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Magnetic Refrigeration at Room Temperature

20th Informatory Note on Refrigerating Technologies

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 magnetization and demagnetization.[1] After the discovery of the "giant" magnetocaloric effect (GMCE) in $Gd_5(Si_2Ge_2)$ in 1997 by Gschneidner and Pecharsky,[2] 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. The main reason for such an attitude is the possibility to replace the HFC refrigerants by environmentally benign magnetocaloric alloys. HFCs, with a typical global warming potential (GWP) of 1000 to 3000 times that of CO_2, at present show an increasing sales market, which has its cause in the phasing out of the more destructive HCFCs and CFCs. This phasing out process is still ongoing and in most developing countries HCFCs and CFCs are still allowed. Systems with natural refrigerants (ammonia, CO_2, propane, etc.) are good solutions for numerous applications, but to date, none of them have reached a remarkable breakthrough on a wide scale of applications in refrigeration. Other advantages include the higher cycle efficiencies of magnetic refrigeration processes compared with those of gas-compression refrigeration and the noiseless operating conditions of a magnetic refrigerator. This IIR informatory note briefly highlights the state-of-the-art, the advantages and disadvantages of this promising technology.

Introduction

The refrigeration-technology market is closely related to beverage and food production, industrial process, the chemical and pharmaceutical industry, the automotive sector, etc. Some of these sectors have strongly growing markets, thanks to the rising incomes of Eastern European, Indian and Chinese customers, with their desire for modern consumer goods driving such development. The retail market, supermarket and hypermarket chains are strongly benefiting from this development. Because the number of built alternative refrigeration technologies such as absorption or adsorption refrigeration, thermoelectric and thermoacoustic refrigeration, etc. is negligible, this leads to positive prospects for the gas-compression system producers.

Furthermore, the tendency to cool domestic buildings in southern areas is also increasing. The business-as-usual scenario, based on dynamic numerical climatological system simulations, was published by the European Commission. The prediction for the year 2010 is an HFC emission level the equivalent of 66 Mtonnes CO_2. This is an increase of 62% based on the value of 1995. Refrigeration and air conditioning are responsible for the main fraction, namely 43%. What are the alternatives, if HFCs also will have to be reduced? This is a desire of an increasing number of politicians that already has been announced in some countries. Maybe new less harmful refrigerants will be discovered. A new blend H has just been developed and announced by an industrial company, but up until now, reliable experience is missing.

The time would be ideal for an alternative refrigeration technology such as for example magnetic refrigeration. For the interested reader, who wants to gain a greater insight into magnetic heat pumps and refrigerators than given in this short informatory note, several review articles are available.[3-7] This promising technology works without a gaseous refrigerant and its energy efficiency (coefficient of performance, COP) in principle can be higher than that of a conventional refrigeration system. As a result, its breakthrough in certain domains of the refrigeration market would lead to less CO_2 output into the atmosphere. This informatory note gives an overview of this spectacular technology, discusses ideal and not-so-promising applications and reports on some problems which have to be solved in order to enter industrializing phases for the various refrigeration applications envisaged.

The magnetocaloric effect

A magnetocaloric material may provide three different contributions to the total entropy, a magnetic, an electronic and a lattice contribution.[3] The entropy is a measure of order in the magneto-thermodynamic system. A high order is related to a low entropy and vice versa. Dipoles, i.e. electronic spins, may show different orientations. If in a paramagnet, ferromagnet or diamagnet these entities are oriented in the same direction, the order and also the magnetization is high. It is clear that applying a magnetic field aligns electronic spins, and lowering the temperature (by releasing energy from the system) also leads to a more ordered system. Therefore, in the sense of the theory of critical phenomena the external magnetic field yields the stress parameter and the magnetization the order parameter of such magnetic materials.

In *Figure 1,* the magnetization of pure gadolinium is shown as a function of the "magnetic field" $\mu_0 H$ and the temperature T. If all the moments or spins are aligned, the maximal magnetization M_{max} occurs. The actual magnetization $M(T,H)$ is divided by this maximal value $M_{max} = 2.47$ T (tesla) to obtain the normalized magnetization $\hat{m} = M/M_{max}$. The temperature is also normalized; it is divided by the Curie temperature T_c of the material: $\hat{t} = T/T_c$. For gadolinium, the Curie temperature is just at room temperature, namely at $T_c \cong 293$ K. The maximal magnetization $(\hat{m} = 1)$ occurs at the absolute zero point ($T = 0$ K or $\hat{t} = 0$), independent of the applied magnetic field. At higher temperatures, the magnetization is lower. And here one can observe a magnetic field dependence. It is clear that a higher field leads to a higher ordering, respectively a higher magnetization $\hat{m}$.

If a magnetocaloric material is moved into a magnetic field, this is usually a fast process. Practically no heat will be exchanged with the environment. Then for this adiabatic process the total entropy s — which in usual cases is the sum of the magnetic s_M, electronic s_E and lattice entropy s_L — remains constant: $s = s_M + s_E + s_L = const.$[3] But the magnetization increases. This means that the magnetic entropy s_M decreases. Therefore, the remaining electronic and lattice entropies, s_E and s_L, must increase. By spin lattice couplings — which occur in milliseconds — phonons or lattice vibrations are created. These oscillatory movements may be compared with Brown's motion of atoms or molecules in a gas.

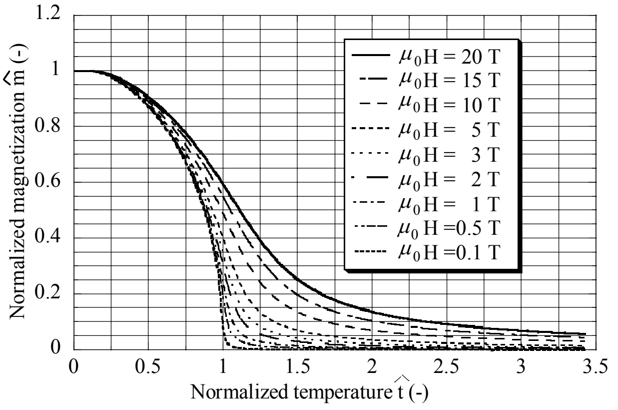

Figure 1. The normalized magnetization curves of pure gadolinium for different "magnetic fields" $\mu_0 H$. The quantity μ_0 is the permeability of vacuum. This figure was taken from Reference 9

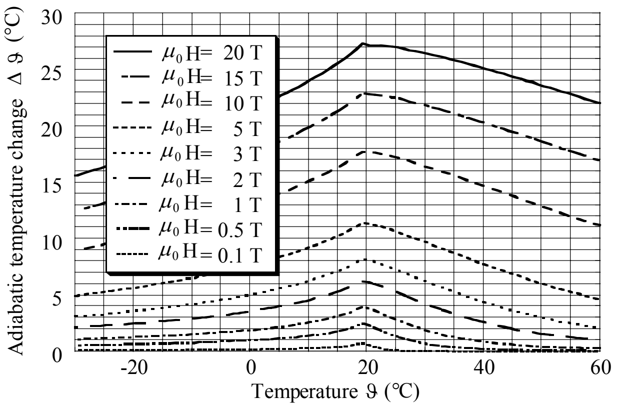

Figure 2. The adiabatic temperature change of gadolinium in the vicinity of the Curie temperature Tc ≅ 20°C. As in Figure 1, here also, the internal field $\mu_0 H$ is shown (from Reference 9)

They increase the temperature of the solid material. Now it becomes clear that removing the magnetocaloric material from the magnetic field lowers its lattice vibrations and its temperature, because now the magnetic moments and spins take up energy from the lattice and become disordered again. The achievable temperature increases $\Delta\vartheta$ of gadolinium for "magnetic field" changes $\mu_0 H$ of 1 and 2 T are shown in *Figure 2.* For both field changes, the temperature decrease occurs at the higher temperature $\vartheta + \Delta\vartheta$, with the same absolute value of the temperature change, $|\Delta\vartheta|$, in the heating and cooling case.[8] For a magnetic refrigerator with permanent magnets of reasonable weight, 2 T is at present the maximal obtainable "magnetic field" strength. For zero magnetic field, the described process is a second order phase transition. For higher magnetic fields, this transition becomes continuous. The described exchange of degrees of freedom between the magnetic moment/spin and the lattice system is the key process for magnetic refrigeration. It was discovered in 1881 by the German physicist Emil Warburg.

Processes of magnetic refrigeration

In *Figure 3* 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.

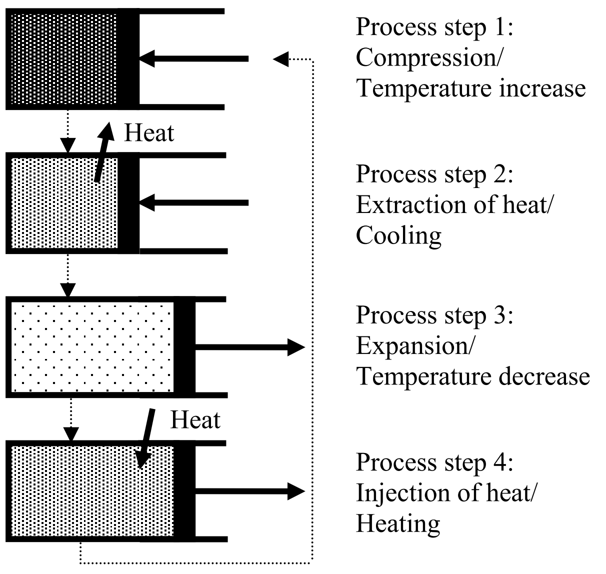

Figure 3. The conventional gas-compression process is driven by continuously repeating the four different basic processes shown in this figure

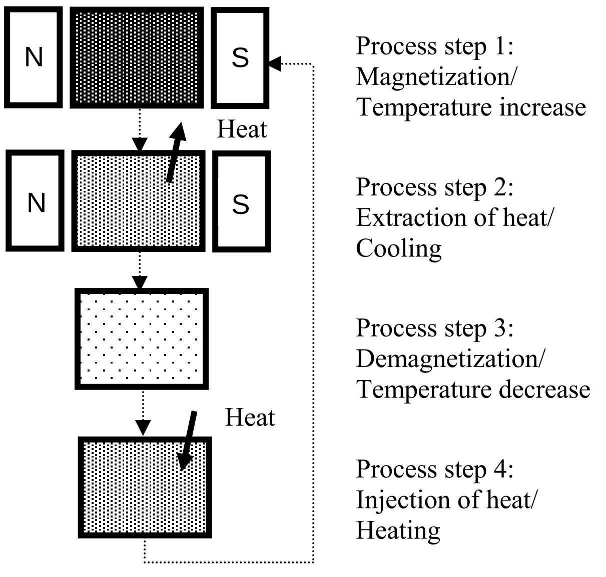

Figure 4. The magnetic refrigeration cycle comparison. Compression is replaced by adiabatic magnetization and expansion by adiabatic demagnetization

The steps of a magnetic refrigeration process are analogous. By comparing *Figure 3* with *Figure 4,* 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. Furthermore, the not very large adiabatic temperature differences of magnetocaloric materials will require more often a design of cascade or regenerative magnetic refrigerators[8] than in conventional refrigerators and hence require additional heat transfer steps.

Magnetocaloric materials and their properties

To apply the magnetocaloric effect with a high performance, optimal properties of magnets and magnetocaloric materials are required. For this, the different families — which show a large GMCE — have to be taken into consideration. The properties of presently best magnets can not be discussed in this brief note, but they are described in the literature: see Reference 6 for instance.

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 (see below). One advantage of pure gadolinium is that its physical properties may be described by basic physical laws such as the Brillouin function for the magnetization or the Debye function for the specific heat, etc. This allows the numerical calculation of magnetothermodynamic charts of high resolution.[9] To produce such charts for magnetocaloric alloys would demand a tremendous amount of high-quality experimental data, which usually is not available. Therefore, it generally makes sense to begin initial testing of a magnetic refrigerator prototype with a gadolinium filling. After the teething problems of a new machine have been solved with the gadolinium content, the latter may be replaced by better magnetocaloric alloys.

Gschneidner and Pecharsky[10] 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.[4,10] Currently, the total entropies and the related refrigeration capacity, the adiabatic temperature change and the costs of the materials are under investigation. Brück 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.[4]

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[9] 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.

Magnetothermodynamic machines

Application of the GMCE calls for a magnetic field change in a magnetocaloric material. This can be performed using different magnetic refrigeration principles:

- alternatively changing magnetic fields in static blocks of magnetocaloric material by application of electromagnets
- rectilinear motion of magnetocaloric material with static permanent magnet assemblies
- rectilinear motion of permanent magnet assemblies with static magnetocaloric material blocks
- rotary motion of magnetocaloric material with static permanent magnet assemblies
- rotary motion of permanent magnet assemblies with static magnetocaloric material blocks.

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).[10]

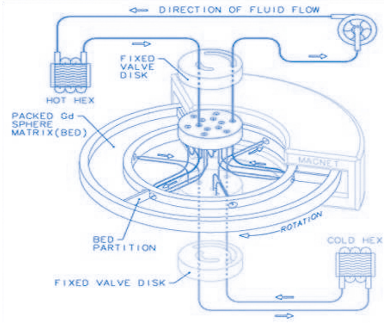

Figure 5. A sketch of the magnetic refrigerator prototype of Astronautics. The device was designed and built by Astronautics and exhibited at the G-8 Meeting with US DOE Ames Laboratory — Iowa State University. Printed with permission from Astronautics Corporation of America

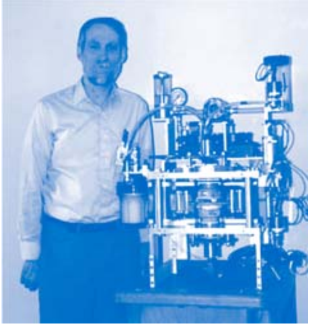

Figure 6. A pioneer of magnetic refrigeration, Dr Carl Zimm, at Astronautics beside the built magnetic refrigerator prototype, which is schematically shown in *Figure 5*. Printed with permission from Astronautics Corporation of America

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, and is shown in *Figure 5*. 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.[10] 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.[11] 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.

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.

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 realization 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.[12]

Conclusion

Magnetic refrigeration is undoubtedly a promising technology that should be encouraged because of its numerous advantages, in particular energy saving and environmental benefits. Efficient prototypes for specific applications must now be built so that the refrigeration industry can be convinced to enter industrializing phases for the production of new magnetic refrigerators.

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