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# The magnetocaloric effect

## *Introduction*

The Magnetocaloric effect (MCE), or adiabatic temperature change ($\Delta T_{ad}$), is defined as the heating or cooling of a magnetic material due to the application of a magnetic field.

It was first discovered in 1881 by Warburg, who was investigating iron, and was later independently explained by Debye and Giauque. They also suggested the first practical use of the MCE: the adiabatic magnetization, for reaching temperatures lower than that of liquid helium, which had been the lowest achievable experimental temperature.

To show why the MCE is arising, let us consider a system of spins, which is paramagnetic or ferromagnetic near its ordering temperature. The entropy of such a system can be considered as a sum of two contributions—the entropy related to magnetic ordering and the entropy related to the temperature of the system. Application of a magnetic field will order the magnetic moments comprising the system, which are disordered by thermal agitation energy, and, consequently, the entropy depending on the magnetic ordering (the magnetic entropy) will be lowered. If a magnetic field is applied under adiabatic conditions when any heat exchange with the surroundings is absent, then the entropy related to the temperature should increase in order to preserve the total entropy of the system constant. Increasing of this entropy implies the system heating up, and an increase in temperature. The opposite process—adiabatic removal of the magnetic field—will cause cooling of the magnetic system under consideration. The size of the MCE depends upon the magnetic field change and the temperature at which it is measured.

Most magnetic materials exhibit a large MCE only at low temperatures, which is not suitable for domestic usage. But with the discovery of giant MCE (GMCE) in $Gd_5Si_2Ge_2$, which is due to a simultaneous magnetic and crystallographic first order transition in 1997 by Pecharsky and Gschneidner the magnetic refrigeration (MR) became a viable and competitive technology with vapor cycle refrigeration.

Now with the competition on the way, everybody is trying to introduce the first commercial acceptable magnetic refrigerator, which would be cleaner, quieter and more energy efficient then regular vapor cycle refrigerators.

## *Basics*

In order to explain the origin of the magnetocaloric effect, we use thermodynamics, which relates the magnetic variables (magnetization and magnetic field) to entropy and temperature. All magnetic materials intrinsically show MCE, although the intensity of the effect depends on the properties of each material. The physical origin of the MCE is the coupling of the magnetic sublattice to the applied magnetic field, *H*, which changes the magnetic contribution to the entropy of the solid.

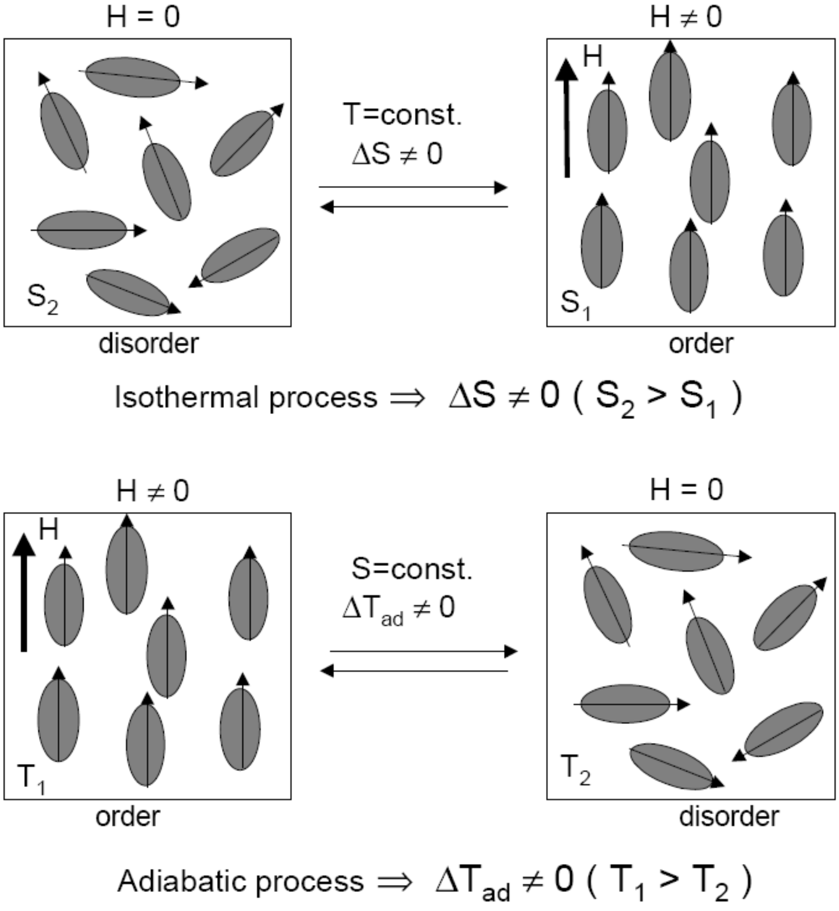


**Figure 1 – Schematic picture that shows the two basic processes of the magnetocaloric effect when a magnetic field is applied or removed in a magnetic system: the isothermal process,which lead to an entropy change, and the adiabatic process, which yields a variaton in temperature.**

The equivalence to the thermodynamics of a gas is evident (Figure 1): the isothermal compression of a gas (we apply pressure and the entropy decreases) is analogous to the isothermal magnetization of a paramagnet or a soft ferromagnet (we apply $H$ and the entropy decreases), while the subsequent adiabatic expansion of a gas (we lower pressure at constant entropy and temperature decreases) is equivalent to adiabatic demagnetization (we remove H, the total entropy remains constant and temperature decreases since the magnetic entropy increases).

Important characteristics of a magnetic material are its total entropy $S$ and the entropy of its magnetic subsystem $S_M$ (magnetic entropy). Entropy can be changed by variation of the magnetic field, temperature and other thermodynamic parameters. The total entropy of a magnetic material can in general, at constant pressure, be presented as:

$$S(H,T) = S_M(H,T) + S_l(T) + S_e(T) \tag{1}$$

where $S_M$ is the magnetic entropy, $S_l$ is the lattice and $S_e$ is the electron contribution to the total entropy.

In Figure 2 one can see the relationship between the entropy and temperature for a ferromagnet near the Curie temperature. The total entropy and the magnetic part are displayed for an applied external field $H_1$, and for zero field, $H_0$.

Two processes are shown in the diagram:

- When the magnetic field is applied adiabatically (i.e., the total entropy remains constant) in a reversible process, the magnetic entropy decreases, but the total entropy does not change, i.e.,

  $$S(T_0, H_0) = S(T_1, H_1)\,, \tag{2}$$

  then, the temperature increases. This adiabatic rise ($\Delta T_{ad}=T_1-T_0$) can be visualized as the isentropic difference between the corresponding $S(T,H)$ functions as shown in Fig. 2 by the horizontal arrow.
- When the magnetic field is applied isothermally ($T$ remains constant), the total entropy decreases due to the decrease in the magnetic contribution, and therefore the entropy in the process is defined as $\Delta S_m=S_1-S_0$, which is shown in Fig.2 by the vertical arrow.

Both, $\Delta T_{ad}$ and $\Delta S_m$ are characteristic values of the MCE and are functions of the initial temperature $T_0$ and the magnetic field change.

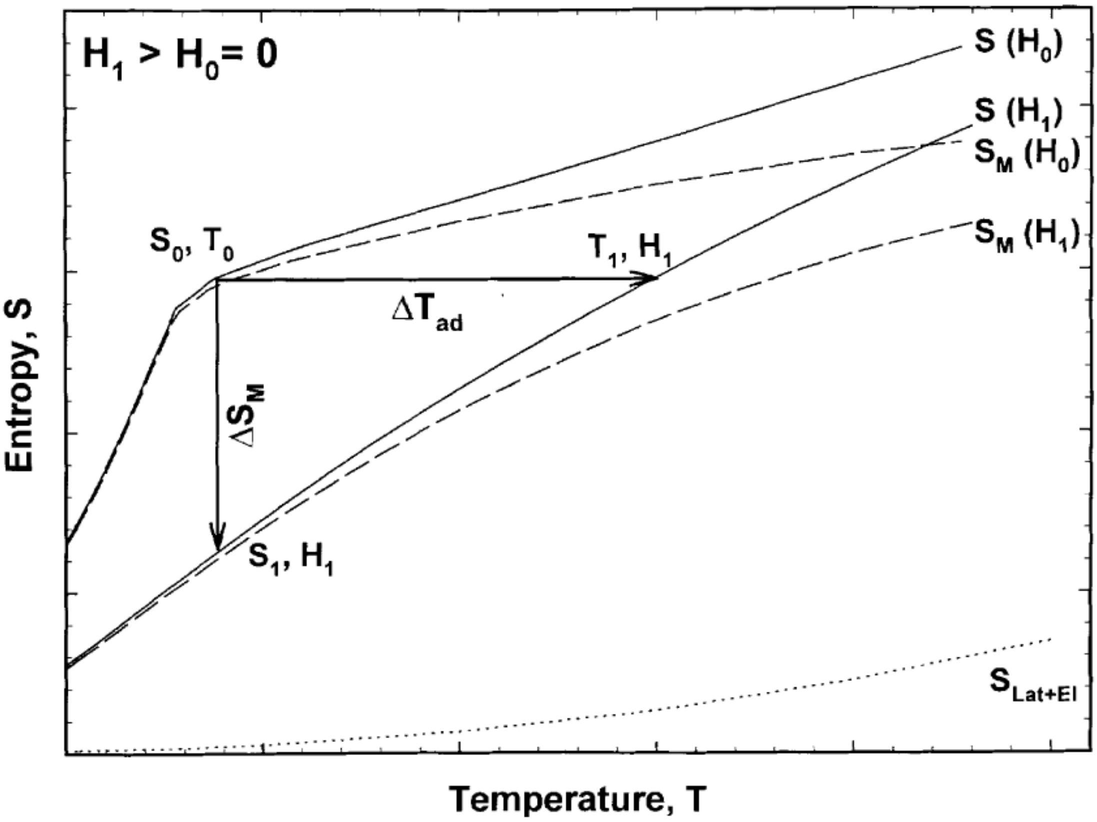


**Figure 2 – S – T diagram showing the MCE. The solid line represents the total entropy in two different magnetic fields, the dashed line shows the magnetic entropy in two fields, and the dotted line shows the electronic and lattice contribution to the entropy (the magnetic field does not affect them).**

By increasing the field the magnetic order increases and the magnetic entropy decreases, which results in a positive $\Delta T_{\mathrm{ad}}(T,\Delta H)$ and the solid heats up, while $\Delta S_{\mathrm{m}}(T,\Delta H)$ is negative. The signs of those two values are correspondingly reversed when the magnetic field is reduced.

To show the relation between $H$ and $T$ to the MCE values $\Delta T_{ad}(T,\Delta H)$ and $\Delta S_m(T,\Delta H)$ the following thermodynamic functions are used: the internal energy $U$, the free energy $F$ and the Gibbs free energy $G$.

The internal energy is represented as a function of entropy $S$, the volume $V$ and the magnetic field $H$:

$$U = U(S,V,H) \tag{3}$$

Correspondingly, the total differential of $U$ can have the form:

$$dU = TdS - pdV - MdH \tag{4}$$

where $p$ is the pressure and $T$ is the absolute temperature.

The magnetic field *H* is usually used as an external parameter in the free energy *F* and Gibbs free energy *G*.

The free energy *F*, which is a function of *T*, *V* and *H*, is used for systems with constant volume and is defined as

$$F = U - TS \,. \tag{5}$$

Its total differential has the form

$$dF = -SdT - pdV - MdH \,. \tag{6}$$

The Gibbs free energy *G* is a function of *T*, *p* and *H* and is used for systems with constant pressure:

$$G = U - TS + pV - MH \tag{7}$$

with the total differential

$$dG = Vdp - SdT - MdH \,. \tag{8}$$

For the Gibbs free energy the internal parameters *S, M* and *V*, conjugated to the external variables *T*, *H* and *p*, can be determined by the following equations of state:

$$S(T,H,p) = -\left(\frac{\partial G}{\partial T}\right)_{H,p} \tag{9}$$

$$M(T,H,p) = -\left(\frac{\partial G}{\partial H}\right)_{T,p} \tag{10}$$

$$V(T,H,p) = -\left(\frac{\partial G}{\partial p}\right)_{T,H} \,. \tag{11}$$

So-called Maxwell equations can be obtained from equation (9) and (10), and equations (9) and (11):

$$\left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{H,p} \tag{12}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,H} = -\left(\frac{\partial V}{\partial T}\right)_{H,p} \,. \tag{13}$$

Integrating equation 12 for an isothermal (and isobaric) process, we obtain

$$\Delta S(T,\Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_{H,p} dH \,. \tag{14}$$

This equation indicates that the entropy change is proportional to both the derivative of magnetization with respect to temperature at constant field and to the field variation.

The heat capacity $C$ at constant parameter $x$ is defined as:

$$C_x = \left(\frac{\delta Q}{dT}\right) \tag{15}$$

where $\delta Q$ is the heat quantity changing the system temperature on d$T$. Using the second law of thermodynamics:

$$dS = \frac{\delta Q}{T} \tag{16}$$

the heat capacity can be represented as

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x . \tag{17}$$

The total differential of the total entropy of the magnetic system expressed as a function of $T$, $H$, and $p$ can be written as

$$dS = \left(\frac{\partial S}{\partial T}\right)_{H,p} dT + \left(\frac{\partial S}{\partial H}\right)_{t,p} dH + \left(\frac{\partial S}{\partial p}\right)_{T,H} dp . \tag{18}$$

With equations (12), (17) and (18), one can obtain for an adiabatic process (d$S$=0) the following equation:

$$\frac{C_{H,p}}{T} dT + \left(\frac{\partial M}{\partial T}\right)_{H,p} dH - \left(\frac{\partial S}{\partial p}\right)_{T,H} dp = 0 . \tag{19}$$

Under an adiabatic-isobaric process (d$p$=0, this process is usually realized in magnetocaloric experiments) the temperature change due to the change of the magnetic field can be obtained from equation (19) as

$$dT = -\frac{T}{C_{H,p}}\left(\frac{\partial M}{\partial T}\right)_{H,p} dH . \tag{20}$$

After integrating this equation, we obtain another expression that characterizes the magnetocaloric effect,

$$\Delta T(T, \Delta H) = -\int_{H_1}^{H_2} \frac{T}{C_{H,p}}\left(\frac{\partial M}{\partial T}\right)_{H,p} dH \tag{21}$$

From equations 14 and 21 information about the MCE can be gained:

1. Magnetization at constant field in both paramagnets and ferromagnets decrease with increasing temperature, i.e., ($\left(\frac{\partial M}{\partial T}\right)_H$ < 0). Hence

$\Delta T_{ad}(T, \Delta H)$ should be positive, while $\Delta S_m(T, \Delta H)$ sould be negative for positive field changes, > 0.

2. In ferromagnets, the absolute value of the derivative of magnetization with respect to temperature, $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$, is maximum at $T_C$, and therefore $\left|\Delta S_m(T, \Delta H)\right|$ should show a peak at $T = T_C$.
3. For the same $\left|\Delta S_m(T, \Delta H)\right|$ value, the $\Delta T_{ad}(T, \Delta H)$ value will be larger at higher *T* and lower heat capacity.
4. In paramagnets the $\Delta T_{ad}(T, \Delta H)$ value is only significant at temperatures close to absolute zero, since $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$ is otherwise small. Only when the heat capacity is also very small (same order as $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$), can a reasonable $\Delta T_{ad}(T, \Delta H)$ value be obtained, which also happens only close to absolute zero. Significant MCE at higher temperatures is only possible in solids that order spontaneously.

## Electrocaloric effect

Electrocaloric materials have a similar effect. Here the electrocaloric (EC) effect is induced by an electric field. With the application or withdrawal of an electric field the temperature of the material changes. This effect is very small and till now it has not been exploited commercially. For example, bulk $Pb_{0.99}Nb_{0.02}(Zr_{0.75}Sn_{0.20}Ti_{0.05})_{0.98}O_3$ shows the highest reported EC effect measured so far, with direct measurements giving a peak value of 2.5 K in 750 V. But, a giant EC effect is reported of 12 K in 25 V in thin films of Zr-rich $Pb(Zr,Ti)O_3$ (PZT).

## *MCE in paramagnets*

MCE in paramagnets can be only seen at temperatures close to absolute zero, where the enhanced, but still limited $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$ is easily offset by the negligible lattice heat capacity of a solid. They were used as the first practical application, the so-called adiabatic magnetization. At the beginning they used paramagnetic salts. The problem for the practical application lies in the low thermal conductivity of PM salts. PM intermetallic compounds have higher thermal conductivity and the most studied material $PrNi_5$ is still in use with the lowest working temperature reached of 22 μK. Another group of materials that have extensively been studied are PM garnets, because of their high thermal conductivity, low lattice heat capacity and very low ordering temperature (below 1K). A noticeable MCE was reported in ytterbium and gadolinium iron garnets, as in neodymium gallium garnet.

## *MCE in order-disorder magnetic phase transition*

Below a given temperature spontaneous magnetic ordering of PM occurs. The ordering temperature depends on the strength of the exchange interaction and on the nature of the magnetic sublattice in the material. When this occurs, the magnetization strongly varies in a very narrow temperature range which allows a large MCE. This temperature is called the Néel temperature for antiferromagnets and the Curie temperature for ferromagnets.

Most research was done on soft ferromagnetic materials ordering from ~4 to ~77 K for gas liquification and materials ordering near room temperature for magnetic refrigeration and aircooling.

The best low-temperature magnetic refrigerant materials are intermetallic compounds that contain lanthanide metals, like $REAl_2$, GdPd and $RENi_2$ (RE=rare earth metals).

The material that orders near room temperature (294K) is Gadolinium. This rare earth metal has been extensively studied and $\Delta T_{ad}$ values at $T_C$ are 20K for magnetic field changes $\mu_0 \Delta H = 10T$. Because Gd is so expensive many ways are exploid to replace Gd with cheaper elements. Many different alloys with Gd were studied to improve the MCE in Gd, but they only lower the $T_C$ or the MCE effect. The only intermetallic materials where the MCE approaches that of Gd is $Gd_5Si_4$ with the

$T_C = 335K$ and germanium substituted $Gd_5(Si_xGe_{1-x})_4$ alloys (x is between 0.5 and 1) with $T_C$ varying between 290 and 335K.

## MCE in first-order magnetic phase transitions

Existence of short-range order and spin fluctuations well above $T_C$ reduces the maximum $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$ in the order-disorder magnetic phase transition. A first-order phase transformation theoretically should occur at constant temperature, and therefore, $\left|\left(\frac{\partial M}{\partial T}\right)_H\right|$ may be infinitively large, consequently giving rise to a large, i.e. giant magnetocaloric effect. The first intermetallic with a giant MCE reported was FeRh. Here an antiferromagnetic to ferromagnetic first-order phase transition at 308K occurs. The effect is negative with a value of -13K for $\Delta H = 2T$. The only drawback is, that this is an irreversible process.

$Gd_5(Si_xGe_{1-x})_4$ alloys (x is between 0 and 0.5) display a $\Delta S_m$ at least two times larger than that of Gd near room temperature. The Curie temperature can be tuned from 20 to 286 K by varying the Si to Ge ratio and small additions of Ga. This way one can tune the GMCE between 20 and 305 K. This process has also the benefit to be reversible and does not disappear after the first application of the magnetic field, like in FeRh. The difference between these two materials is most likely associated with the difference in the nature of the first order phase transition, which for FeRh is a magnetic order-order transformation, while for $Gd_5(Si_xGe_{1-x})_4$ it is a simultaneous magnetic and crystallographic phase transition, i.e. it is a magnetic order-disorder, and crystallographic order-order phase transformation.

## Measuring the MCE

### Direct measurements

Direct techniques to measure MCE always involve the measurement of the initial $T_0$ and the final $T_F$ temperatures of the sample, when the external field is changed from an initial $H_0$ to a final value $H_F$. Then the measurement of the adiabatic temperature change is simply given by

$$\Delta T_{ad}(T_0, H_F - H_0) = T_F - T_0 . \qquad (22)$$

Direct measurements can be done with contact and non-contact techniques. To do a direct measurement, a rapid change of the magnetic field is needed. This can be done either by an immobilized sample and a changing field or by moving the sample in and out of a constant magnetic field. With pulsed magnetic fields we get up to 40 Tesla (*T*), with an electromagnet less than 2 *T* and with permanents or superconducting magnets, for moving samples, from 0,1-10 *T*.

The accuracy of these kind of measurements depends on the errors in thermometry, the thermal insulation and conduction of the sample and field settings. The accuracy lies between 5-10%.

For a second-order phase transition ac, relaxation and adiabatic calorimetry are commonly used for determining the heat capacity $C_p$. This can not be done for a first-order phase transition, due to the uncertainties in determining $C_p$ due to the latent heat release.

A new technique, used for first-order transitions, is the differential scanning calorimeter (DSC). The DSC measures the differential heat flow, $\dot{Q}(t)$, between the sample and a reference sample, against temperature. At the first-order transition a peak in $dQ/dT$ is observed. The temperature where this happens is called the transition temperature $T_t$. The T-integration of the peak in $dQ/dT$, yields the value of the latent heat (*L*) and the entropy change ($\Delta S$):

$$L = \int_{T_L}^{T_H} \frac{dQ}{dT} dT \, ; \; \Delta S = \int_{T_L}^{T_H} \frac{1}{T} \frac{dQ}{dT} dT \, , \qquad (23)$$

where $T_H$ and $T_L$ are respectively temperatures above and below the starting and finishing of the transition.

## Indirect measurements

Two techniques are commonly used for indirect measurements. Heat capacity measurements allows us to calculate $\Delta T_{ad}(T, \Delta H)$ and $\Delta S_m(T, \Delta H)$, while magnetization measurements allows us to calculate only $\Delta S_m(T, \Delta H)$. Magnetization must be measured as a function of *T* and *H* and by numerical integration with Eq. 14 it is very useful as a rapid search for potential magnetic refrigerant materials. With accurate magnetic measurements one can achieve an error of only 3-10%.

The measurement of the heat capacity as a function of temperature in constant magnetic fields and pressure provides the most complete characterization of MCE in magnetic materials. The entropy of a solid can be calculated from the heat capacity as:

$$S(T)_{H=0} = \int_0^T \frac{C(T)_{P,H=0}}{T} dT + S_0 \qquad (24)$$

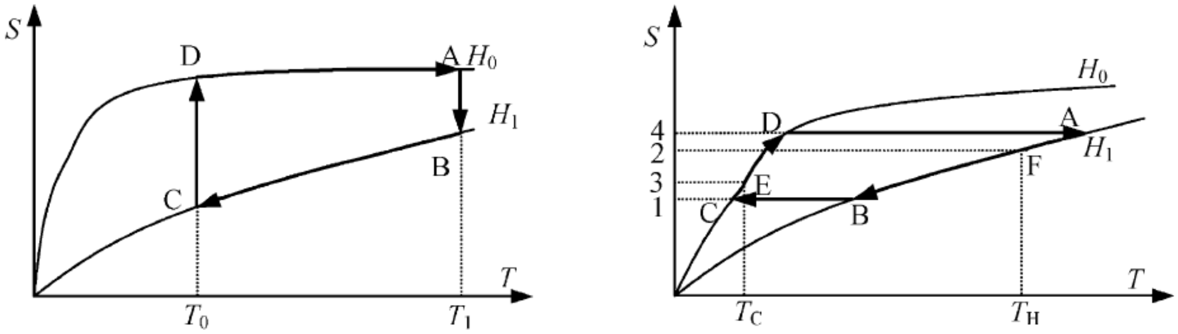
$$S(T)_{H\neq 0} = \int_0^T \frac{C(T)_{P,H}}{T} dT + S_{0,H}$$

Where $S_0$ and $S_{0,H}$ are the zero temperature entropies. In a condensed system $S_0 = S_{0,H}$. Hence, if $S(T)_H$ is known, both $\Delta T_{ad}(T, \Delta H)$ and $\Delta S_m(T, \Delta H)$ can be obtained. However this evaluation is not valid if a first-order transition takes place within the evaluated range, since the value of $C_p$ is not defined at a first order transition.

## Magnetic refrigeration

Magnetic refrigerator completes cooling/refrigeration by magnetic material through magnetic refrigeration cycle. In general a magnetic refrigeration cycle consists of magnetization and demagnetization in which heat is expelled and absorbed respectively, and two other middle processes.

The magnetic Ericsson and Brayton cycle are applicable for room temperature magnetic refrigeration because they achieve a large temperature span and are easy to operate. Fig. 3 shows the Ericsson and Brayton cycles.



(a) magnetic Ericsson cycle (b) magnetic Brayton cycle

**Figure 3 – Magnetic refrigeration cycle**

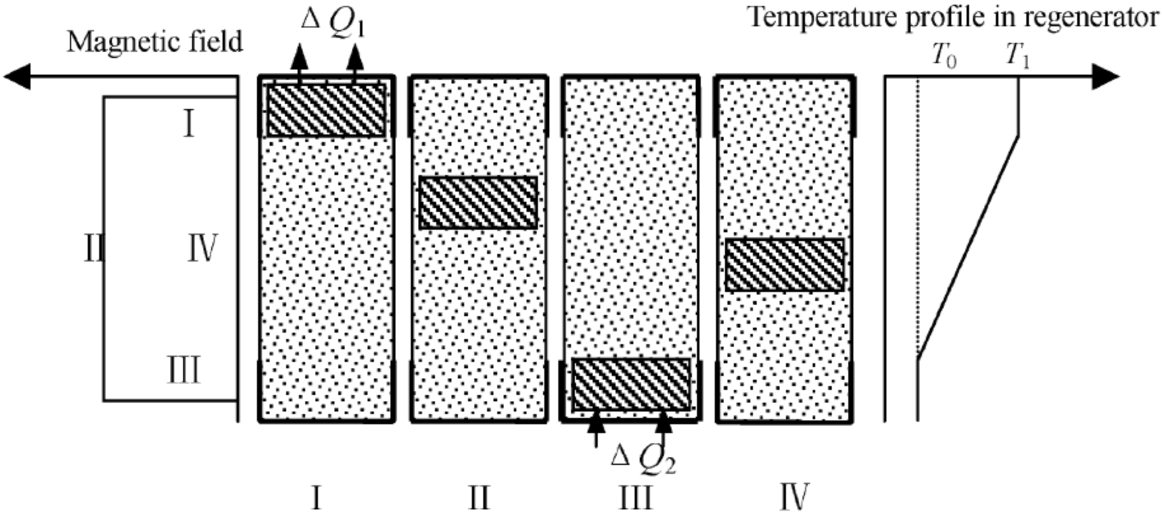


**Figure 4 – Principle of magnetic Ericsson cycle**

## Ericsson cycle

The Ericsson cycle consist of two isothermal processes/stages and two isofield processes (Fig. 4 and 3(a)). The first stage (A→B,I) is a isothermal magnetization, with the working material in the upper position in the magnetic field of the electromagnet. During this stage the magnetic material rejects heat by the hot heat exchanger. Then, at a constant field (B→C,II) the magnetic material is moved downwards. The field is switched of (C→D,III) and the magnetic material absorbs heat from the load at the temperature of the cold end. At the last (D→A,IV) the working material passes through the regenerator column. The cycle is then repeated. For best performances parallel *T-S* curves are required. This can be achieved by using composite materials for MCE. With the Ericsson cycle they achieved temperature differences between the lower cold and higher hot zone of 47 K.

### Brayton cycle

Magnetic Brayton cycle consists of two adiabatic processes and two isofield processes as shown in Fig. 3(b). During the isofield cooling process A→B, magnetic refrigerant expels heat of the area of AB14. During the isofield heating process C→D, magnetic refrigerant absorbs heat of the area DC14. No heat flows from and out of the magnetic refrigerant during the adiabatic magnetization process D→A and the adiabatic demagnetization B→C process.

## *Conclusion*

This paper shortly explains the principle of the MCE, which materials have till now the best properties and what process are suitable for magnetic refrigeration. However, the development of room temperature magnetic refrigeration is not in a mature status yet. Room-temperature magnetic refrigeration will be a new refrigeration method with extreme potential, an account of high efficiency and environment-safe. But before wide application can be achieved, a breakthrough in material science is needed.

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