A Review Paper on Development of Magnetic Refrigerator at Room Temperature

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Abstract: Magnetic refrigeration is an adiabatic cooling method which applies the magnetocaloric effect (MCE). From the point of view of basic physics, it shows an analogy to the conventional gas compression/expansion method. It has been applied for many years in Cryogenics, to reach very low temperatures. In 1976, Brown presented the first room temperature refrigerator applying adiabatic magnetisation and demagnetisation. After the discovery of the "giant" magnetocaloric effect (GMCE) in Gd5(Si2Ge2) in 1997 by Gschneidner and Pecharsky.

Which increases the MCE, many scientists and industrial representatives of the refrigeration community concede that this "new" technology (applying permanent magnets and the GMCE) has a good future potential for a remarkable penetration into the refrigeration market. They are convinced that in several different market domains, conventional refrigeration could be replaced by magnetic refrigeration.

Some magnetocaloric materials were used successfully in magnetic refrigeration application and became one of the critical parts of magnetic refrigeration technology whose delightful progresses were made worldwide in the past 30 years. At the same time, the research on giant magnetocaloric materials will accelerate the development of room temperature magnetic refrigeration.

Based on the magnetocaloric effect, magnetic refrigeration at room temperature has for the past decade been a promising, environmentally friendly new energy technology predicted to have a significantly higher efficiency than the present conventional methods. However, so far only a few prototype refrigeration machines have been presented worldwide and there are still many scientific and technological challenges to be overcome.

Key words: magnetic material; refrigeration; magnetocaloric effect; magnetic resistance

I. INTRODUCTION

Emil Gabriel Warburg (1846-1931) was a German physicist who during his career was professor of physics at the Universities of Strassburg, Freiburg and Berlin. He carried out research in the areas of kinetic theory of gases, electrical conductivity, gas discharges, ferromagnetism and photochemistry (Wikipedia,2007). In 1881 he discovered the magneto caloric effect in an iron sample, which heated a few Milli kelvins when moved into a magnetic field and cooled down again, when removed out of it .This technology was successfully applied in low temperature physics since the 1930's to cool down samples from a few Kelvin to a few hundreds of a Kelvin above the absolute zero point (-273.15 K). But today, because of two important aspects, also applications for the refrigeration market seem feasible. The first one is the availability of magneto caloric effect new magneto caloric effect new magneto caloric effect new magneto caloric effect new magneto caloric materials have become a factor two to three more performing.

Some magnetic materials, such as lanthanide metal Gd, MnAs, and lanthanide transition-metal-based compounds, generate magnetocaloric effect (MCE). Therefore, these magnetic materials can be adopted in magnetic refrigeration application. Gadolinium (Gd), is the mainly used magnetocaloric material at present. It was firstly applied in room temperature magnetic refrigeration by BROWN in 1976 and then its magnetocaloric physical properties were widely focused.

Room temperature magnetic refrigeration is an environment-safe refrigeration technology with many excellent features, such as compact configuration, low noise, high efficiency, high stability and longevity. The newly designed magnetic refrigeration components and systems use water-based heat transfer fluids, and these environmentally desirable products make minimal contributions to global warming.

Moreover, efficiency improvements of 20%–30% compared with those of currently available vapour compression-based systems are envisioned once technology development is completed [1]. Many investigators in America, China, Japan, and some European countries have focused on the performance research of room temperature magnetic refrigeration since the 1990s because of its great applicable prospect.

As a result, room temperature magnetic refrigeration has been one of the hot topics in the world. Currently, it has been regarded as one of the nine advanced subjects of the International Institute of Refrigeration (IIR) and a corresponding international workgroup has been built.

II. MAGNETOCALORIC EFFECT

The magnetocaloric effect, which is intrinsic to all magnetic materials, is a consequence of magneto-thermal couplings between the magnetic entropy and the lattice entropy. When a magnetic field is applied to the material, the atomic magnetic moments of paramagnetic or soft ferromagnetic materials become aligned, making the material more ordered. Consequently, the materials expel heat and their magnetic entropy decreases. Otherwise, the magnetic moments return to their random directions, and the materials absorb heat and their magnetic entropy increases when the magnetic field is reduced isothermally.

The MCE can be related to the isothermal magnetic entropy change (ΔSM) and the adiabatic temperature change (ΔTad), which are shown in the following expression [2-3] :

$$\Delta S_{\rm M} = \mu_0 \int_{H_0}^{H_t} \left(\frac{\partial M}{\partial T} \right)_H dH \tag{1}$$
$$\Delta T_{\rm ad} = -\mu_0 \int_{H_0}^{H_t} \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H dH \tag{2}$$

Where μ_0 is the permeability of vacuum; H_0 and H_i are the initial and the final magnetic field strength, respectively; *CH* is the heat capacity in constant magnetic field; and $(\partial M/\partial T) H_o$ is the derivative of magnetization with respect to temperature in a constant magnetic field.

Other parameters for comparing magnetic materials are the refrigerant capacity, q, which indicates that how much heat can be transferred between the cold and hot sinks in one ideal refrigeration cycle, and the relative cooling power (*P*RCP). q and *P*RCP can be established as Follows:

$$q = \int_{T_0}^{T_i} \Delta S_{\mathbf{M}} dT$$

$$P_{\text{RCP}}(S) = -\Delta T_{FWHM} \Delta S_M(T.H) \qquad (3)$$

$$P_{\text{RCP}}(T) = -\Delta T_{FWHM} \Delta T_{\text{ad}}(T.H) \qquad (4)$$

Where ΔT_{FWHM} is the full-width at half maximum of ΔS_M or ΔT_{ad}

In Figure 1 the four basic steps of a conventional gas compression/expansion refrigeration process are shown. These are a compression of a gas, extraction of heat, expansion of the gas, and injection of heat. The two process steps extraction of heat and expansion are responsible for a cooling process in two steps. The main cooling usually occurs through the expansion of the gas.



FIG 1: The conventional gas-compression process is driven by continuously repeating the four different basic processes shown in this figure.

The steps of a magnetic refrigeration process are analogous. By comparing Figure 1 with Figure 2, one can see that instead of compression of a gas, a magnetocaloric material is moved into a magnetic field and that instead of expansion it is moved out of the field.

As explained in the previous section, these processes change the temperature of the material and heat may be extracted, respectively injected just as in the conventional process.

There are some differences between the two processes. The heat injection and rejection in a gaseous refrigerant is a rather fast process, because turbulent motion transports heat very fast. Unfortunately, this is not the case in the solid magnetocaloric materials. Here, the transport mechanism for heat is slow molecular diffusion. Therefore, at present filigree porous structures are considered to be the best solution to overcome this problem. The small distances from the central regions of the material to an adjacent fluid domain, where a heat transport fluid captures the heat and transports it out of the material, are ideal to make the magnetic cooling process faster.



FIG 2: The magnetic refrigeration cycle comparison. Compression is replaced by adiabatic magnetisation and expansion by adiabatic demagnetisation.

Furthermore, the not very large adiabatic temperature differences of magnetocaloric materials will require more often a design of cascade or regenerative magnetic refrigerators [4] than in conventional refrigerators and hence require additional heat transfer steps.

III. THEORETICAL APPROACH OF MCE: MOLECULAR FIELD THEORY:

The theoretical calculation of the MCE is based on the model of Weiss (MFT: Molecular Field Theory) and the thermodynamic relations (Huang, 2004). To interpret quantitatively the ferromagnetism, Weiss proposed a phenomenological model in which the action of the applied magnetic field **B** was increased from that of an additional magnetic field proportional to the volume magnetization density Bv as:

$$Bv = \lambda \mu_o M$$
 (5)

The energy of a magnetic moment is then:

$$\mathbf{E} = -\mu(B + Bv) \tag{6}$$

The magnetic moments will tend to move in the direction of this new field. Adapting the classical Weiss-Langevin classical calculations to a system of quantum magnetic moments, one finds:

$$M(x) = ng_j \,\mu_B B_J(x) \tag{7}$$

Where:

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(9)

$$x = \frac{Jg_J \mu_B \{B + \lambda \mu_o M(x)\}}{k_B T}$$
(8)

and

$$B_{J}(x) = \frac{2J+1}{2J} \operatorname{coth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \operatorname{coth}\left(\frac{1}{2J}x\right)$$

Where $J(N \ s \ m)$ is the total angular momentum, $n(mol^{-1})$ is the Avogardro number, g_J is the Lande factor, $\mu_B(J \ T^{-1})$ is the Bohr magnetron $k_B(J \ K-1)$ is the Boltzmann constant, $B_J(x)$ is the Brillouin function λ is the Weiss molecular field coefficient and $\mu_{o(T \ mA^{-1})}$ is the Permeability of vacuum.

The magnetic entropy is given by the relationship of Smart (Allab 2008) The lattice contribution can be obtained using the Debye model of phonons(Allab 2008) it is given by the following equation:

$$S_m(x) = R\left(\ln\left(\sinh\left(\frac{2J+1}{2J}x\right)\right) / \sinh\left(\frac{1}{2J}x\right)\right) - xB_J(x)\right)$$
(10)

A. Application of MFT to gadolinium (Gd)

x

In this section the theoretical study based on the MFT developed in the previous section is applied to the gadolinium. Table 1 gives the parameters used to calculate the magneto caloric Properties

J	N	gj	$\mu_{\rm B}$	k _B	μο	T _C	T _D
3.5	6.023X10 ²³	2	9.2740154X10 ⁻ 24	1.380662X10 ⁻ 23	4πX10 ⁻ 7	293	184



Table 1: Parameters used for applying MFT to the gadolinium





FIG 3: Results of the theoretical study applied to Gd

The numerical solution of equations (14), (15) and (16) allows getting the isotherms of magnetization and its evolution as a function of temperature calculated by the method of Weiss as shown in Fig. 3 (a) and Fig. 3 (b). Fig. 3 (c) represents the total heat capacity calculated from the equation (3) for different levels of induction. The magnetic entropy and Its variation with temperature is shown respectively in Fig. 3 (d) and Fig. 3 (e). Finally, Fig.3 (f) shows the magnetocaloric effect calculated by the MFT.

B. Application of MCE to produce cold

The magnetic cycles are generally composed of the process of magnetization and demagnetization, in which heat is discharged or absorbed in four steps as depicted by Fig. 3.

From thermodynamic point of view, the magnetic cooling can be realized by: Carnot, Stirling, Ericsson and Brayton, where the Ericsson and Brayton cycles are believed to be the most suitable for such medium or room temperature cooling. Such cycles are predisposed toyield high cooling efficiency of the magnetic materials (Bouchekara, 2008).

Fig. 4(a) shows the conventional gas compression process that is driven by continuously repeating the four different basic processes shown while Fig. 4 (b) shows the magnetic refrigeration cycle comparison. The steps of the magnetic refrigeration process are analogous to those of the conventional refrigeration. By comparing (a) with (b) in Fig. 4, one can see that the compression and expansion are replaced by adiabatic magnetization and demagnetization, respectively. These processes change the temperature of the material and heat may be extracted and injected just as in the conventional process.





FIG 4: Analogy between magnetic refrigeration and conventional refrigeration

IV. CRITERIA FOR SELECTING ROOM TEMPERATURE MAGNETIC MATERIAL

On the basis of the corresponding theoretical analysis and the nature of MCE, magnetic materials in magnetic refrigeration should satisfy several features for application, including [5,6, 7]: (1) the large ΔSM and ΔTad (i.e. large total angular momentum number (*J*) and Lande factor (*g*) for ferromagnetic material); (2) the large density of magnetic entropy, which is an important factor contributing to the working efficiency of materials; (3) the small lattice entropy (i.e. the high Debye temperature); (4) the modest Curie temperature (*T*C) in the vicinity of room temperature to guarantee that the large magnetic entropy change can be obtained in the whole temperature range of the cycle; (5) the nearly zero magnetic hysteresis; (6) the very small thermal hysteresis; (7) the small specific heat and large thermal conductivity, which ensure remarkable temperature change and rapid heat exchange; (8) the large electric resistance (i.e. the lowering eddy current heating or the small eddy current loss); (9) the high chemical stability and simple sample synthetic route.

V. MAGNETIC MATERIALS FOR MAGNETIC REFRIGERATION

Pure gadolinium may be regarded as being the ideal substance for magnetic refrigeration, just as the ideal gas is for conventional refrigeration. But just as conventional systems are usually not operated with ideal gases, magnetic refrigerators will perform better with specially designed alloys Gschneidner and Pecharsky [8] have published the following list of promising categories of magnetocaloric materials for application in magnetic refrigerators:

- Binary and ternary intermetallic compounds
- Gadolinium-silicon-germanium compounds
- manganites
- Lanthanum-iron based compounds
- Manganese-antimony arsenide
- Iron-manganese-arsenic phosphides
- Amorphous fine met-type alloys (very recent).

At present, a number of toxic substances in such compounds are being replaced by more acceptable elements. A discussion on the different types of materials with their distinct properties is found in extended topical reviews [8,9]. Currently, the total entropies and the related refrigeration capacity, the adiabatic temperature change and the costs of the materials are under investigation. Bruck states that in the near future, other properties such as corrosion resistance, mechanical properties, heat conductivity, electrical resistivity, and the environmental impact will also become important [9]. Currently, the best, not too expensive materials were reported with cooling capacities at a change of 2 T "magnetic field" strength of approximately 1500 J/kg at constant temperature [10] and an adiabatic temperature change of 7–8 K. Materials with low magnetic hysteresis are favourable, because the area of a hysteresis curve on coordinates of M vs H corresponds to energy dissipated to the environment in each cycle.

A. Gd and its alloys

Gadolinium, a rare-earth metal, exhibits one of the largest known magnetocaloric effects. It was used as the refrigerant for many of the early magnetic refrigeration designs. The problem with using pure gadolinium as the refrigerant material is that it does not exhibit a strong magnetocaloric effect at room temperature. More recently, however, it has been discovered that arc-melted alloys of gadolinium, silicon, and germanium are more efficient at room temperature. The prototype magnetic material available for room temperature magnetic refrigeration is the lanthanide metal gadolinium (Gd). At the Curie temperature of 294 K, Gd

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Undergoes a second-order paramagnetic – ferromagnetic phase transition. The MCE and the heat capacity of Gd have been studied in many research activities. [11-14] Table 1. Presents the magnetic entropy of some magnetic materials in the range of near room temperature, from which it can be seen that _SM of the GdSiGe alloys are all considerably large in the presence of a 5 T magnetic field and most of those Curie temperatures are in the room temperature range. Therefore, this series of alloys meet the requirements of room temperature magnetic refrigeration. However, many urgent problems such as easy oxidation, hard preparation, and high price, need to be settled before they are applied in room temperature magnetic refrigeration.

Magnetic Material		Tc (K)	$\Delta H(T)$	ΔS _M (Jkg K')
Gd		294	5.0	10.2
Gdo 5Dyo 5		230	5.0	10.2
Gdo 74 Tbo 28		280	5.0	11.5
Gd ₇ Pd ₃		323	5.0	100000
Gds (SixGe1-x)4	x=0.43	247	5.0	39.0
	x=0.5	276	5.0	18.4
	x=0.505	280	5.0	11.7
Gds (SilessGelesGa.os)2		290	5.0	
Nise 6Mines 1 Gaza 5		300	5.0	18.0
MnAs		318	5.0	30.0
MnAs _{0.9} Sb _{0.1}		286	5.0	30.0
MnFePo.4sASo.36		300	5.0	18.0
Gd		294	1.5	3.8
		294	3.0	7.1
		294	6.0	11.4
La _{1-x} Ca _x MnO ₃	x=0.2	230	1.5	5.5
	x=0.33	267	3.0	6.4
	x=0.35	255	3.0	5.2
	x=0.4	263	3.0	5.0
La _{0.9} K _{0.1} MnO ₃	10000000000000000000000000000000000000	283	1.5	1.5
Lao.75Cao.15Sro.1 MnO3		327	1.5	2.8
Lagra(Ca,Pb) raMnOa		296	7.0	7.5

Table 2: Magnetic entropy change some near room temperature magnetic materials

	Rare-earth metal								
Parameter	Gd	Tb	Dy	Ho	Er	Tm			
gi	2	1.5	1.33	1.25	1.2	1.7			
i	3.5	6	7.5	8	7.5	6			
T _C (K)	294	•		•	•				
T _N (K)	-	230	178	133	85	60			
T _D (K)	184	177	179	194	192	190			

Table 3: Parameters of rare-earth elements used in theoretical MFA calculations by Tishin

Table 3 present the basic parameters for magnetocaloric effect of some rare-earth elements, where gj is the g factor of the atom, j is the total angular momentum quantum number, for the determine of the magnetic moment of an atom. TC is the Curie temperature of element; TN and TD are the Neel and Debye temperature of these rare - earth elements as shown Table 3. Table 4 present of the Advantages and disadvantages of various near room temperature magnetic refrigerant materials.

B. Perovskite and perovskite-like compounds

Large magnetic entropy change has been found in the perovskite manganese oxides in recent years, so that these materials attract more and more attention. The main advantages of this series of compounds over Gd and GdSiGe alloys are low cost, non-active chemical property (no oxidation), little coercive force as well as high electric resistance. Many studies on these compounds are led mainly in China, Spain and United States [11]. From Table 1, it is clear that their Curie temperature also can be easily tuned to the needed range by introducing some kinds of metal additions. However, _SM will decrease much in the meantime, lowering their practicability. For instance, _SM of La0.8Ca0.2MnO3 in the presence of 1.5 T magnetic fields reaches 5.5 J/kg K, about 1.5 times of Gd, but its Curie temperature is only 230 K. After adjusting Ca ratio to La0.6Ca0.4MnO3, its Curie point increases to 263 K but _SM decreases to 70% of Gd at 3 T. To improve the Curie temperatures by adding Sr and Pb, the Curie temperatures reach 327 and 296 K, however _SM decreases obviously. In addition, the behaviour of heat transfer of these compounds is incompetent because they are oxides [15].

Gd	GdsT4	RMnO ₂	LaFeSI	MnAs	FeMnPAs	Ni ₂ MnGa
0	*	**		**	++	· •
0	1.00	**				0.000
0	0	0	0			0
0	+		+1.1			
0	0	2	0	2	?	?
0	**	1.42		+	+	+
0		1.6	- 20		0	
0	+	?	+	?	+	?
0		0		1.000		
0		?		?	?	?
0	0	0	0			0
0	**	?	-	?	2	0
0		2		2		1
	Gd 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Gd GdsTs 0 - 0 0 0 0 0 0 0 - 0 0 0 ++ 0 ++ 0 0 0 0 0 0 0 0 0	Gd Gd ₃ T ₄ RMnO ₂ 0 - ++ 0 - ++ 0 0 0 0 0 0 0 - - 0 0 ? 0 + - 0 + ? 0 + ? 0 + ? 0 - ? 0 - ? 0 - ? 0 0 0	Gd Gd ₃ T ₄ RMnO ₂ LaFeSi 0 - ++ ++ 0 - - 0 0 0 0 0 0 - - - 0 0 0 0 0 0 - - - - 0 0 ? 0 0 0 ++ - + + 0 + ? + + 0 + ? + + 0 - ? - - 0 0 0 0 0 0 0 ++ ? - - - - 0 0 0 0 0 0 - -	Gd Gds_1 RMnOs LaFeSi MnAs 0 - ++ ++ ++ 0 - 0 0 0 0 0 0 0 0 0 0 ? 0 ? ? ? 0 0 ? 0 ? ? ? 0 ++ - + + + ? ? ? ? 0 ++ ? + ? - ? ? 0 + ? - ? ? ? ? 0 0 0 0 - ? ? ? 0 0 0 0 - ? ? ? 0 0 0 0 - ? ? ? ? </td <td>Gd Gd₃T₄ RMnO₃ LaFeSI MnAs FeMnPAs 0 - ++ ++ ++ ++ 0 - 0 0 0 0 0 0 0 0 0 0 ? 0 ? ? ? 0 0 ? 0 ? ? ? 0 + - + + + + 0 + ? + ? + + 0 + ? + ? + ? 0 + ? - ? ? ? ? 0 - ? ? ? ? ? ? 0 - ? ? ? ? ? 0 0</td>	Gd Gd ₃ T ₄ RMnO ₃ LaFeSI MnAs FeMnPAs 0 - ++ ++ ++ ++ 0 - 0 0 0 0 0 0 0 0 0 0 ? 0 ? ? ? 0 0 ? 0 ? ? ? 0 + - + + + + 0 + ? + ? + + 0 + ? + ? + ? 0 + ? - ? ? ? ? 0 - ? ? ? ? ? ? 0 - ? ? ? ? ? 0 0

Table 4: Advantages and disadvantages of various near room temperature magnetic refrigerant materials

VI. GIANT MAGNETOCALORIC EFFECT MATERIALS

The discovery of the GMCE is a landmark in the development of room temperature magnetic refrigeration [11]. The GMCE results from the fact that a structural transformation takes place simultaneously with the magnetic ordering. In this case, both the magnetic sub-lattice and crystallographic sub-lattice are easily affected by the magnetic field. Therefore, the MCE in the first-order phase transition materials undergoing the coupled magneto-structural transformations (or the GMCE compounds) arises from the added difference of the entropies of the two crystallographic modifications (polymorphs) of the material [8]. Further research on the GMCE shall focus on its nature and mechanism. For the GMCE materials, the added entropy change resulted from structural transformation in the first-order phase transition can be expressed by ΔS st, and hence the total entropy change is given by

$$\Delta S_{\rm M} = \mu_0 \int_{H_0}^{H_t} \left(\frac{\partial M}{\partial T}\right)_{H} \mathrm{d}H + \Delta S_{\rm st}$$

An estimation based on comparison of the MCEs exhibited by closely related materials with and without the magnetic field-induced structural transformation indicates that ΔS st may account for more than a half of the total magnetic entropy change in magnetic fields less than 5 T [8, 12]. Fig.1 schematically compares the magnetocaloric effects in the first-order magnetic phase transition (FOMT) compounds (GMCE materials) and the second order magnetic phase transition (SOMT) compounds (conventional MCE materials) [8], where *T*C is the transition temperature. It can be seen from the figure that the GMCE materials have much larger magnetic entropy changes compared with those of the conventional MCE compounds at any temperature, and the former have much wider applicable prospect.



FIG 5: Comparison between GMCE materials and conventional MCE materials at $\mu_o \Delta H=5T$

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VII. MAGNETOTHERMODYNAMIC MACHINES

The basic magnetothermodynamic cycles are the Carnot cycle, the Brayton cycle and the Ericsson cycle. A review of the magnetothermodynamics of magnetic refrigeration is given in Reference 8. Also, cascade and regeneration processes are explained. Another concept is the application of the active magnetic refrigeration principal (AMR) [8]. Until now, studies on 28 prototypes have been published and some of their characteristics were listed (for a partial overview, see Reference 10). One of the most successful machines was built by Astronautics Corporation, USA. This rotary type of magnetic refrigerator is operated with a frequency of up to 4 Hz. It has a magnetic field induction of 1.5 T, is filled with gadolinium spheres and has a cooling capacity of 95 W with a maximum temperature span of 20 K [8]. Other prototypes have been built by the Material Science Institute in Barcelona, Spain; Chubu Electric/Toshiba, Yokohama, Japan; a group at the University of Victoria, British Columbia, Canada; Sichuan Institute of Technology/Nanjing University, Nanjing, China; the Laboratoire d'Electronique Grenoble in Grenoble and Cooltech Applications, France [16].

The prototype designed by the University of Victoria applies the layered bed technique with two different materials. By choosing different alloys at different positions in the refrigerator, the performance of the refrigerator is increased. The refrigerator prototype built at the Sichuan Institute of Technology was the first which applied a material with the GMCE exceeding the adiabatic temperature difference of gadolinium.



FIG 6: Magnetocaloric effect with gadolinium

In Figure 6, the maximum temperature change induced by a 2 T magnetic field is only 5°C (9°F). Stronger magnetic fields induce a larger temperature change, at 10 T, the maximum temperature change equals approximately 25°C. This level of magnetic field strength is, however, only obtained in superconducting electromagnets (such as those used in magnetic resonant imaging [MRI] systems). For a practical, efficient magnetic refrigeration cycle, the cycle needs to operate with magnetic field strengths that attainable by permanent magnets that provide the magnetic field without parasitic energy consumption. As the best high energy permanent magnets can provide fields in the range of 1 to 2 T, achieving the temperature lifts needed for air conditioning and refrigeration requires the use of a regenerative cycle. In essence, the sensible heat cycling of the magnetocaloric material needs be provided by regenerative heat transfer and the magnetic field induced temperature changes are used to remove heat from the cooling load and reject heat to the heat sink [17].

VIII. LINEAR AND ROTARY MAGNETIC REFRIGERATORS

The four basic processes of magnetic refrigeration are most simply realized by machines as described e.g. in a patent of the University of Applied Sciences of Western Switzerland (Kitanovski *et al.*, 2004). It describes an axial machine (Figure 4, left), whereas a second recently deposited patent idea describes a machine of a radial type of refrigerator (Figure 4, right). There also exist prototypes with rectilinear motion. These prototypes work like rotary heat recovery machines applied with success for decades in air conditioning. A first step is the magnetization of a porous solid magneto caloric structure in a magnetic field, followed by a simultaneous heating up of the material (see (A)). By a fluid flow this structure is cooled (also in region (A)), and after that it turns out of the magnetic field and shows a demagnetization process (B). Here the magneto caloric alloy becomes cold and is heated by a fluid flow, which preferable has the opposite direction to the first flow (also in region (B)). If the hot fluid on side (A) is used it's anheat pump application, if the cold fluid is applied then the machine is a cooler or a refrigerator.

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FIG 7: An axial magnetic refrigerator is shown on the left and a radial machine on the right. The first has the advantage of a constant axial fluid velocity and the second a preferable positioning of the magnets assembly

IX. THE THERMODYNAMIC CYCLES

The basic thermodynamic cycle of a machine is the Brayton cycle. A machine following the Brayton cycle operates between two adiabatic and iso-magnetic field lines (see FIG. 5 on the left). The processes 1-2 and 3-4 are the magnetisation from a magnetic field H_0^{-1} to H_0^{-2} , respectively the inverse demagnetisation.



Not all the details of the thermodynamics of magnetic refrigeration can be discussed in this overview. A comprehensive review on magneto-thermal cycles was published by Kitanovski and Egolf (2006).

FIG 9: Temperature of two stage machine

X. MULTI-STAGE MACHINES

To show good performance magnetic refrigerators should operate with permanent magnets. At present a "field strength" $\mu oH= 2$ T (Tesla) seems a realistic value for their induction. By optimized structures a field line convergence may locally even allow higher values. If we assume an induction of 2 T, best materials have an adiabatic temperature difference of 7 to 8 K, but only if their hysteresis effects are negligible. A hysteresis leads to irreversibility's, which lower the coefficient of performance of a machine. From this one concludes that applications with smaller temperature differences are more adapted to magnetic refrigerationas those with very large temperature spans. Furthermore, the ideal operation around the Curie temperature of the magneto caloric material favors applications with rather stable operation temperature levels. Because of the first mentioned reason cascade machines (see FIG. 6) or machines with regeneration must be envisaged (more on this subject is found in Kitanovski and Egolf, 2006). To design a multi-stage machine the following design drawing - showing

a two stage refrigerator, respectively heat pump - may be very helpful (see FIG. 7). For more stages the drawing may easily be adapted.



FIG 8 : The connections between the stages have to be contiously guaranteed. For this purpose in the case of four machines, one needs three pumps. Furthermore a pump each is necessary at the heat sink and heat source. Because of leakages the fluids should be the same in all hydraulic parts.



FIG 10: The most important temperatures of a two-stage machine are shown in this figure. The two processes overlap a little. Only then heat may be transferred from the higher to the lower stage. The diagram is presented for a machine with a high thermal inertia of the rotor and a counter flow of the fluids (from Egolf *et al.*, 2006b).

XI. ESTIMATE OF THE COEFFICIENT OF PERFORMANCE

In the case that the proposed magnetic refrigerator cannot achieve the required temperature difference between the temperatures of the heat source and the heat sink in a single stage, a cascade or a multi-stage regenerative cycle has to be performed. The number of stages depends on the strength of the magnetic field change, on the

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heat transfer efficiency, etc. In order to transfer heat from one stage to the other a temperature difference must exist and this leads to irreversible losses. To determine the final temperature difference, an assumption of overlapping cycles of different stages takes into account the heat transfer rate between them as well as the heat transfer in the heat exchangers at the source and sink. A magnetic refrigerator thermodynamic cycle may reach at least 80 % of Carnot efficiency. But this is only valid for a single stage refrigerator with magneto caloric material with a small hysteresis. One has to be aware that this thermodynamic coefficient of performance *COPtherm* does not yet contain all losses of a magnetic refrigerator. Further irreversibility effects are:

1) The "energy loss" by friction between the cylindrical wheel and its housing, *Pfriction*

- 2) Energy losses by a non-ideal motor turning the wheel with efficiency $\Box mot$
- 3) Energy loss of the two counter current flows in the porous structure, *Pmatrix*
- 4) Energy losses by the pumps with a hydraulic and electric efficiency, Ppumps
- 5) Energy loss of fluid flows in connecting tubes, *Ptubes*.

To minimize all these losses the rotation frequency should not be too high. Also the fluid velocities must be rather low, because otherwise the power losses given by a flow through the porous structures decreases the final *COP* value remarkably. The losses by pumps and fluid flows in connecting tubes are almost negligible. For numerous applications higher COP values are expected than those of analogous conventional refrigeration technologies.

XII. MAGNETIC FIELD CALCULATIONS

More sophisticated investigations call for theoretical models and numerical simulations of the magnetic and thermodynamic behaviour of the operation of such machines. Even more appropriate is a coupled thermomagnetic treatment of the problems. Then optimization calculations for a defined prototype show, which parameters give best results. Even a simplified approach leads to a 16-dim. space for an optimization calculus (Egolf *et al.*, 2006b). In FIG. 12 an example of a magnetic field calculation is shown.



FIG 11: Magnetic scalar field shown by a color shade presentation. The results were calculated by applying the finite element method. The colors show different inductions μ_0 H. The lower half cylinder shows high field intensities and the higher half low field intensities,

XIII. THERMODYNAMIC CALCULATIONS

Nine different temperature fields in the rotary porous heat exchanger were calculated by a model presented in Kitanovski *et. al.*, 2005 and shown in FIG. 12. The cylindrical wheel is mapped on a rectangle. One can see the cold lower and the warm higher side separated by the adiabatic temperature differences.



are constant in azimuth and axial direction. The axial direction is the one going back to the left. where the azimuth direction is leading to the back on the right. The parameters of these calculations are found in Egolf et al., 2006b. The simpler cases are also described by analytical solutions.

FIG 12: The most simple case is the one in the left lowest corner. Here the temperature fields are constant in azimuth and axial direction. The axial direction is the one going back to the left, where the azimuth direction is leading to the back on the right. The parameters of these calculations are foung in Egolf et al. 2006b. The simpler cases are also described by analytical solutions.

XIV. ADVANTAGES AND DRAWBACKS

The potential advantages of magnetic refrigeration are valid in comparison with the direct evaporation refrigerating machines:

• "Green" technology, no use of conventional refrigerants.

• Noiseless technology (no compressor). This is an advantage in certain contexts such as medical applications.

• Higher energy efficiency. Thermodynamic cycles close to Carnot process are possible due to the reversibility of the MCE.

• Simple design of machines, e.g. rotary porous heat exchanger refrigerator.

• Low maintenance costs.

• Low (atmospheric) pressure. This is an advantage in certain applications such as in air-conditioning and refrigeration units in automobiles.

On the other hand, some disadvantages include:

· GMCE materials need to be developed to allow higher frequencies of rectilinear and rotary magnetic refrigerators.

• Protection of electronic components from magnetic fields. But notice that they are static, of short range and may be shielded.

• Permanent magnets have limited field strength. Electro magnets and superconducting magnets are (too) expensive.

• Temperature changes are limited. Multi-stage machines lose efficiency through the heat transfer between the stages.

• Moving machines need high precision to avoid magnetic field reduction due to gaps between the magnets and the magnetocaloric material[18,19].

POSSIBLE FUTURE APPLICATIONS:

The list of possible applications involves all domains of refrigeration, heat pump technology and power conversion. But there are two conditions which limit the applications of the technology in its current state. The first is the temperature span. If the difference between the upper and lower temperature levels is large, then the number of stages becomes also large and a practical realisation is no longer economic.

The second condition is the stability of the running conditions. Because the MCE is limited to a domain around the Curie temperature where the continuous phase transition occurs, it is difficult to operate magnetic refrigerating machines under highly fluctuating conditions. More or less stable temperature levels are required

for a reliable and efficient operation of a magnetic refrigeration system. The potential for cost-effective magnetocaloric air-conditioning systems was outlined by Russek and Zimm in the Bulletin of the IIR [20].

CONCLUSION

The number of research papers puplished 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. Furthermore while Figure.4 shows that the importance of magnetocaloric effect for magnetic refrigeration year after year Figure.5 shows that the number of near room temperature magnetic refrigerators reported per decade since 1970. If we say future perspectives of room temperature magnetic Refrigeration; It can be seen from the earlier description that main progresses have been made in America. However, with the continual phasic progresses of room temperature magnetic refrigerated in the research. Nevertheless, it is notable that main work is concentrated on investigations of magnetic materials, lack of experimental explorations of magnetic refrigerator. From the former results achieved by researchers, it can be seen that there is still a great performance difference between magnetic refrigerator and vapor compression refrigerator in terms of cooling capacity and temperature span.



FIG 13: The number of research paper published



FIG 14: The number of near room temperature magnetic refrigerators reported

At the end of this study we can say;

- Large MCE of magnetic material is investigated for room temperature magnetic cooling application
- Strong magnetic field is required
- Magnetic materials available for room temperature magnetic refrigeration are mainly Gd, GdSiGe alloys, MnAs-like materials, perovskitelike materials

- Materials under development for room temperature magnetic refrigeration are La(FexSi1-x)13 and La(Fe0.88Si0.12)13Hy
- Excellent behavior of regeneration and heat transfer is required
- Room temperature magnetic refrigeration is a new highly efficient
- It can be use household refrigerator, central cooling systems, room air conditioners and supermarket refrigeration applications
- It is environmentally protective technology
- This technology must be universalized worldwide

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