MAGNETIC REFRIGERATION

ALTERNATING REFRIGERATION TECHNIQUES

ABSTRACT

Chlorofluorocarbons refrigerants that were used widely today in refrigeration and air conditioning causes the depletion of ozone layer, which is very hazardous to earth. With the goal of making refrigerators and air conditioners more efficient, several groups around the world are developing magnetic refrigerant materials. A magnetic cooling system could also be less polluting than current systems because it wouldn't use environmentally harmful chemicals, such as ammonia or chlorofluorocarbons.

Instead of ozone depleting refrigerants and energy consuming compressors found in conventional vaporcycle refrigerators, this new style of refrigerator uses gadolinium metal that heats up when exposed to a magnetic field, then cools down when the magnetic field is removed.

Magnets are big time materials, finding roles in products ranging from motors to medical imaging systems. Now, a team of engineers' improvement of a custom-made magnetic material increases the odds that refrigeration will soon join the roster of magnet based technologies.

What's more, the technology requires few moving parts, so it can be simple, silent, and reliable. When a magnetic refrigerant material is exposed to a magnetic field, the forces the spins of electrons in the material to align. As a result, the material heats up. Removing the field permits the electrons to relax into less-ordered states, and the material cools down. By cycling the material through these hot and cold states and venting away the heat, the system can generate an overall cooling effect.

Introduction:

Refrigeration is defined as the process of removing heat from an enclosed space or from a substance and rejecting it elsewhere, for the primary purpose of lowering the temperature of the enclosed space or substance and then maintaining that lower temperature.

Magnetic refrigeration, or adiabatic demagnetization, is a cooling technology based on the magneto caloric effect presently (2006) being developed by several research institutes and companies worldwide. It is an intrinsic property of magnetic solids. The refrigerant is often a paramagnetic salt, such as cerium magnesium nitrate. The active magnetic dipoles in this case are those of the electron shells of the paramagnetic atoms.

A strong magnetic field is applied to the refrigerant, forcing its various magnetic dipoles to align and putting these degrees of freedom of the refrigerant into a state of lowered entropy. A heat sink then absorbs the heat released by the refrigerant due to its loss of entropy. Thermal contact with the heat sink is then broken so that the system is insulated, and the magnetic field is switched off. This increases the heat capacity of the refrigerant, thus decreasing its temperature below the temperature of the heat sink.

The Magneto caloric effect:

The Magneto caloric effect (MCE, from *magnet* and *calorie*) is a magneto thermodynamic phenomenon which is the reversible change in temperature caused by a material's exposure to a magnetic field. This is also known as adiabatic demagnetization by low temperature physicists. It produces a change in entropy when a ferromagnetic object's temperature crosses the Curie point. Above the Curie point the material becomes merely paramagnetic. This phase transition to the paramagnetic state can be exploited to turn heat into electricity.

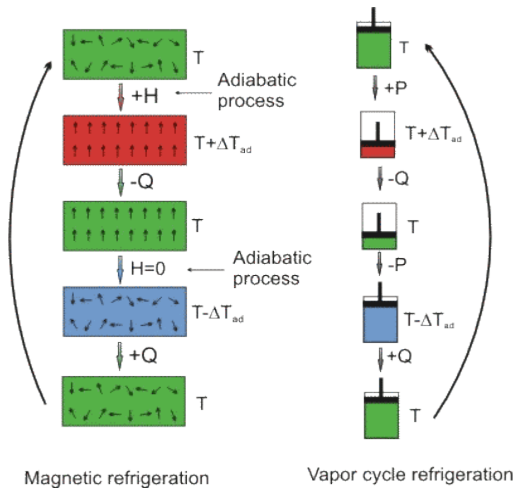
One of the most notable examples of the magneto caloric effect is that which occurs between the chemical element gadolinium and some of its alloys. Gadolinium's temperature is observed to increase when it enters certain magnetic fields. When it leaves the magnetic field, the temperature returns to normal.

Effect:

The magneto caloric effect is an intrinsic property of a magnetic solid. It is the response of a solid to the application or removal of magnetic fields, which is maximized when the solid is near its magnetic ordering temperature. When subjected to a magnetic field the magnetic moments are aligned and the magnetic entropy is lower.

Under adiabatic conditions the total entropy remains constant, and thus the sample heats up (i.e. the adiabatic temperature change). When the field is removed the magnetic entropy is increased and the temperature is lowered.

To illustrate what are the physics behind the magnetic refrigeration, lets look what happens with the magneto caloric material when it is put into a magnetic field. The external magnetic field (+H) causes the magnetic spins of the atoms to align, thereby decreasing the material's magnetic entropy and heat capacity. Since energy cannot be lost and the entropy cannot be reduced according to thermodynamic laws, the net result is that the item heats up ($T + \Delta T_{ad}$).



What happens is that this decrease in the magnetic entropy results an increase in the entropy of the material's lattice, consequently increasing the material's temperature. This added heat can then removed by a fluid like water or helium, for example (-Q). Once the magnetocaloric material and the field are parted (H=0), the material will be cooler than before entering the field, and thus is inclined to absorb heat from its surroundings (+Q).

The magnitudes of the magnetic entropy and the adiabatic temperature changes are strongly dependent upon the magnetic order process: the magnitude is generally small in antiferromagnets, ferrimagnets and spin glass systems; it can be substantial for normal ferromagnets which undergo a second order magnetic transition; and it is generally the largest for a ferromagnet which undergoes a first order magnetic transition.

Also, crystalline electric fields and pressure can have a substantial influence on magnetic entropy and adiabatic temperature changes.

History:

The effect was discovered in pure iron in 1881. Major advances first appeared in the late 1920s when cooling via adiabatic demagnetization.

Currently, alloys of gadolinium producing 3 to 4 °K per Tesla of change in a magnetic field can be used for magnetic refrigeration or power generation purposes. Recent research on materials that exhibit a giant entropy change showed that $Gd_5(Si_xGe_{1-x})_4$, $La(Fe_xSi_{1-x})_{13}H_x$ and $MnFeP_{1-x}As_x$ alloys, for example, are some of the most promising substitutes for Gadolinium and its alloys (GdDy, GdTy, etc...). These materials are called giant magnetocaloric effect materials (GMCE).

Gadolinium and its alloys are the best material available today for magnetic refrigeration near room temperature since they undergo second-order phase transitions which have no magnetic or thermal hysteresis involved.

Current and future uses:

This effect is currently being explored to produce better refrigeration techniques, especially for use in spacecraft. This technique is already used to achieve cryogenic temperatures in the laboratory setting (below 10K). As an object displaying MCE is moved into a magnetic field, the magnetic spins align, lowering the entropy. Moving that object out of the field allows the object to increase its entropy by absorbing heat fromenvironment and disordering the spins. In this way, heat can be taken from one area to another. Should materials be found to display this effect near room temperature, refrigeration without the need for compression may be possible, increasing energy efficiency.

Basic technique:

The basic operating principle of an ADR is the use of a strong magnetic field to control the entropy of a sample of material, often called the "refrigerant." Magnetic field constrains the orientation of magnetic dipoles in the refrigerant. The stronger the magnetic field, the more aligned the dipoles are, and this corresponds to lower entropy and heat capacity because the material has (effectively) lost some of its internal degrees of freedom. If the refrigerant is kept at a constant temperature through thermal contact with a heat sink (usually liquid helium) while the magnetic field is switched on, the refrigerant must lose some energy because it is equilibrated with the heat sink. When the magnetic field is subsequently switched off, the heat capacity of the refrigerant rises again because the degrees of freedom associated with orientation of the dipoles are once again liberated, pulling their share of equipartitioned energy from the motion of the molecules, thereby lowering the overall temperature of a system with decreased energy. Since the system is now insulated when the magnetic field is switched off, the process is adiabatic, i.e. the system can no longer exchange energy with its surroundings (the heat sink), and its temperature decreases below its initial value, that of the heat sink.

The operation of a standard ADR proceeds roughly as follows. First, a strong magnetic field is applied to the refrigerant, forcing its various magnetic dipoles to align and putting these degrees of freedom of the refrigerant into a state of lowered entropy. The heat sink then absorbs the heat released by the refrigerant due to its loss of entropy. Thermal contact with the heat sink is then broken so that the system is insulated, and the magnetic field is switched off, increasing the heat capacity of the refrigerant, thus decreasing its temperature below the temperature of the He heat sink. In practice, the magnetic field is decreased slowly in order to provide continuous cooling and keep the sample at an approximately constant low temperature. Once the field falls to zero (or to some low limiting value determined by the properties of the refrigerant), the cooling power of the ADR vanishes, and heat leaks will cause the refrigerant to warm up.

Implementations:

Paramagnetic salts:

The simplest choice of refrigerant is a sample of a paramagnetic salt, such as cerium magnesium nitrate. The active magnetic dipoles in this case are those of the electron shells of the paramagnetic atoms.

In a paramagnetic salt ADR, the heat sink is usually provided by a pumped ^{4}He (~1.2 K) or ^{3}He (~0.3 K) cryostat. An easily attainable 1 tesla magnetic field is generally required for the initial magnetization. The minimum temperature attainable is determined by the self-magnetization tendencies of the chosen refrigerant salt, but temperatures from 1 to 100 mK are accessible. Dilution refrigerators had for many years supplanted paramagnetic salt ADRs, but interest in space-based and simple to use lab-ADR's has recently revived the field.

Eventually paramagnetic salts become either diamagnetic or ferromagnetic, limiting the lowest temperature which can be reached using this method.

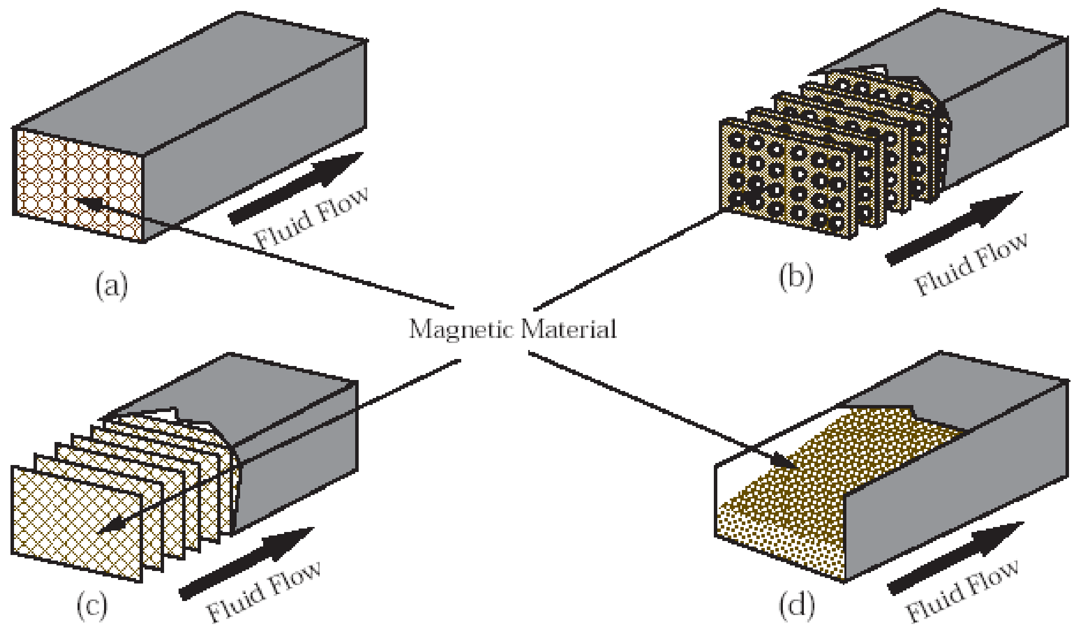
Nuclear demagnetization:

One variant of adiabatic demagnetization that continues to find substantial research application is nuclear demagnetization refrigeration (NDR). NDR follows the same principle described above, but in this case the cooling power arises from the magnetic dipoles of the nuclei of the refrigerant atoms, rather than their electron configurations. Since these dipoles are of much smaller magnitude, they are less prone to self-alignment and have lower intrinsic minimum fields. This allows NDR to cool the nuclear spin system to very low temperatures, often 1 μK or below. Unfortunately, the small magnitudes of nuclear magnetic dipoles also makes them less inclined to align to external fields. Magnetic fields of 3 teslas or greater are often needed for the initial magnetization step of NDR.

In NDR systems, the initial heat sink must sit at very low temperatures (10–100 mK). This precooling is often provided by the mixing chamber of a dilution refrigerator or a paramagnetic salt ADR stage.

Regenerators

Magnetic refrigeration requires excellent heat transfer to and from the solid magnetic material. Efficient heat transfer requires the large surface areas offered by porous materials. When these porous solids are used in refrigerators, they are referred to as "regenerators". Typical regenerator geometries include tubes (a), perforated plates (b), wire screens (c) and particle beds (d):



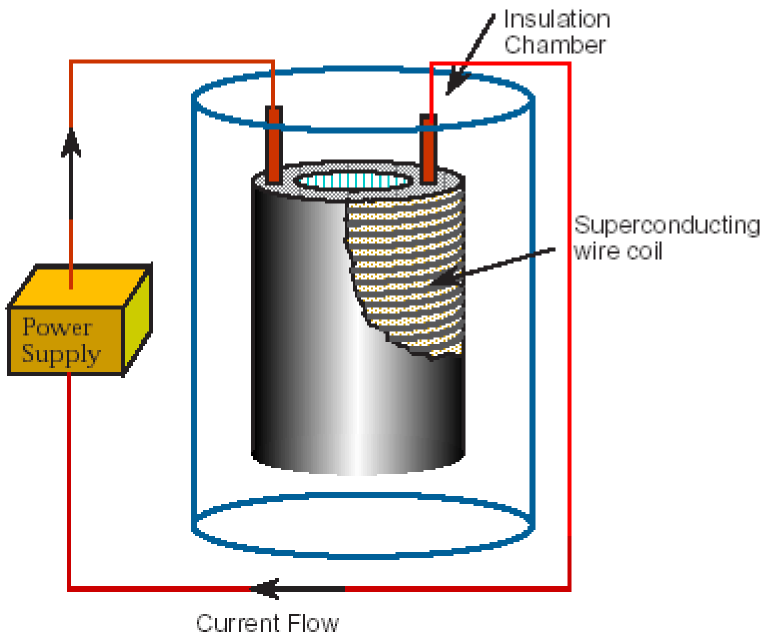
Superconducting Magnets

Most practical magnetic refrigerators are based on superconducting magnets operating at cryogenic temperatures (i.e., at –269ºC or 4 K). These devices are electromagnets that conduct electricity with essentially no resistive losses. The superconducting wire most commonly used is made of a Niobium-Titanium alloy.

Only superconducting magnets can provide sufficiently strong magnetic fields for most refrigeration applications.

A typical field strength is 8 Tesla (approximately 150,000 times the Earth's magnetic field).

An 8 Tesla field can produce a magnetocaloric temperature change of up to 15ºC in some rare-earth materials.



Active Magnetic Regenerators (AMR's)

A regenerator that undergoes cyclic heat transfer operations and the magnetocaloric effect is called an Active Magnetic Regenerator (AMR).

An AMR should be designed to possess the following attributes:

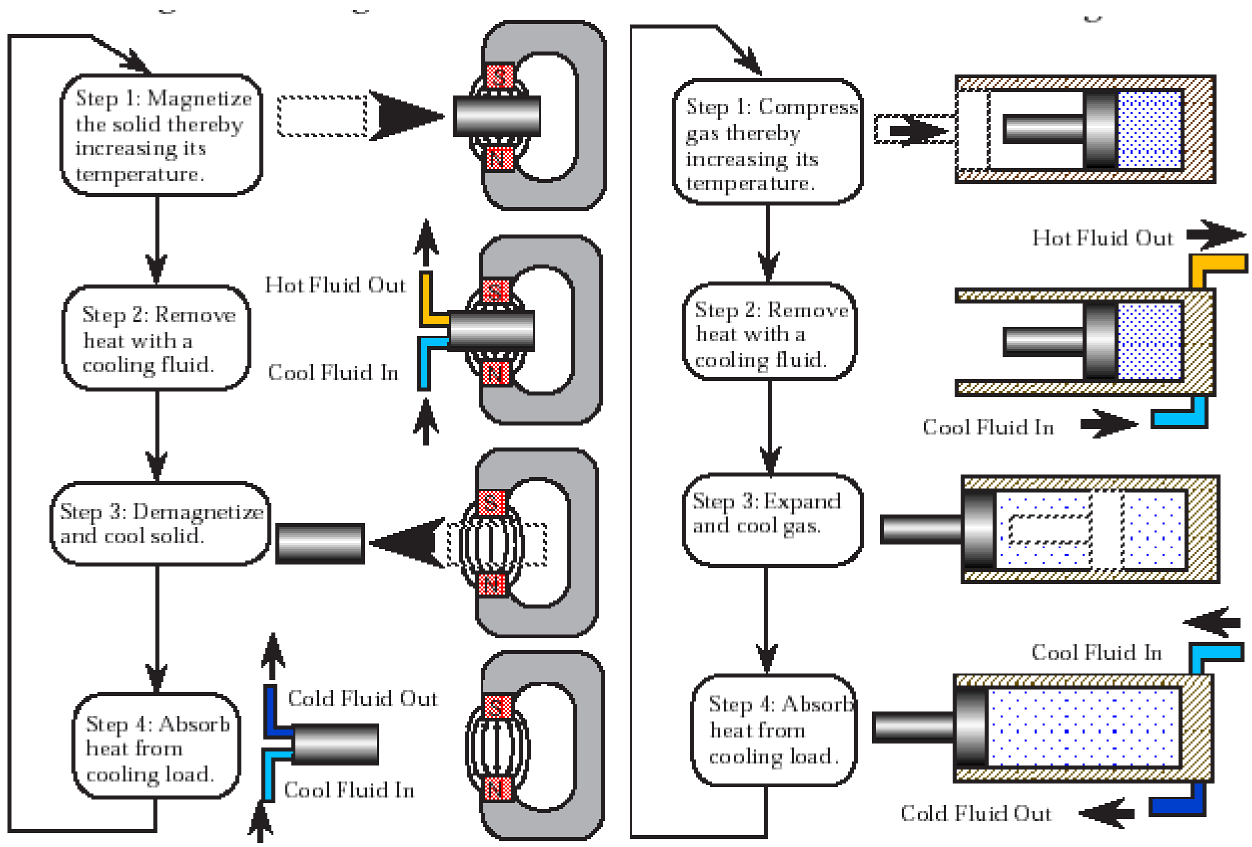
- High heat transfer rate
- Low pressure drop of the heat transfer fluid
- High magnetocaloric effect
- Sufficient structural integrity
- Low thermal conduction in the direction of fluid flow
- Low porosity
- Affordable materials
- Ease of manufacture

These requirements are often contradictory, making AMR's difficult to design and fabricate.

Refrigeration Cycles

The magnetocaloric effect can be utilized in a thermodynamic cycle to produce refrigeration. Such a cycle is analogous to conventional gas-compression refrigeration:

Magnetic Refrigeration **Conventional Refrigeration**

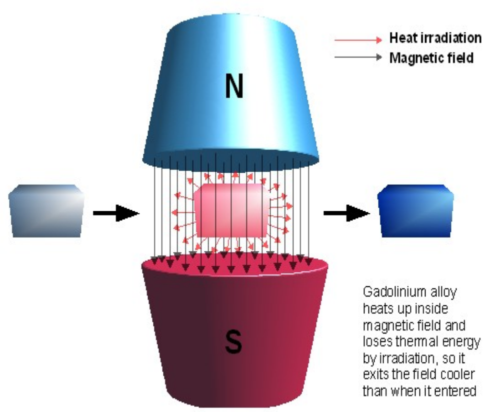


<u>Applications:</u>

This refrigeration, once proven viable, could be used in any possible application where cooling, heating or power generation is used today. Since it is only at an early stage of development, there are several technical and efficiency issues that should be analyzed. The magnetocaloric refrigeration system is composed of pumps, electric motors,

Secondary fluids, heat exchangers of different types, magnets and magnetic materials. These processes are greatly affected by irreversibilities and should be adequately considered. Appliances using this method could have a smaller environmental impact if the method is perfected and replaces hydrofluorocarbon (HFCs) refrigerators (some refrigerators still use HFCs which have some greenhouse effect). At present, however, the superconducting magnets that are used in the process have to themselves be cooled down to the temperature of liquid nitrogen, or with even colder, and relatively expensive, liquid helium. Considering these fluids have boiling points of 77.36 K and 4.22 K respectively, the technology is clearly not cost-efficient and efficient for home appliances, but for experimental, laboratorial, and industrial use only.

Recent research on materials that exhibit a large entropy change showed that $\boldsymbol{Gd_5(Si_xGe_{1-x})_4}$, $\boldsymbol{La(Fe_xSi_{1-x})_{13}H_x}$ and $\boldsymbol{MnFeP_{1-x}As_x}$ alloys are some of the most promising substitutes of Gadolinium and its alloys (GdDy, GdTy, etc...). Gadolinium and its alloys are the best material available today for magnetic refrigeration near room temperature. There are still some thermal and magnetic hysteresis problems to be solved for them to become really useful and scientists are working hard to achieve this goal. Recent discovery has succeeded using commercial grade materials and permanent magnets on room temperatures to construct a magnetocaloric refrigerator which promises wide use.



Other methods:

Other methods of refrigeration include the Air cycle machine used in aircraft; the Vortex tube used for spot cooling, when compressed air is available; and Thermoacoustic refrigeration using sound waves in a pressurised gas to drive heat transfer.

References:

- Lounasmaa, *Experimental Principles and Methods Below 1* K, Academic Press (1974).

- Richardson and Smith, *Experimental Techniques in Condensed Matter Physics at Low Temperatures*, Addison Wesley (1988).