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Introduction to magnetic refrigeration: magnetocaloric materials

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Abstract

This work presents a review of research work on the magnetic refrigerator, of which different research is presented. The principle of magnetic refrigeration at room temperature and its interests has been shown. The phase transitions, first-order and second-order, have been shown with the advantages and disadvantages of both. Indeed, the first-order materials benefit from high magnetic entropy and adiabatic temperature change. Their negative point consists in their great magnetic hysteresis. It is quite the opposite for second-order phase transition materials. An overview of existing materials and characterization of magnetocaloric effect have been explained.

Keywords Magnetic refrigerator, Magnetocaloric materials, Room temperature, Magnetocaloric effect, Magnetic entropy change, Adiabatic temperature change, Hysteresis, Room temperature

1 Introduction

According to the 20th Information Note of the IIR on refrigeration techniques (2007), it is possible to replace HFC refrigerants by magnetocaloric alloys harmless to the environment by using magnetic refrigeration at room temperature. This principle is ancient, based on a thermomagnetic observations made in 1600 by W. Gilbert [1] better interpreted by the German physicist Emil Warburg [2], who in 1881 discovered the magnetocaloric effect in iron at the Curie temperature of $T_C \approx 1043$ K. This effect is manifested by a temperature rise (or drop) during a sudden application (or deactivation) of an external magnetic field. In 1918, physicists Pierre Weiss and Auguste Picard demonstrated the reversibility of this "Magneto-Caloric effect" (MCE) [3], paving the way for the creation of many prototypes and a very wide literature. The first system, reaching 0.25 K for 0.08 Tesla under 1 W, was produced by the Nobel chemist W. F. Giauque in 1933 when he used the gadolinium salt $Gd_2 (SO_4)_3 8H_2O$ in his cryogenics demonstration [4].

In 1951, Darby et al. create a two-stage magnetocaloric regenerator with materials having different Curie points. They go down to 3 mK for an induction of 0.42 T. Subsequently a large number of prototypes with multiple Curie points have been designed [5].

Magnetic refrigeration at room temperature began almost a hundred years after the discovery of the magnetocaloric effect, when in 1976 Brown developed an efficient refrigeration system using gadolinium as an active material and an electro-magneticMagnet developing a magnetic field of 7 Tesla. This resulted in a temperature difference of about 47 K between the hot and cold sources. For heat transfer, he used a fluid based on water and alcohol [6].

In 1997, Gschneidner discovered "giant magnetocaloric materials" at room temperature in gadolinium-germanium-silicon alloys (Ga-Ge-Si) [7]. In 1998, Zimm developed a prototype demonstrating the feasibility of magnetic cold close to room temperature [8]. These last three advances have enabled magnetic cold to experience exponential development (Fig. 1) [9].

In 2001, the first magnetic refrigerator operating at room temperature equipped with a permanent magnet

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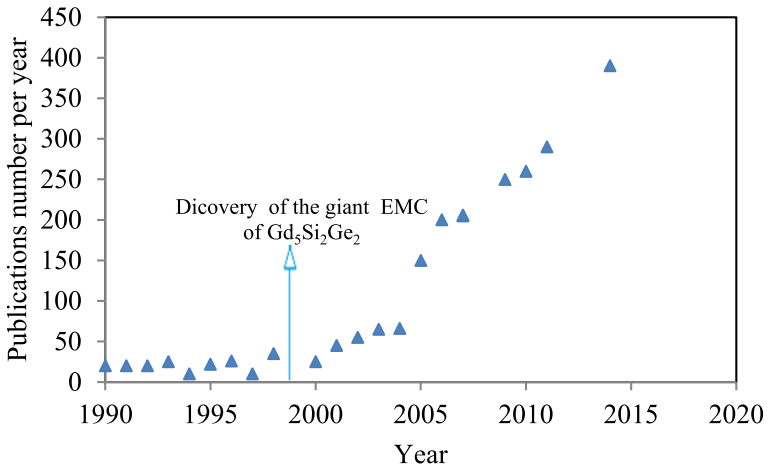

Fig. 1 Number of publications published annually containing the word "magnetocaloric" [10]

was made by the members of the Astronautics Cooperation of America [11].

The different expressions of the magnetic work ($-MdB$) linked to the system yet essential to the establishment of the first law of thermodynamics have been presented by [10, 12–15].

The interests of magnetic refrigeration are no compressor, free of ozone-depleting gases, reduction in the energy required by approximately 35%, according to certain studies (the only energy required is that necessary to run the engine and the water pumps), safe cooling with no impact on the environment, can reach temperatures of 4 K (− 269 °C), high reversibility (quasi reversibility), and therefore greater efficiency. This leads to a much better energy efficiency, compact, silent, and practically without mechanical vibration. These advantages offer potential applications of magnetic refrigeration in many areas of industry where it can compete with conventional thermodynamic refrigeration systems such as domestic or industrial refrigeration, residential air conditioning, automotive air conditioning, cooling of portable systems (electronics, medical...), and gas liquefaction.

This review article aims to highlight the most popular magnetic materials in the field of magnetic refrigeration at room temperature and present the three methods of characterization of the magnetocaloric effect. The present paper puts more emphasis on demonstrating the advantages and disadvantages of first-order and second-order phase transition magnetic materials.

2 Characterization of magnetocaloric effect

Magnetic refrigeration is a system for reducing the entropy of a paramagnetic or even ferromagnetic material [16], based on the physical property of certain magnetic materials, which see their intrinsic temperature rise when they are subjected to a magnetic field (Fig. 2); conversely, demagnetization leads to cooling (Fig. 3). This phenomenon is called the magnetocaloric effect "MCE". This effect depends on the critical paramagnetic transition (randomly orientated spins)/ferromagnetic transition (aligned and parallel spins) of the material. If one draws an analogy between the traditional vapor compression cycle and magnetic refrigeration, one can see that evaporation and condensation correspond respectively to

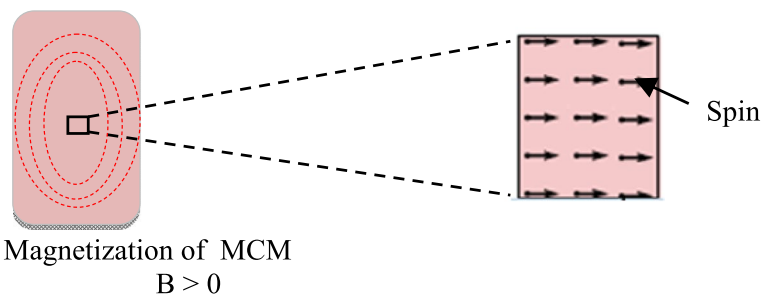

Fig. 2 Ferromagnetic behavior (Aligned and parallel magnetic moments)

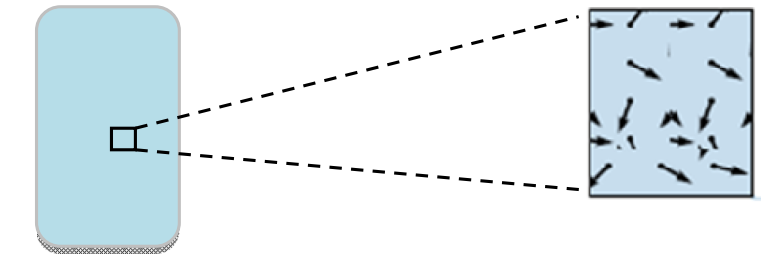

Fig. 3 Paramagnetic behavior (randomly oriented magnetic) moments

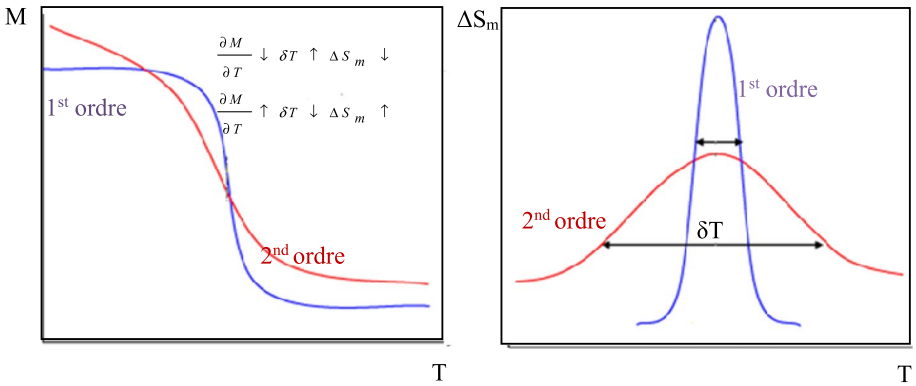

Fig. 4 Phase transitions and associated magnetic entropy variations [17]

the demagnetization and magnetization of the magnetocaloric material "MCM".

In the vicinity of the Curie temperature, magnetic variations are very important and cause strong evolutions of magnetic entropy. In addition to the applied magnetic field, the magnetocaloric effect also depends significantly on the nature of the magnetic transition in the material, as illustrated in Fig. 4 [17].

Materials with a first order of transition phase have the following characteristics: (i) large variations of the magnetic entropy ΔS_m (T); (ii) large variations in the temperature ΔT_{ad} but over a small temperature range δT because the first order transitions are abrupt and the magnetization changes very quickly with the temperature; (iii) however, as the losses by hysteresis (or magnetic losses) lead to the irreversibilities of these systems. Indeed, the magnetization of a magnetic circuit absorbing the energy, this energy is not completely restored during the demagnetization, a part of the energy is dissipated as heat; (iv) heir slow kinetics can reduce the efficiency of materials with a magnetocaloric effect, because Maxwell's relation which links entropy and magnetization can only be used in the case of a system in equilibrium. In addition, these materials may have other disadvantages such as early aging due to structural modifications generally accompanying these transitions.

The materials with the second order of transition include the following specifications: (i) involve a small variation in magnetic entropy ΔS_m (T); (ii) involve a small variation ΔT_{ad}, but their effects extend over a wider range of temperatures δT; (iii) are free from penalizing phenomena such as hysteresis (Fig. 5), slow kinetics and structural modifications.

An example hysteresis loop is shown below (Fig. 5). A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). The B-H curve will only determine the behavior of ferromagnetic material when it is placed in a magnetic field. Indeed, under the application of an external magnetic field H (created for example by circulation of a current in a solenoid and expressed in Am^{-1}), a magnetic induction field B_0 is created in vacuum, capable of to elicit magnetic behavior in a material. The magnetic field B is proportional to the field H; the combination of the coercive field H_C necessary for demagnetization and the remanent induction B_R implies that the curve presents a hysteresis loop [18].

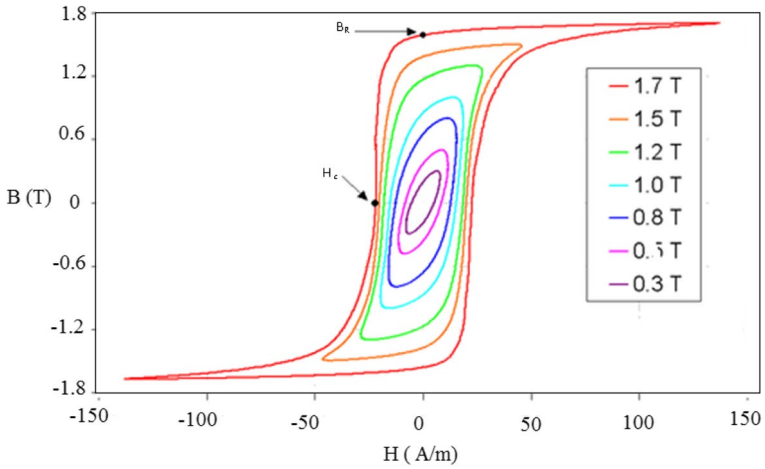

Fig. 5 Hysteresis cycles of the magnetization of a ferromagnetic material (standard grain-oriented electrical steel) [18]

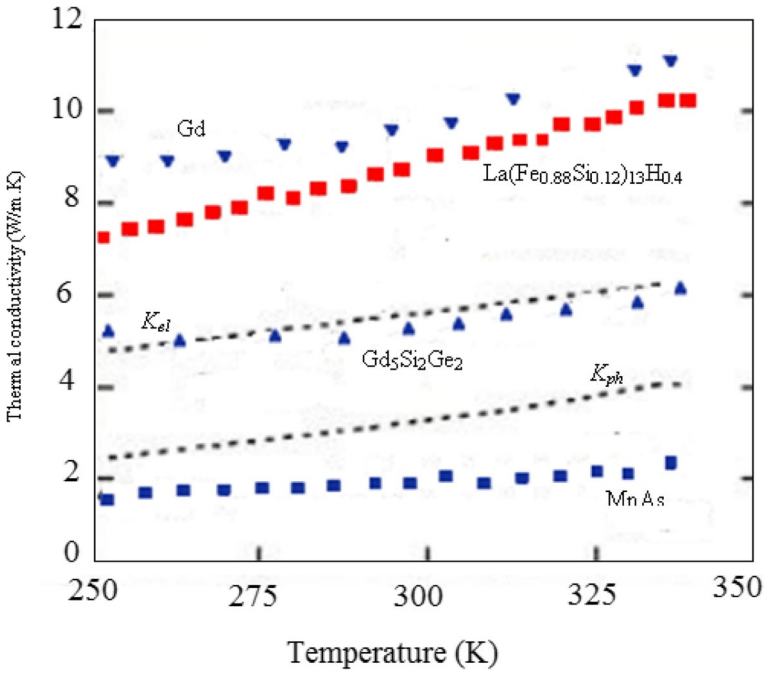

Fig. 6 Thermal conductivity as a function of temperature of different MCM [20]

Chennabasappa showed in his thesis that the thermal conductivity which partly depends on the microstructure (Fig. 6), the magnetocaloric cyclability and the sensitivity to corrosion are essential for a concrete use of the material [19].

Magnetic entropy is maximum at zero fields (demagnetized state) in the paramagnetic phase above the transition temperature called T_C Curie temperature which has been demonstrated by [21]. It is reduced by the action of a magnetic field, which is explained by the alignment of magnetic moments in the ferromagnetic phase. This means that the magnetocaloric effect is maximum around the Curie temperature (Fig. 7).

To characterize MCE, there are three methods which are: direct measurements of temperature variation ΔT_{ad}, calorimetric measurements and magnetic measurements.

The direct measurement of temperature variation as a function of applied field and temperature have used by [22, 23]. They have shown that the accuracy of this measurement depends on the accuracy of the temperature measurement and the adiabatic quality of the system and that the decrease in exchanges is achieved, either by

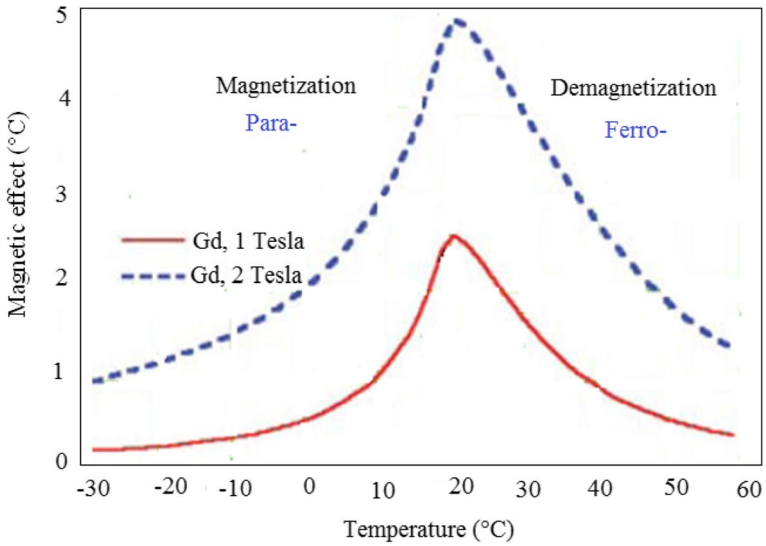

Fig. 7 Magnetocaloric effect of gadolinium by Astronautics Technology Center cited by [21]

reinforcing the thermal insulation, or by performing very fast measurements. They also showed that this method also allows evaluating the entropy *crée* due to the irreversibility of the cycle. Despite, seems the most obvious principle, but only allows measurements at a fixed temperature and at relatively weak fields of 1 Tesla.

Calorimetric measurements of the heat flux and temperature of the sample to determine entropy variations by Eq. (1) were used by [24–27].

$$\Delta T_{ad}(T, \Delta B) = -\frac{T}{C_B(T,B)}\Delta S_m(T.\Delta B) \tag{1}$$

As the measurements of the thermal flow between the sample and the thermal source, while the field or the temperature of the source evolves, are difficult, these researchers used differential techniques DSC (differential scanning calorimeter).

The method of measuring the magnetic moment (T, B) gives the magnetization $M(T, \mathrm{B})$ at thermodynamic equilibrium and on a reversible path, which excludes metastable states and hysteresis phenomena, Maxwell's relation is used to obtain information on entropy and heat capacity [28, 29]. From magnetic measurement performed at discrete temperature intervals, the magnetic entropy change can be approximated as Eq. (2):

$$\Delta S_m = -\sum_j \frac{M_{i+1} - M_i}{T_{i+1} - T_i}\Delta B_i \tag{2}$$

Where M_{i+1} and M_i are the magnetization values measured in a magnetic field B, at temperatures T_{i+1} and T_i, respectively.

The magnetic measurement is the best and most used method, especially at a temperature close to room temperature, and it allows rapid evaluation of the magnetocaloric performance of materials with a relative error from 3 to 10% but whether it is better to work at a fixed field or temperature.

3 Magnetocaloric materials

The magnetocaloric characteristics of 4f lanthanide metals where the gadolinium metal of the second-order phase transition was the first MCE analyzed by Brown [6]. This one is readily available and has good characteristics with an adiabatic temperature change of about 3 K for an applied magnetic induction of 1Tesla and has a relatively high magnetocaloric effect of 2.6 K/Tesla of a Curie temperature around room temperature 294 K. However, gadolinium is easily corroded, oxidizable, has a cooling capacity limited to a temperature of 300 K and is quite expensive.

Afterwards, Pecharsky and Gschneidner [7] discovered an extraordinarily large magnetic entropy change in Gd_5 (Si_2Ge_2) of 3.65 K/T twice that of gadolinium due to a first- order (ferromagnetic (I) ↔ferromagnetic (II)) phase transition at around the Curie temperature 276 K with an adiabatic temperature change of about 15 K. The magnetic entropy change is about $13 J.kg^{-1}.K^{-1}$ in comparatively low magnetic fields up to 2 Tesla. Nevertheless, it can only be operated below room temperature (Fig. 8). This is the main concept that has revolutionized the field of magnetic refrigeration at room temperature [7]. Gd_5 (Si_2Ge_2) compounds covered a wide range of applications by simply varying the concentrations

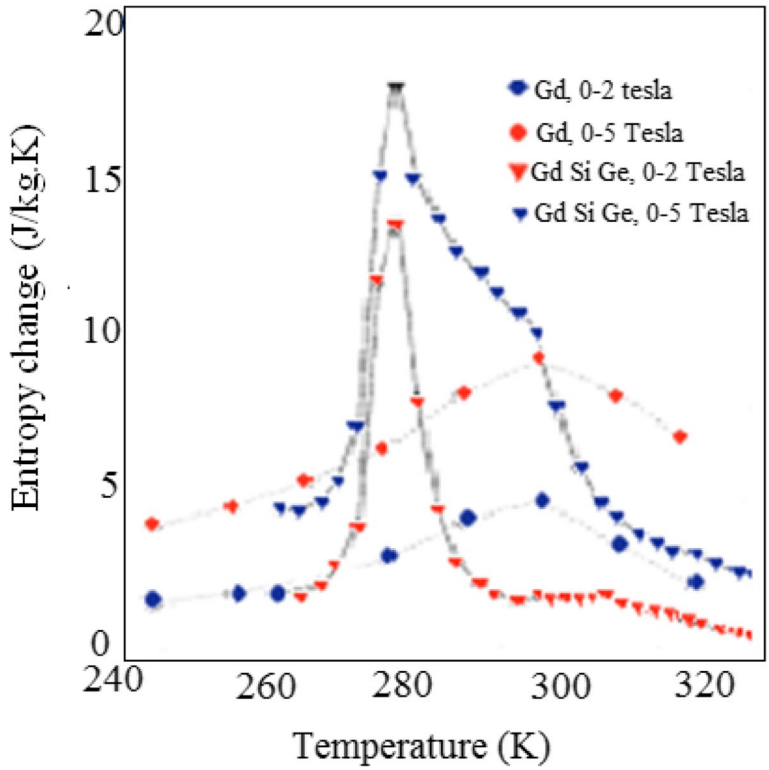

Fig. 8 Magnetic entropy change of first-order material (G_d S_iG_e) and second-order material (G_d) for B=2 and 5Tesla

of germanium and silicon. A concentration ranging from 0.5 to 1.0, allowing having a Curie temperature between 290 K and 335 K. These compounds have as the main disadvantages their high price and a significant hysteresis.

Since the discovery of the giant magnetocaloric effect of $Gd_5(Si_2Ge_2)$ in 2000, a new series of magnetocaloric materials has been developed. Phospho-arsenide $MnFeP_{1-x}As_x$ is a material derived from iron-Fe_2P phosphide where the variation of the phosphorus and arsenic fraction between 0.25 and 0.65 gives a Curie temperature variation of 150 to 340 K allowing magnetic refrigeration at room temperature. For example, the magnetic entropy changes of $MnFeP_{0.45}As_{0.55}$ reach values of 14.5 $J.kg^{-1}.K^{-1}$ and 18 $J.kg^{-1}$ K^{-1} for field changes of 2 and 5 Tesla respectively (Fig. 9). The current adiabatic temperature change values are approximately 4–7 K in 2 Tesla. The variation in magnetic entropy of the $MnFeP_{1-x}As_x$ is twice that observed for pure gadolinium and similar to that exhibited by $Gd_5(Si_2Ge_2)$. The large entropy change of $MnFeP_{1-x}As_x$ is attributed to a field-induced first-order phase transition, enhancing the effect of the applied magnetic field. However, two difficulties appear in their implementation. First difficulty, these materials are complex to prepare on a large scale due to the high volatility of certain components (boiling temperature of As at 600 °C). Second, the presence and use of toxic arsenic is regulated [30, 31].

In a study of the magnetocaloric effect of three generations of MnFe (*P*, *X*=As, Ge, Si) materials, it was found that by combining the large change in magnetic entropy and adiabatic temperature in intermediate magnetic fields, The limited thermal magnetic hysteresis, easy adjustment of Curie temperatures and other practical advantages such as cheap and non-toxic raw materials, makes the $MnxFe_{1.95-x}P_{1-y}$ Si_y family very promising for magnetic refrigeration applications. The negative point of $MnFeP_{1-x}$ As_x materials are the presence of toxic As [32].

Manganese compounds The MnAs, although having a transition of the first order, they displayed bad results, they have a very small change of adiabatic temperature about 2.5 K for 1Tesla, because of the hysteresis of important transition. The magnetic entropy change is around 40 $J.kg^{-1}.K^{-1}$ for 5Tesla, the first-order ferromagnetic to paramagnetic transition takes place at $T_C = 318$ K [33]. MnAs0.9 Sb0.1 was obtained by substituting 10% of As by Sb which reduces the thermal hysteresis of MnAs and lowers the Curie temperature to 280 K. the magnetic transition, previously of the first order, is of the second order; which has the effect of reducing the giant magnetocaloric effect but in this case the giant magnetocaloric properties are maintained. From an economic point of

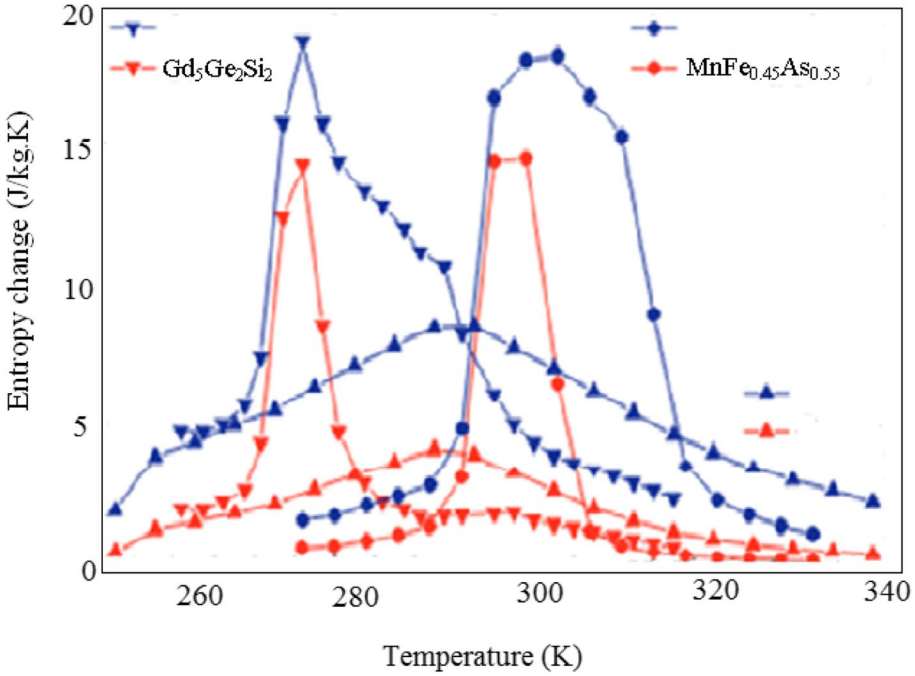

Fig. 9 Magnetic entropy change of MnFeP0.45As0.55, G_d , $Gd_5Ge_2Si_2$. Data are shown for external magnetic field changes of 0 to 2 T (red), and 0 to 5 T (blue), calculated from the magnetization data

view, MnAs and $Mn(As_{1-x}Sb_x)$ consist of inexpensive elements but are difficult to manufacture given the high toxicity of arsenic and antimony [33].

A study of $Mn_5Ge_{3-x}Sb_x$ compounds showed that with $x = 0$, 0.1, 0.2, and 0.3 the temperature range ranges from 5 to 350 K. The adiabatic temperature change is in the order of 298 K, 304 K, 307 K, and 312 K, corresponding to the changes in magnetic entropy 9.3 $J.kg^{-1}.K^{-1}$, 66 $J.kg^{-1}.K^{-1}$, 6.2 $J.kg^{-1}.K^{-1}$, and 5.6 $J.kg^{-1}.K^{-1}$, respectively, for 5Tesla. For $x = 0$, the Curie temperature of Mn_5Ge_3 in a field of 5 Tesla is 298 K (Fig. 10) this is in good agreement with the reported value of 296 K. It is clear that the compounds retain their ferromagnetic order. The Sb substitution results in an increase of the Curie temperature and decreases of magnetic entropy change. The other effect is the MCE peak that becomes broadened [34].

The $CoMnSi_{1-x}Ge_x$ material exhibits a significant magnetocaloric effect in large fields 5 Tesla with the size of the effect at lower fields being inhibited by the proximity of the metamagnetic transition to the Curie temperature transition of this material. The rate at which the metamagnetic transition temperature changes with applied field is very large as high as 50 K $.T^{-1}$ in low fields. As it can be seen that in Fig. 11, the isothermal entropy change at the metamagnetic transition in CoMnSiGe is smaller than CoMnSi [35].

The compositional dependence of magnetic entropy change was investigated experimentally by when they exhibited a significant magnetocaloric effect of Heusler alloys $Ni_{2+x}Mn_{1-x}Ga$. They noted that, the best magnetic entropy change of 20.7 ± 1.5 J/K kg in the magnetic field of 1.8Tesla was revealed in the $Ni_{2.18}Mn_{0.82}Ga$ alloy at a Curie temperature of 333.2 K (Fig. 12) [36]. Given these good performances, the alloys Ni–Mn–Ga would be suitable for magnetic refrigeration as a regenerator for operating temperatures between 300 and 350 K. However, the disadvantages of these intermetallics generally containing Ga or Ge associated with first-order transitions limit the use of these alloys due a large thermal hysteresis of the order of 7 K [37].

The researchers discovered in a polycrystalline sample of $La_{0.5}Gd_{0.2}Sr_{0.3}MnO_3$ oxides a large change in magnetic entropy with a large peak around the Curie temperature of 270.5 K (Fig. 13). Moreover, the maximum of magnetic entropy change of the colossal magnetoresistance material $La_{0.5}Gd_{0.2}Sr_{0.3}MnO_3$ exhibits a nearly linear dependence with the applied high magnetic field. These results suggest that this material is a suitable candidate as the working substance in magnetic refrigeration near room temperature. However, the performances of these materials remain modest around ambient, being at best "comparable" to those of gadolinium [38].

The polycrystalline La1−xK $xMnO_3$ perovskites it is reported $T_C = 287$ K for $x = 0.1$ and $T_C = 310$ K for $x = 0.15$ [39] $x = 0.125$ for $T_C \approx 295$ K on the weak field [40].

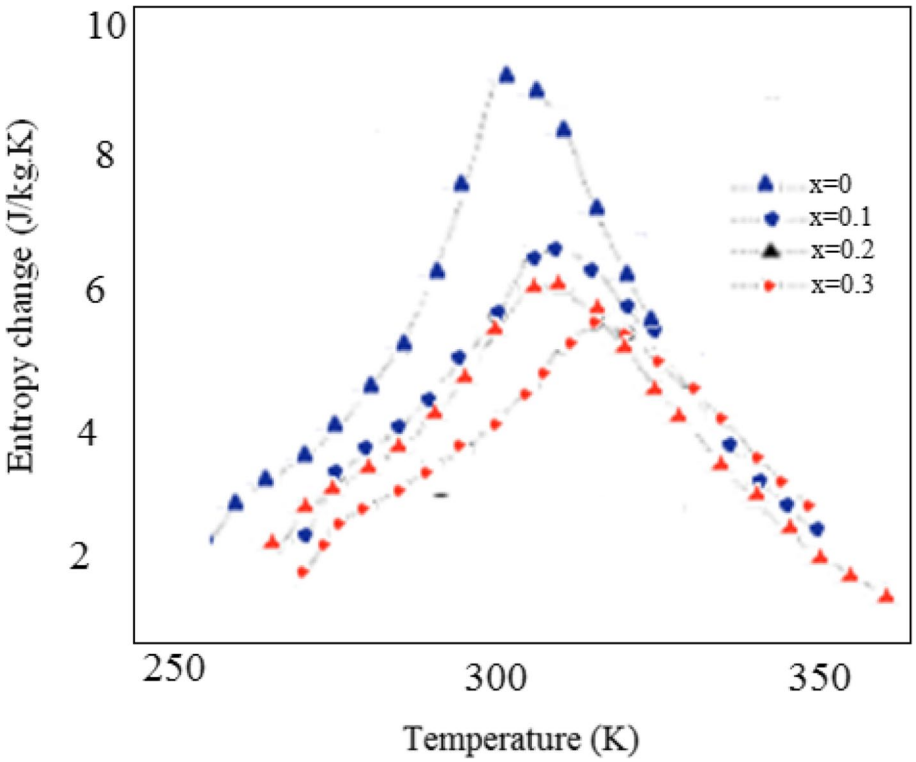

Fig. 10 Magnetic entropy change of $Mn_5Ge_{3-x}Sb_x$, calculated the magnetization data for a field change of 5Tesla

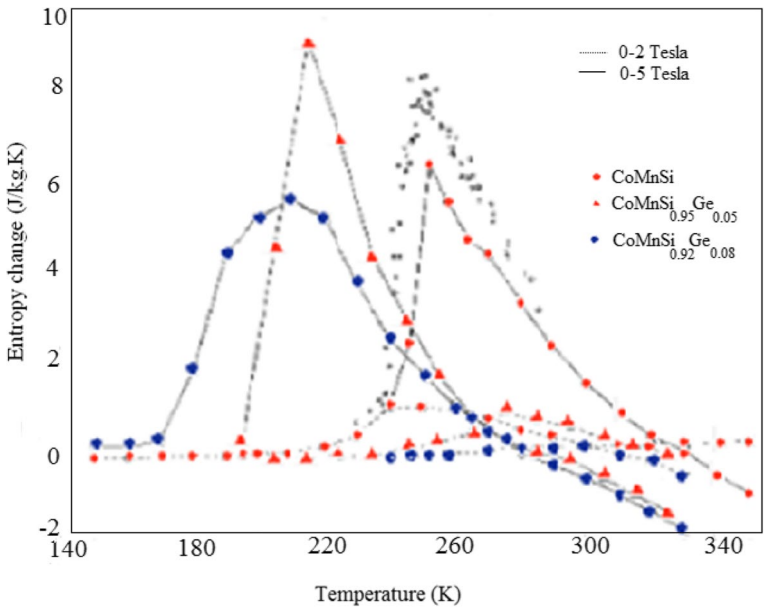

Fig. 11 The isothermal entropy change of $CoMn_5Si_{1-x}Ge_x$ ($x = 0$, 0.05, and 0.08), on changing the applied field from zero to either 2Tesla or 5 Tesla. Also shown is the magnitude of the negative adiabatic change of CoMnSi when the applied field is raised from 0 to 5 T, together with estimate of ΔT using ΔS data

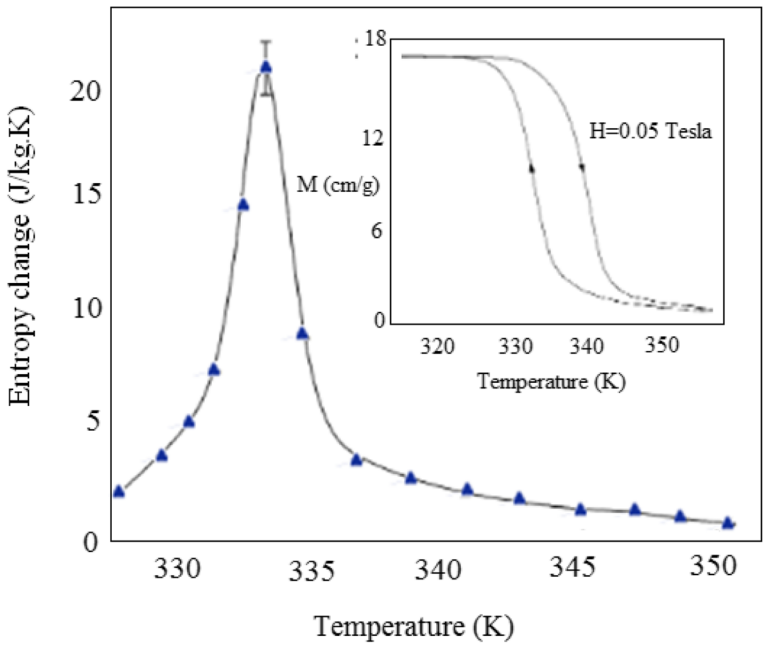

Fig. 12 Magnetic entropy change, the insert displays magnetization at $H = 0.05$T with T_C and SPT temperatures of $Ni_{2.18}Mn_{0.82}Ga$ at 326–351 K

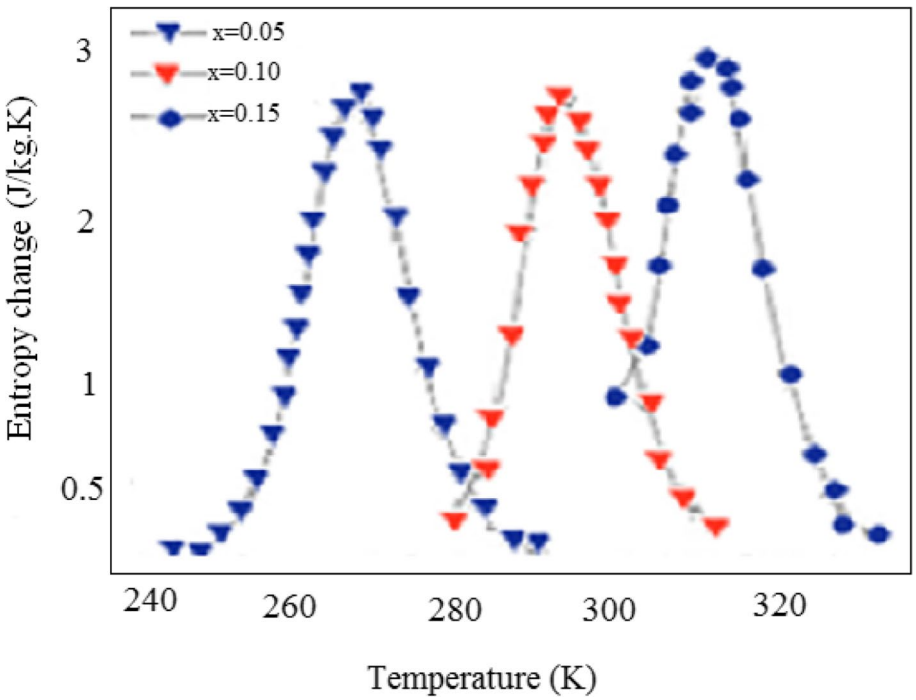

Fig. 13 Temperature dependence of magnetic entropy change for $(La_{0.5}\ Gd_{0.2})Sr_{0.3}MnO_3$

As for the unique crystal of the $Pr_{1-x}\ Sr_x\ MnO_3$ system, it was co-observed that for $x = 0.37$ there is a large magnetocaloric effect in $Pr_{0.63}Sr_{0.37}MnO_3$ that undergoes a very strong ferromagnetic-ferromagnetic phase transition at 305 K. Magnetic entropy variations and maximum temperatures were determined in an applied field of 1 Tesla which were 2.6 $J.kg^{-1}.K^{-1}$ and 5.65 K, respectively. The large magnetic entropy change originates mainly from the abrupt drop in magnetization which is associated with a magnetic first-order phase transition near the Curie temperature [41]. For $x = 0.4$ the maximum magnetic entropy

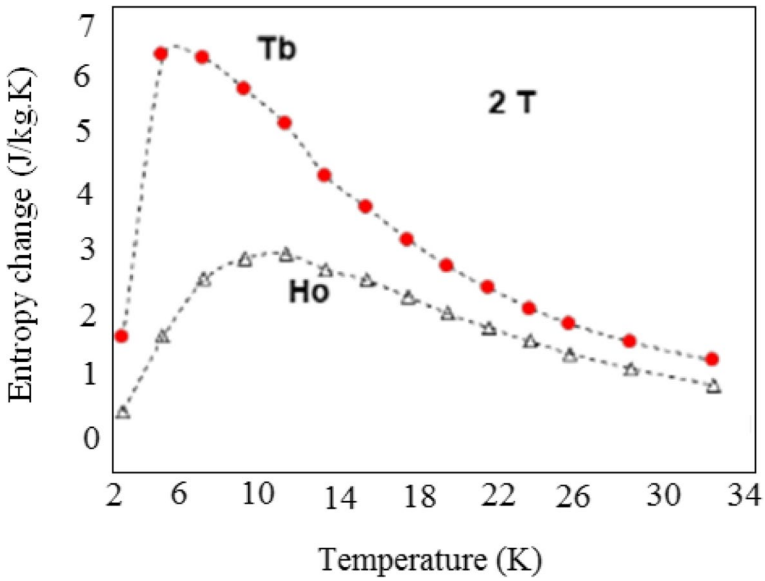

Fig. 14 Temperature dependence of the rotating isothermal entropy change in RMn_2O_5 (R = Ho, Tb) under 2Tesla

change as determined in an applied field of 1 Tesla was 1.05 J.kg^{-}K^{-} at $T_C = 322$ K [42]. According to Guillou 2011, for $x = 0.33$ the material can truly be considered representative of the "best oxide" available at ambient temperature [40].

However, the size of the rare earths could play a crucial role in determining the magnetic order and consequently the rotational magnetocaloric properties of multiferroic RMn2O5 single crystal compounds (R = Tb and Ho) via the modulation of exchange interactions and distortions of the network. A large adiabatic temperature change can be induced (about 10 K) by rotating them in constant magnetic fields instead of the standard magnetization-demagnetization method. The maximum magnetic entropy change of $TbMn_2O_5$ was 6.5 J.kg^{-}K^{-1} in 2 Tesla (Fig. 14) [43].

$Fe_{1-x}Rh_x$ compounds with a first-order transition resulting from coupling between magnetic and structural transitions; however, its MCE is not fully reversible in the applied laboratory fields [44, 45]. Applying a magnetic field of approximately 2 T to a soaked sample of 0.49 Rh0.51 to 313 K results in a remarkable temperature change of 12.9 K under adiabatic conditions. Therefore, $Fe_{0.49}Rh_{0.51}$ compounds are interesting working materials for magnetic refrigeration technology. However, are both expensive and loses its negative ECM on the applied field multiple cycle [46].

The first-order material $LaFe_{13-x}Si_x$ family has high magnetocaloric power. An analysis yields an optimum adiabatic temperature change of 13 K in 2Tesla [47, 48]. In this regard, the compounds based on $LaFe_{13-x}Si_x$ are the most promising, they are considered the best alternative to gadolinium due to their excellent magnetic and magnetocaloric properties, as well as their attractive price. They usually have a giant low temperature MCE around their Curie point, around 200 K, and low hysteresis. For applications near room temperature (domestic or industrial), the Curie point can be raised in two ways. One by inserting certain interstitial elements, notably hydrogen, without affecting the EMC, $LaFe_{13-x}Si_xH_y$ where the Curie temperature reaches 278 K [32]. The other way, by replacing a small amount of iron with cobalt $La(Fe, Co)_{13-x}Si_x$ to increase the Curie temperature by nearly 300 K [49].

Given the chemical and mechanical instability of hydrides, $La(Fe,Co)_{13-x}Si_x$ compounds currently seem to be the most suitable for magnetic refrigeration applications (Fig. 15).

Recently, a surprising first-order phase transition of isosymmetrical Eu2In in a rare intermetallic earth has been discovered. What makes this transition in Eu2In even more remarkable is that it is associated with large latent heat and an unusually high magnetocaloric effect in weak magnetic fields but with tiny lattice discontinuities and negligible hysteresis. MCE is about 3.5 K. T^{-1}, the change of magnetic entropy is around 26 J.kg^{-1}.K^{-1} and the latent heat is around 1.4 J.kg^{-1} at T_C 55 K [50].

To overcome the critical problems of mechanical fatigue and magnetic hysteresis which limit the applicability of conventional mechanical materials such as alloys, research has been carried out on two types of materials. The first type are elastic compounds with phase

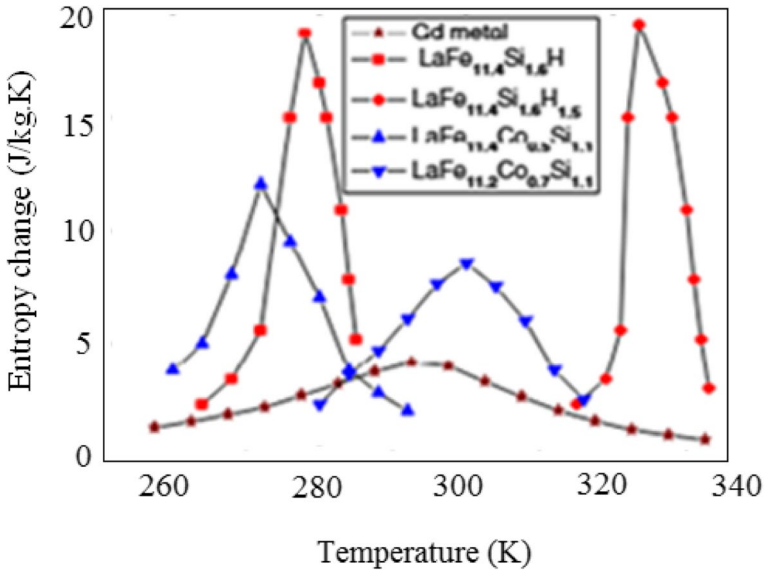

Fig. 15 Magnetic entropy change for different $LaFe_{13}$-based sample at a field of 2Tesla

transitions of order/field-induced disorder involving ions or molecules (such as polymers, fast-conducting ions and plastic crystals) and the second type are multiferroics whose structural parameters are strongly coupled to degrees of polar and/or magnetic freedom (magnetic alloys and perovskite oxides) [51].

4 Conclusion

The new materials at Giant EMC must have a large magnetic entropy change and large adiabatic temperature change with a low applied magnetic field, for example, with superconductors, the main obstacle to industrialization is the particularly high magnetic field (5 Tesla) that must be generated to be able to obtain significant yields. Permanent magnets constitute an interesting field source solution for magnetic refrigeration devices, in particular for relatively low powers (< 10 kW). A large application temperature (δT) is desirable, unfortunately, the giant magnetocaloric materials being first-order transition, they therefore have a reduced application margin by exploring further the study of cascade systems composed of several magnetocaloric materials. It is necessary to select materials with reversible MCE, for this it is necessary to reduce the loss of unwanted magnetic hysteresis inherent in the first transition order. Knowing that hysteresis losses are proportional to the area of the hysteresis cycle, magnetic losses can then be limited by using narrow-cycle materials as shown in Fig. 5. Optimize heat exchange between the material and the heat transfer fluid in order to limit losses by diffusion in the material. The new materials must have a low fatigue, indeed, the materials with a giant magnetocaloric effect are transition of first- order, and therefore, they have the disadvantage of aging prematurely due to structural changes that usually accompany these transitions. It is obvious to use magnetic materials without environmental impact. Fortunately the fluids used in the dispositive of magnetic refrigeration are water or glycol instead of refrigerants such as the famous CFC, HCFC, or HFC fluorocarbons which either are powerful greenhouse gases (2000 to 8000 times their weight in CO_2 equivalent). Last but not least, get an inexpensive material with optimal properties.

At present, research is therefore focused in order to find magnetocaloric materials or more efficient alloys. The first-order phase transition La–Fe–Si family or $(Mn–Fe)_2(P,As,Si)$ materials derive from iron phosphide Fe_2P are the most promising magnetocaloric materials for room temperature magnetic refrigeration applications. They offer a large isothermal entropy change and adiabatic temperature change in low magnetic fields in combination with small thermal hysteresis first-order ferromagnetism where gives away to a continuous Curie temperature transition and low raw material cost.

Author's contributions
The author(s) read and approved the final manuscript.

Availability of data and materials
Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

Declarations

Competing interests
The author declares no competing interests.

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