

## MAGNETO CALORIC EFFECT BASED REFRIGERATION SYSTEM

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### **Abstract**

A cooling system consists of a device or devices used to lower the temperature of a defined region in space through some cooling process. Currently, the most popular commercial cooling medium is the refrigerant. A refrigerant in its general sense is what makes refrigerator cool foods, and it also use to makes air conditioners and other cooling products. A typical consumer based refrigerator lowers temperatures by modulating a gas vapour compression-evaporation cycle, to cool a refrigerant fluid which has been heated by the contents of the refrigerator (i.e. the food inside). Typical refrigerants used in refrigerators are ammonia, methyl chloride, and sulfur dioxide, all of which are toxic. To mitigate the risks associated with toxic refrigerants, a collaboration by Frigidaire, General Motors, and DuPont netted the development of Freon (or R12), a chlorofluorocarbon. Freon is a non-flammable and non-toxic, but ozone- depleting gas<sup>1</sup>. Because of the damaging effects of Freon to the ozone layer, there has been much interest in targeting other refrigerants. The future seems ripe for new refrigeration technology.

There are two main reasons why magnetic refrigeration research continues. While a magnetic refrigerator would cost more than today's refrigerator, it could consume 20% more energy than current evaporation-compression refrigerators, The other attraction to magnetic refrigeration is the ecological impact a magnetic refrigerator would bring should it supplant current technologies. Not only would ozone-depleting refrigerant concerns be calmed, but the energy savings itself would lessen the strain our household appliances put on our environment.

## Introduction

It is a newest cooling technology based on the magneto caloric effect. Magnetic refrigeration can be used to attain extremely low temperatures (well below 1 Kelvin), as well as the ranges used in common refrigerators, depending on the design of the system.

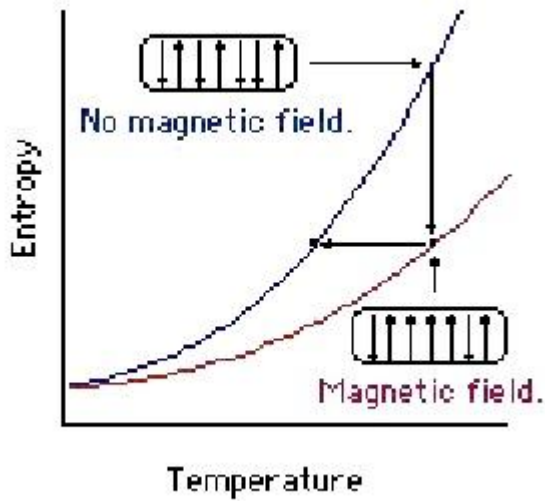
The fundamental principle was suggested by Debye (1926) and Giauque (1927) and the first working magnetic refrigerators were constructed by several groups<sup>2</sup> beginning in 1933. Magnetic refrigeration was the first method developed for cooling below about 0.3 Kelvin (a temperature attainable by<sup>3</sup>He/<sup>4</sup>He dilution refrigeration).

## The Magneto caloric effect

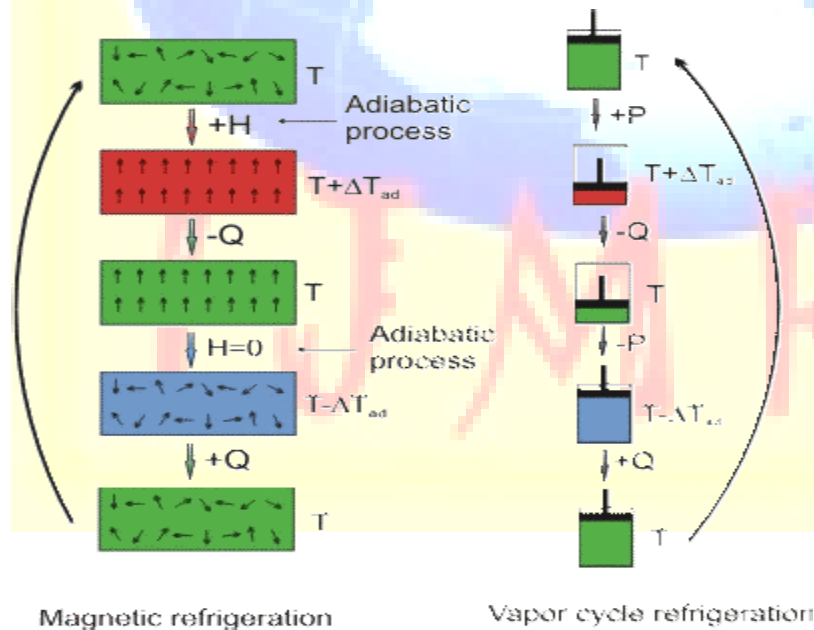
The Magneto caloric effect (MCE, from magnet and calorie) is a magneto- thermodynamic phenomenon in which a reversible change in temperature of a suitable material is caused by exposing the material to a changing magnetic field. This is also known as adiabatic demagnetization by low temperature physicists, due to the application of the process specifically to effect a temperature drop. In that part of the overall refrigeration process, a decrease in the strength of an externally applied magnetic field allows the magnetic domains of a chosen (magneto caloric) material to become disoriented from the magnetic field by the agitating action of the thermal energy (phonons) present in the material. If the material is isolated so that no energy is allowed to (e)migrate into the material during this time (i.e. an adiabatic process), the temperature drops as the domains absorb the thermal energy to perform their reorientation. The randomization of the domains occurs in a similar fashion to the randomization at the Curie temperature, except that magnetic dipoles overcome a decreasing external magnetic field while energy remains constant, instead of magnetic domains being disrupted from internal ferromagnetism as energy is added.

One of the most notable examples of the magnetocaloric effect is in 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. The effect is considerably stronger for the gadolinium alloy Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>).

Praseodymium alloyed with nickel (PrNi5) has such a strong magnetocaloric effect that it has allowed scientists to approach within one thousandth of a degree of absolute zero.



Thermodynamic cycle



## Magnetic Refrigeration Cycle

The cycle is performed as a refrigeration cycle, analogous to the Carnot cycle, and can be described at a starting point whereby the chosen working substance is introduced into a magnetic field (i.e. the magnetic flux density is increased). The working material is the refrigerant, and starts in thermal equilibrium with the refrigerated environment.

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**Adiabatic magnetization:** The substance is placed in an insulated environment. The increasing external magnetic field (+H) causes the magnetic dipoles of the atoms to align, thereby decreasing the magnetic entropy and heat capacity. Since overall energy is not lost (yet) and therefore total entropy is not reduced (according to thermodynamic laws), the net result is that the item heats up ( $T + \Delta T_{ad}$ ).

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**Isomagnetic enthalpy transfer:** This added heat can then be removed by a fluid like water or helium for example (-Q). The magnetic field is held constant to prevent the dipoles from reabsorbing the heat. Once sufficiently cooled, the magneto caloric material and the coolant are separated ( $H=0$ ).

**Adiabatic demagnetization:** The substance is returned to another adiabatic (insulated) condition so the total entropy remains constant. However, this time the magnetic field is decreased, the thermal energy causes the domains to overcome the field, and thus the sample cools (i.e. an adiabatic temperature change). Energy (and entropy) transfers from thermal entropy to magnetic entropy (disorder of the magnetic dipoles).

**Isomagnetic entropic transfer:** The magnetic field is held constant to prevent the material from heating back up. The material is placed in thermal contact with the environment being refrigerated. Because the working material is cooler than the refrigerated environment (by design), heat energy migrates into the working material (+Q).

Once the refrigerant and refrigerated environment is in thermal equilibrium, the cycle begins anew.

### Applied 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.

### Used materials

The magneto caloric effect is an intrinsic property of a magnetic solid. This thermal response of a solid to the application or removal of magnetic fields is maximized when the solid is near its magnetic ordering temperature.

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.

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.

### **Paramagnetic salts**

The originally suggested refrigerant was 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  $^4\text{He}$  (about 1.2 K) or  $^3\text{He}$  (about 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 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  $\mu\text{K}$  or below.

Unfortunately, the small magnitudes of nuclear magnetic dipoles also make 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.

### Commercial development

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 irreversibility's and should be adequately considered. Appliances using this method could have a smaller environmental impact if the method is perfected and replaces hydro fluorocarbon (HFCs) refrigerators (some refrigerators still use HFCs which have considerable 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  $Gd_5(SixGe_{1-x})_4$ ,  $La(FexSi_{1-x})_{13}H_x$  and  $MnFeP_{1-x}As_x$  alloys are some of the most promising substitutes of Gadolinium and its alloys (GdDy, GdT<sub>y</sub>, etc...).

### History

The effect was discovered in pure iron in 1881 by E. Warburg. Originally, the cooling effect varied between 0.5 to 2 K/T.

Major advances first appeared in the late 1920s when cooling via adiabatic demagnetization was independently proposed by two scientists: Debye (1926) and Giauque (1927).

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