Chapter 2
Magnetocaloric Materials for Freezing, Cooling, and Heat-Pump Applications

Magnetocaloric materials (MCM) are the 'heart' of every magnetic refrigeration or heat-pump application. Apart from having a crucial role in the heat-regeneration process, they also exhibit a special and vital phenomenon for magnetic refrigeration called the magnetocaloric effect. As mentioned in the previous chapter on the Thermodynamics of magnetocaloric energy conversion and as described later in the book in the Chap. 7 (*Overview of existing magnetocaloric prototype devices*) the first real magnetic devices working near room temperature were not built until the middle of the 1970s. However, the discovery of the magnetocaloric effect (MCE) in ferromagnetic materials dates back more than 90 years to 1917.

The MCE was discovered by the French and Swiss physicists Weiss and Piccard [1, 2]. This is an important historical fact that needs to be emphasized, since in the past 15 years a misconception has arisen in the magnetocaloric research community, wrongly attributing the discovery of the MCE to the work of Warburg [3]. At this point we have to address the recent paper of Smith [4], who did a thorough and interesting review of the research on thermodynamics that led to the discovery of the MCE. The next few lines are a brief summary of the historical events according to Smith's findings. He reviewed the original works of scientists that date back to the nineteenth century, starting with Joule in 1843 [5]. Joule observed that heat was evolved from iron samples when they were subjected to a magnetic field. Later, in 1860, Thomson (Lord Kelvin) [6] was already aware of the fact that ferromagnetic materials lose their magnetic properties when heated above a certain temperature (now known as the Curie temperature). Thomson correctly predicted that ferromagnetic materials would experience a heating effect when magnetized and a cooling effect when demagnetized, and that these effects would be the largest around the temperature where they lose their magnetization. However, he did not associate these predictions with the magnetocaloric effect. Then, in 1881, Warburg published a paper [3], which is nowadays wrongly cited when referencing the discovery of the MCE. Nevertheless, the work of Warburg was of great significance, since he was the first to explain magnetic hysteresis. He correctly predicted that the magnetization of a material is larger when the magnetic field is decreasing than when it is increasing. One year later, in 1882, Ewing [7] discovered the same phenomenon and was the first to name it "hysteresis". It was not until the works of

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Weiss and Piccard were published in 1917 and 1918 [1, 2], where they discovered a reversible heating of a nickel sample near its Curie temperature (354 °C) when a magnetic field was applied. They found that the nickel sample increased its temperature by 0.7 K when a magnetic field of 1.5 T was applied. Furthermore, they also stated that the reversibility of the effect and also its larger order of magnitude could distinguish it from the heat that emerges from the hysteresis. Finally, they called their discovery a "novel magnetocaloric phenomenon", thereby coining the word "magnetocaloric".

The discovery of Weiss and Piccard was undoubtedly acknowledged and well known in the scientific community until the end of twentieth century, when the sudden misconception arose, attributing the discovery of the MCE to Warburg. The reasons for this misconception will not be discussed here. However, we encourage the reader of this book to investigate the paper of Smith [4], where this is explained in detail.

The first ideas that ferromagnetic materials could be usefully applied in power generation, refrigeration or heat pumping emerged with the works of the Slovenian physicist Stefan in the last quarter of the nineteenth century [8, 9]. Stefan explained how a thermomagnetic motor should work by exploiting the transition from the ferromagnetic to the paramagnetic state of the material by heating it above its Curie temperature. Edison [10, 11] and Tesla [12, 13] then patented their versions of thermomagnetic generators at the end of nineteenth century. In 1926 Debye [14] and in 1927 Giauque [15] independently discussed that if paramagnetic salts are adiabatically demagnetized, extremely low temperatures (under 1 K) could be achieved. This was experimentally proven in 1933 by Giauque and MacDougall [16]. In 1935, Urbain et al. [17] discovered ferromagnetism in gadolinium. This was the first ferromagnetic material discovered that has a Curie temperature near room temperature. However, it was not until the middle of the 1960s that the MCE of gadolinium was investigated [18, 19] by researchers from West Virginia University. This opened up the possibility of magnetic refrigeration devices operating near room temperature. In this manner Brown showed in his paper from 1976 [20] that gadolinium could be a possible MCM to be used in magnetic refrigeration. He built and experimentally tested the first-ever magnetic refrigeration prototype working near room temperature. From that point on the amount of research in magnetic refrigeration near room temperature started to increase. For example, Barclay and Steyert presented and patented the idea of an active magnetic regenerator in 1982 [21]. Active magnetic regeneration is an important invention in magnetic refrigeration. Active magnetic regeneration also implies that not only are the magnetocaloric properties of a material important, but also its thermal properties, as well as the manufacturability and processing properties to enhance the heat-transfer characteristics.

Another important milestone in magnetic refrigeration happened in 1997 with the discovery of the so-called giant MCE close to room temperature in a first-order transition material $Gd_5Si_2Ge_2$ by Pecharsky and Gschneidner [22]. The giant MCE observed at a transition temperature of 276 K was much higher (in terms of magnetic entropy change) than that of other known MCMs at that time. This discovery further increased the research on magnetic refrigeration near room

temperature. Nowadays, a lot of effort is put into the research and design of magnetocaloric devices; however, even more effort is directed at the research of new MCMs that would be suitable for use in near-room-temperature applications.

There are a number of different MCMs available for use near room temperature; these are thoroughly described in various reviews in the literature [23–28]. Furthermore, there is also a book written by Tishin and Spichkin [29] which describes numerous different MCMs in details.

In general, MCMs can be divided into two groups based on the order of their phase transition from the ferromagnetic to paramagnetic state, thus calling them second-order or first-order materials [30]. The phase transition happens at the certain temperature, referred to as the Curie temperature. Above the Curie temperature the spontaneous magnetization disappears and the material becomes paramagnetic. Furthermore, the MCE is most noticeable at this phase transition. The difference between first-order and second-order materials is how this transition takes place (Fig. 2.1).

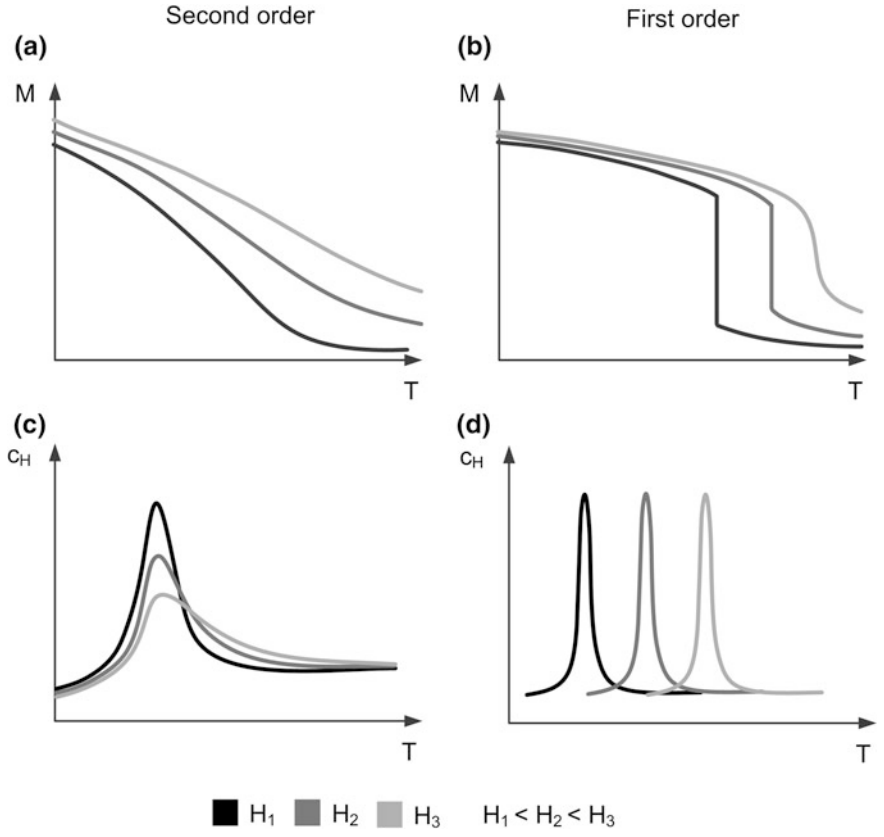

Fig. 2.1 Schematic general distinctions between second-order and first-order materials via magnetization (**a** and **b**) and specific heat (**c** and **d**) in relation to temperature and magnetic field

The characteristic of a second-order phase transition is the continuous change of the magnetization around the Curie temperature (Fig. 2.1a), while in the first-order phase transition the magnetization changes discontinuously at some temperature (Fig. 2.1b) with associated structural-deformation.

Regarding the magnetic entropy change, in second-order materials the magnetic entropy change increases with a larger magnetic field. In the first-order magnetic materials the entropy change only increases drastically to a certain value of magnetic field. However, with a larger field the magnetic entropy change becomes considerable over a wider temperature range.

Adiabatic temperature changes for both phase transitions increase their values with increasing field. However, in second-order materials the peak is broader than in first-order materials. Another important distinction between second- and first-order is in the specific heat (Fig. 2.1c, d). In second-order materials the specific heat is sharply peaked with a lower field and then decreases and broadens the peak without any significant shift in the peak temperature, while in first-order materials the specific heat significantly changes its peak-temperature position with larger magnetic fields, whilst not changing the peak values drastically.

Since this book is focussed more on an engineering approach to research and the design of magnetocaloric devices, the next pages of this chapter will present different MCMs from the engineering point of view rather than that of a material scientist. Some of the MCMs that are, at least at the moment, the most promising, will be presented. In this way, an engineer reading this book could get some initial impression about which direction she or he could focus her or his research and design of magnetic devices. Furthermore, some important issues and aspects regarding other characteristics (e.g. thermal, mechanical, chemical properties) will also be discussed.

2.1 General Criteria for the Selection of the Magnetocaloric Material

The MCMs as the coolants and the regeneration materials represent the most crucial elements of the magnetic refrigerator. Therefore, it is very important to apply the best material possible for a particular application. In general, they should have the following properties (see also e.g. [31]):

2.1.1 Suitable Curie Temperature of the Material

A precondition for the application of a MCM for a particular application is the suitability of its Curie temperature. With this we ensure that the MCE occurs at the required temperature or temperature range. The Curie temperature represents the

temperature of the phase transition of the magnetic material between the ferromagnetic and paramagnetic phases, which is related to the most pronounced magnetocaloric effect. It should be noted that the magnetocaloric effects at temperatures that are relatively far away from the Curie temperature are practically negligible (depending on the width of the temperature range of the magnetocaloric effect).

2.1.2 The Intensity of the Magnetocaloric Effect

The most important criterion for the selection of a MCM is the intensity of its magnetocaloric effect. The MCE manifests itself as the adiabatic temperature change and/or isothermal entropy change, which are related through the specific heat of the material (see Eqs. (1.14) and (1.19)). It should be noted that for applications of the MCM in the AMR its adiabatic temperature change is more important than the isothermal entropy change. The material is, therefore, more suitable for an application if it has a greater adiabatic temperature change on account of the smaller isothermal entropy change. This is strongly related to the heat-transfer characteristics between the material and the heat-transfer medium, since the heat-transfer irreversibility losses can strongly reduce the device's performance in the case of a small adiabatic temperature change, as is also explained in Sect. 4.5. A detailed analysis of the impact of the adiabatic temperature change and the isothermal entropy change on the AMR's performance is presented in [32].

2.1.3 The Wide Temperature Range of the Magnetocaloric Effect

It is a great advantage for the MCM to have a (large) MCE over as wide a temperature range as possible. This is especially important in an AMR where the temperature span is established over the material. With a wide temperature range for the MCE we ensure that the intense MCE occurs over the entire material, even in the parts of the material that are temperature-wise away from its Curie temperature. Since the great majority of currently known MCMs exhibit a MCE over a relatively narrow temperature range, a layering of different MCMs with different Curie temperatures along the length of the AMR (in a direction of the temperature gradient) is required. As also explained and shown in Sect. 4.2, the layering also ensures an intense MCE over the entire length of the AMR (with the established temperature profile). It should also be noted that the MCE of second-order phase-transition materials like Gd occurs over a relatively wide temperature range compared to the first-order phase-transition materials, e.g. Mn–Fe–P and La–Fe–Si alloys (see Sect. 4.2), where layering is therefore more important.

2.1.4 Near-Zero Hysteresis of the Magnetocaloric Effect

The MCMs should have as small a hysteresis as possible. The hysteresis occurs as the magnetic hysteresis (during an alternating magnetic field) and the thermal hysteresis (during heating and cooling). It should be noted that the hysteresis is, in general, related with the first-order phase transition and its structural changes, and in general does not occur in a second-order phase transition materials (e.g. Gd), which is a great advantage. However, both hystereses result in an energy loss and therefore, an increase in the input work of the thermodynamic cycle as the result of the entropy generation [33]. This can drastically reduce the MCE during the cycling operation as well as the efficiency of the magnetocaloric device. The impact of the hysteresis on the performance of the magnetic refrigerator can be found in [34, 35].

2.1.5 High Thermal Conductivity and Diffusivity

In general, the thermal conductivity and thermal diffusivity of the MCM should be as high as possible, since it ensures a faster temperature response and a more intense heat transfer between the material and the heat-transfer fluid. However, the high thermal conductivity of the MCM can also reduce the AMR's performance due to the heat flux along the direction of the temperature gradient in material, parallel to the fluid flow. This is especially pronounced in the case of a shorter AMR with an ordered geometry (where the material in AMR is continuous along its length) and a large temperature span. As shown in Nielsen and Engelbrecht [36], the optimal thermal conductivity of the MCM applied in a parallel-plate AMR strongly depends on the length of the AMR and the operating frequency. They showed that in the case of a long AMR (200 mm) the thermal conductivity should be as high as possible (up to 30 $Wm^{-1}K^{-1}$), regardless of the operating frequency (up to 4 Hz) and the temperature span, while in the case of a shorter AMR (50 mm) there is an optimal thermal conductivity for each operating frequency (the higher the frequency the higher the optimal thermal conductivity will be: around 10 $Wm^{-1}K^{-1}$ at 1 Hz and 30 $Wm^{-1}K^{-1}$ at 4 Hz). For example, Gd and its alloys with Er and Tb have a thermal conductivity around 10 $Wm^{-1}K^{-1}$, La–Fe–Co–Si alloys around 8 $Wm^{-1}K^{-1}$ and La–Ca–Sr–MnO_3 ceramics around 1 $Wm^{-1}K^{-1}$.

2.1.6 Good Manufacturing Properties

It is desirable for the MCMs to have good manufacturing, casting, mechanical and processing properties, which allow them to be fabricated into the desired shape, suitable for use in an efficient AMR. The impact of the geometrical properties of the

AMR on its performance is presented in Sect. 4.4, while the review of the different applied fabrication techniques for the AMRs is given in Sect. 4.7.

2.1.7 High Electrical Resistivity

The high electrical resistivity of the MCM prevents the generation of eddy currents (which results in energy dissipation and heating of the material) under the influence of the changing of the external magnetic field. However, in a typical AMR, operating with frequencies up to 10 Hz, the impact of the eddy currents are, in general, negligible, but for applications at higher operating frequencies this might play an important role. For details of the energy dissipation due to the eddy currents in magnetic materials see, e.g. [37].

2.1.8 Good Corrosion Properties

It is preferable that the MCM does not corrode when in contact with water (or other heat-transfer fluids). From this point of view the ceramic manganite MCMs (e.g. La–Ca–Sr–MnO_3) have a certain advantage as they are non-corrosive. However, as explained in Sect. 4.6 the corrosion of other MCMs can be prevented by adding the proper inhibitors to the heat-transfer fluid.

2.2 Most Common Magnetocaloric Materials with a Near-Room-Temperature MCE

The subsequent subsections are intended to present groups of different MCMs that are currently the most promising in the field of magnetic refrigeration near room temperature. Only a brief description of the different materials are given to show the design engineer of the magnetocaloric prototypes basic idea of how to approach MCMs so as to apply them in the AMR. Detailed descriptions, reviews and studies of MCMs are already well covered in the known literature and are also more of the domain of material scientists.

Note that the majority of studies on different MCMs report their MCEs in the form of magnetic entropy change. This is, of course, a fundamental physical property for defining the MCE; however, in terms of system design and heat transfer it would be more useful to also have the data for the adiabatic temperature change and the specific heat for given MCMs. In this way, one could quickly consider the different MCMs to be suitable for the AMR design, at least during the initial design stages.

2.2.1 Gd and Its Alloys

Gadolinium (Gd) is definitely the most common MCM for magnetic refrigeration near room temperature. It is the only pure element that exhibits a MCE near room temperature ($\sim$293 K). Furthermore, its magnetocaloric properties are fairly good ($\Delta T_{\text{ad}} = 3.3$ K, $c_H = 300$ Jkg^{-1}K^{-1}, $\Delta s_M = 3.1$ Jkg^{-1}K^{-1} at magnetic field change of 1 T [38]), making it a strong candidate for use in magnetic refrigeration. Actually, gadolinium has already been thoroughly investigated and characterized for use as a constituent of various AMRs in different magnetic refrigeration devices as it is reviewed later in Chap. 7 on magnetic prototypes. As a result, Gd is known as a kind of reference material when considering different MCM candidates for an AMR design. However, one of the most important factors when choosing Gd is its purity. As was shown by Dan'kov et al. [39], different impurities in Gd may significantly alter its magnetocaloric properties.

However, introducing different amounts of other elements to make alloys with Gd can also have positive effects. Especially in terms of designing layered AMRs. For instance, different ratios of Gd and Mn in Gd–Mn alloys can lower the T_C to 278 K without any drastic changes in the MCE, as was shown by Jayaraman et al. [40, 41]. Furthermore, for example, in Gd–R alloys, where R is some other rare-earth element (Tb, Dy, Ho, Er) the T_C may also be shifted to lower temperatures [42]; however, without any drastic changes in their MCEs. For instance, Kaštil et al. [43] presented the MCE in Gd–Tb alloys. By changing the Tb content they could shift the Curie temperature of Gd–Tb alloys in the temperature range from 269 to 294 K, with an average adiabatic temperature change of approximately 2.5 K for a 1 T magnetic field change.

On the other hand, the Curie temperature T_C may also be shifted above that of pure Gd, which can be suitable in magnetic heat pumping or magnetic power generation. For instance, Couillaud et al. [44] presented the magnetocaloric properties of two MCMs, Gd–Sc–Ge and Gd–Sc–Si. The former has a T_C of 348 K and a magnetic entropy change Δs_M of 2.5 Jkg^{-1}K^{-1} from 0 to 1.5 T, while the latter has a T_C of 252 K and Δs_M of 2 Jkg^{-1}K^{-1} when changing the magnetic field from 0 to 1.5 T. Furthermore, Law et al. [45] showed that different ratios of elements in Fe–Gd–Cr–B alloys can lead to an increase in T_C above 400 K. However, the magnetic entropy change for the materials with a Curie temperature around such high temperatures can decrease to approximately 1 Jkg^{-1}K^{-1} for magnetic field change from 0 T to 1.5 T.

However, there is a group of Gd-based alloys that exhibit a remarkable MCE, noticeably higher than that of pure Gd and the above-mentioned alloys. These are the first-order Gd–Si–Ge alloys. These alloys exhibit the so-called giant magnetocaloric effect. The giant MCE was discovered in 1997 in $Gd_5Si_2Ge_2$ by Pecharsky and Gschneidner [22]. The same researchers later showed that by varying the Si-to-Ge ratio and by introducing small amounts of Ga into the Gd–Si–Ge the giant MCE may be tuned in the temperature range between approximately 20 and 305 K [42]. The MCE (in terms of magnetic entropy change) of Gd–Si–Ge is near room

temperature at least two times higher than that of pure Gd. However, due to its first-order nature, Gd–Si–Ge alloys display a high magnetic hysteresis, which can drastically contribute to the parasitic losses in the magnetocaloric device.

However, the main drawback of Gd (and its second-order transition alloys) is its price, which limits its practical application. However, its magnetocaloric, thermal and manufacturing properties and the absence of hysteresis make it currently the best MCM for room-temperature magnetic refrigeration.

2.2.2 La–Fe–Si-Based MCMs

La–Fe–Si-based MCMs are well represented in magnetic refrigeration and are considered to be one of the possible alternatives to the expensive Gd-based MCMs.

The basis of La–Fe–Si materials is a hypothetical compound $LaFe_{13}$, which does not exist. However, by substituting a certain proportion of the Fe for Si or Al one can make a stable compound. For instance, in 2001 Hu et al. [46] discovered a first-order transition at 208 K in the compound $LaFe_{11.4}Si_{1.6}$. Later researchers discovered that the Curie temperature can be tuned by adding H to the structure of La–Fe–Si, as, for example, was presented by Fujita et al. in 2003 [47, 48]. Furthermore, researchers also found that the T_C may also be tuned by partially substituting Fe with Al, Co or Mn. This was presented by several authors, such as Katter et al. [49], Hansen et al. [50] and Bjørk et al. [38]. These kinds of substitutions may also alter a material's transition from first to second order.

Nowadays, there is a substantial number of different La–Fe–Si-based MCMs, which were thoroughly reviewed by Shen et al. [24]. One of the major issues regarding such materials is their long-term stability. However, this can be avoided by properly processing the material [51]. La–Fe–Si-based MCMs have a great potential to be used in layered AMRs, since their T_C may be tuned in a temperature range from approximately 200 to 340 K. Regarding their magnetocaloric properties, La–Fe–Si-based materials exhibit a larger magnetic entropy change than that of Gd. It may vary from approximately 5 to 12 $Jkg^{-1}K^{-1}$ (regarding magnetic field change of 1.6 T) [49, 51], depending on the material. The adiabatic temperature change is, for a magnetic field change from 0 to 1.4 T, in the range of 2.8 K [38]. La–Fe–Si-based materials have a substantially higher specific heat than Gd (from approx. 1,200 $Jkg^{-1}K^{-1}$ at 0 T to 700 $Jkg^{-1}K^{-1}$ at 1.4 T [38, 51]).

The reasons why La–Fe–Si-based MCMs are so appealing for use in magnetocaloric devices lie mostly in their low cost (in comparison to Gd). Some of the materials also exhibit no or low magnetic hysteresis, which is positive from the device-performance point of view. Moreover, the technology for producing such materials and then processing them is available for large-scale industrial production [49].

2.2.3 Mn-Based MCMs

Compounds with Mn are another large group of MCMs with the potential to be used in magnetic refrigeration. A comprehensive review on Mn-based MCMs was recently presented by Brück et al. [25]. In 2001, Wada et al. [52] presented a giant MCE in the compound Mn-As. It has a Curie temperature around 317 K with a magnetic entropy change of approximately 40 $Jkg^{-1}K^{-1}$ (when changing the magnetic field from 0 to 2 T), which is substantially larger than that of $Gd_5Si_2Ge_2$. Wada et al. [52] also showed that increasing the magnetic field above 2 T does not contribute much more to the increase in Δs_M. One of the issues associated with Mn–As is that it exhibits a large hysteresis due to its first-order nature. However, the hysteretic behaviour as well as the Curie temperature may be adjusted, to some extent, by substituting a certain proportion of As with Sb [52], making a Mn–As–Sb compound. Later in 2002, Tegus et al. [53] presented a new Mn-based compound Mn–Fe–P–As. By adjusting the P/As ratio, their T_C may be significantly tuned in a large temperature range from 150 to 335 K. For example, the compound $MnFeP_{0.5}As_{0.5}$ has a T_C at 280 K with a magnetic entropy change of 25 $Jkg^{-1}K^{-1}$ (2 T) [54]. A slight change of the P/As ratio in the compound $MnFeP_{0.45}As_{0.55}$ shifts its T_C to 306 K, while the magnetic entropy change decreases to 13 $Jkg^{-1}K^{-1}$ (2 T) [25, 55], which is still quite substantial. In 2011 Dung et al. [56] discovered that the hysteresis in Mn–Fe–P–As may be tuned by changing the Mn/Fe ratio. Furthermore, adjusting the Mn/Fe ratio may also lead to a change from a first- to second-order transition.

Another interesting group of Mn-based MCMs is the Mn–Fe–P–Si–Ge alloys [57]. Their main advantage is that they do not contain toxic As. Mn–Fe–P–Si–Ge materials exhibit a similar MCE to Mn–Fe–P–As. However, Mn–Fe–P–Si–Ge materials have a large hysteresis, which can also be tuned by changing the concentrations of Fe and Mn. In this manner, the Curie temperature can also be varied to some extent [58].

2.2.4 Manganites

Another group of materials that show a potential for use in magnetic refrigeration near room temperature are the perovskite manganites, which are basically ceramic materials. Their general formula may be expressed as $R_{1-x}M_xMnO_3$, where R = La, Nd or Pr and M = Ca, Sr or Ba. There is a large number of different manganite MCMs, which were comprehensively reviewed by Phan and Yu [26]. Manganites are second-order materials, thus exhibiting a low MCE (lower than Gd). However, their Curie temperature may be tuned over a large temperature range. For example, the manganites $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ (LCSM) can be tuned for their Curie temperature in the range from 267 to 369 K by changing the x value from 0 to 0.33 [59]. The LCSM compound (x = 0) with a Curie temperature of 267 K has a

magnetic entropy change of 5.9 $Jkg^{-1}K^{-1}$ and an adiabatic temperature change of 2 K (from 0 to 1.2 T). However, the MCE decreases with increasing x value. Therefore, the LCSM compound (x = 0.055) with a Curie temperature of 285 K (which is relevant for near-room-temperature magnetic applications) has a magnetic entropy change of 2.8 $Jkg^{-1}K^{-1}$ and an adiabatic temperature change of 1 K for a magnetic field change from 0 to 1.2 T. In spite of the LCSMs having a rather low MCE, they are still a promising group of MCMs that could be used in magnetic refrigeration. This is mostly due to their low price, good corrosion resistance, the easy tunability of the T_C and the ease of processing [30].

2.2.5 *Layered MCMs*

As stated in Sect. 2.1 (*General criteria for the selection of the MCM*), one of the important characteristics of MCMs is to have a large MCE over as wide a temperature range as possible, since the AMR should operate with a large temperature span. Since the MCMs exhibit their largest MCE around their Curie temperature, the idea has been developed to build the AMR from different MCMs along the regenerator. Each material should have its Curie temperature (and therefore the largest MCE) in a different temperature range. In this way, the AMR could have a significant MCE across its full operating temperature span. As was presented in the previous sections on different MCMs, the tuning of Curie temperatures is of course possible by changing the concentrations of the certain elements in magnetocaloric compounds. Building the AMR from several MCMs with different Curie temperatures will lead to a step-wise change in the Curie temperatures along the AMR's length (Fig. 2.2a).

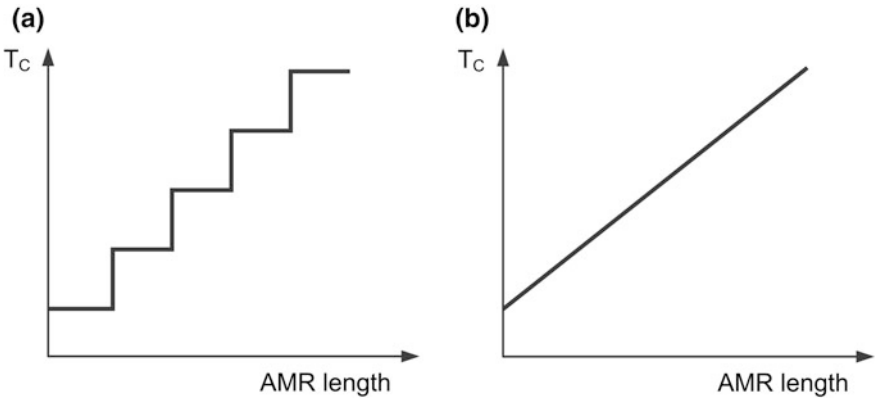

Fig. 2.2 **a** A schematic diagram of a step-wise T_C; **b** Linearly continuously T_C layered AMR

Table 2.1 Some MCMs with their magnetocaloric properties near room temperature

Material	T_C (K)	$-\Delta s_M$ ($Jkg^{-1}K^{-1}$)	ΔT_{ad} (K)	ΔB (T)	$q_{R,max}$ (Jkg^{-1})	References
Gd	~293	3.1	3.3	1	913	[38]
$Gd_{0.9}Tb_{0.1}$	~286	2.3	1.9	1	1,148	[43]
$Gd_5Si_2Ge_2$	~278	14	7.3	2	3,943	[22]
$LaFe_{11.06}Co_{0.86}Si_{1.08}$	~276	6.1	2.3	1	1,690	[38]
$LaFe_{11.05}Co_{0.94}Si_{1.01}$	~287	5.1	2.1	1	1,469	[38]
$LaFe_{10.96}$ $Co_{0.97}Si_{1.07}$	~289	5.3	2.2	1	1,537	[38]
$La(Fe_{0.88}Si_{0.12})_{13}H$	~274	19	6.2	2	5,264	[48]
$La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$	~291	24	6.9	2	7,066	[48]
$La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$	~323	19	6.8	2	6,201	[48]
MnAs	~318	31	4.7	2	9,930	[52]
$MnFeP_{0.45}As_{0.55}$	~306	12.5	2.8	1	3,842	[55]
$Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$	~292	11	2.8	1	3,227	[55]
LCSM ($x = 0$)	~267	5.9	2.0	1.2	1,581	[59]
LCSM ($x = 0.055$)	~285	2.8	1	1.2	800	[59]
LCSM ($x = 0.165$)	~332	1.8	0.93	1.2	598	[59]

An overview of a numerical and experimental analysis of layered AMRs is presented in Sect. 4.2. However, recently, a new material was presented by Barcza et al. [60]. They presented a layered $LaFe_{13-x-y}Co_xSi_y$ material in which the Curie temperature changes continuously along the length. They managed to produce such a layered material by pressing several powders with different Curie temperatures on top of each other with a subsequent sintering and diffusion treatment [60]. In this manner gradients of the Curie temperature between 0.3 and 10 Kmm^{-1} were obtained. The general idea is to make such a material in which the Curie temperature gradient would linearly and continuously change along the length (Fig. 2.2b).

2.2.6 Conclusions

In the above sections a brief review of some of the most common MCMs that exhibit a MCE close to room temperature were presented. In this way the reader can obtain a general impression about which direction to search in the study of magnetic refrigeration, heat pumping or power generation. There are a number of extensive and thorough reviews on MCMs of different sorts already published in the literature, if the reader needs to study MCMs in more detail.

In conclusion, Table 2.1 shows some of the most interesting types of MCMs with regards to their MCE.

Only materials for which the data regarding their magnetic entropy change and adiabatic temperature change were available are shown. In this manner the maximum specific cooling energy $q_{R,\max}$ can also be given. The maximum specific cooling energy $q_{R,\max}$ is explained in more details in Chap. 4 (Active magnetic regeneration, Sect. 4.1.4). However, in general, it can be expressed using the following equation:

$$q_{R,\max} = \frac{(2T_R + \Delta T_{\mathrm{ad}})\Delta s_M}{2} \tag{2.1}$$

where for the examples in Table 2.1 T_R is the Curie temperature T_C with the corresponding magnetic entropy change $-\Delta s_M$ and adiabatic temperature change ΔT_{ad}. As is clear from Table 2.1 different MCMs have different Curie temperatures.

In this manner, the parameter $q_{R,\max}$ could be significant when designing layered AMRs. For example, when designing a magnetic refrigerator that would operate at a certain temperature span it would make sense to choose the material at the cold end of the AMR with the highest maximum specific cooling energy $q_{R,\max}$.

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