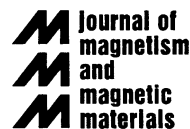




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Magnetocaloric effect and magnetic refrigeration

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Abstract

The phenomenon of the magnetocaloric effect along with recent progress and the future needs in both the characterization and exploration of new magnetic refrigerant materials with respect to their magnetocaloric properties are discussed. Also the recent progress in magnetic refrigerator design is reviewed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Magnetocaloric effect

1.1. Discovery and fundamentals

Magnetocaloric effect (MCE), or adiabatic temperature change (ΔT_{ad}), which is detected as the heating or the cooling of magnetic materials due to a varying magnetic field, was originally discovered in iron by Warburg [1]. The nature of the MCE was explained and its practical use to reach ultra-low temperatures in a process known as adiabatic demagnetization was suggested independently by Debye [2] and by Giauque [3].

The MCE is intrinsic to all magnetic materials and is due to the coupling of the magnetic sublattice with the magnetic field, which changes the magnetic part of the entropy of a solid. Just as the

compression of a gas, the isothermal magnetizing of a paramagnet or a soft ferromagnet reduces the entropy and, in a reversible process, demagnetizing (which is similar to the expansion of a gas) restores the zero-field magnetic entropy of a system. The thermodynamics of the MCE in a ferromagnet near its magnetic ordering temperature (Curie temperature, T_C) is illustrated schematically in Fig. 1. At constant pressure the entropy of a magnetic solid, $S(T, H)$, which is a function of both the magnetic field strength (H) and the absolute temperature (T), is the combined total of the magnetic, S_M , lattice, S_{Lat} , and electronic, S_{El} contributions:

$$S(T, H) = S_M(T, H) + S_{Lat}(T) + S_{El}(T). \quad (1)$$

It is shown for a ferromagnetic material in two constant magnetic fields (zero magnetic field, H_0 , and a non-zero magnetic field, H_1), together with the corresponding magnetic and non-magnetic terms. When the magnetic field is applied adiabatically (i.e. when the total entropy of the system

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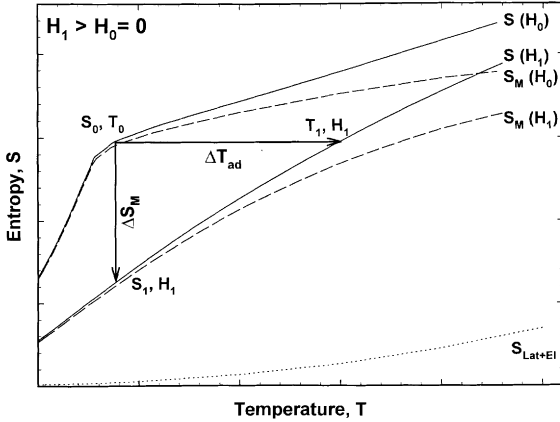


Fig. 1. The S - T diagram illustrating the existence of the magnetocaloric effect. The solid lines represent the total entropy in two different magnetic fields: $H_0 = 0$ and $H_1 > 0$. The horizontal arrow shows ΔT_{ad} and the vertical arrow shows ΔS_{M} when the magnetic field is changed from H_0 to H_1 . The dotted line shows the combined lattice and electronic (non-magnetic) entropy, and dashed lines show the magnetic entropy in the two fields. S_0 and T_0 are zero field entropy and temperature, S_1 and T_1 are entropy and temperature at the elevated magnetic field H_1 .

remains constant during the magnetic field change) in a reversible process, the magnetocaloric effect (i.e. the adiabatic temperature rise, $\Delta T_{\text{ad}} = T_1 - T_0$) can be visualized as the isentropic difference between the corresponding $S(T)_H$ functions as shown in Fig. 1 by the horizontal arrow. The MCE can be also expressed by means of the isothermal magnetic entropy change (or simply magnetic entropy change), $\Delta S_{\text{M}} = S_1 - S_0$, when the magnetic field is applied isothermally. In the latter case it is equal to the isothermal difference between the corresponding $S(T)_H$ functions as shown in Fig. 1 by the vertical arrow. Therefore ΔT_{ad} and ΔS_{M} represent the two quantitative characteristics of the magnetocaloric effect, and it is obvious that both ΔT_{ad} and ΔS_{M} are functions of the initial temperature, T_0 (i.e. the temperature before the magnetic field was altered), and the magnetic field change, $\Delta H = H_1 - H_0$. It is easy to see (Fig. 1) that if raising the magnetic field increases magnetic order (i.e. reduces magnetic entropy, which is the case for simple paramagnetic and ferromagnetic materials), then $\Delta T_{\text{ad}}(T, \Delta H)$ is positive and magnetic solid heats up, while $\Delta S_{\text{M}}(T, \Delta H)$ is negative. The signs of

$\Delta T_{\text{ad}}(T, -\Delta H)$ and $\Delta S_{\text{M}}(T, -\Delta H)$ are correspondingly reversed when the magnetic field is reduced.

The ΔT_{ad} and ΔS_{M} are correlated with the magnetization (M), the magnetic field strength, the heat capacity at constant pressure (C), and the absolute temperature by one of the fundamental Maxwell's relations [4]

$$\left(\frac{\partial S(T, H)}{\partial H} \right)_T = \left(\frac{\partial M(T, H)}{\partial T} \right)_H, \quad (2)$$

which for an isothermal-isobaric process after integration yields

$$\Delta S_{\text{M}}(T, \Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH. \quad (3)$$

Eq. (3) indicates that the magnetic entropy change is proportional to the derivative of magnetization with respect to temperature at constant field and to the magnetic field change. By combining Eq. (2) with the corresponding $T dS$ equation it is easy to show [4] that the infinitesimal adiabatic temperature rise for the reversible adiabatic-isobaric process is equal to

$$dT = - \left(\frac{T}{C(T, H)} \right)_H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH. \quad (4)$$

Hence, the adiabatic temperature rise is directly proportional to the absolute temperature, to the derivative of magnetization with respect to temperature at constant field and to the magnetic field change; and it is inversely proportional to the heat capacity. After integrating Eq. (4) one gets the value of the magnetocaloric effect as

$$\begin{aligned} \Delta T_{\text{ad}}(T, \Delta H) \\ = - \int_{H_1}^{H_2} \left(\frac{T}{C(T, H)} \right)_H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH. \end{aligned} \quad (5)$$

Eqs. (2)–(5) have a fundamental importance on the understanding of the behavior of the MCE in solids, and serve as a guide for the search of new materials with a large magnetocaloric effect. First, since the magnetization at constant field of paramagnets and simple ferromagnets decreases with

increasing temperature [i.e. $(\partial M/\partial T)_H < 0$], then $\Delta S_M(T)_{\Delta H}$ should be negative (Eqs. (2) and (3)), while $\Delta T_{ad}(T)_{\Delta H}$ should be positive (Eqs. (4) and (5)), which agrees with Fig. 1. Second, in ferromagnets $|\partial M/\partial T)_H|$ is the largest at the T_C , and therefore, $|\Delta S_M(T)_{\Delta H}|$ should peak at T_C (Eqs. (2) and (3)). Third, although it is not straightforward from Eqs. (4) and (5) because the heat capacity at constant field is also anomalous near the T_C , it has been shown [5] that $\Delta T_{ad}(T)_{\Delta H}$ in ferromagnets peaks at the Curie temperature when $\Delta H \rightarrow 0$. The behavior of $\Delta T_{ad}(T)_{\Delta H}$ should be similar to the behavior of $|\Delta S_M(T)_{\Delta H}|$, i.e. it will be gradually reduced both below and above the T_C . Fourth, for the same $|\Delta S_M(T)_{\Delta H}|$, the $\Delta T_{ad}(T)_{\Delta H}$ will be larger at a higher absolute temperature, and also when the total heat capacity of the solid is lower (Eq. (5)). The latter point is critical in understanding the fact that paramagnets display significant $\Delta T_{ad}(T, \Delta H)$ only at temperatures close to absolute zero, where the limited value of $|\partial M/\partial T)_H|$ is easily offset by the negligible lattice heat capacity. Furthermore, at high temperatures the measurable adiabatic heating (or cooling) is expected only if the solid orders spontaneously, i.e. when value of $|\partial M/\partial T)_H|$ becomes significant.

1.2. Measurement of the magnetocaloric effect

The magnetocaloric effect can be measured directly or it can be calculated indirectly from the measured magnetization or field dependence of the heat capacity. Direct techniques always involve measurements of the sample temperatures (T_0 and T_F) in magnetic fields H_0 and H_F , where subscripts 0 and F designate initial and final magnetic field, respectively. The $\Delta T_{ad}(T)_{\Delta H}$ is then determined as the difference between T_F and T_0 for a given T_0 and $\Delta H = H_F - H_0$.

Direct MCE measurements can be carried out using contact (i.e. when the temperature sensor is in direct thermal contact with the sample) and non-contact techniques (i.e. when the sample temperature is measured without the sensor being directly connected to the sample) [6–14]. Since during the direct MCE measurements a rapid change of the magnetic field is required, the measurements can be carried out on immobilized samples when the mag-

netic field change is provided either by charging/discharging the magnet, or by moving the sample in and out of a uniform magnetic field volume. Using immobilized samples and pulse magnetic fields direct MCE measurements in magnetic fields from 1 to 40 T have been reported. The use of electromagnets usually limits the magnetic field strength to less than 2 T. Experimental apparatus, where the sample or the magnet are moved to provide the varying magnetic field environment usually employ superconducting or permanent magnets, which limit the magnetic field range to 0.1–10 T. The accuracy of the direct experimental techniques depends on the errors in thermometry, errors in field setting, the quality of thermal insulation of the sample (this becomes a critical source of error when the MCE is large and thus disrupts the adiabatic conditions), the quality of the compensation scheme to eliminate the effect of the changing magnetic field on the temperature sensor reading. Considering all these effects the accuracy is claimed to be in the 5–10% range [6–14].

Unlike the direct MCE measurements, which only yield the adiabatic temperature change, the indirect experiments allow the calculation of both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ — heat capacity measurements, or just $\Delta S_M(T)_{\Delta H}$ — magnetization measurements. Magnetization measured experimentally as a function of temperature and magnetic field provides $\Delta S_M(T)_{\Delta H}$ after numerical integration of Eq. (3), and has been rightfully suggested as a useful technique for the rapid screening of prospective magnetic refrigerant materials [15]. The accuracy of $\Delta S_M(T)_{\Delta H}$ calculated from magnetization data depends on the accuracy of the magnetic moment, temperature, and magnetic field measurements. Because numerical integration is involved, and because the exact differentials (dM , dT , and dH) are substituted, respectively, by the measured ΔM , ΔT , and ΔH , the typical accuracy of $\Delta S_M(T)_{\Delta H}$ from magnetization measurements is reported to be in the range of 3–10% [15]. The relative error may become significantly larger particularly for small $|\Delta S_M(T)_{\Delta H}|$ values.

The heat capacity measured as a function of temperature in constant magnetic fields, $C(T)_H$, provides the most complete characterization of magnetic materials with respect to their magnetocaloric

effect, since the entropy of magnetic solid can be calculated from heat capacity as

$$S(T)_{H=0} = \int_0^T \frac{C(T)_0}{T} dT + S_0$$

and

$$S(T)_{H \neq 0} = \int_0^T \frac{C(T)_H}{T} dT + S_{0,H}, \quad (6)$$

where S_0 and $S_{0,H}$ are the zero temperature entropies. In a condensed system these are the same (i.e. $S_0 = S_{0,H}$) [16], and therefore, the calculation of both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ is straightforward [17], also see Fig. 1. The accuracy of the MCE calculations using heat capacity data is critically dependent on the accuracy of the heat capacity measurements and data processing (Eq. (6)) because both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ are small differences between two large quantities (temperatures and total entropies). The error in $\Delta S_M(T)_{\Delta H}$ from heat capacity is given [17] as

$$\sigma \Delta S_M(T)_{\Delta H} = \sigma S(T)_{H=0} + S(T)_{H \neq 0}, \quad (7)$$

where $\sigma S(T)_{H=0}$ and $\sigma S(T)_{H \neq 0}$ are the errors in the zero magnetic field entropy and non-zero magnetic field entropy, respectively. The error in $\Delta T_{ad}(T)_{\Delta H}$ is also proportional to the errors in the entropy, but it is inversely proportional to the derivative of the entropy with respect to temperature [17]

$$\sigma \Delta T_{ad}(T)_{\Delta H} = \sigma S(T)_{H=0} / (dS(T)_{H=0} / dT) + \sigma S(T)_{H \neq 0} / (dS(T)_{H \neq 0} / dT). \quad (8)$$

It should be noted that Eqs. (7) and (8) yield the absolute uncertainty in the calculated magnetocaloric effect, and therefore, the relative errors rise significantly for small MCE values (Figs. 2 and 3). Hence, assuming that the accuracy of the heat capacity measurements is magnetic field independent, the relative error in both $\Delta T_{ad}(T)_{\Delta H}$ and $\Delta S_M(T)_{\Delta H}$ will be reduced for larger ΔH .

1.3. Magnetocaloric effect in paramagnets

As mentioned above, the MCE in paramagnets is only expected to be measurable at temperatures close to absolute zero, where the enhanced, but still limited $|\partial M / \partial T|_H$ is easily offset by the negligible

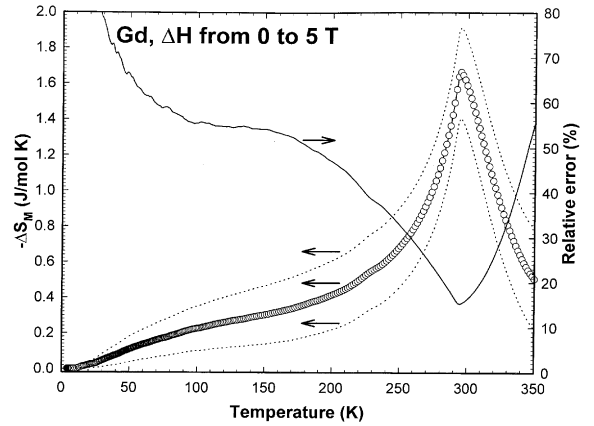


Fig. 2. The ΔS_M in Gd for a magnetic field change from 0 to 5 T calculated from the experimental heat capacity data measured in 0 and 5 T magnetic fields (open circles, left-hand scale). The dotted lines (left-hand scale) indicate the range of absolute errors and the solid line shows the relative error (right-hand scale).

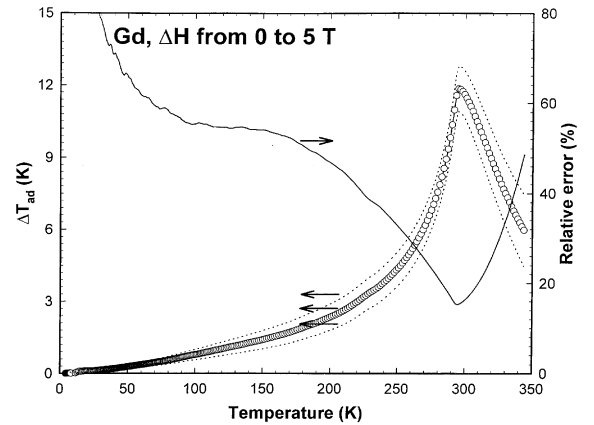


Fig. 3. The ΔT_{ad} in Gd for a magnetic field change from 0 to 5 T calculated from the experimental heat capacity data measured in 0 and 5 T magnetic fields (open circles, left-hand scale). The dotted lines (left-hand scale) indicate the range of absolute errors and the solid line shows the relative error (right-hand scale).

lattice heat capacity of a solid. Early research on the magnetocaloric effect in paramagnets was carried out because of the drive to reach ultra-low temperature by adiabatic demagnetization cooling. It is worth noting that the pioneering work of Giauque and MacDougall, who studied low-temperature magnetocaloric properties of paramagnetic

$\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, showed that a temperature of less than 1 K could be reached [3,18]. This work and other important contributions to the low-temperature behaviors of solids resulted in Giaugue winning the 1949 Nobel prize in chemistry. Many years later the low-temperature magnetocaloric effect was reported in a variety of paramagnetic salts including ferric ammonium alum [19], chromic potassium alum [20], and cerous magnesium nitrate [21].

The low thermal conductivity of paramagnetic salts is detrimental for adiabatic demagnetization applications, and therefore, paramagnetic intermetallic compounds have attracted some attention with respect to their magnetocaloric properties. One of the most studied materials was PrNi_5 [22–32], which is still successfully used in nuclear adiabatic demagnetization devices. In conjunction with Cu as the low-temperature nuclear magnetic demagnetization stage and PrNi_5 as the upper stage a record was set for the lowest working temperature (27 μK) at which useful experiments could be performed on materials, other than on the refrigerant itself [29]. Recent experimental and theoretical data [32] show that at higher temperatures ($\sim 3 \text{ K} < T < \sim 13 \text{ K}$) the magnetocaloric effect in paramagnetic PrNi_5 is anomalous due to the crystalline electric field effects, which cause the paramagnetic system to *cool upon magnetizing and to warm upon demagnetizing*.

A considerable effort has been devoted to the studies of the MCE in paramagnetic garnets mainly because of their high thermal conductivity, low lattice heat capacity and very low ordering temperature (generally below 1 K). With an ordering temperature close to absolute zero it is possible to obtain a large ΔS_M to maintain a significant MCE up to $\sim 20 \text{ K}$. Clark and Alben [33] report ΔT_{ad} approaching 6–10 K for $\Delta H = 11 \text{ T}$ in ytterbium and gadolinium iron garnets between 10 and 30 K. Noticeable magnetocaloric effects were also reported in neodymium gallium garnet ($\text{Nd}_3\text{Ga}_5\text{O}_{12}$) at 4.2 K [34], and in gadolinium gallium garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$) below 15 K [35,36]. A large enhancement of the ΔS_M in magnetic nanocomposites based on iron-substituted gadolinium gallium garnets $\text{Gd}_3\text{Ga}_{5-x}\text{Fe}_x\text{O}_{12}$ ($x \leq 2.5$) was recently observed by Shull and co-workers [35,37,38].

1.4. Magnetocaloric effect and order–disorder magnetic phase transition

Spontaneous magnetic ordering of paramagnetic solids upon lowering the temperature is a cooperative phenomenon, which occurs at various temperatures depending both on the nature of the magnetic sublattice and on the strength of exchange interaction. When spontaneous magnetic ordering occurs, the magnetic order parameter as well as the bulk magnetization of a solid undergo large changes in relatively narrow temperature interval close to the respective Curie or Néel temperature contributing to a large $|\partial M / \partial T|_H$ and thus making it possible for a practical utilization of the MCE (see Eqs. (2)–(5)). Even though it is not the absolute magnetization, but the derivative of the magnetization with respect to temperature, which must be large to yield a large MCE, the 4f metals (lanthanides) and their alloys have been studied much more extensively than 3d metals and their alloys simply because the available theoretical magnetic entropy in the former is considerably larger than in the latter. Most of the research on the MCE has been associated with either soft ferromagnetic materials ordering from ~ 4 to $\sim 77 \text{ K}$ for applications such as helium and hydrogen liquefaction, or materials ordering near room temperature for applications such as conventional air conditioning and refrigeration. The scope and the size of this article do not allow us to review all of the available data, and therefore we will briefly discuss only the most interesting results.

1.4.1. Low temperatures: MCE in the range ~ 10 –80 K

One of the most natural choices for low-temperature magnetic refrigerant materials are the pure lanthanide metals which order at low temperatures, such as Pr, Nd, Er, and Tm. Of these four, the MCE was studied for all but Pr (which does not order magnetically) and the expectations for large MCE values were not realized. Zimm et al. [39] report that the MCE in Nd reached a ΔT_{ad} of $\sim 2.5 \text{ K}$ at $T = 10 \text{ K}$ for $\Delta H = 7 \text{ T}$. The presence of several magnetic phase transitions, which occur in Er between ~ 20 and $\sim 80 \text{ K}$ brings about an almost

constant but quite small MCE (averaging between 4 and 5 K for a 7 T magnetic field change) in the 20–90 K temperature range [40]. Pure Tm orders magnetically in a sinusoidally modulated ferromagnetic structure at ~ 56 K and becomes ferrimagnetic at ~ 32 K. These features of the Tm magnetic structure restrict its MCE, which barely tops ~ 3 K at ~ 56 K for $\Delta H = 7$ T [41]. It has been also observed that the MCE in Tm becomes negative between ~ 32 and ~ 56 K in a weak magnetic field of 1 T [41]. The main reason for these low ΔT_{ad} values is that most of magnetic phases in Nd, Er and Tm are antiferromagnetic and ferrimagnetic, and much of the entropy is involved in flipping spins to a ferromagnetic alignment.

The materials which display the largest MCE between ~ 10 and ~ 80 K are intermetallic compounds containing lanthanide metals. Among them the best are RAI_2 , where $R = \text{Er, Ho, Dy}$ and $Dy_{0.5}Ho_{0.5}$ [42–44], $R = Dy_xEr_{1-x}$, $0 < x < 1$ [45,46], $GdPd$ [47], and RNi_2 , where $R = Gd$ [48,49], Dy [49,50] and Ho [49,50]. The ΔT_{ad} for selected materials is shown in Fig. 4. It is easy to see, that the maximum MCE is significantly reduced as temperature rises from ~ 10 to ~ 80 K, which is associated with the rapid increase of the lattice heat capacity in these alloys. The field dependence of the MCE in this temperature range varies from ~ 1 to ~ 2 K/T.

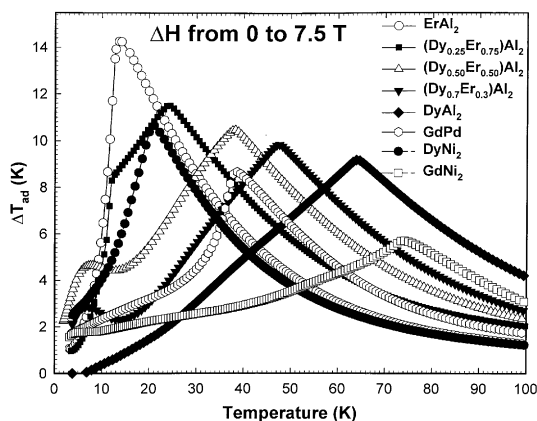


Fig. 4. The ΔT_{ad} in the best magnetic refrigerant intermetallic materials in the temperature range from ~ 10 to ~ 80 K for a magnetic field change from 0 to 7.5 T [42–50].

1.4.2. Intermediate temperatures: MCE in the range ~ 80 – ~ 250 K

This temperature range has not received nearly as much attention as the other two ranges (10–80 K and > 250 K). First, there is the lack of the driving force for magnetocaloric cooling to these temperatures. The second reason is the inherent minimum of the T/C ratio (where C is only the lattice and electronic heat capacity) as shown for typical metal (Cu) in Fig. 5 suggesting that the adiabatic heating and cooling would be minimal in this temperature range (Eqs. (4) and (5)). One of the best magnetic refrigerant materials for the intermediate temperatures is pure Dy [11,51–54], with ΔT_{ad} reaching ~ 12 K at ~ 180 K for $\Delta H = 7$ T. Similarly, as discussed earlier for the MCE in Tm, the complexity of the magnetic structure of Dy brings about a negative MCE for small magnetic field changes ($\Delta H < 2$ T). Recent studies of amorphous $R_x(T_1, T_2)_{1-x}$ alloys, where R is a lanthanide metal, and T_1 and T_2 are 3d transition metals [55–58] indicate that these materials may be useful magnetic refrigerant materials between 100 and 200 K. The field dependence of the MCE is just under 2 K/T for Dy, but rarely reaches more than 1 K/T for all other studied magnetocaloric materials, including the amorphous alloys. However, a recent study [59,60] shows that the $Gd_5(Si_xGe_{1-x})_4$ alloys for $0.08 \leq x \leq 0.43$ have extremely large ΔS_M and ΔT_{ad} values, 2–10 times larger than any of the above mentioned materials (also see below, Section 1.5).

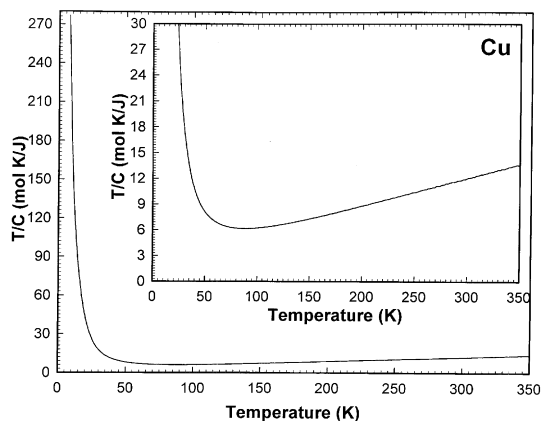


Fig. 5. The T/C versus T from lattice and electronic contribution in a typical metallic material.

1.4.3. Near room temperature MCE

The prototype material for the room temperature range is the lanthanide metal Gd which orders ferromagnetically at 294 K. Its magnetocaloric effect has been studied independently by many authors [5,8,14,61–66] and the ΔT_{ad} values at T_C are $\sim 6, 12, 16$, and 20 K for $\Delta H = 2, 5, 7.5$ and 10 T, respectively, reaching an impressive field dependence of the MCE of ~ 3 K/T in low magnetic fields which falls to ~ 2 K/T in higher magnetic fields. A variety of Gd–R alloys, where R is another lanthanide metal (such as Tb, Dy, Ho, or Er) and/or Y were prepared in an attempt to improve the MCE in Gd [67–74]. However, all alloying additions just shift the Curie temperature of Gd to lower temperatures without any noticeable improvement in its MCE. The only known exception is the probable enhancement of the low magnetic field ($\Delta H = 1$ T) MCE in nanocrystalline Gd–Y alloys [75–77].

Most intermetallic compounds which order magnetically near the room temperature but above ~ 290 K show a significantly lower MCE than that of Gd. A theoretical estimate [78] that the MCE in Y_2Fe_{17} ($T_C = \sim 310$ K) would be equal to $\sim 50\%$ of the MCE in Gd was recently verified experimentally [79]. Approximately, the same magnitude of the MCE was also measured experimentally in Nd_2Fe_{17} with $T_C = \sim 324$ K [79]. It has been suggested by [80] that there may be an enhancement of the MCE in $(Pr_{1.5}Ce_{0.5})Fe_{17}$, but it has not been verified experimentally. The only intermetallic materials where the MCE approaches that of Gd are Gd_5Si_4 [60] with the $T_C = \sim 335$ K and germanium substituted $Gd_5(Si_xGe_{1-x})_4$ alloys, where $0.5 < x \leq 1$ [59] with $\sim 290 < T_C \leq \sim 335$ K.

1.5. First-order magnetic phase transition and the giant MCE

In an order–disorder magnetic phase transition the existence of short-range order and spin fluctuations well above the T_C often reduces the maximum possible $|(\partial M / \partial T)_H|$ thus effectively reducing the maximum MCE. A first-order phase transformation theoretically should occur at constant temperature, and therefore, $|(\partial M / \partial T)_H|$ may be infi-

nately large, consequently giving rise to a large, i.e. giant magnetocaloric effect. One of the first intermetallics, in which a giant, but also *negative*, MCE was experimentally observed, is FeRh. It undergoes an antiferromagnetic to ferromagnetic first-order phase transition at ~ 308 K, which is accompanied by a MCE as large as -13 K for $\Delta H = 2$ T [81–83]. Unfortunately the giant MCE in FeRh is irreversible and observed only upon the application of the magnetic field to a virgin sample.

Recently a series of $Gd_5(Si_xGe_{1-x})_4$ alloys, where $0 \leq x \leq 0.5$, was reported [59,84–87] to display a ΔS_M at least two times larger than that of Gd near room temperature and between 2 and 10 times larger than the best magnetocaloric materials in the low and intermediate (see above) temperature regions. Besides the extremely large ΔS_M two additional features make these alloys unique, and likely candidate magnetic refrigerant materials for the use in highly efficient magnetic refrigerators. The first is the fact that their Curie temperature can be tuned between ~ 20 and ~ 286 K by varying the Si to Ge ratio and by introducing small alloying additions of Ga to $Gd_5(Si_2Ge_2)$ [87]. This allows one to tune the maximum giant magnetocaloric effect between ~ 20 and ~ 305 K. The second is the fact, that unlike FeRh, the giant magnetocaloric effect in the $Gd_5(Si_xGe_{1-x})_4$ alloys, where $0 \leq x \leq 0.5$, is reversible, i.e. it does not disappear after the first application of the magnetic field. The difference in the behavior of the MCE in FeRh and $Gd_5(Si_xGe_{1-x})_4$ alloys is most likely associated with the difference in the nature of the first order phase transition, which in the former case is a magnetic order–order transformation, while in the latter case it is a simultaneous magnetic and crystallographic phase transition, i.e. it is a magnetic order–disorder, and crystallographic order–order phase transformation [86,88].

The third class of materials also displaying a large magnetocaloric effect (comparable to Gd) is based on differently substituted perovskite-like $LaMnO_3$ materials with Y, Ca, Li and/or Na substituting for La, and Ti for Mn [89–92]. The reversibility of the MCE as well as possible mechanisms of its existence in these compounds has not been reported.

2. Application of the magnetocaloric effect – magnetic refrigeration

2.1. History of continuous magnetic refrigeration

The history of continuous magnetic refrigeration can be traced to the work of Collins and Zimmerman [93], and Heer et al. [94], who built and tested magnetic refrigerators (MR) operating between ~ 1 and 0.73 K [93] and 0.2 K [94] by periodically magnetizing and demagnetizing iron ammonium alum. The latter apparatus extracted 123 erg/s (12.3 μ J/s) from the cold reservoir at 0.2 K operating at 1/120 Hz frequency. It was not, however, until Brown [95] reported a near room temperature continuously operating MR, when it became clear that magnetic refrigeration may be successfully utilized at significantly higher temperatures and achieve much larger temperature spans than the maximum observed MCE. Brown [95] was able to attain a 47°C no-load temperature difference between the hot end (46°C) and cold end (-1°C) by regenerating a column of fluid (80% water and 20% ethyl alcohol) using the lanthanide metal Gd and a magnetic field change from 0 to 7 T. Following the early work of Brown the concept of active magnetic regenerator (AMR) refrigeration was introduced by Steyert [96] and developed by Barclay [97,98], and subsequently was brought to life in various MR units operating at different temperatures [99–110]. Both the AMR concept and the successful proof-of-principle room temperature magnetic refrigerator are briefly described below.

2.2. Active magnetic regenerator cycle

A description of the AMR cycle was presented by Zimm and DeGregoria [111]. In the AMR cycle, a porous bed of a magnetic refrigerant material acts as both the refrigerant (coolant) that produces refrigeration and the regenerator for the heat transfer fluid. A schematic of the process is shown in Fig. 6. Assume that the bed is at a steady state condition with the hot heat exchanger at 75°F ($\sim 24^\circ\text{C}$) and the cold heat exchanger at 40°F ($\sim 5^\circ\text{C}$). In Fig. 6a, the initial temperature profile for the bed is in its demagnetized state in zero magnetic field (dashed

line). When a magnetic field is applied to the refrigerant, each particle in the bed warms because of the MCE to form the final magnetized bed temperature profile (solid line). The amount each particle warms is equal to ΔT_{ad} reduced by the effect of the heat capacity of the heat transfer fluid in the pores between the particles. Next, the 40°F ($\sim 5^\circ\text{C}$) fluid flows through the bed from the cold end to the hot end (Fig. 6b). The bed is cooled by the fluid lowering the temperature profile across the bed (the dashed line to the solid line), and the fluid in turn is warmed by the bed, emerging at a temperature close to the temperature of the bed at the warm end. This temperature is higher than 75°F ($\sim 24^\circ\text{C}$), so heat is removed from the fluid at the hot heat sink as the fluid flows through the hot heat exchanger. After the fluid flow is stopped, the magnetic field is removed, cooling the bed by the MCE (the dashed line to the solid line in Fig. 6c). The refrigeration cycle is completed by forcing the 75°F fluid to flow from the hot to the cold end of the bed (Fig. 6d). The fluid is cooled by the bed, emerging at a temperature below 40°F ($\sim 5^\circ\text{C}$) and removes heat from the cold sink as the fluid passes through the cold heat exchanger.

The AMR cycle outlined above has several positive features useful for practical application in MR devices. First, the temperature span of a single stage can greatly exceed that of the MCE of the magnetic refrigerant because the MCE of each individual particle changes the entire temperature profile across the bed. Second, because the bed acts as its own regenerator, heat need not be transferred between two separate solid assemblies, but rather between the solid particles in a single bed via the action of a fluid. Third, the individual particles in the bed do not encounter the entire temperature span of the stage, and hence the bed may be made into layers, each containing a magnetic material with properties optimized for a particular temperature range.

2.3. Recent achievements in near room temperature refrigeration

The successful proof-of-principle MR, which was recently described by Zimm et al. [112,113], operates near room temperature in a magnetic field

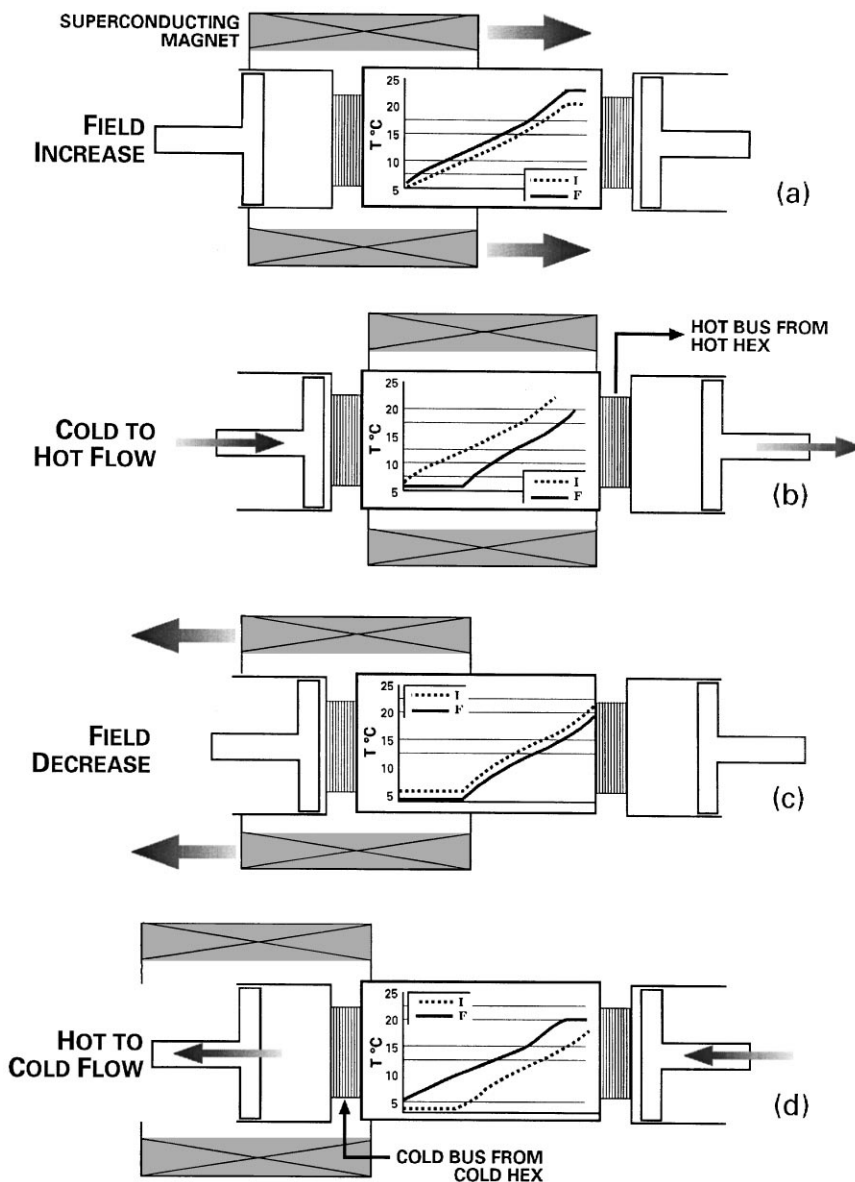


Fig. 6. The four steps of the active magnetic regenerator cycle: magnetizing (a), flow from cold to hot (b), demagnetizing (c), and flow from hot to cold (d) [111].

between 1.5 to 5 T and uses approximately 3 kg of Gd spheres packed in two magnetocaloric beds. The heat transfer fluid is water. The beds are periodically magnetized and demagnetized and the fluid flows are arranged as described above (AMR cycle). A simple reciprocating machine, shown schematically in Fig. 7, operates at low frequency

($\sim \frac{1}{6}$ Hz) and generates up to 600 W of cooling power in a 5 T magnetic field (200 W of cooling power in a 1.5 T field). Its efficiency approaches 60% at 5 T (30% at 1.5 T) of Carnot with a coefficient of performance (COP) approaching 15 at 5 T (3 at 1.5 T). The efficiency and COP are calculated with the seal friction subtracted off. The maximum

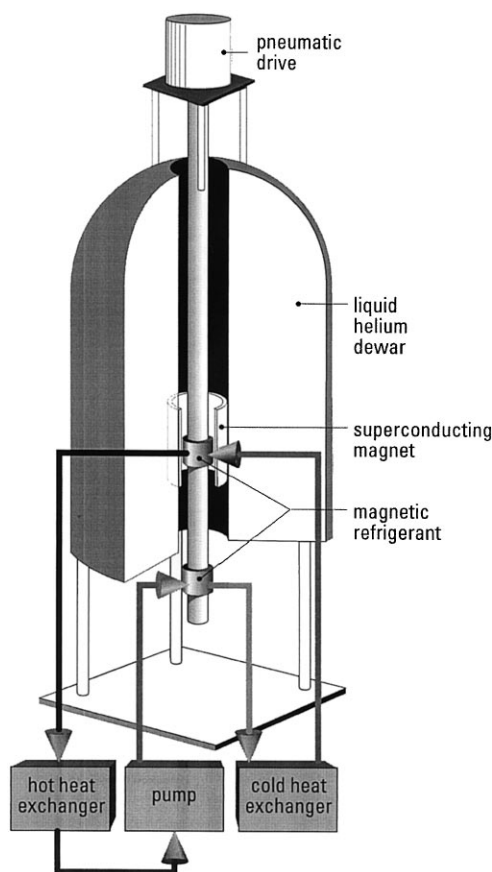


Fig. 7. A schematic sketch of the reciprocating proof-of-principle magnetic refrigerator [112,113].

cooling power and COP are reported for a temperature span equal to approximately $\frac{1}{3}$ of the maximum observed temperature span of 38°C for $\Delta H = 5$ T.

3. Magnetocaloric effect and magnetic refrigeration – future perspectives

The last quarter of the 20th century has seen a continuous increase of interest in the magnetocaloric effect and magnetic refrigeration. The number of publications, worldwide, has been rising continuously during the last 35 years (Fig. 8) from a total of 11 in 1965–1969 to a total of 127 in 1990–94 and an estimated 155 in 1995–1999 period. This is about an 8% growth rate per year. Judging

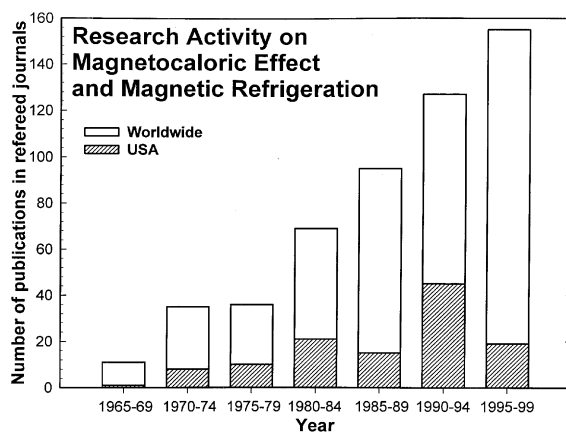


Fig. 8. The number of publications concerning the magnetocaloric effect and magnetic refrigeration for the last 35 years as cited in Chemical Abstracts. The figure for 1995–1999 includes our projection for the second-half of 1998 and the entire year for 1999.

by the number of publications, the research activities in the US are lagging behind the rest of the world, although the major achievements [the discovery of the giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, and the design and the testing of a reliable proof-of-principle, near room temperature magnetic refrigerator] were accomplished recently in the United States [59,84–87,112,113]. The reduction in the US publication rate in the past five years is probably associated with significant reduction of the US defense, NIST and NASA research expenditures, which occurred in late 1980s and early 1990s. Research in Japan also has decreased significantly in the past 5 to 10 years, but this has been more than offset by recent increased research on the magnetocaloric effect in China, Canada and Europe. Furthermore, many of the new findings are being published in letter-type journals (particularly those which originate in China), which also increases the number of non-US produced reports.

We expect future developments in all aspects of magnetic refrigeration to be rapidly forthcoming because the traditional vapor compression technology is asymptotically approaching its technical limitations for additional increases in energy efficiency, and because of environmental concerns, while magnetic refrigeration promises significant

improvements in both. Magnetic refrigerant materials and magnetic refrigerator design represent the two sides of the same scientific and technological problem — the development of new magnetic refrigeration technology as an energy efficient and environmentally safe alternative to existing vapor compression refrigeration. First, it is without a doubt that new and better magnetic refrigerant materials will be discovered as more research effort will be concentrated on the search for and characterization of new classes of metallic and non-metallic magnetic materials for potential applications in different ranges of temperatures, from close to absolute zero to well above room temperature. This will also include basic studies on the fundamental nature of magnetic ordering and how it affects the magnetocaloric properties. Extensive basic research is required, not only with regard to the exploration and characterization of new magnetic refrigerant materials, but also with respect to methods of economical production and processing them into porous media (including parallel plates, spheres, jelly rolls, wires, etc.) suitable for making magnetocaloric beds. Second, there is also no doubt that new designs of magnetic refrigerators using superconducting and permanent magnets will be developed for a variety of large- and small-scale applications for cooling from well above room temperature to temperatures as low as 1 K. Extensive basic and applied research is required not only with respect to improvements in the thermodynamic behavior and the mechanical configuration of the new magnetic refrigeration devices, but also with respect to creating the varying magnetic field environment to power-up the refrigerator to improve the temperature lift across differently configured magnetocaloric beds, and in turn to improve the overall magnetic refrigerator performance.

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