

# Magnetic refrigeration: an eco-friendly technology for the refrigeration at room temperature

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**Abstract.** Magnetic refrigeration is an emerging, environment-friendly technology based on a magnetic solid that acts as a refrigerant by magneto-caloric effect (MCE). In the case of ferromagnetic materials MCE is a warming as the magnetic moments of the atom are aligned by the application of a magnetic field, and the corresponding cooling upon removal of the magnetic field. There are two types of magnetic phase changes that may occur at the Curie point: first order magnetic transition (FOMT) and second order magnetic transition (SOMT). The reference cycle for magnetic refrigeration is AMR (Active Magnetic Regenerative cycle) where the magnetic material matrix works both as a refrigerating medium and as a heat regenerating medium, while the fluid flowing in the porous matrix works as a heat transfer medium. Regeneration can be accomplished by blowing a heat transfer fluid in a reciprocating fashion through the regenerator made of magnetocaloric material that is alternately magnetized and demagnetized. In this paper, attention is directed towards the near room-temperature range. We compare the energetic performance of a commercial R134a refrigeration plant to that of a magnetic refrigerator working with an AMR cycle. Attention is devoted to the evaluation of the environmental impact in terms of a greenhouse effect. The comparison is performed in term of TEWI index (Total Equivalent Warming Impact) that takes into account both direct and indirect contributions to global warming. In this paper the AMR cycle works with different magnetic refrigerants: pure gadolinium, second order phase magnetic transition ( $\text{Pr}_{0.45}\text{Sr}_{0.35}\text{MnO}_3$ ) and first order phase magnetic transition alloys ( $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ,  $\text{LaFe}_{11.384}\text{Mn}_{0.356}\text{Si}_{1.26}\text{H}_{1.52}$ ,  $\text{LaFe}_{11.05}\text{Co}_{0.94}\text{Si}_{1.10}$  and  $\text{MnFeP}_{0.45}\text{As}_{0.55}$ ). The comparison, carried out by means of a mathematical model, clearly shows that  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  and  $\text{LaFe}_{11.384}\text{Mn}_{0.356}\text{Si}_{1.26}\text{H}_{1.52}$  has a TEWI index always lower than that of a vapor compression plant. Furthermore, the TEWI of the AMR cycle working with FOMT materials is always better than that of SOMT materials.  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  is the best FOMT material.

## 1. Introduction

Worldwide, about 15% of the overall energy consumption originates from refrigeration. Most modern refrigeration units are based on vapor compression plants, whose development is strictly related to the characteristics of the working fluids, since the very beginning of their commercial diffusion. The traditional refrigerant fluids, i.e. CFCs and HCFCs, have been banned because of their contribution to the disruption of the stratospheric ozone layer (Ozone-Depleting substances ODs).



Human activities have increased the concentration of greenhouse gases in the atmosphere, thus resulting in a substantial warming of both earth surface and atmosphere that adversely affect the natural ecosystem. The impact of greenhouse gases on global warming is quantified by their GWP (Global Warming Potential). The GWP is defined as the mass of CO<sub>2</sub> that would result in the same net impact on global warming as the release of a single unit (kg) of the component.

The Kyoto Protocol (1987), pursuant to the United Nations Framework Convention on Climate Change (UNFCCC), sets binding targets for greenhouse gas emissions.

A vapor compression plant produces both a direct and an indirect contribution to global warming. The former depends on the GWP of refrigerant fluids and on the fraction of refrigerant charge which is either directly released in the atmosphere during operation and maintenance, or is not recovered when the system is scrapped. The indirect contribution is related to energy-consumption of the plant. In fact, a vapor compression refrigerator requires electrical energy produced by a power plant that typically burns a fossil fuel, thus releasing CO<sub>2</sub> into the atmosphere. The amount of CO<sub>2</sub> emitted is a strong function of the COP of the vapor compression plant.

Magnetic refrigeration is an emerging new technology. It is based on the magneto-caloric effect taking place in solid-state refrigerants (MCE). Compared to conventional vapor compression systems, magnetic refrigeration can be an environment-friendly and efficient technology. The magnetic refrigerant is a solid, has essentially zero vapor pressure, and therefore is ecologically sound with no direct Ozone Depletion Potential (ODP) and zero direct Global Warming Potential (GWP). The Active Magnetic Regenerator (AMR) is the core of a magnetic refrigerator system. It is a special kind of thermal regenerator made of magnetic material which works both as a refrigerating and as a heat regenerating medium.

The present paper compares a commercial R134a refrigerator and a 1.5T AMR cycle using different magnetic materials and water as a secondary fluid. The higher efficiency of the magnetic refrigeration unit resulted in a reduced CO<sub>2</sub> release and in a lower electric energy consumption. Thus, the development of magnetocaloric air conditioners would provide a relevant contribution to energy conservation and to the reduction of global warming. Magnetic refrigeration is not yet a commercial technology because of a number of challenges that have still to be overcome. Improved engineering to overcome are: limitations of the currently available magnetic refrigerant materials, developing new magnetic materials with giant magnetocaloric effect, producing magnetic refrigerants on large scale, developing processes to inexpensively fabricate these materials into useable forms for regenerators (spheres, wires, foils, plates, etc.) without losing the magnetocaloric effect, increase of the magnetic field strength of the permanent magnets while reducing the size, mass and costs.

## 2. Magnetic materials and magnetocaloric effect

The performances of an AMR refrigerator are mostly influenced by the particular solid materials employed, which is for sure a magnetocaloric material (MM) [1-6]. In fact, only magnetocaloric materials experience magnetocaloric effect (MCE) which is a coupling between MM entropy and the variation of an external magnetic field applied to the material, providing an amount of cooling that needs to be transferred out of the regenerator by a secondary fluid, used only as heat vector. The explanation of the MCE lies in the coupling between the magnetic spin and the crystal lattice. When a ferro- or paramagnetic material is magnetized there will be some ordering of the magnetic spins, forcing them towards the direction of the applied field. If this is done isothermally, this will lower the material's magnetic entropy by the isothermal entropy change ( $\Delta S_M$ ). However, if the magnetization is done adiabatically, the total sample entropy remains constant and the decrease in magnetic entropy is countered by an increase in the lattice and electron entropy. This causes a heating of the material and a temperature increase given by the adiabatic temperature change ( $\Delta T_{ad}$ ). The inverse procedure also applies: under adiabatic demagnetization the magnetic entropy increases, causing a decrease in lattice vibrations and by that a temperature decrease. At its Curie temperature, where is located its own magnetic phase transition, a MM shows the peak of MCE, in terms of  $\Delta T_{ad}$  and  $\Delta S_M$ . The two possible

magnetic phase changes that one can observe at the Curie point are first order magnetic transition (FOMT) and second order magnetic transition (SOMT).

At the Curie point a magnetic transition has FOMT characteristics when the material exhibits a discontinuity in the first derivative of the Gibbs free energy (G.f.e.), whereas has a SOMT behavior when the gap is detected in the second derivative of G.f.e. while its first derivative is a continuous function.

The most employed material for the refrigeration at room temperature is gadolinium, a rare-earth metal which exhibits a second order paramagnetic to ferromagnetic transition at its Curie temperature of 294 K. It exhibits excellent magnetocaloric properties that are difficult to improve upon. Nowadays a huge part of researchers is orienting its attention on some new alloys of magnetocaloric materials. The most promising are  $Gd_5Si_{4-x}Ge_x$  compounds (where  $0 < x < 0.5$ ), alloys of gadolinium, silicon and germanium which show a FOMT characterized by a peak of  $\Delta T_{ad}$  and  $\Delta S_M$  much greater than gadolinium ones, but the whole function is quite sharper in  $Gd_5Si_{4-x}Ge_x$  alloys. In particular,  $Gd_5Si_2Ge_2$  exhibits the larger MCE among  $Gd_5Si_{4-x}Ge_x$  compounds, named GIANT magnetocaloric effect of Pecharsky [7-10].  $Gd_5Si_2Ge_2$  presents two different phase transitions: at 276 K one can observe a FOMT which constitute the MCE highest temperature peak, whereas at 299K it is possible to appreciate a SOMT where, according to it, the material orders paramagnetically. MnAs alloys also assume the role of candidates for new magnetic refrigeration materials at room temperature because those compounds have a giant MCE exhibiting a first order magnetic transition; by varying alloy's composition, the Curie temperature could be switched in the range 220÷318 K. Among Mn-based compounds,  $MnFeP_{1-x}As_x$  compounds that are stable for  $0.15 < x < 0.66$  and exhibit interesting magnetic properties associated with a first order metamagnetic transition. The Curie temperature of the alloy increases linearly with the As contents. In the present paper compound  $MnFeP_{0.45}As_{0.55}$  [11] has been investigated; it undergoes a FOMT from paramagnetic to ferromagnetic at 307 K (on heating) according to a rapid decrease of the material parameters which changes its Debye temperature and its electronic structure. The adiabatic temperature change for these compounds is relatively low and the thermal conductivity is significantly lower than that of gadolinium and other magnetic materials.

Other interesting compounds for magnetic refrigeration are the rare-earth transition-metal  $La(Fe_xSi_{1-x})_{13}$  because of the large MCE exhibiting around room temperature ( $\Delta S_T$  of up to 30 J/kgK under a 0-5T magnetic field variation). The main advantages of employing  $La(Fe_xSi_{1-x})_{13}$  alloys are cheap, readily available and easy preparation. They present a first-order itinerant electron metamagnetic transition producing a giant magnetocaloric effect. In this paper  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$  and  $LaFe_{11.05}Co_{0.94}Si_{1.10}$  [12-14] have been considered. Both compounds have a first order transition at 290 and 287 K, respectively.

In the present work also  $Pr_{0.45}Sr_{0.35}MnO_3$  [15,16] is considered. It belongs to  $Pr_{1-x}Sr_xMnO_3$  compounds, which are an easy synthesizable series, and it presents a second order phase transition at 295 K where it shows a modest MCE.

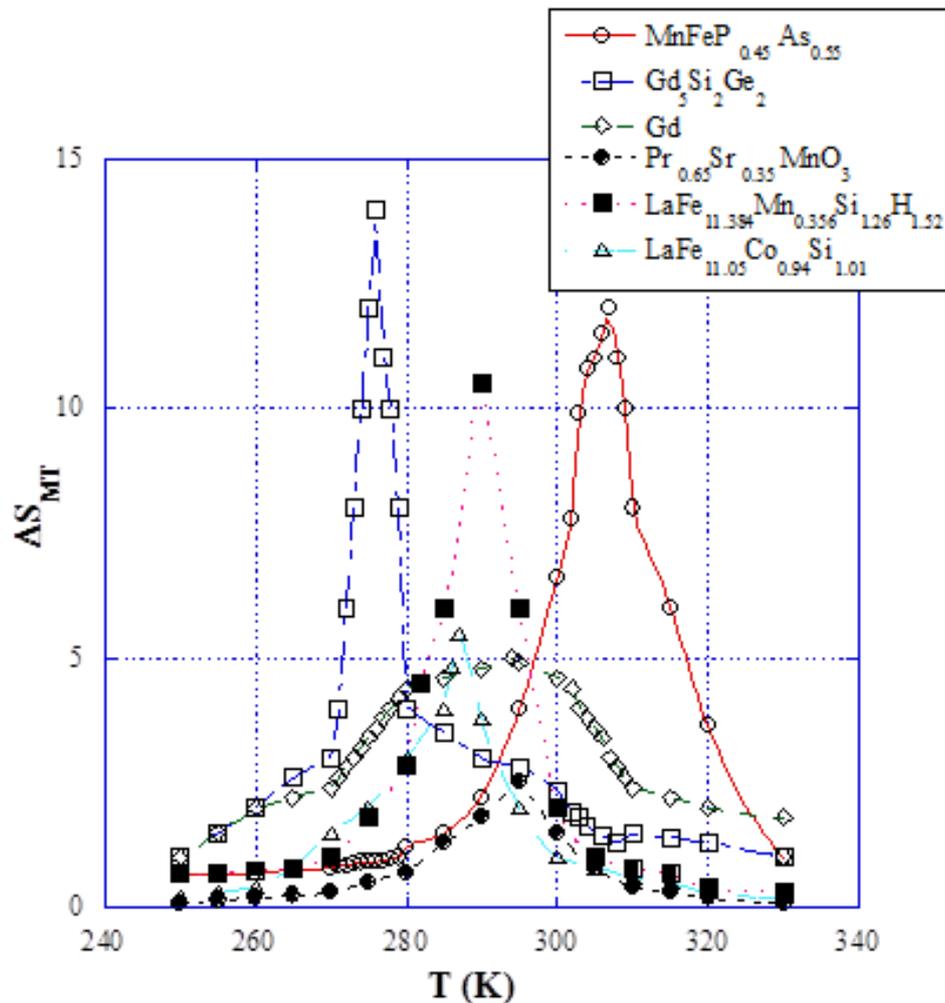
Table 1 summarizes the characteristics of the presented magnetic materials in the room temperature range. The main parameters of the different materials allow a fast comparison in terms of cost vs performance analysis.  $\Delta T_{ad}$  and  $\Delta S_M$  reported are the peak value with a magnetic field variation  $\Delta H$  of 1.5 T.

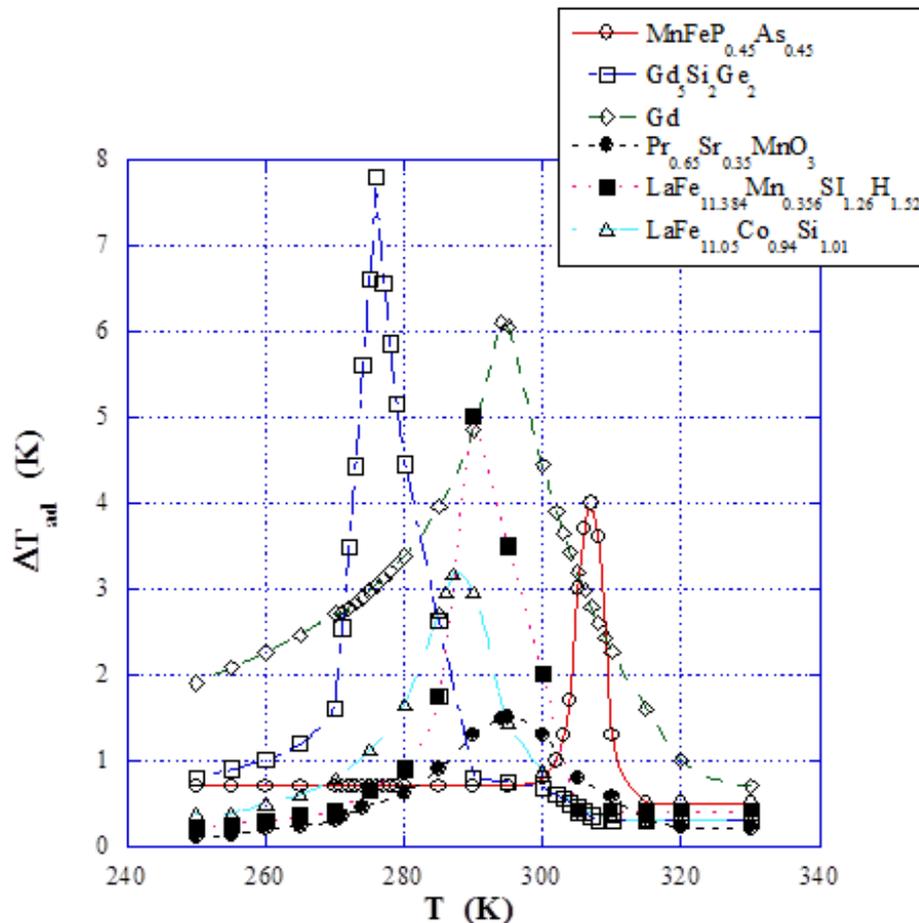
Table 1 allow a quick comparison between the different magnetic materials. The FOMT materials show peak values of  $\Delta T_{ad}$  and  $\Delta S_{MT}$  always higher than that of Gd.  $Gd_5(Si_xGe_{1-x})_4$  shows the higher peak values, but out of the room temperature range. The greater thermal conductivity is that of Gd, but also LaFeSi alloys show high values. From a commercial point of view,  $Gd_5(Si_xGe_{1-x})_4$  and Gd are too expensive and the magnetic transition metals are more adequate than the rare earths for an industrial production of magnetic cooling engines. La is the cheapest element of the rare-earths series, and Fe, Si, Mn are available in large amounts. The material costs of  $MnFeP_{0.45}As_{0.55}$  are quite low, but processing of As is complicated due to its toxicity.

**Table 1.** The different magnetic materials.

Materials	T <sub>c</sub>	ΔH	ΔT <sub>ad</sub>	ΔS <sub>M</sub>	ρ	k	Cost
	(°C)	(T)	(°C)	(J/kgK)	(kg/m <sup>3</sup> )	(W/mK)	(€/kg)
Gd	294	1.5	6	5	7900	10.9	3000
Gd <sub>5</sub> (Si <sub>x</sub> Ge <sub>1-x</sub> ) <sub>4</sub>	276	1.5	7.8	14	7205	5.8	9000
LaFe <sub>11.384</sub> Mn <sub>0.356</sub> Si <sub>1.26</sub> H <sub>1.52</sub>	290	1.5	5	10.5	7100	9	1200
LaFe <sub>11.05</sub> Co <sub>0.94</sub> Si <sub>1.10</sub>	287	1.5	3.17	5.5	7290	8.9	1200
MnFeP <sub>0.45</sub> As <sub>0.55</sub>	307	1.5	4	12	7300	2.5	1500
Pr <sub>0.65</sub> Sr <sub>0.35</sub> MnO <sub>3</sub>	295	1.5	1.5	2.5	5800	1.8	1050

In figure 1 and 2 are reported ΔS<sub>MT</sub> and ΔT<sub>ad</sub> as a function of temperature for the above mentioned magnetic materials for a magnetic field change of 1.5 T.

**Figure 1.** ΔS<sub>MT</sub> vs T for the different magnetic materials.



**Figure 2.**  $\Delta T_{ad}$  vs T for the different magnetic materials.

Figure 1 clearly shows that  $Gd_5(Si_xGe_{1-x})_4$ ,  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$  and  $MnFeP_{0.45}As_{0.55}$  materials shows the greater values of  $\Delta S_{MT}$ . These materials are FOMT and therefore the magnetic entropy variation is centered in a restricted temperature interval. Whereas Gd shows lower values of  $\Delta S_{MT}$  but over a broad temperature range.  $Pr_{0.45}Sr_{0.35}MnO_3$  shows a very low magnetic entropy variation in the whole temperature range.  $Gd_5(Si_xGe_{1-x})_4$  and Gd show high values of  $\Delta T_{ad}$ . Whereas,  $MnFeP_{0.45}As_{0.55}$  has the disadvantage that the adiabatic temperature change is not very large due to the relatively high heat capacity. The main goal of this paper is to investigate the effect of the different magnetic materials on the energetic performances of an AMR cycle and to compare the energetic performance of a commercial R134a refrigeration plant to that an AMR cycle. Attention is devoted to the evaluation of the environmental impact in terms of a greenhouse effect. To this hope, a practical 2D model for predicting the refrigeration capacity and the efficiency of an AMR cycle in the room temperature range has been developed. Different magnetic materials have been considered as refrigerant: pure gadolinium [17], second order phase magnetic transition  $Pr_{0.45}Sr_{0.35}MnO_3$  and first order phase magnetic transition alloys  $Gd_5(Si_xGe_{1-x})_4$ ,  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$ ,  $LaFe_{11.05}Co_{0.94}Si_{1.10}$  and  $MnFeP_{0.45}As_{0.55}$ .

### 3. The TEWI concept

Human activities have increased the concentration of greenhouse gases in the atmosphere. This resulted in a substantial warming of earth surface and atmosphere that adversely affected the natural ecosystem. The impact that greenhouse gases on global warming is quantified by their GWP (Global

Warming Potential). The GWP is defined as the mass of CO<sub>2</sub> that would result in the same net impact on global warming as the release of a single unit (kg) of the atmospheric component in question [18].

Vapor compression plants produce both a direct and an indirect contribution to global warming. The former depends on the GWP of refrigerant fluids and on the fraction of refrigerant charge released in the atmosphere during operation and maintenance, or not recovered when the system is scrapped. The indirect contribution consists in the so-called energy-related contribution. In fact, a vapor compression refrigerator requires electrical energy produced by a power plant that typically burns a fossil fuel releasing CO<sub>2</sub> to the atmosphere. The amount of CO<sub>2</sub> emitted is a strong function of the COP of the vapor compression plant. The Total Equivalent Warming Impact (TEWI) index takes into account both contributions to global warming of the system.

The concept of total equivalent warming impact (TEWI) was developed to combine the effect of direct refrigerant emission with those due to energy consumption and the related combustion of fossil fuels for the electric energy production. TEWI provides a measure of the environmental impact of greenhouse gases originating from operation, service and end-of-life disposal of the equipment. TEWI is the sum of the direct contribution of the greenhouse gases used to make or operate the systems and the indirect contribution of carbon dioxide emissions resulting from the energy required to run the systems over their normal lifetimes.

The TEWI is calculated as :

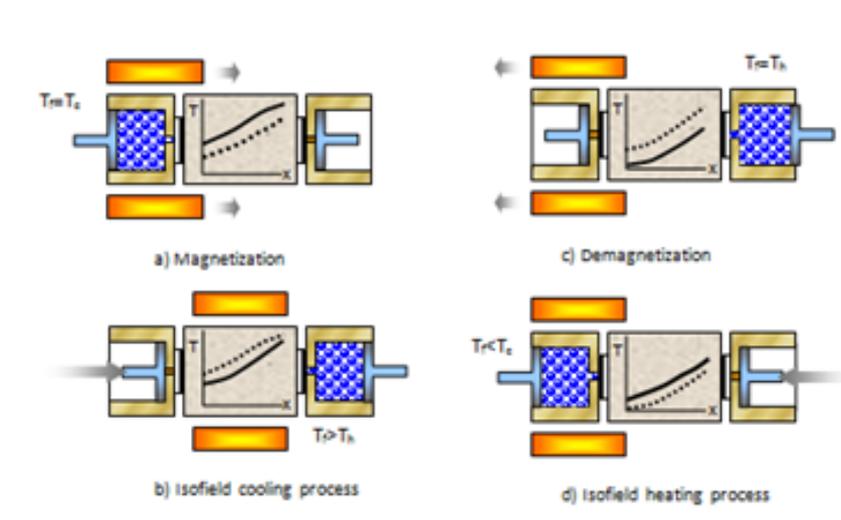
$$\begin{aligned} \text{TEWI} &= \text{CO}_{2,\text{dir}} + \text{CO}_{2,\text{indir}} && [\text{kg CO}_2] \\ \text{CO}_{2,\text{dir}} &= \text{RC} \left[ P_L + \left( \frac{1 - P_R}{V} \right) \right] V \cdot \text{GWP} && [\text{kg CO}_2] \\ \text{CO}_{2,\text{indir}} &= \alpha \cdot \frac{\dot{Q}_{\text{ref}}}{\text{COP}} \cdot H \cdot V && [\text{kg CO}_2] \end{aligned} \quad (1)$$

The direct global warming effect of refrigerant fluids, stemming from the absorption they produce of long-wave radiations, depends on their GWP and on the fraction of refrigerant charge released in the atmosphere. The last is mainly due to leakage during the operational plant life time (PL) and to the residual amounts which, according to the current state of technology, are not recyclable and thus are released to the atmosphere when taking the plant out of operation (1-PR). In the simulation PL is assumed as 5%, whereas PR has not been considered. As already stated, the indirect contribution to TEWI consists in the so-called energy-related contribution. Indeed, an electrical refrigerator requires electrical energy from a CO<sub>2</sub> releasing power plant that typically burns a fossil fuel. The amount of CO<sub>2</sub> emitted is a function of the refrigerator COP, of the power plant efficiency and of the fuel used in the conversion plant that affect the emissions per unit energy converted. The typical power-plant technology adopted varies from one country to another. The literature provides some indicative, average levels of CO<sub>2</sub> release per kWh of electrical energy for various countries. For Italy, the value is 0.6 kg CO<sub>2</sub>/kWh. The annual power consumption in the TEWI simulation is 290 kWh per year that corresponds to a commercial medium size wine cooler. R134a is an HFC with zero ODP and a GWP of 1300.

#### 4. The AMR cycle

Barclay firstly introduced the Active Magnetic Regenerative refrigeration cycle, well known as AMR, in 1982 [20]. It considers a magnetic Brayton cycle. The main innovation consists of introducing the AMR regenerator concept, i.e. the employ of the magnetic material itself as refrigerant and as regenerator. A secondary fluid is used to transfer heat from the cold to the hot end of the regenerator. Substantially every section of the regenerator experiments its own AMR cycle, according to the proper working temperature. Through an AMR one can appreciate a larger temperature span between the regenerator material and the auxiliary fluid.

The principle of operation of the presented magnetic refrigerator is based on the AMR thermodynamic cycle. The working principle of an AMR is presented in figure 3. Let us assume that the bed is at a steady state condition with the hot heat exchanger at  $T_h$  whereas the cold heat exchanger is at  $T_c$ . Four processes are simultaneously present in the AMR cycle: (a) adiabatic magnetization: each particle in the bed warms up; (b) isofield cooling: the high field is present, the fluid is blown from the cold end to the hot end, and absorbs heat from the bed and expels heat at a temperature higher than  $T_h$  in the hot heat exchanger; (c) adiabatic demagnetization: each particle in the bed cools again; (d) isofield heating: the field is zero, the fluid is blown from the hot end to the cold one, and it expels heat to the particles of the bed and absorbs heat at a temperature lower than  $T_c$  in the cold heat exchanger. In Figure 3 the dashed line represents the initial temperature profile of the bed in each process, while the solid line depicts the final temperature profile of the process.



**Figure 3.** Four schematic processes of an AMR cycle: solid and dashed lines referred to final and initial temperature profile respectively.

## 5. Model description

The model presented in this paper is of a two-dimensional porous regenerator operating at room temperature. The regenerator has a rectangular shape with a height of 20mm and a length of 45 mm. The area of the regenerator is filled with a regular matrix of 3600 circles that constitute the porous media; every circle has a diameter of 0.45mm and the amount of the area occupied by all of the circles is 63% of the total rectangular area. A group of channels is formed by stacking particles in the regenerator area: the fluid flows through these interstitial channels.

In this paper the 2D simulations of the numerical model are performed according to operate in the same conditions of a Rotary Permanent Magnet Magnetic Regenerator (RPMMR) [21-23], so that a comparison between the model and the RPMMR could be done. The rotary permanent magnet magnetic refrigerator (RPMMR) presents a rotating magnet while the magnetocaloric material (MCM) is stationary and is made of 8 regenerators.

In this model are taken into account both the fluid flow and heat transfer between the solid and the fluid. The regenerator of the proposed model has a porous media geometry: it is made of a porous matrix of gadolinium circles and the fluid flows through interstitial channels paragraphs are indented.

The fluid flow in the positive  $x$  direction during the isofield cooling process and in the opposite direction during isofield heating.

The assumption for the porous region of the AMR are:

(1) the magnetic material is isotropic and the magnetic particles are rigid spheres with the same diameter;

- (2) heat radiation is neglected;
- (3) the porosity of porous medium is constant;
- (4) the bed is adiabatic.

The mathematical formulation that describes the AMR cycle includes several distinct groups of equations according to the different processes of the AMR cycle that the regenerator experience. paragraphs are indented (BodytextIndented style).

The equations that rule the regenerative fluid flow processes, in both directions, are: the Navier-Stokes equations for the fluid flow and the energy equations for both the fluid and the solid particles. With the assumptions that the fluid is incompressible, the viscous dissipation is neglected, due to low mass flow, the above equations are as follows:

$$\left\{ \begin{array}{l} \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \\ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho_f} \frac{\partial p}{\partial x} + \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \\ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho_f} \frac{\partial p}{\partial y} + \nu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) \\ \frac{\partial T_f}{\partial t} + u \frac{\partial T_f}{\partial x} + v \frac{\partial T_f}{\partial y} = \frac{k_f}{\rho_f C_{fp}} \left( \frac{\partial^2 T_f}{\partial x^2} + \frac{\partial^2 T_f}{\partial y^2} \right) \\ \frac{\partial T_s}{\partial t} = \frac{k_s}{\rho_s C_{sp}} \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right) \end{array} \right. \quad (2)$$

The fluid is sufficiently low speed to be considered laminar. The solid and the fluid temperature are strictly related and they are constantly evolving during the whole AMR cycle.

The equations that model the magnetization and the demagnetization process of the cycle must take into account the MCE which elevates or lowers the temperature of the solid by the variation of the external magnetic field applied to the regenerator. Hence the MCE temperature variation is converted into a heat source  $Q$ :

$$Q = Q(H, T_s) = \frac{\rho_s C_{sp}(H, T_s) \Delta T_{ad}(H, T_s)}{\Delta t} \quad (3)$$

which has the dimensions of a power density and included in the solid energy equation, only for magnetization and demagnetizations phases, as follows:

$$\rho_s C_{sp} \frac{\partial T_s}{\partial t} = k_s \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right) + Q \quad (4)$$

The term  $Q$  is positive during magnetization, negative during demagnetization.  $\Delta t$  is the period of the magnetization/demagnetization process. Therefore, the equations that govern the magnetization and the demagnetization phases are:

$$\left\{ \begin{array}{l} \rho_f C_{fp} \frac{\partial T_f}{\partial t} = k_f \left( \frac{\partial^2 T_f}{\partial x^2} + \frac{\partial^2 T_f}{\partial y^2} \right) \\ \rho_s C_{sp} \frac{\partial T_s}{\partial t} = k_s \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right) + Q \end{array} \right. \quad (5)$$

The magnetic properties of the magnetocaloric materials have been evaluated interpolating experimental data available from the literature. From the construction of a table function, who describes  $Q$  in a range of temperature and magnetic field intensity, and by the help of a mathematical

function finder software, a mathematical expression for  $Q$  has been found both for magnetization and demagnetization processes. The intensity of the magnetic field varies from 0 to the maximum value of 1.2 T during magnetization and from 1.2T to 0 during demagnetization.

The coupled equations that govern the AMR cycle, imposed on this model, are solved using Finite Element Method. The AMR cycle is modelled as four sequential steps. The same time step  $\Delta t$  has been chosen for the resolution during all the four periods of the cycle. The cycle is repeated several times with constant frequency until the regenerator reaches steady state operation.

The refrigeration energy and the energy supplied in the environment are calculated according to the following equations:

$$Q_{ref} = \int_{t_M+t_{CF}+t_D}^{t_M+t_{CF}+t_D+t_{HF}} \dot{m}_f C_f (T_C - T_f(0, y, t)) dt \quad (6)$$

$$Q_{rej} = \int_{t_M}^{t_M+t_{CF}} \dot{m}_f C_f (T_f(L, y, t) - T_H) dt \quad (7)$$

The work of the secondary fluid circulation pump is:

$$W_p = \frac{\dot{m}(\Delta p_{CF} + \Delta p_{HF})}{\eta_p \rho_f} (t_{CF} + t_{HF}) \quad (8)$$

The Coefficient of Performance is:

$$COP = \frac{Q_{ref}}{Q_{rej} - Q_{ref} + W_p} \quad (9)$$

The COP of the vapor compression plant working under the same operating conditions of the above mentioned AMR cycle was predicted with the DOE/ORNL Heat Pump model (Rice 2006). The vapour compression plant used in the simulation is a commercial, small size, R134a refrigerator with a semi-hermetic compressor, air cooled condenser, forced air circulating evaporator [24].

## 6. Results and discussion

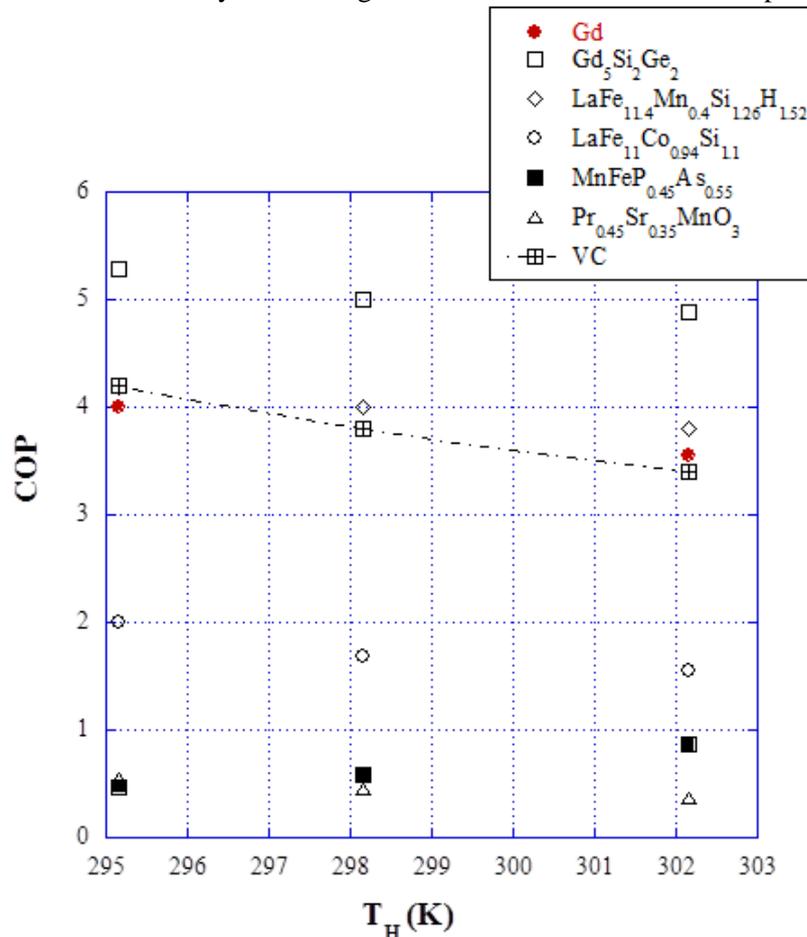
Several AMR cycles with different magnetocaloric materials employed as refrigerant, were simulated. The MCE materials kept under investigation have been Gd,  $Gd_5Si_2Ge_2$  and alloys of  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$ ,  $LaFe_{11.05}Co_{0.94}Si_{1.10}$ ,  $MnFeP_{0.45}As_{0.55}$ ,  $Pr_{0.45}Sr_{0.35}MnO_3$ . In all of the cases, the secondary fluid is pure water. The simulations were performed with fixed flow rate (5 l/min), AMR cycle frequency (1.25 Hz) and cold heat exchanger temperature  $T_C$  (288 K). The hot heat exchanger temperature  $T_H$  was varied in the range 295÷302 K to characterize the performance sensitivity of the heat rejection temperature in proximity of the refrigerant Curie temperature. The results presented were generated for a magnetic induction, which varies from 0 to 1.5 T.

TEWI is the sum of the direct and indirect contribution to global warming. The direct contribution of the AMR cycle is zero because the refrigerant is solid and therefore has essentially zero vapor pressure and zero GWP. The direct contribution of the vapor compression plant accounts about 10 % of the whole value. The parameter that affects the indirect contribution of the TEWI is the COP of the plant. In Figure 4 is shown the Coefficient of Performance (COP) as a function of hot heat exchanger temperature for all the materials presented in this work and for the vapor compression plant.

The Figure clearly shows that  $Gd_5Si_2Ge_2$  and  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$  have the highest values of COP and always over performs a vapor compression plant. The results of the simulation clearly show that  $Gd_5(Si_xGe_{1-x})_4$  is the best magnetic material with a COP that is always greater than that of a traditional vapor compression plant in the same operating conditions (from a minimum of + 26 to a

maximum of +44 %). Gd show energetic performances similar to a vapor compression plant. Instead  $\text{LaFe}_{11.05}\text{Co}_{0.94}\text{Si}_{1.10}$ ,  $\text{MnFeP}_{0.45}\text{As}_{0.55}$  and  $\text{Pr}_{0.45}\text{Sr}_{0.35}\text{MnO}_3$  always underperform vapor compression.

Therefore the COP of the AMR cycle working with these materials needs an improvement



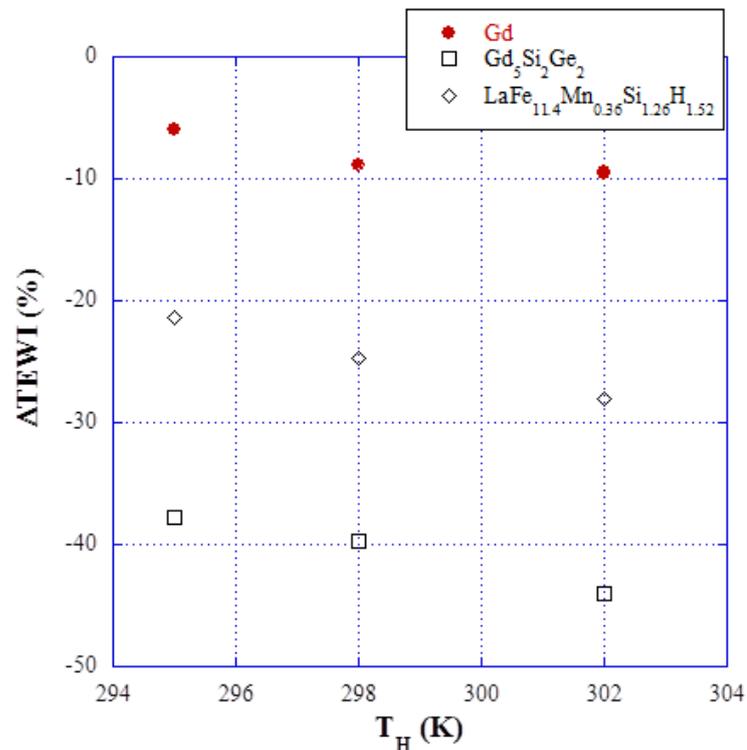
**Figure 4.** COP as a function of the hot heat exchanger temperature.

In order to make a comparison  $\Delta\text{TEWI}$  has been defined according to the following equation:

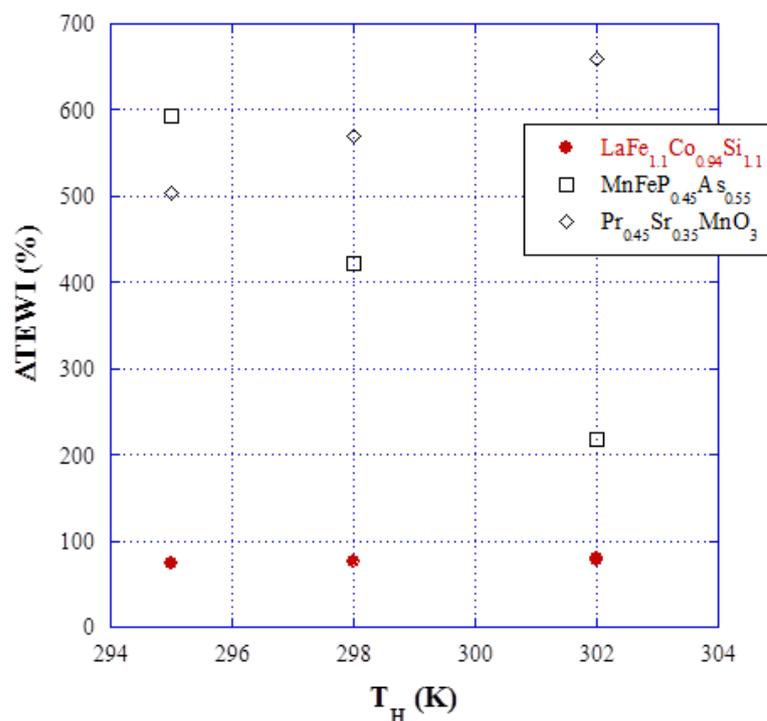
$$\Delta\text{TEWI} = \frac{\text{TEWI}_{\text{AMR}} - \text{TEWI}_{\text{VC}}}{\text{TEWI}_{\text{VC}}} \quad (10)$$

In figure 5 is reported  $\Delta\text{TEWI}$  of Gd,  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  and  $\text{LaFe}_{11.384}\text{Mn}_{0.356}\text{Si}_{1.26}\text{H}_{1.52}$  as a function of  $T_H$ .

The figure clearly shows that the AMR cycle working with these magnetic materials shows a lower greenhouse effect with respect to a vapor compression plant. In particular with  $\text{Gd}_5\text{Si}_2\text{Ge}_2$   $\Delta\text{TEWI}$  varies between a minimum of -44 to a maximum of -38 %. In figure 6 is reported  $\Delta\text{TEWI}$  of  $\text{LaFe}_{11.05}\text{Co}_{0.94}\text{Si}_{1.10}$ ,  $\text{MnFeP}_{0.45}\text{As}_{0.55}$  and  $\text{Pr}_{0.45}\text{Sr}_{0.35}\text{MnO}_3$  as a function of  $T_H$ .



**Figure 5.**  $\Delta TEWI$  of Gd,  $Gd_5(Si_xGe_{1-x})_4$  and  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$  as a function of the hot heat exchanger temperature.



**Figure 6.**  $\Delta TEWI$  of  $LaFe_{11.05}Co_{0.94}Si_{1.10}$ ,  $MnFeP_{0.45}As_{0.55}$  and  $Pr_{0.45}Sr_{0.35}MnO_3$  as a function of the hot heat exchanger temperature.

The Figure clearly shows that the AMR cycle working with these magnetic materials strongly under performs a vapor compression plant. Therefore, these magnetic materials cannot be considered for a commercial use because show a contribution in term of greenhouse effect greater than that of a vapor compression plant.

## 7. Conclusions

In the present paper, a practical model for predicting the performance and efficiency of an AMR refrigerator system has been introduced. The model is able to simulate an AMR made of FOMT and SOMT materials. In particular: Gd,  $Gd_5Si_2Ge_2$ ,  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$ ,  $LaFe_{11.05}Co_{0.94}Si_{1.10}$ ,  $MnFeP_{0.45}As_{0.55}$  and  $Pr_{0.45}Sr_{0.35}MnO_3$  have been considered as solid magnetic refrigerants. In order to make a comparison, the energetic performances of a vapor compression plant working in the same operating conditions have been evaluated by means of a computer program. Attention has been devoted to the evaluation of the greenhouse effect of both AMR and vapor compression cycle. The greenhouse effect has been evaluated by means of TEWI index. The latter takes into account both direct and indirect contribution to global warming.

The simulations clearly show that:

- $Gd_5Si_2Ge_2$  and  $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$  has a TEWI index always lower than that of a vapor compression plant. In particular  $GdSi_2Ge_2$  is the best magnetic material because an AMR cycle working with the latter material shows a greenhouse effect lower than that of a traditional plant of around -40%.
- Gd, that is the benchmark material for magnetic refrigeration, shows a greenhouse effect similar to that of a vapor compression plant.
- $LaFe_{11.05}Co_{0.94}Si_{1.10}$ ,  $MnFeP_{0.45}As_{0.55}$  and  $Pr_{0.45}Sr_{0.35}MnO_3$  cannot be considered because show a contribution in term of greenhouse effect greater than that of a vapor compression plant.

These results indicate that magnetic refrigeration is a promising refrigeration technology that will be used in chiller applications. An AMR cycle can be an eco-friendly technology if used with magnetic materials that show a significant magnetocaloric effect. As expected, from an efficiency point of view, the best candidates to magnetic refrigeration is  $Gd_5(Si_xGe_{1-x})_4$  which exhibits the lower values of TEWI index, but on the other side is a very expensive material, disadvantage which makes it impractical for every economic plan of magnetic refrigerator commercialization. From a global point of view (performances and cost), the most promising material are LaFeSi compounds which are really cheaper than rare earth compounds and they give a contribution to global warming sufficiently lower than that of a vapor compression plant.

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