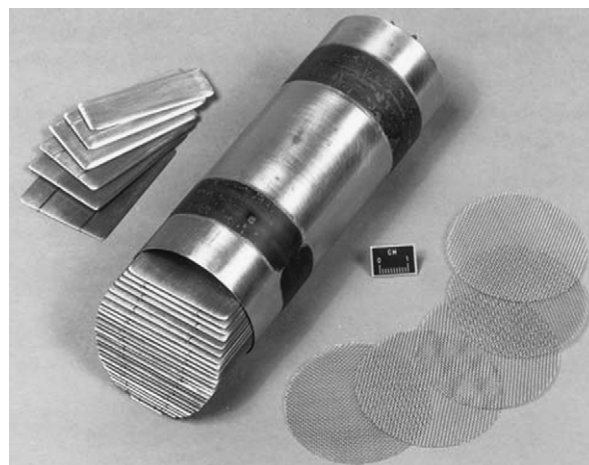
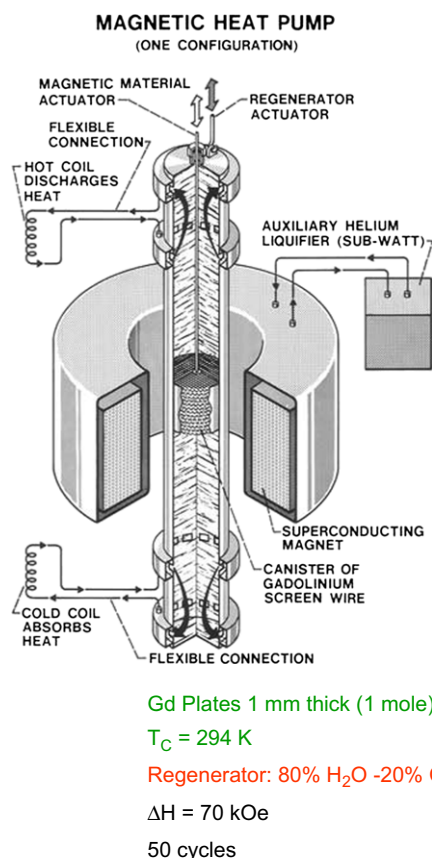
Fig. 1 – The number of research papers published annually over the past 80 years containing the word “magnetocaloric” in the title, abstract, or among the keywords. The values for 2007 (triangle) are based on the number of papers abstracted during the first three-fourths of the year.

a number of reviews (Barclay, 1988; Hull and Uherka, 1989; Gschneidner and Pecharsky, 1997; Pecharsky and Gschneidner, 1999, 2005a; Tishin and Spichkin, 2003; Yu et al., 2003; Gschneidner et al., 2005) this prior history will not be repeated here.

The significance of the Brown refrigerator cannot be emphasized enough. Prior to his work several researchers pursued the use of ferrofluids (a colloidal suspension of ferromagnetic particles) in near room temperature heat engines (see comments and references cited by Barclay, 1982). But because of the low concentration of magnetic particles in the ferrofluid and also because of heat transfer problems this approach was abandoned. Brown (1976) showed that a continuously operating device working near room temperature could achieve much larger temperature spans than the maximum observed magnetocaloric effect (MCE, or the adiabatic temperature change,  $\Delta T_{ad}$ ). Brown's near room temperature reciprocating magnetic refrigerator used one mole of 1 mm thick Gd plates separated by a wire screen (Curie temperature,  $T_C = 294$  K) and an 80% water–20% ethyl alcohol solution as a regenerator in an alternating 70 kOe field produced by a superconducting magnet (see Fig. 2). A maximum temperature span of 47 K was attained after 50 cycles ( $T_{hot} = 319$  K [ $46^\circ\text{C}$ ] and  $T_{cold} = 272$  K [ $-1^\circ\text{C}$ ] where  $T_{hot}$  is the hot end temperature and  $T_{cold}$  is the cold end temperature). This temperature span is more than three times larger than the MCE of Gd metal between 272 K ( $\Delta T_{ad} = 11$  K) and 319 K ( $\Delta T_{ad} = 13$  K); Gd has a maximum  $\Delta T_{ad}$  value of 16 K at its Curie temperature  $T_C = 294$  K. Subsequently, Brown (1978) was able to attain a temperature span of 80 K (from 248 to 328 K) using the same apparatus.

Following the early work of Brown, the concept of using an active magnetic regenerator (AMR) in the cooling device to facilitate heat transfer was introduced by Steyert (1978) who was evaluating the Stirling cycle for magnetic refrigerators and heat engines. This AMR cycle which is a Brayton-like cycle, was further developed by Barclay and Steyert (1982) and Barclay (1983a). In a seminal paper Barclay (1983b) (also described in the patent by Barclay and Steyert, 1982) showed that it is possible to get much larger temperature lifts than just the adiabatic temperature rise of the magnetic refrigerant by using the magnetic material simultaneously as a regenerator and as the active magnetic component. Chen et al. (1992) concluded that for near room temperature magnetic refrigerators a regenerative cycle is more efficient than the Carnot, Ericsson or Stirling cycles. A pure Carnot cycle, which consists of two isothermal and two isentropic processes, will have the maximum thermodynamic efficiency, but the cycle capacity for a given  $T_{hot}$  and  $T_{cold}$  may be limited because of the allowable magnetic field variation. However, the cycle capacity can be increased by employing a regenerative process (Chen et al., 1992). The regenerative cycle was subsequently brought to life in the late 1990s, and early 2000s when various magnetic refrigeration units were built in the USA, Canada, Europe, Japan and China (Gschneidner et al., 2005) (also see Sections 3.2–3.4 and 4).

Other room temperature demonstration units have been constructed since then but no working refrigerator had been constructed before 1988. Kirol and Dacus (1987, 1988) designed, built and tested a recuperative Ericsson cycle rotary



$$\left. \begin{array}{l} T_{\text{hot}} = 319\text{ K} \\ T_{\text{cold}} = 272\text{ K} \end{array} \right\} \Delta T = 47\text{ K}$$

$\Delta T_{\text{ad}} \text{ of Gd} = 16\text{ K at } 294\text{ K } (T_C)$

Fig. 2 – Brown's (1976) magnetic heat pump.

machine (see Fig. 3). They believed that a recuperative design was superior to a regenerative magnetic heat pump because the temperature rise in the regenerator fluid reduces the effectiveness of the latter. In the former, the recuperative fluid is in thermal contact with the magnetic refrigerant except in the magnetization and demagnetization steps. It is interesting to note that the refrigerators built since then are based on a regenerative design. In the Kirol and Dacus refrigerator the heat transfer fluid flows between layers of 0.076 mm thick Gd foils (disks) which are separated by a gap of 0.127 mm. The rotor consists of 126 disks weighing 270 g. A temperature span of 11 K was attained using a  $\text{Nd}_2\text{Fe}_{14}\text{B}$  permanent magnet which generated a field of 9 kOe.

Green et al. (1990) constructed and tested a reciprocating magnetic refrigerator with a layered active regenerator (see Fig. 4). The regenerator (marked "Gd" in Fig. 4) consisted of embossed Gd and Tb metal ribbons in a "jellyroll" configuration wound into discrete sections ("pancakes"). The pancakes were stacked in a fiber glass sleeve: the low temperature end pancake was Tb, the middle pancake consisted of a mixture of Gd and Tb ribbons, and the hot end pancake was made of Gd ribbons. A second passive Cu regenerator was placed in the circuit as the cold temperature heat exchanger and a displacer was used to move the nitrogen gas heat exchange fluid. The changing magnetic field was realized by ramping the current up or down in 30 s in a 70 kOe superconducting magnet. A complete refrigeration cycle took about 70 s. A no load temperature span of 24 K (from 268 to 292 K) was attained after about 100 cycles.

### 3. The Ames Laboratory–Astronautics Corporation connection

#### 3.1. The beginning – hydrogen liquefaction

In the early to mid-1970s, W.A. Steyert at the Los Alamos National Laboratory (LANL) began working on magnetic refrigeration for hydrogen gas liquefaction, and in 1977 he was joined by J.A. Barclay. When Steyert left LANL in 1982 to join APD Cryogenics, Barclay took over the hydrogen gas liquefier research. In the following year C.B. Zimm joined the LANL team as a post-doctoral research associate. In 1985, the magnetic refrigeration technology was transferred from LANL to Astronautics Corporation of America (ACA), whose research facilities are located in Madison, Wisconsin.

Because of the Ames Laboratory's (AL) expertise in the rare earth metals, alloys and intermetallic compounds, and the Laboratory's contribution to the basic research on the magnetic, thermal and electrical properties of rare earth materials, Barclay turned to K.A. Gschneidner, Jr. for advice and assistance in developing new magnetic regenerator materials in 1990. A year later ACA subcontracted a research project to the AL to develop new and inexpensive magnetic rare earth materials as active magnetic regenerator (AMR) materials for the low temperature stage of a magnetic refrigerator for the liquefaction of hydrogen gas, which condenses at 20 K. The goal was to replace the prototype GdPd ( $T_C = 40\text{ K}$ ) magnetic

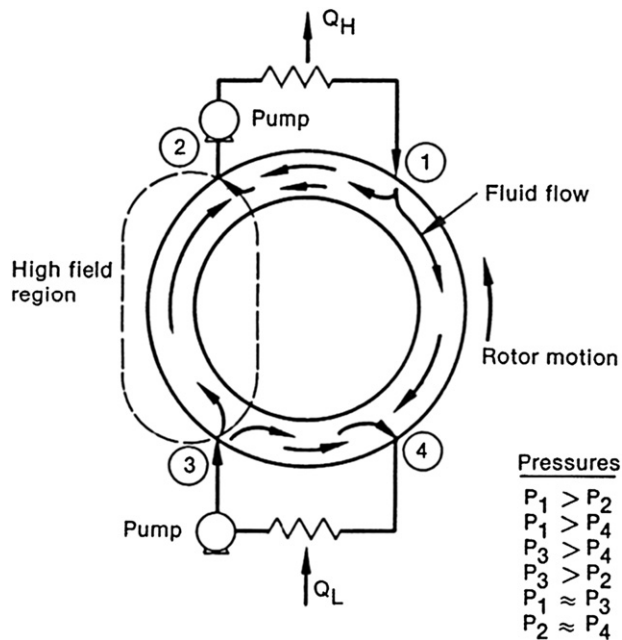


Fig. 3 – Schematic of Kirol and Dacus' (1987,1988) rotary recuperative magnetic heat pump, by permission of the American Institute of Aeronautics and Astronautics, Inc.

refrigerant material because of the cost of Pd metal (in the 1990s it was near \$5000/kg and now is over \$11,000/kg), and because Pd makes up 40% of the compound by weight. Gd, on the other hand, only costs \$120/kg but is an essential component since it is the magnetic constituent which permits the magnetic refrigerator to function.

The AL team of scientists was successful in designing several new materials that replaced GdPd. The best of these materials was  $(\text{Dy}_{0.5}\text{Er}_{0.5})\text{Al}_2$ , which is significantly cheaper since Al only costs a few dollars/kg and the magnetic rare

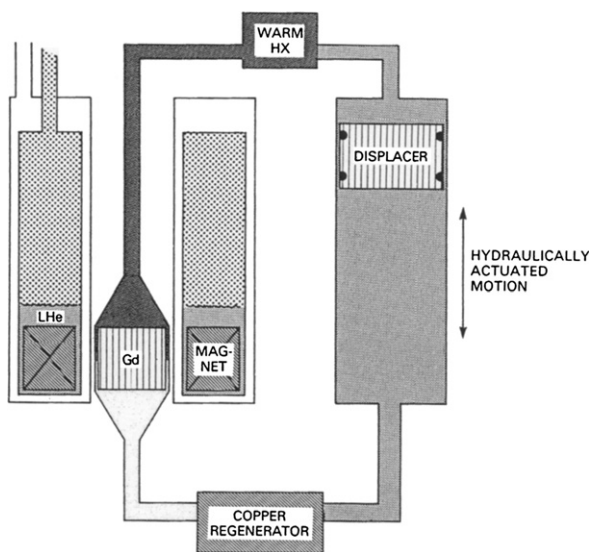


Fig. 4 – Schematic of Green et al.'s (1990) active regenerator reciprocating magnetic refrigerator, by permission of Plenum Press.

earth metals Dy and Er cost only a fraction more than Gd. Furthermore, the magnetocaloric properties of the  $(\text{Dy}_{0.5}\text{Er}_{0.5})\text{Al}_2$  intermetallic compound are 20% better than GdPd. This significant achievement was recognized by the Cryogenic Engineering Conference (CEC) as the best research paper (Gschneidner et al., 1994) given at the previous CEC conference, when the authors received the Russell B. Scott Memorial Award in Columbus, Ohio in 1995.

About six months after the completion of this study, ACA and the AL entered into a CRADA (Cooperative Research and Development Agreement) to develop a better AMR refrigerant material than ErNi, ACA's prototype material for the liquefaction of helium (boiling point 4.2 K). Three of the five materials selected for the study had MCEs which were better than or equal to those of the prototype ErNi. However, modeling of their performances in an AMR/MR by ACA indicated that they would not be as efficient as the prototype material. These results show that new materials, however, promising, must be tested under realistic operating conditions of alternating dynamic fluid flows and alternating magnetic fields before one can state whether or not material A is better than material B. A truly synergistic symbiotic relationship between the materials designer and the bench engineer/scientist is critical if significant advances are to occur in magnetic refrigeration.

### 3.2. Near room temperature refrigeration

Simultaneously with the experimental aspects noted above, an analysis of the various capital and operating costs for a near room temperature refrigerator was carried out by Gschneidner and Barclay. This study indicated that magnetic refrigeration could be competitive with conventional gas compression refrigerators operating below ambient temperatures, with a five-year payback for large scale building air conditioning or supermarket chillers or food processing plants (refrigeration and freezing). The energy savings by replacing a conventional gas-cycle (Freon or ammonia) refrigeration unit with a magnetic refrigerator were estimated to be 30% along with the elimination of Freon or ammonia, as an added environmental benefit. Based on the 1990 USA energy consumption for industrial refrigeration and cooling systems (~15 billion kWh), ~5 billion kWh and \$250 million could be saved if all of the gas compression refrigerators were replaced by AMR magnetic refrigeration units. Based on this favorable analysis, the AL scientists (K.A. Gschneidner, Jr. and I.E. Anderson) together with scientists from ACA (J.A. Barclay and C.B. Zimm) put together and submitted (in 1993) a proposal to the Advanced Energy Projects of the U.S. Department of Energy's Office of Basic Energy Science to design, build and operate a laboratory AMR magnetic refrigerator unit to demonstrate the feasibility of magnetic refrigeration as an alternative refrigeration technology within a three-year period. The project was funded in mid-1994 at the \$1 million level for the three years.

The AL (under the direction of Gschneidner) provided the management of this project and was responsible for providing the materials for the AMR test beds (~5 kg), for designing new materials, and for developing processes for the production of the desired materials in the form of spherical particles ~0.3 mm in diameter. ACA, who was a subcontractor to the AL, designed, built and tested the demonstration unit (see



Fig. 5) under the supervision of C.B. Zimm. On February 20, 1997 the Ames Laboratory/Astronautics Corporation of America held a news conference and announced the results of this three-year project – a successful operating proof-of-principle demonstration unit, showing that magnetic refrigeration is a feasible and competitive technology for large scale building air conditioning, and for refrigeration and freezing units in supermarkets and food processing plants. The demonstration unit ran for over 5000 h during an 18 month period with no significant problems and only minor maintenance. This in itself is a significant achievement since any prior magnetic refrigerator at best had only been operational for a few days. This device operated in magnetic fields up to 50 kOe using a superconducting magnet, and it achieved a cooling power of 600 W with a COP (coefficient of performance) approaching 10, a maximum of 60% of Carnot efficiency with a 10 K temperature span (between 281 K and 291 K) in magnetic fields of 50 kOe (Zimm et al., 1998; Lawton et al., 1999). As to be expected for larger temperature spans (22 K), both the cooling power and COP are much lower, 150 W and 2, respectively, and the Carnot efficiency was reduced to 20%. Later the authors report that they were able to increase the COP to 16 at 50 kOe and the same 10 K temperature span, and to attain a cooling power of  $\sim 100$  W with a 38 K temperature span in a 50 kOe field (Gschneidner et al., 1999a, 2001). They also showed that in a field of 15 kOe (a magnetic field which can be attained by using permanent magnets) and a heat transfer fluid flow rate of 4 l/min, a cooling power of  $\sim 200$  W, a COP of  $\sim 6$ , and a temperature span of 5 K with a hot heat exchanger temperature of  $\sim 295$  K could be realized (Gschneidner et al., 1999a). The AMR material was made from commercial grade gadolinium metal purchased from mainland China. The raw Chinese ingots were cast into rods at the AL, and then commercially fabricated into spheres by Starmet Powders (formerly Nuclear Metals, Inc.) using a plasma rotating electrode

process (PREP) to atomize the Gd metal. The overall yield in processing the raw ingots into usable spheres was 50%. In addition to the values cited above tests were carried out at various magnetic fields (0–50 kOe), under several different flow rates and cycle frequencies to determine the optimum operating conditions for that particular AMR/MR design, and to check the observed data relative to the numerical theoretical models for this demonstration unit (Zimm et al., 1998; Lawton et al., 1999; Gschneidner et al., 1999a, 2001).

In 1998 the AL along with ACA was awarded a Phase I CARAT (Cooperative Automotive Research for Advance Technology) grant to carry out a feasibility study of the development of magnetic cooling for automotive climate control to reduce the power consumption of a vehicle air conditioner by 30%. The AL-ACA team (1) established the cost, size, weight, cooling capacity and operating conditions for a vehicle magnetic air conditioner (VMAC); (2) chose and recommended the appropriate magnetic refrigerant for use in the VMAC; and (3) selected suitable magnetic materials and designed a permanent magnet configuration for the VMAC. For the hot temperature side of the AMR the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  alloys for  $x > 0.6$  were found to be the best materials to meet the design requirements. The permanent magnet configuration consisted of several different magnetic materials, including  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , and it generated a 29 kOe field in a 1.2 cm gap (Lee et al., 2002, 2004).

Phase II, unfortunately, was not carried out because the U.S. Congress did not fund the CARAT program in 1999 or subsequent years.

### 3.3. The second generation magnetic refrigerator

Following the success of the proof-of-principle magnetic refrigerator the ACA scientists and engineers evaluated its performance and concluded that the cycle time of 6 s (operating frequency of 0.16 Hz) for this reciprocating machine was

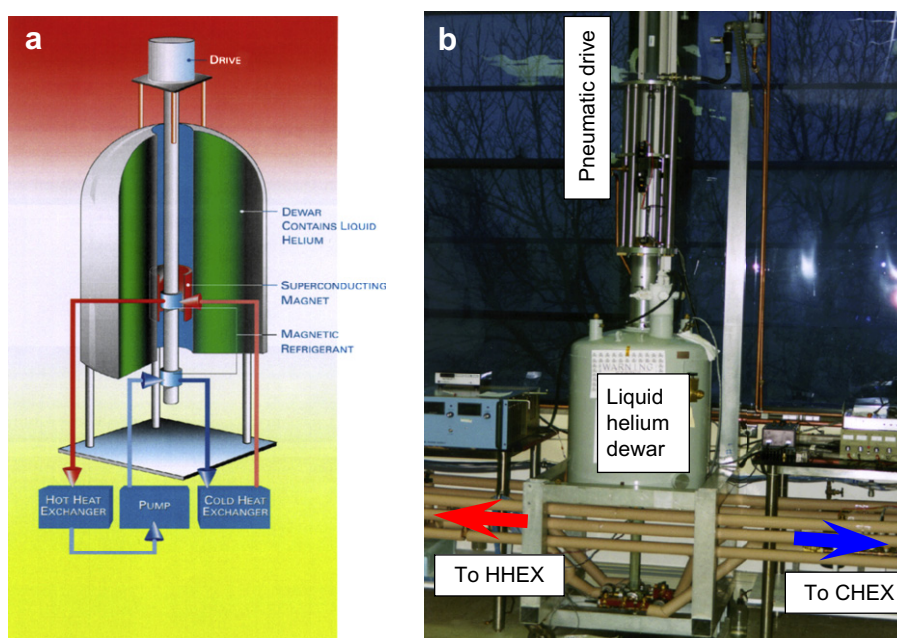


Fig. 5 – Ames Laboratory/Astronautics Corporation of America's reciprocating proof-of-principle magnetic refrigerator: (a) schematic and (b) photograph (Zimm et al., 1998).

too slow to be practical. An analysis indicated that for high frequencies,  $>1$  Hz, a rotary device would be better than a reciprocating machine. Furthermore, a decision was made to build a small cooling machine using a permanent magnet as the field source rather than build a large size magnetic refrigerator using a superconducting magnet as the magnetic field source (Zimm, 2003; Zimm et al., 2003).

Work on the second generation magnetic cooling device – a rotary, room temperature, permanent magnet, magnetic refrigerator (now called the Rotating Bed Magnetic Refrigerator – RBMR) – began in 1998 at ACA. In the meanwhile AL entered into a three-year CRADA (1999–2001) with ACA to assist ACA to bring this apparatus, called a laboratory demonstration magnetic refrigerator (see Fig. 6), to an operational status, which was achieved on September 18, 2001. In early 2002 ACA hired S. Russek to manage the near room temperature magnetic refrigerator project, and his stellar efforts were instrumental in securing additional government funds to continue work on this research project in the following years, see below, Section 3.4. A few months later on May 1, 2002 the laboratory demonstration magnetic refrigerator was unveiled to the public at the Global-8 Energy Ministers Meeting in Detroit, Michigan, and again at the Anniversary Celebration of the President's National Energy Policy at the U.S. Department of Energy Headquarters in Washington, D.C. on May 17, 2002.

In this refrigerator the porous beds of the magnetocaloric material, 160 g (initially spheres of Gd and later both Gd and a 94%Gd–4%Er alloy in a layered bed), are rotated through a magnetic field of 15 kOe produced by a  $\text{Nd}_2\text{Fe}_{14}\text{B}$  permanent magnet with steel flux concentration poles. Water is used as the heat exchange fluid. The design of this laboratory demonstration unit easily allows it to operate over a range of frequencies from 0.5 to 4 Hz and at various fluid flows to achieve a range of cooling powers. The maximum temperature span was 25 K under a no load condition, and the maximum cooling power of 50 W was realized at 0 K temperature

span. In addition a  $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$  alloy, in the form of crushed powders, was tested and a performance similar to that obtained using the Gd and GdEr alloy was realized (Zimm et al., 2003, 2006).

The RBMR operated smoothly and reliably for more than 1500 h between 2001 and 2007 (Zimm et al., 2007). About 1500 tests were carried out on the RBMR. One of the biggest difficulties was instrumenting the moving magnetocaloric beds. Also scaling up of this refrigerator has some difficulties with the central valves and piping. In view of these limitations ACA began investigating a new configuration of the magnet and magnetocaloric beds; and these developments are described in the next section.

### 3.4. The third generation magnetic refrigerator

In 2004 with funding from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, ACA and AL entered into a one year CRADA to: (1) design and evaluate a high efficiency air conditioner based on magnetic refrigeration technology; and (2) prepare and characterize several malleable intra-rare earth Gd-based alloys for the AMR. At about the same time ACA received NIST (National Institute for Standards and Technology) funding for two years to develop and demonstrate a high efficiency permanent magnet-based magnetic refrigeration technology to bring magnetic cooling one step closer to commercialization. In both projects ACA was the lead organization and responsible for the engineering aspects, while the AL provided support for magnetocaloric material synthesis and characterization.

The third generation magnetic refrigerator (the Rotating Magnet Magnetic Refrigerator – RMMR) consists of two 15 kOe modified Halbach magnets which rotate while 12 magnetocaloric beds remain fixed (see Fig. 7) (Zimm et al., 2007). The two rotating permanent magnets are arranged so that the moment of inertia of the magnet is minimized and the

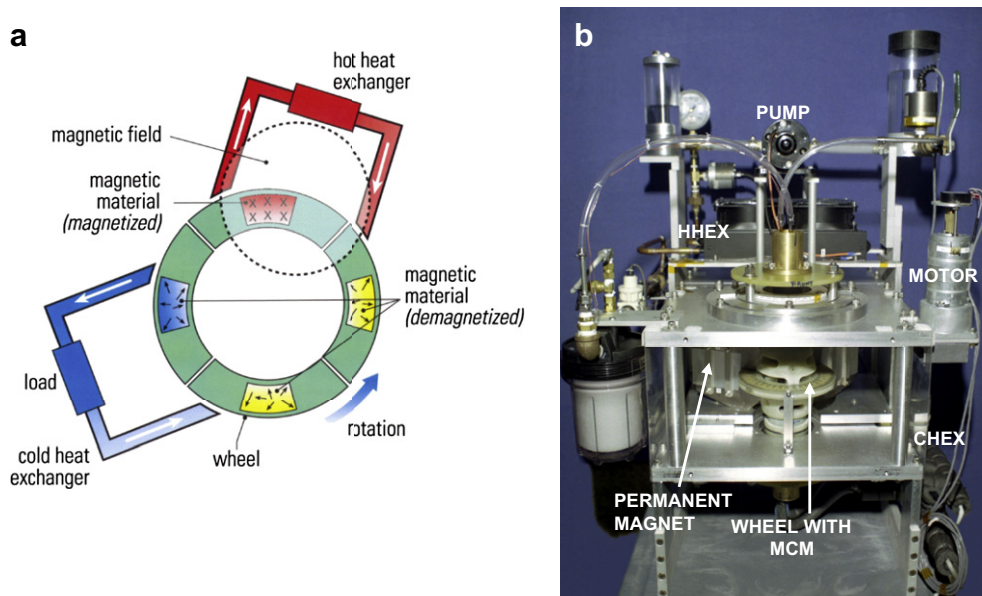


Fig. 6 – Astronautics Corporation of America laboratory prototype permanent magnet, rotating bed magnetic refrigerator (RBMR): (a) schematic and (b) photograph (Zimm, 2003; Zimm et al., 2003, 2006, 2007).

inertial forces are balanced. The main advantage of the fixed beds is that the valving and timing of the fluid flows through the beds and heat exchangers are simpler than that for the second generation machine (RBMR) in which the beds rotate through a gap in the magnet (see Section 3.3 and Fig. 6). The magnetic refrigerant used in the initial tests was Gd foils. The performance at the time of the Thermag II conference in Portoroz, Slovenia (April 11–13, 2007) had not reached the expected theoretical cooling power, e.g. 140 W actual vs. 190 W calculated for a 4 K temperature span at a flow rate of 3 l/min, i.e. ~75% of theoretical. But since this machine is in the early stages of testing, these results are not unexpected.

#### 4. Other groups

Following the seminal work of Zimm et al. (1998), near room temperature magnetic refrigeration has quickly caught the attention of both scientists and engineers, and by the time of the Thermag II conference in April 2007 more than 25 laboratory-scale magnetic cooling units have been built and

tested. Various degrees of success in implementing magnetic refrigeration as a near room temperature cooling technology have been reported by Bohigas et al. (2000), Hirano et al. (2002), Rowe and Barclay (2002a,b), Blumenfeld et al. (2002), Wu (2003), Hirano (2003), Clot et al. (2004), Richard et al. (2004), Shir et al. (2005), Lu et al. (2005), Okamura et al. (2006), and Rowe et al. (2005). More recently (April 11–13, 2007) six new magnetic refrigerators were unveiled by Chen et al. (2007), Zimm et al. (2007), Tang et al. (2007), Tura and Rowe (2007), Buchelnikov et al. (2007), Okamura et al. (2007) and Poredos and Sarlah (2007) at Thermag II. A brief summary of the operational near room temperature refrigerators that have been reported in the literature is presented in Table 1 (1998–2003) and Table 2 (2004–2007). Some of the unique features of these magnetic refrigerators are discussed in the following paragraphs.

Bohigas et al. (2000) used two bar magnets parallel to one another to generate the magnetic field with Gd foils between them. Interestingly they used olive oil as the heat transfer medium. They were able to obtain a maximum temperature span of 5 K, which is quite good considering the magnetic field change was only 5 kOe.

Blumenfeld et al. (2002) designed, built and tested a magnetic refrigerator which uses charging/discharging of a superconducting coil to generate the changing magnetic field. The significant feature is that there are no moving parts (i.e. both the magnet and the magnetocaloric beds are stationary), which makes the engineering of heat transfer system much simpler, see Fig. 8. The main penalty is the slow cycle time, which is 30 s. But on the other hand, the giant magnetocaloric effect materials may be utilized to their maximum potential, which may not be true for most machines built to date because they generally operate between 0.1 and 4 Hz (see Section 5). This novel refrigerator achieved 3 W of cooling power at a 15 K temperature span for a 17 kOe field change.

The magnetic refrigerator built in Nanjing, China, see Fig. 9, was the first reciprocating apparatus using two 14 kOe Halbach permanent magnets (Wu, 2003; Lu et al., 2005) (the previous reciprocating machines used a superconducting magnet). The authors were able to obtain a cooling power of 40 W at a 5 K temperature span using ~1 kg of the magnetic refrigerant material. At a zero heat load, a temperature span of ~25 K was reached in about 20 min of running time using either Gd powders or  $\text{Gd}_5(\text{Si}_{1.895}\text{Ge}_{1.895}\text{Ga}_{0.03})$  powders. Wu (2003) and Lu et al. (2005) were the first to use a giant magnetocaloric effect material (see Section 5) in a magnetic refrigerator, however, the performance of the latter was marginally better than that when Gd metal was used in the magnetocaloric beds, i.e. the temperature span was only 1 K greater. The operating frequency of the reciprocating machine was not given.

A compact rotary permanent magnet magnetic refrigerator was described by Tura and Rowe (2007) at Thermag II. This apparatus utilized two pairs of concentric Halbach arrays which are synchronized such that one magnetocaloric bed is being demagnetized while the second one is being magnetized, see Fig. 10. The maximum field inside the concentric Halbach magnet array was 14 kOe, and the inner cylinder could be rotated to operate at a frequency as high as 5 Hz. Since the magnetocaloric beds are stationary the valving and timing of the fluid flows are simpler than in machines in which the

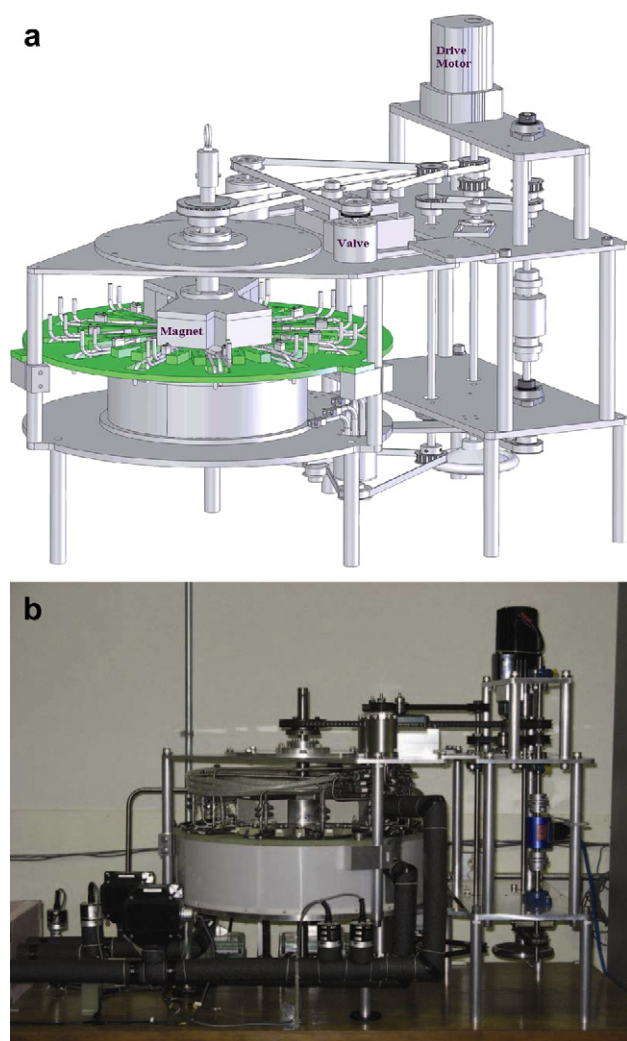


Fig. 7 – Astronautics Corporation of America's rotating magnet magnetic refrigerator (RMMR): (a) schematic and (b) photograph (Zimm et al., 2007).



**Table 1 – Room temperature magnetic refrigerators (1998–2003)**

Name	Location	Announcement date	Type	Max. cooling power (W)	Max. $\Delta T$ (K)	Max. magnetic field <sup>a</sup> (kOe)	Regenerator material	Reference
Ames Laboratory/ Astronautics	Madison, Wisconsin, USA	Feb. 20, 1997	Reciprocating	600	10	50 (S)	Gd spheres	Zimm et al. (1998)
Mater. Science Institute Barcelona	Barcelona, Spain	May 2000	Rotary	?	5	9.5 (P)	Gd foil	Bohigas et al. (2000)
Chubu Electric/Toshiba	Yokohama, Japan	Summer 2000 <sup>b</sup>	Reciprocating	100	21	40 (S)	Gd spheres	Hirano et al. (2002)
University of Victoria	Victoria, British Columbia Canada	July 2001	Reciprocating	2	14	20 (S)	Gd & Gd <sub>1-x</sub> Tb <sub>x</sub> L.B. <sup>c</sup>	Rowe and Barclay (2002a,b)
Astronautics	Madison, Wisconsin, USA	Sept. 18, 2001	Rotary	95	20	15 (P)	Gd spheres	Zimm et al. (2003)
Los Alamos Natl. Lab.	Los Alamos, New Mexico, USA	March 2002	Charging- discharging a coil	3	15	17 (S)	Gd powdr.	Blumenfeld et al. (2002)
Sichuan Inst. Tech./ Nanjing University	Nanjing, China	April 23, 2002 <sup>d</sup>	Reciprocating	?	23	14 (P)	Gd spheres; Gd <sub>5</sub> (Si,Ge) <sub>4</sub> powdr. <sup>e</sup>	Wu (2003)
Chubu Electric/Toshiba	Yokohama, Japan	Oct. 5, 2002 <sup>f</sup>	Reciprocating	40	27	6 (P)	Gd <sub>1-x</sub> Dy <sub>x</sub> L.B. <sup>c</sup>	Hirano (2003)
Chubu Electric/Toshiba	Yokohama, Japan	Mar. 4, 2003	Rotary	60	10	7.6 (P)	Gd <sub>1-x</sub> Dy <sub>x</sub> L.B. <sup>c</sup>	Hirano (2003)
Lab. d'Electronique Grenoble	Grenoble, France	April 2003	Reciprocating	8.8	4	8 (H)	Gd foil	Clot et al. (2004)

a Magnetic field source: S = superconducting magnet; P = permanent magnet; H = Halbach magnet.

b Local announcement only.

c L.B. = layered bed.

d Privately to K.A. Gschneidner, Jr.; publicly March 4, 2003.

e Actual composition Gd<sub>5</sub>(Si<sub>1.985</sub>Ge<sub>1.985</sub>Ga<sub>0.03</sub>).

f Electric Industry News, October 5, 2002.



**Table 2 – Recent room temperature magnetic refrigerators (2004–2007)**

Name	Location	Announcement date	Type	Max. cooling power (W)	Max. $\Delta T$ (K)	Max. magnetic field <sup>a</sup> (kOe)	Regenerator material	Reference
Univ. Quebec, Trois Rivières	Trois Rivières, Quebec, Canada	Feb. 2004	Reciprocating	2	14	20 (S)	Gd–R alloys <sup>b</sup>	Richard et al. (2004)
George Washington Univ.	Ashburn, Virginia, USA	June 2005	Reciprocating	?	5	20 (P)	Gd powdr.	Shir et al. (2005)
Nanjing Univ.	Nanjing, China	Sept. 27, 2005	Reciprocating	40	25	14 (H)	Gd powdr. Gd <sub>5</sub> (Si,Ge) <sub>4</sub> powdr.	Lu et al. (2005)
Tokyo Inst. Tech.	Yokohama, Japan	Sept. 27, 2005	Rotary	60	4	7.7 (P)	Gd–R alloys <sup>b</sup>	Okamura et al. (2006)
Univ. Victoria	Victoria, Canada	Sept. 27, 2005	Reciprocating	?	50	20 (S)	Gd–R alloys <sup>b</sup>	Rowe et al. (2005)
Astronautics	Madison, Wisconsin, USA	Sept. 27, 2005	Rotary	50	25	15 (P)	Gd, Gd alloys <sup>b</sup> La(Fe,Si) <sub>13</sub> H <sub>x</sub>	Zimm et al. (2006)
Sichuan Univ.	Chengdu, China	April 11, 2007	Rotary	40	11.5	15 (P)	Gd particles	Chen et al. (2007)
Astronautics	Madison, Wisconsin, USA	April 12, 2007	Rotating magnet	220	11	14 (H)	Gd plates	Zimm et al. (2007)
Sichuan Univ.	Chengdu, China	April 12, 2007	Rotary	?	6.2	7.8 (P)	Gd sheets in water	Tang et al. (2007)
Univ. Victoria	Victoria, British Columbia, Canada	April 13, 2007	Rotary	?	13	14 (H)	Gd particles	Tura and Rowe (2007)
Chelyabinsk State Univ.	Chelyabinsk, Russia	April 13, 2007	Rotary	?	?	9 (P)	Gd and Heusler alloy	Buchelnikov et al. (2007)
Tokyo Inst. Tech.	Yokohama, Japan	April 13, 2007	Rotary	540	7.5	11 (P)	Gd spheres	Okamura et al. (2007)
Univ. Ljubljana	Ljubljana, Slovenia	April 13, 2007	Rotary	?	?	9.7 (P)	Various	Poredos and Sarlah (2007)

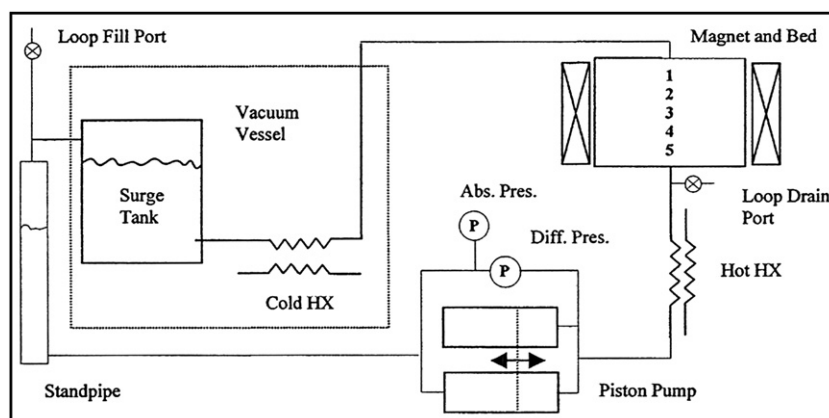
a Magnetic field source: S = superconducting magnet; P = permanent magnet; H = Halbach magnet.

b Layered bed.

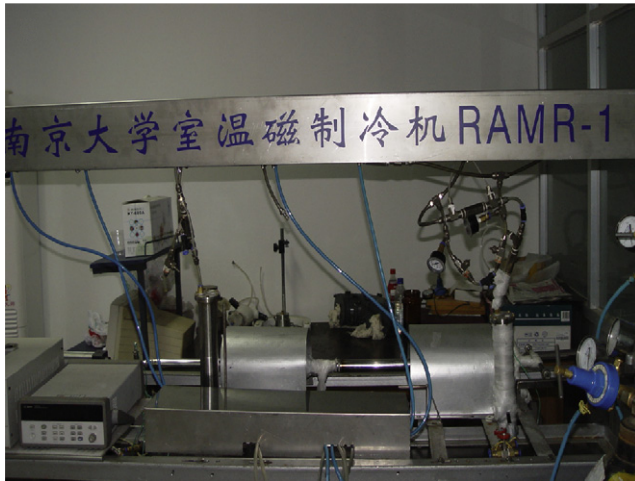
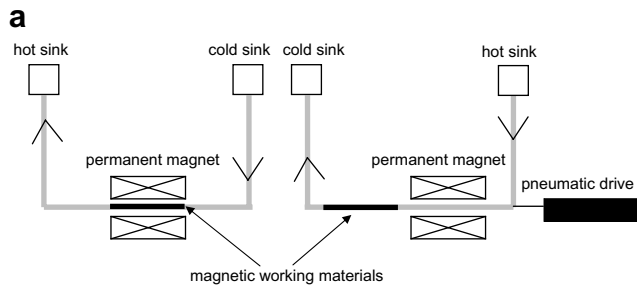
beds are rotated. Preliminary results showed that a maximum temperature span of 15 K could be reached under no load conditions.

Okamura et al. (2007) reported at Thermag II on their improvements of a rotating permanent magnet magnetic refrigerator first described at Thermag I in September 2005 (Okamura et al., 2006). In the Tokyo Institute of Technology (TIT) device a permanent magnet rotates inside a four segmented

magnetocaloric ring (the four “AMR ducts” shown in Fig. 11a) which is surrounded by an iron yoke (Fig. 11). The magnetic field in the AMR ducts when the poles of the inner permanent magnet are next to the duct is 11 kOe. The authors tested four different Gd-based alloys as the magnetic refrigerant, each weighing 4 kg. They realized a cooling power of 540 W, and a COP of 1.8 when the hot end of the AMR duct was 21 °C with a 0.2 K temperature span and the water flow



**Fig. 8 – Schematic of Los Alamos National Laboratory's superconducting magnetic refrigerator (Blumenfeld et al., 2002), by permission of American Institute of Physics.**

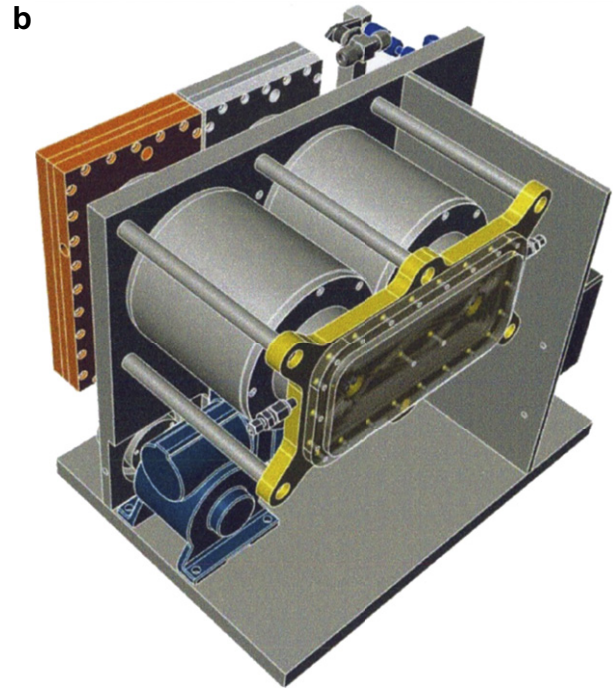
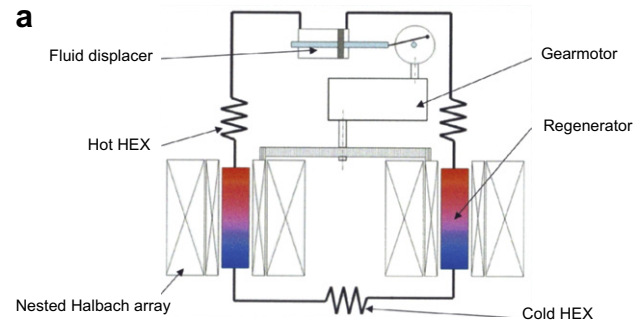


**Fig. 9 – Nanjing reciprocating dual permanent magnet magnetic refrigerator: (a) schematic and (b) photograph, by permission of Wu (2003) (Sichuan Institute of Technology, Chengdu, Sichuan, PR China) and Lu et al. (2005) (Nanjing University, Nanjing, PR China).**

rate was 13.3 l/min. The cycle time is 2.4 s. The major disadvantage is that the rotation is not continuous, i.e. magnet stops after each quarter turn next to the AMR duct for 0.7 s before the next quarter turn, which takes 0.5 s.

An important advance in regenerator design was presented by Rowe and Tura (2007) who showed both theoretically and experimentally that the temperature span of the AMR could be increased up to 35% by reducing the demagnetization at the hot and cold ends of the regenerator beds by adding ferromagnetic shims at the two ends. By adding a 1010 stainless steel (which is ferromagnetic and is far below its Curie temperature at 298 K) 12 mm thick shim at the hot end of the regenerator the temperature span increased by ~28% for a 25 mm long Gd AMR and ~17% for a  $\text{Gd}_{0.74}\text{Tb}_{0.26}$  AMR. When shims were added at both the hot and cold ends of the Gd AMR, the temperature span was increased by ~35%. All the tests were run under a no load condition using a 20 kOe magnetic field change. However, because the addition of a shim(s) increases the heat load of the AMR, the cooling power of the device probably will not be increased as much as these percentages. Further tests will show how much or an improvement in the cooling power of a magnetic refrigerator will be, but at this stage this development looks quite promising.

Many of the other magnetic refrigerators have not been discussed in detail in this paper, except for what is presented in Tables 1 and 2, because they are similar to one of the



**Fig. 10 – University of Victoria's compact permanent magnet magnetic refrigerator: (a) schematic and (b) artist's rendition; by permission of Tura and Rowe (2007).**

magnetic cooling machines described above in either this section or in Sections 2, 3.2–3.4 and shown in Figs. 2–11.

Furthermore, as far as the authors of this paper are aware, a few more units have been built and either tested or are undergoing rigorous evaluation. Indeed, one of the authors (Gschneidner) participated in an all-Chinese workshop on Magnetic Refrigeration Materials and Magnetic Cooling Machines in April 4–6, 2005, and the attending Chinese scientists and engineers described the characteristics and behaviors of six magnetic refrigerators that have been built and tested. Three of them were no longer operational because the scientists have moved to more advanced versions. Only two of the six have been described in the open literature by Wu (2003), and later by Lu et al. (2005), see Tables 1 and 2, respectively. Details of two more Chinese magnetic refrigerators which may be advanced versions of the machines discussed at the 2005 Chinese workshop, were described at Thermag II.

As one can see from the information given in Tables 1 and 2, a total of 23 working machines have been described in the

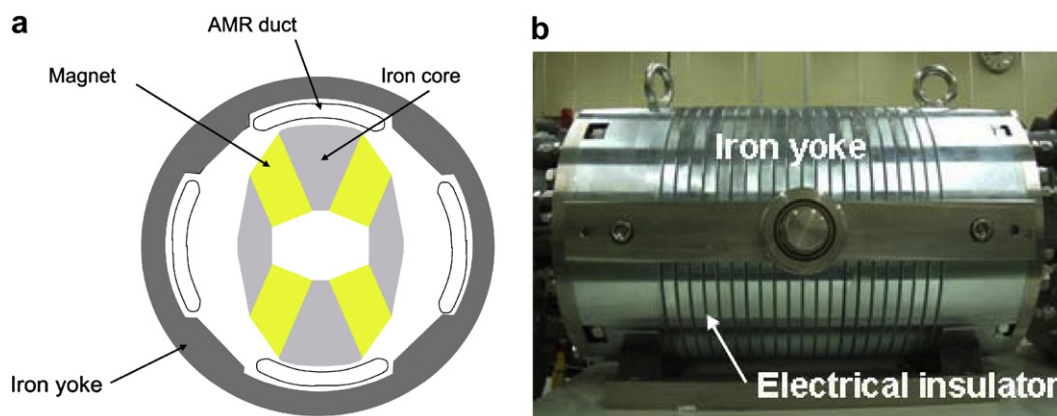


Fig. 11 – Tokyo Institute of Technology's rotating magnet magnetic refrigerator: (a) schematic and (b) photograph; by permission of Okamura et al. (2007).

open literature, while six other magnetic cooling devices have been described privately to one or both of the authors.

In addition to the four Chinese refrigerators noted above, Profs. O. Sari and P. Egolf described their two magnetic cooling machines while the authors visited the University of Applied Science of Western Switzerland, on April 17, 2007. Thus we are aware of 29 magnetic refrigerators, but there are probably several other working devices which have not yet been disclosed as of June 2007. The geographical distribution of these magnetic refrigerators is fairly broad: Canada – 4, China – 8, France – 1, Japan – 5, Russia – 1, Slovenia – 1, Spain – 1, Switzerland – 2 and USA – 6.

As one might suspect the number of near room temperature magnetic cooling machines being built and tested is growing annually, see Fig. 12. The shape of this growth curve is typical of the start of the introduction of a new technology to the world – the skewed “S” curve. We have boldly predicted that the number of machines publicized will grow rapidly over the next few years, and that we can consider magnetic refrigeration to be commercialized when 1000 machines are produced in one year which we estimate to be about 2015.

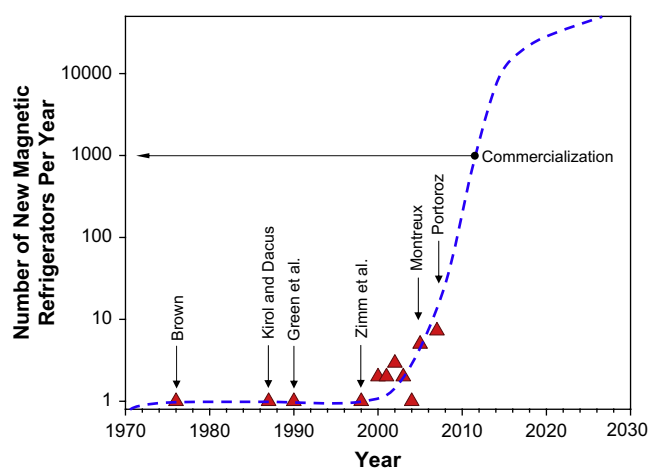


Fig. 12 – The number of near room temperature magnetic refrigerators reported vs. the year.

## 5. The giant magnetocaloric effect

### 5.1. The discovery of the giant magnetocaloric effect

The AL alloy design team (V.K. Pecharsky and K.A. Gschneidner, Jr.) also made a significant advance during the 1994–1997 Advanced Energy Projects sponsored study. They discovered a giant magnetocaloric effect (MCE) in  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ , which is  $\sim 50\%$  larger than that of Gd metal, with a magnetic ordering temperature ( $T_C = 270$  K) about 25 K lower than that of Gd ( $T_C = 294$  K). This large MCE is due to a coupled first order magnetic-structural transformation (Pecharsky and Gschneidner, 1997a,b, 2001). Additional research showed that it is possible: (1) to raise the Curie temperature to 285 K without any significant loss of the MCE by substituting a small amount of Ga for the Si + Ge content (Pecharsky and Gschneidner, 1997c; Gschneidner and Pecharsky, 1998); and (2) to vary the Curie temperature from 40 to 270 K while maintaining or even increasing the MCE by changing the Si to Ge ratio, the more Si the higher the ordering temperature (Pecharsky and Gschneidner, 1997b; Gschneidner and Pecharsky, 1998). It is noted that when the Si content is greater than 50%, there is no structural transformation and the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  material exhibits a second order ferromagnetic to paramagnetic transition and thus the giant MCE is lost. But these alloys still have a significant MCE and the Curie temperature rises to 335 K at  $x = 1$  (Gschneidner et al., 1999b). This is important since AMR materials with ordering temperatures  $> 25^\circ\text{C}$  are needed for the hot temperature end of a layered regenerator bed.

### 5.2. Other giant magnetocaloric effect materials

Within a few years of the discovery of the giant MCE in  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  intermetallics, several other families of materials have been found to exhibit the large MCEs near ambient temperatures. These include  $\text{Tb}_5\text{Si}_2\text{Ge}_2$  (Morellon et al., 2001);  $\text{MnAs}$  and  $\text{MnAs}_{1-x}\text{Sb}_x$  compounds (Wada and Tanabe, 2001; Gama et al., 2004);  $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$  alloys (Hu et al., 2001; Saito et al., 2004) and their hydrides  $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}\text{H}_y$  (Fujita et al., 2003);  $\text{MnFeP}_{0.45}\text{As}_{0.55}$  and related  $\text{MnFeP}_x\text{As}_{1-x}$  alloys (Tegus



et al., 2002; Brück et al., 2003); and the  $\text{Ni}_{2\pm x}\text{Mn}_{1\pm x}\text{Ga}$  ferromagnetic Heusler shape memory alloys (Albertini et al., 2004; Pasquale et al., 2004; Zhou et al., 2004). More detailed information about additional studies (and references) on the giant MCE materials and the ordinary MCE alloys and compounds can be found in the review by Tishin (1999), Gschneidner and Pecharsky (2000, 2002), Tishin and Spichkin (2003), Gschneidner et al. (2005), Brück (2005), and Pecharsky and Gschneidner (2005a,b, 2007a,b).

The giant magnetocaloric effect arises from a magnetic field induced magnetostructural first order transformation. When a magnetic field is applied to the material, the magnetic state changes from a paramagnet or an antiferromagnet to a ferromagnet simultaneously with either a martensitic-like structural change (Morellon et al., 1998; Choe et al., 2000), or a substantial phase volume discontinuity but without a clear crystallographic modification (Fujita et al., 2004). When the system undergoes a first order phase transition, the total entropy as a function of temperature exhibits a discontinuous (however, in reality it almost always continuous) change of entropy at a critical temperature.

Indeed many scientists have assumed that entropy is at least semicontinuous near the ordering temperatures and that Maxwell's relations apply, and have reported the existence of a colossal MCE (Gama et al., 2004). Quite recently, however, Liu et al. (2007) have shown that spike in the entropy vs. temperature at the low temperature side of skyscraper-shaped MCE is a spurious result. They noted after a careful analysis that the Maxwell relation cannot be used in the immediate vicinity of the Curie temperature because of the coexistence of the paramagnetic and ferromagnetic phases. Thus it is possible that some of the other large entropy changes reported for other giant MCE materials may also be too high.

This entropy change can be partitioned into a structural entropy change and a magnetic entropy change, and the magnitudes of these two entropy terms are about the same when the magnetic field change is  $\geq 2.5$  T (Pecharsky and Gschneidner, 2005b; Pecharsky et al., 2003). It is the structural entropy change which accounts for the significant

difference between magnetocaloric properties of materials which exhibit a first order magnetostructural transformation and those which exhibit a second order magnetic transformation. In addition to a large entropy change, the adiabatic temperature change should be large, which is only true for some of these giant magnetocaloric effect refrigerant materials.

As noted by Gschneidner et al. (2005) there are a number of other factors which must be taken into account before a final decision is made concerning the magnetic regeneration material to be used in a commercial magnetic refrigerator in addition to the magnetic entropy change,  $\Delta S_m$ , and  $\Delta T_{ad}$ . These include: raw material costs, preparation (and production) costs, fabrication costs, hysteresis, environmental concerns (e.g. are the components of the magnetic material poisonous, or carcinogenic), corrosion, stability, and the time dependence of  $\Delta T_{ad}$ ; see Table 3, which is an updated version of Table 9 in Gschneidner et al. (2005). The preparation and production costs include: the method of making the alloy (e.g. does one or more of its components have a high vapor pressure?), special handling because it is a poison or a carcinogen, heat treating times and protocols, reactivity with air and crucible materials, etc. In addition to the 11 criteria (factors) in Gschneidner et al. (2005), two more categories have been added: (1) large scale production, i.e. 1 kg or greater, and (2) friability. The large scale production is discussed below in the following paragraph (5.3). The friability category was added because the magnetic refrigerant materials will be subject to magnetic field and the corresponding fluid flow cycling between 0.5 and 10 Hz in a fully operational magnetic refrigerator which is expected to have a lifetime of 15 years minimum. Any friability will tend to clog up the regenerator beds and reduce the amount of fluid flow and thus the cooling power and capacity of the refrigeration device. Since Gd is a ductile metal its friability is zero – non-existent. Personal experience or discussions with other scientists/engineers indicate the  $\text{Gd}_5\text{T}_4$ ,  $\text{La}(\text{Fe-Si})_{13}\text{H}_x$ ,  $\text{FeMnPAs}$ -base materials and  $\text{Ni}_2\text{MnGa}$  are at least somewhat brittle and dealing with friability presents a real challenge.

**Table 3 – Advantages and disadvantages of various near room temperature magnetic refrigerant materials**

Factor	Gd	$\text{Gd}_5\text{T}_4$	$\text{RMnO}_3$	$\text{LaFeSi}$	MnAs	$\text{FeMnPAs}$	$\text{Ni}_2\text{MnGa}$
Raw material costs	0	–	++	++	++	++	+
Preparation	0	–	–	–	–	–	–
Vapor pressure	0	0	0	0	–	–	0
Fabrication (sheet)	0	–	–	–	–	–	–
$\geq 1$ kg production	0	0	?	0	?	?	?
MCE, $\Delta S_m$	0	++	–	+	+	+	+
MCE, $\Delta T_{ad}$	0	+	–	–	–	0	–
Refrigeration capacity	0	+	?	+	?	+	?
Hysteresis	0	–	0	–	–	–	–
Time dependence of $\Delta T_{ad}$	0	–	?	–	?	?	?
Environmental concerns	0	0	0	0	–	–	0
Corrosion	0	++	?	–	?	?	0
Friability	0	–	?	–	?	–	–

Elemental Gd is taken as the baseline.

### 5.3. Large scale production of giant magnetocaloric effect materials

To date only one study of the large scale production of a magnetic refrigerator regenerator material has been reported in detail – that of the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  alloys by AL scientists (Gschneidner et al., 2000a, 2003; Pecharsky et al., 2006). These scientists described a kilogram scale process for the production of  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  alloys from commercial grade Gd metal. Over 10 kg of the  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$  alloy was produced with giant MCE values of about two-thirds of that made by using high-purity Gd.

More recently Fujita et al. (2007) reported that they produced  $\text{La}(\text{Fe}_{0.86}\text{Si}_{0.14})_{13}$  spheres by the plasma-arc rotating electrode process (PREP). One hundred grams of the hydrided alloy powder (0.5 mm spheres) was tested in a magnetic refrigerator and they obtained encouraging results with a temperature span of 16 K near room temperature. No processing details were given; however, knowing that the PREP technique requires an ingot that is about 5 cm in diameter and at least 10 cm long the authors must have prepared about a 2 kg ingot. After the components had been melted together to form the  $\text{La}(\text{Fe}_{0.86}\text{Si}_{0.14})_{13}$  alloy, it was first heat treated for 10 days at 1050 °C before the powder was prepared by the PREP method, and then spheres were hydrogenated to give the final composition.

Since the publication of the initial version of Table 3 in 2005 (Gschneidner et al., 2005), the criteria for two materials have been upgraded from a double minus to a single minus: (1) the preparation of the  $\text{LaFeSi}$  alloy, and (2) the environmental concerns for FeMnPNAs; and FeMnPNAs from minus to neutral (zero) (Brück et al., 2005). Gutfleisch (2007) reported that he has been able to prepare the base  $\text{La}(\text{Fe,Si})_{13}$  alloy by melt spinning followed by a 1 h anneal. The major improvement is that the one week anneal at ~1000 °C has been reduced to a much shorter anneal. However, this is still an extra step in the preparation process, and furthermore the alloy needs to be hydrogenated to raise the Curie temperature up to room temperature. For the FeMnPNAs-base alloys, the Dutch scientists have been able to replace the As by doping with Si + Ge without losing the good MCE properties (Dagula et al., 2005; Cam Thanh et al., 2006). However, since the alloy still contains P, special handling techniques in preparing these alloys are required because white P is a poison and every allotrope of this element has a high vapor pressure. Furthermore, when As is replaced by Si + Ge the thermal hysteresis is increased from about 4 K to 15–22 K (depending upon the amount of doping Cam Thanh et al., 2006).

### 5.4. Potential problems for the use of giant magnetocaloric effect materials in magnetic refrigerators

The three major problems with the giant MCE materials as magnetic regenerator materials are due to the facts that they undergo a first order magnetostructural transition, which results in (1) a large volume change (Morellon et al., 1998; Choe et al., 2000; Fujita et al., 2004); (2) hysteresis (Provenzano et al., 2004); and (3) a finite time for the  $\Delta T_{\text{ad}}$  to reach its maximum equilibrium value (Gschneidner et al., 2000b, 2005).

The large volume change presents a problem since all of the giant magnetocaloric materials are intermetallic

compounds (except for the complex manganites) and are notorious for their brittleness (the manganites are also brittle). Assuming a lifetime of 15 years and 10% runtime for a commercial cooling device, the magnetic refrigerant material will undergo 50 (at 1 Hz) to 500 (at 10 Hz) million cycles, it is quite likely that most of these brittle materials will undergo some fracture, i.e. decrepitate. Thus, it is likely that in time small particles of the refrigerant material will break off (friable) and would clog the regenerator bed, reducing the flow of the heat transfer fluid and lowering the cooling power, and eventually the refrigerator will stop cooling altogether. This problem may be solved by alloying (but one needs to be careful not to reduce the favorable magnetocaloric properties), or perhaps by coating the particles with a ductile material which would reduce the regenerator capacity because of the coating material. In the first case, the brittleness in the magnetostrictive lanthanide (R)-iron Laves phase  $\text{RFe}_2$  material, known as Terfenol-D, was ameliorated by the addition of excess lanthanides (Tb, Dy) to the stoichiometric 1:2 Laves phase, i.e.  $(\text{Tb}_{0.27}\text{Dy}_{0.73})\text{Fe}_{1.9}$  (Verhoeven et al., 1987). In the second case, Mérida and Barclay (1998) made a monolithic regenerator by bonding irregular shaped particles using an epoxy coating that prevents the motion of the particles relative to one another during the operation of the regenerator.

The temperature hysteresis values for the various first order materials range from 2 to 14 K and the magnetic field hysteresis values range from 2 to 11 kOe (Gschneidner et al., 2005). This problem can be overcome by layering the regenerator bed so that the temperature swing in a given elemental volume of the regenerator is such that  $T_{\text{hot}}$  is higher than the upper temperature of the hysteresis loop of magnetization step of the magnetocaloric material, and that  $T_{\text{cold}}$  is less than the lower temperature of the hysteresis of the demagnetization step.

Another solution to the hysteresis problem was suggested by Provenzano et al. (2004). They added Fe to  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  which destroyed the first order giant MCE, but the resultant entropy change was significantly smaller than that for the unalloyed  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ , and somewhat larger than that of pure Gd metal. The same effect was reported seven years earlier by Pecharsky and Gschneidner (1997c) and the measured MCE was about 30% larger for Fe additions than the results reported by Provenzano et al. Furthermore, the 1997 study showed that: Cu and Ni additions are even more effective than Fe, the magnetic entropy changes were higher by ~10% and ~20%, respectively.

Of even greater concern is delay time for the  $\Delta T_{\text{ad}}$  rise to achieve its maximum value in a cycle. For  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$  and  $\text{La}(\text{Fe}_{1.44}\text{Si}_{1.56})_{13}$  the directly measured temperature changes may be 30–50% smaller than the equilibrium values because of the kinetics of the phase transformation when magnetic fields are near critical. This is a problem because the magnetic refrigerators will operate between 0.5 and 10 Hz and much of the giant MCE may not be utilized during the rapid magnetic field increase and the field decrease.

These last two effects probably account for the fact that the cooling capacity of the two magnetic refrigerators that tested the giant MCE materials  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  (Wu, 2003; Lu et al., 2005), and  $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}\text{H}_y$  (Zimm et al., 2006) was about the same as when Gd (Zimm et al., 2006; Wu, 2003; Lu et al., 2005) and/or a Gd–Er alloy (Zimm et al., 2006) was used as

the magnetic refrigerant in the same refrigerator. More research and clever engineering may be able to overcome these two disadvantages of first order magnetostructural magnetic regenerator materials.

## 6. Rare earth metal markets

The rising cost of rare earth materials is also of concern, even if the magnetic refrigerant does not contain any rare earth metal. At the present time most of the research efforts are concentrated on household (air conditioners, refrigerators, freezers, etc.) or small scale commercial (e.g. display cases and vending machines) applications. In all of these uses, Nd-Fe-B permanent magnets will likely be employed as the magnetic field source, and since 0.5–10 kg of Nd will be used per refrigerating unit, the cost of the device will critically depend on the cost of Nd. As shown in Fig. 13 the cost of Nd metal has risen by a factor of 3.5 over a two year period, January 2005–December 2006. Will this trend continue? Probably not, because now most of the Nd metal comes from China, which has a tremendous advantage over the rest of the world because of its abundant rare earth resources and low cost of labor. However, at the current price Nd metal from other countries, such as Russia, USA, Brazil, Australia is becoming competitive with the Chinese prices. As a matter of fact, we expect that the price for Nd will fall and perhaps level off in the \$12–15 per kg range in the next two or three years, as new manufacturing facilities in other non-Chinese countries come on stream. Furthermore, when magnetic refrigeration becomes of age the large demand for Nd-Fe-B permanent magnets will also help to reduce the price of Nd just due to scaling up the production processes.

The price for the magnetic refrigerant compounds La and Gd will remain fairly constant because these rare earths are by-products from the Nd processing for the permanent magnet market and we expect that the total weight of the rare earth metals in the refrigerant will be smaller than in the permanent magnet.

## 7. Epilogue

The future of magnetic cooling is bright but there are still a number of challenges to overcome. Improved engineering

to overcome the limitations of the currently available magnetic refrigerant regenerator materials, and the increase of the magnetic field strength of the permanent magnets while reducing the size, mass and cost are two critical areas which need to be continually addressed. On the other hand scientists need to continue looking for new, and hopefully better magnetic materials, and to improve the critical properties of existing materials (Table 3), i.e. changes some of minuses to zeros or pluses and reduced the double and triple minuses to single or double minuses, respectively. Also we need to address the problems: of producing the magnetic refrigerants on large scale – kilograms instead of grams, and even larger; and of developing processes to inexpensively fabricate these materials into useable forms for regenerators (spheres, wires, foils, screens, etc.) without losing the precious magnetocaloric effect.

The design, building and testing of large scale air conditioning and refrigeration systems (hundreds of kilowatts) is an area where little if any effort is being made. Some of the problems of small magnetic field systems, which are being extensively studied today, will be ameliorated with the higher fields, but new problems will be introduced when going to high magnetic field systems (> 5 T). But work on such systems may leap-frog the permanent magnet systems and actually accelerate near room temperature cooling technology.

Environmental concerns may be a major push in the not too distant future with the strong worldwide apprehension about global warming. The improved efficiency of ~20% of the magnetic cooling technology over conventional cooling devices may overcome the current cost disadvantage considering the ever rising energy costs and be the deciding factor in moving magnetic refrigeration into the realm of commercial products.

It is also worthwhile to note that a number of leading scientists and engineers from around the world have formed a society to promote magnetic refrigeration as a viable energy efficient and environmentally friendly cooling technology – the IIR (International Institute for Refrigeration) Working Party on Magnetic Refrigeration. The IIR Working Party was organized several years ago and held its first meeting at the First International Conference on Magnetic Refrigeration at Room Temperature (Thermag I) in Montreux, Switzerland, September 27–30, 2005 (Anonymous, 2005), where officers were elected and a strategy to coordinate research and development activities on an international level was developed.

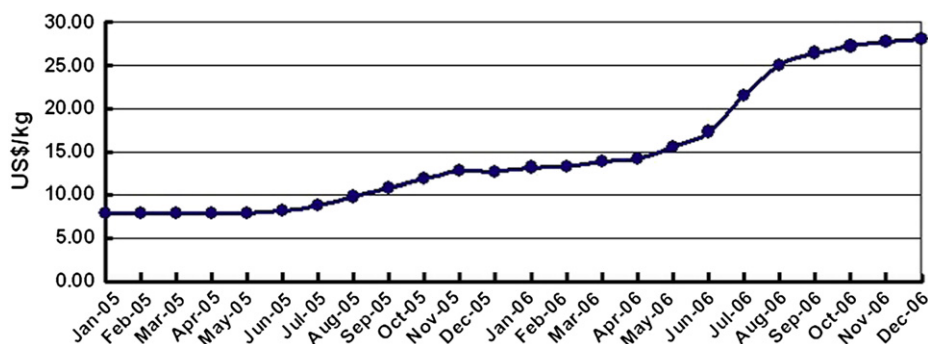


Fig. 13 – The price of neodymium metal (Nd) from January 2005 through December 2006, courtesy of Dr. Peter Campbell, consultant.



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## REFERENCES

- Albertini, F., Canepa, F., Cirafici, S., Franceschi, E.A., Napoletano, M., Paoluzi, A., Pareti, L., Solzi, M., 2004. Composition dependence of magnetic and magnetothermal properties of Ni–Mn–Ga shape memory alloys. *J. Magn. Magn. Mater.* 272–276, 2111–2112.
- Anonymous, 2005. The IIR working party on magnetic refrigeration. In: Egolf, P.W. (Ed.), *Proceedings of the First International Conference on Magnetic Refrigeration at Room Temperature*, 2005 September 27–30, Montreux Switzerland. International Institute of Refrigeration, Paris, p. 8.
- Barclay, J.A., 1982. Use of a ferrofluid as a heat-exchange fluid in a magnetic refrigerator. *J. Appl. Phys.* 53, 2887–2894.
- Barclay, J.A., 1983a. Wheel-type magnetic refrigerator. U.S. Patent No. 4,408,463.
- Barclay, J.A., 1983b. The theory of an active magnetic regenerative refrigerator. In: *Proceedings of the Second Biennial Conference on Refrigeration for Cryocooler Sensors and Electronic Systems*, NASA-CP 2287. Goddard Space Flight Center, Greenbelt, MD. 13p. Also available as Los Alamos National Laboratory Report LA-UR-82-1792.
- Barclay, J.A., 1988. Magnetic refrigeration: a review of a developing technology. *Adv. Cryog. Eng.* 33, 719–731.
- Barclay, J.A., Steyert, W.A., 1982. Active magnetic regenerator. U.S. Patent 4,332,135.
- Blumenfeld, P.E., Prenger, F.C., Sternberg, A., Zimm, C.B., 2002. High temperature superconducting magnetic refrigeration. *Adv. Cryog. Eng.* 47, 1019–1026.
- Bohigas, X., Molins, S., Roig, A., Tejada, J., Zhang, X.X., 2000. Room-temperature magnetic refrigerator using permanent magnets. *IEEE Trans. Magn.* 36, 538–544.
- Brown, G.V., 1976. Magnetic heat pumping near room temperature. *J. Appl. Phys.* 47, 3673–3680.
- Brown, G.V., 1978. Practical and efficient magnetic heat pump. NASA Tech. Brief 3, 190–191.
- Brück, E., 2005. Developments in magnetocaloric refrigeration. *J. Phys. D Appl. Phys.* 38, R381–R391.
- Brück, E., Tegus, O., Li, X.W., de Boer, F.R., Buschow, K.H.J., 2003. Magnetic refrigeration – towards room-temperature applications. *Physica B: Condens. Matter* 327, 431–437.
- Brück, E., Ilyn, M., Tishin, A.M., Tegus, O., 2005. Magnetocaloric effects in  $\text{MnFeP}_{1-x}\text{As}_x$ -based compounds. *J. Magn. Magn. Mater.* 290–291, 8–13.
- Buchelnikov, V.D., Taskaev, S.V., Bychkov, I.V., Chernets, I.A., Denisovskiy, A.M., 2007. The prototype of effective device for magnetic refrigeration. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 371–376.
- Cam Thanh, D.T., Brück, E., Tegus, O., Klaasse, J.C.P., Gortenmulder, T., Buschow, K.H.J., 2006. Magnetocaloric effect in  $\text{MnFe(P,Si,Ge)}$  compounds. *J. Appl. Phys.* 99, 08Q107/1–08Q107/3.
- Coulomb, D., 2007. The IIR and environmental challenges facing the refrigeration sector. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 3–5.
- Chen, F.C., Murphy, R.W., Mei, V.C., Chen, G.L., 1992. Thermodynamic analysis of four magnetic heat-pump cycles. *J. Eng. Gas Turbine Power* 114, 715–720.
- Chen, Y.G., Tang, Y.B., Wang, B.M., Xue, Q.X., Tu, M.J., 2007. A permanent magnet rotary magnetic refrigerator. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 309–313.
- Choe, W., Pecharsky, V.K., Pecharsky, A.O., Gschneidner Jr., K.A., Young Jr., V.G., Miller, G.J., 2000. Making and breaking covalent bonds across the magnetic transition in the giant magnetocaloric material  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ . *Phys. Rev. Lett.* 84, 4617–4620.
- Clot, P., Viallet, D., Allab, F., Kedous-Leboc, A., Fournier, J.M., Yonnet, J.P., 2004. A magnet-based device for active magnetic refrigeration. *IEEE Trans. Magn.* 39, 3349–3351.
- Dagula, W., Tegus, O., Fuquan, B., Zhang, L., Si, P.Z., Zhang, M., Zhang, W.S., Brück, E., deBoer, F.R., Buschow, K.H.J., 2005. Magnetic-entropy change in  $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{1-x}\text{Ge}_x$  compounds. *IEEE Trans. Magn.* 41, 2778–2780.
- Fujita, A., Fujieda, S., Hasegawa, Y., Fukamichi, K., 2003. Itinerant-electron metamagnetic transition and large magnetocaloric effects in  $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$  compounds and their hydrides. *Phys. Rev. B* 67, 104416/1–104416/12.
- Fujita, A., Fukamichi, K., Koyama, K., Watanabe, K., 2004. X-ray diffraction study of magnetovolume effect in itinerant-electron metamagnetic  $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$  compound. *J. Appl. Phys.* 95, 6687–6689.
- Fujita, A., Koiwai, S., Fujieda, S., Fukamichi, K., Kobayashi, T., Tsuji, H., Kaji, S., Saito, A.T., 2007. Active magnetic regenerator behavior of spherical hydrogenated  $\text{La}(\text{Fe}_{0.86}\text{Si}_{0.14})_{13}$  fabricated by rotating electrode process. *Jpn. J. Appl. Phys.* 46, L154–L156.
- Gama, S., Coelho, A.A., de Campos, A., Carvalho, A.M.G., Gandra, F., C.G. von Ranke, P.J., de Oliveira, N.A., 2004. Pressure-induced colossal magnetocaloric effect in  $\text{MnAs}$ . *Phys. Rev. Lett.* 93, 237202/1–237202/4.
- Green, G., Chafe, J., Stevens, J., Humphrey, J., 1990. A gadolinium-terbium active regenerator. *Adv. Cryog. Eng.* 35, 1165–1174.
- Gschneidner Jr., K.A., Pecharsky, V.K., 1997. Magnetic refrigeration. In: Bautista, R.G., Bounds, C.O., Ellis, T.W., Kilbourn, B.T. (Eds.), *Rare Earths: Science, Technology and Applications III*, The Minerals. Metals & Materials Society, Warrendale, PA, pp. 209–221.
- Gschneidner Jr., K.A., Pecharsky, V.K., 1998. Active magnetic refrigerants based on Gd–Si–Ge material and refrigeration apparatus and process. U.S. Patent 5,743,095.
- Gschneidner Jr., K.A., Pecharsky, V.K., 2000. Magnetocaloric materials. *Ann. Rev. Mater. Sci.* 30, 387–429.
- Gschneidner Jr., K.A., Pecharsky, V.K., 2002. Magnetic refrigeration. In: Westbrook, J.H., Fleischer, R.L. (Eds.), *Intermetallic Compounds. Principles and Practice*, vol. 3. John Wiley & Sons, Ltd., Chichester, England, pp. 519–539.

- Gschneidner Jr., K.A., Takeya, H., Moorman, J.O., Pecharsky, V.K., Malik, S.K., Zimm, C.B., 1994. New magnetic refrigeration materials for the liquefaction of hydrogen. *Adv. Cryog. Eng.* 39, 1457–1465.
- Gschneidner Jr., K.A., Pecharsky, V.K., Zimm, C.B., 1999a. Magnetic cooling for appliances. In: *Proceedings of the Fiftieth Anniversary of the International Appliance Technology Conference*, 1999 May 10–12, West Lafayette, Indiana, International Appliance Technical Conference, Largo, Florida, pp. 144–154.
- Gschneidner Jr., K.A., Pecharsky, V.K., Pecharsky, A.O., Zimm, C.B., 1999b. Recent developments in magnetic refrigeration. *Mater. Sci. Forum* 315–317, 69–76.
- Gschneidner Jr., K.A., Pecharsky, A.O., Pecharsky, V.K., Lograsso, T.A., Schlager, D.L., 2000a. Production of the giant magnetocaloric effect  $Gd_5(Si_xGe_{1-x})_4$  magnetic refrigerant materials from commercial gadolinium metal. In: Bautista, R. G., Mishra, B. (Eds.), *Rare Earths and Actinides: Science, Technology and Applications IV*, The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, pp. 63–72.
- Gschneidner Jr., K.A., Pecharsky, V.K., Brück, E., Duijn, H.G.M., Levin, E.M., 2000b. Comment on “Direct measurement of the ‘giant’ adiabatic temperature change in  $Gd_5Si_2Ge_2$ ”. *Phys. Rev. Lett.* 85, 4190.
- Gschneidner Jr., K.A., Pecharsky, V.K., Zimm, C.B., Sternberg, A., 2001. Magnetic refrigerators/freezers and air conditioners. In: *Proceedings of the Domotecnica Appliance Engineering Conference*, 2001 March 7–9, Cologne, Germany, International Appliance Technical Conference, Largo, Florida, pp. 170–182.
- Gschneidner Jr., K.A., Pecharsky, A.O., Pecharsky, V.K., 2003. Method of making active magnetic refrigerant, colossal magnetostriction and giant magnetoresistive materials based on Gd–Si–Ge alloys. U.S. Patent 6,589,366.
- Gschneidner Jr., K.A., Pecharsky, V.K., Tsokol, A.O., 2005. Recent developments in magnetocaloric materials. *Rep. Prog. Phys.* 68, 1479–1539.
- Gutfleisch, O., 2007. Melt-spinning as a novel processing route for  $MnFe(P,Ge,Si)$ . Paper no. 3A7, presented at the Second International Conference on Magnetic Refrigeration at Room Temperature, 2007 April 11–13, Portoroz, Slovenia.
- Hirano, M., 2003. Room temperature magnetic refrigerator using permanent magnets. Paper No. K7.002, presented at the American Physical Society Meeting, 2003 March 4, Austin, TX, <http://www.aps.org/meet/MAR03/baps/tocK.html>.
- Hirano, N., Nagaya, S., Takahashi, M., Kuriyama, T., Ito, K., Nomura, S., 2002. Development of magnetic refrigerator for room temperature application. *Adv. Cryog. Eng.* 47, 1027–1034.
- Hu, F.X., Shen, B.G., Sun, J.R., Cheng, Z.H., Rao, G.H., Zhang, X.X., 2001. Influence of negative lattice expansion on magnetic entropy change in the compounds  $LaFe_{11.4}Si_{1.6}$ . *Appl. Phys. Lett.* 78, 3675–3677.
- Hull, J.R., Uherka, K.L., 1989. Magnetic heat pumps for near-room-temperature applications. *Energy* 14, 177–185.
- Kirol, L.D., Dacus, M.W., 1987. Magnetic heat pump design. In: *Twenty Second Intersociety Energy Conversion Engineering Conference*, vol. 22, pp. 1133–1137.
- Kirol, L.D., Dacus, M.W., 1988. Rotary recuperative magnetic heat pump. *Adv. Cryog. Eng.* 33, 757–765.
- Lawton Jr., M.L., Zimm, C.B., Jastrab, A.G., 1999. Reciprocating active magnetic regenerator refrigeration apparatus. U.S. Patent 5,934,078.
- Lee, S.J., Kenkel, J.M., Pecharsky, V.K., Jiles, D.C., 2002. Permanent magnet array for the magnetic refrigerator. *J. Appl. Phys.* 91, 8894–8896.
- Lee, S.J., Jiles, D., Gschneidner Jr., K.A., Pecharsky, V., 2004. Permanent magnet structure for generation of magnetic fields. U.S. Patent 6,680,663.
- Liu, G.J., Sun, J.R., Shen, J., Gao, B., Zhang, H.W., Hu, F.X., Shen, B.G., 2007. Determination of entropy changes in compounds with a first order magnetic transition. *Appl. Phys. Lett.* 90, 032507/1–032507/3.
- Lu, D.W., Xu, X.N., Wu, H.B., Jin, X., 2005. A permanent-magnet magneto-refrigerator study using Gd/Gd–SiGe/Gd–SiGe–Ga alloys. In: Egolf, P.W. (Ed.), *Proceedings of the First International Conference on Magnetic Refrigeration at Room Temperature*, 2005 September 27–30, Montreux, Switzerland. International Institute of Refrigeration, Paris, pp. 291–296.
- Mérida, W.R., Barclay, J.A., 1998. Monolithic regenerator technology for low temperature (4 K) Gifford-McMahon cryocoolers. *Adv. Cryog. Eng.* 43, 1597–1604.
- Morellon, L., Algarabel, P.A., Ibarra, M., Blasco, J., García-Landa, B., Arnold, Z., Albertini, F., 1998. Magnetic-field-induced structural phase transition in  $(Gd_5Si_{1.8}Ge_{2.2})$ . *Phys. Rev. B* 58, R14721–R14724.
- Morellon, L., Magen, C., Algarabel, P.A., Ibarra, M.R., Ritter, C., 2001. Magnetocaloric effect in  $Tb_5(Si_xGe_{1-x})_4$ . *Appl. Phys. Lett.* 79, 1318–1320.
- Okamura, T., Yamada, K., Hirano, N., Nagay, N., 2006. Performance of a room-temperature rotary magnetic refrigerator. *Int. J. Refrigeration* 29, 1327–1331.
- Okamura, T., Rachi, R., Hirano, N., Nagaya, S., 2007. Improvement of 100W class room temperature magnetic refrigerator. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 377–382.
- Pasquale, M., Sasso, C.P., Lewis, L.H., 2004. Magnetic entropy change in  $Ni_2MnGa$  single crystals. *J. Appl. Phys.* 95, 6918–6920.
- Pecharsky, V.K., Gschneidner Jr., K.A., 1997a. Giant magnetocaloric effect in  $Gd_5(Si_2Ge_2)$ . *Phys. Rev. Lett.* 78, 4484–4497.
- Pecharsky, V.K., Gschneidner Jr., K.A., 1997b. Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K. *Appl. Phys. Lett.* 70, 3299–3301.
- Pecharsky, V.K., Gschneidner Jr., K.A., 1997c. Effect of alloying on the giant magnetocaloric effect of  $Gd_5(Si_2Ge_2)$ . *J. Magn. Magn. Mater.* 167, L179–L184.
- Pecharsky, V.K., Gschneidner Jr., K.A., 1999. Magnetocaloric effect and magnetic refrigeration. *J. Magn. Magn. Mater.* 200, 44–56.
- Pecharsky, V.K., Gschneidner Jr., K.A., 2001.  $Gd_5(Si_xGe_{1-x})_4$ : an extremum material. *Adv. Mater.* 13, 683–686.
- Pecharsky, V.K., Gschneidner Jr., K.A., 2005a. Magnetocaloric effect. In: Bassani, G.F., Liedl, G.L., Wyder, P. (Eds.), *Encyclopedia of Condensed Matter Physics*. Elsevier, Amsterdam, The Netherlands, pp. 236–244.
- Pecharsky, V.K., Gschneidner Jr., K.A., 2005b. Magnetocaloric effect associated with magnetocrystallographic transitions. In: Planes, A., Mañosa, L., Saxena, A. (Eds.), *Magnetism and Structure in Functional Materials*. Springer-Verlag, Berlin, pp. 199–222.
- Pecharsky, V.K., Gschneidner Jr., K.A., 2007a. Structure, magnetism, and thermodynamics of the novel rare earth-based  $R_5T_4$  intermetallics. *Pure Appl. Chem.* 79, 1383–1402.
- Pecharsky, V.K., Gschneidner Jr., K.A., 2007b. Magnetocaloric materials. In: Kronmüller, H., Parkin, S. (Eds.), *Handbook of Magnetism and Advanced Magnetic Materials*. Novel Materials, vol. 4. John Wiley & Sons, Ltd., Chichester, England, pp. 2363–2377.
- Pecharsky, V.K., Holm, A.P., Gschneidner Jr., K.A., Rink, R., 2003. Massive magnetic-field-induced structural transformation in  $Gd_5Ge_4$  and the nature of the giant magnetocaloric effect. *Phys. Rev. Lett.* 91, 197204/1–197204/4.
- Pecharsky, A.O., Gschneidner Jr., K.A., Pecharsky, V.K., 2006. Method of making active magnetic refrigerant materials based on Gd–Si–Ge alloys. U.S. Patent 7,114,340.

- Poredos, A., Sarlah, A., 2007. Presented a motion picture of their magnetic refrigerator at the Second International Conference on Magnetic Refrigeration at Room Temperature, 2007 April 11–13, Portoroz, Slovenia. Details of their apparatus were transmitted privately to the authors of this review.
- Provenzano, V., Shapiro, A.J., Shull, R.D., 2004. Reduction of hysteresis losses in the magnetic refrigerant  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  by the addition of iron. *Nature* 429, 853–857. 430 (2004) 810.
- Richard, M.A., Rowe, A.M., Chahine, R., 2004. Magnetic refrigeration: single and multimaterial active magnetic regenerator experiments. *J. Appl. Phys.* 95, 2146–2150.
- Rowe, A.M., Barclay, J.A., 2002a. Design of an active magnetic regenerator test apparatus. *Adv. Cryog. Eng.* 47, 995–1002.
- Rowe, A.M., Barclay, J.A., 2002b. Static and dynamic force balancing in reciprocating active magnetic refrigerators. *Adv. Cryog. Eng.* 47, 1003–1010.
- Rowe, A., Tura, A., 2007. Active magnetic regenerator performance enhancement using passive magnetic materials. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 289–297.
- Rowe, A., Dikeos, A., Tura, A., 2005. Experimental studies of a near-room temperature magnetic refrigeration. In: Egolf, P.W. (Ed.), *Proceedings First International Conference on Magnetic Refrigeration at Room Temperature*, 2005 September 27–30, Montreux, Switzerland. International Institute of Refrigeration, Paris, pp. 325–334.
- Saito, A., Kobayashi, T., Sawa, T., Sahashi, M., 2004. Magnetic material. U.S. Patent 6,676,772.
- Shir, F., Bennet, L.H., Della Torre, E., Mavriplis, C., Shull, R.D., 2005. Transient response in magnetocaloric refrigeration. *IEEE Trans. Magn.* 41, 2129–2134.
- Steyert, W.A., 1978. Stirling-cycle rotating magnetic refrigerators and heat engines for use near room temperature. *J. Appl. Phys.* 49, 1216–1226.
- Tang, Y.B., Chen, Y.G., Wang, B.M., Xue, Q.X., Tu, M.J., 2007. A room-temperature magnetic refrigerator using heat exchange of free convection. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 359–361.
- Tegus, O., Brück, E., Buschow, K.H.J., de Boer, F.R., 2002. Transition-metal-based magnetic refrigerants for room-temperature applications. *Nature* 415, 150–152.
- Tishin, A.M., 1999. Magnetocaloric effect in the vicinity of phase transitions. In: Buschow, K.H.J. (Ed.), *Handbook of Magnetic Materials*, vol. 12. Elsevier Science B.V., Amsterdam, pp. 395–524.
- Tishin, A.M., Spichkin, Y.I., 2003. The magnetocaloric effect and its applications. Institute of Physics Publishing, Bristol.
- Tura, A., Rowe, A., 2007. Design and testing of a permanent magnet magnetic refrigerator. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 363–370.
- Verhoeven, J.D., Gibson, E.D., McMasters, O.D., Baker, H.H., 1987. The growth of single crystal Terfenol-D crystals. *Metall. Trans.* 18A, 223–231.
- Wada, H., Tanabe, Y., 2001. Giant magnetocaloric effect of  $\text{MnAs}_{1-x}\text{Sb}_x$ . *Appl. Phys. Lett.* 79, 3302–3304.
- Wu, W., 2003. Development of a magnetic refrigeration prototype for operation at ambient temperature. Paper No. K7.004, presented at the American Physical Society Meeting, 2003 March 4, Austin, TX, <http://www.aps.org/meet/MAR03/baps/tocK.html>.
- Yu, B.F., Gao, Q., Zhang, B., Meng, X.Z., Chen, Z., 2003. Review on research of room temperature magnetic refrigeration. *Int. J. Refrigeration* 26, 622–636.
- Zhou, X., Li, W., Kunkel, H.P., Williams, G., 2004. A criterion for enhancing the giant magnetocaloric effect: (Ni–Mn–Ga) – a promising new system for magnetic refrigeration. *J. Phys.: Condens. Matter* 16, L39–L44.
- Zimm, C., 2003. Development of a magnetic refrigeration prototype for operation at ambient temperature. Paper No. K7.003, presented at the American Physical Society Meeting, 2003 March 4, Austin, TX, <http://www.aps.org/meet/MAR03/baps/tocK.html>.
- Zimm, C., Jastrab, A., Sternberg, A., Pecharsky, V., Gschneidner Jr., K., Osborne, M., Anderson, I., 1998. Description and performance of a near room temperature magnetic refrigerator. *Adv. Cryog. Eng.* 43, 1759–1766.
- Zimm, C.B., Sternberg, A., Jastrab, A.G., Boeder, A.M., Lawton, L.M., Chell, J.J., 2003. Rotating bed magnetic refrigeration apparatus. U.S. Patent 6,526,759.
- Zimm, C., Boeder, A., Chell, J., Sternberg, A., Fujita, A., Fujieda, S., Fukamichi, K., 2006. Design and performance of a permanent magnet rotary refrigerator. *Int. J. Refrigeration* 29, 1302–1306.
- Zimm, C., Auringer, J., Boeder, A., Chells, J., Russek, S., Sternberg, A., 2007. Design and initial performance of a magnetic refrigerator with a rotating permanent magnet. In: Poredos, A., Sarlah, A. (Eds.), *Proceedings of the Second International Conference on Magnetic Refrigeration at Room Temperature*, 2007 April 11–13, Portoroz, Slovenia. International Institute of Refrigeration, Paris, pp. 341–347.