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Magnetocaloric refrigeration near room temperature (invited)

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Abstract

Modern society relies on readily available refrigeration. The ideal cooling machine would be a compact, solid state, silent and energy-efficient heat pump that does not require maintenance. Magnetic refrigeration has three prominent advantages compared to compressor-based refrigeration. First, there are no harmful gases involved, second it may be built more compact as the working material is a solid and third magnetic refrigerators generate much less noise. Recently, a new class of magnetic refrigerant materials for room-temperature applications was discovered. These new materials have important advantages over existing magnetic coolants: They exhibit a large magnetocaloric effect (MCE) in conjunction with a magnetic phase transition of first order. This MCE is, larger than that of Gd metal, which is used in the demonstration refrigerators built to explore the potential of this evolving technology. In the present review, we compare the different materials considering both scientific aspects and industrial applicability.

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1. Introduction

This decade has seen an immense increase in interest in magnetic refrigeration, based on the magnetocaloric effect (MCE). This is because it is considered as a promising alternative to the well-established compression–evaporation cycle for room-temperature applications. Magnetic materials contain two energy reservoirs; the usual phonon excitations connected to lattice degrees of freedom and magnetic excitations connected to spin degrees of freedom. These two reservoirs are generally well coupled by the spin–lattice coupling that ensures loss-free energy transfer within millisecond time scales. An externally applied magnetic field can strongly affect the spin degree of freedom that results in the MCE. In the magnetic refrigeration cycle, depicted in Fig. 1, initially randomly oriented magnetic moments are aligned by a magnetic field, resulting in heating of the magnetic material. This heat is removed from the material to the ambient by heat transfer. On removing the

field, the magnetic moments randomise, which leads to the cooling of the material below the ambient temperature. Heat from the system to be cooled can then be extracted using a heat-transfer medium. Depending on the operating temperature, the heat-transfer medium may be water (with antifreeze) or air, and for very low-temperatures helium. Therefore, magnetic refrigeration is an environmentally friendly cooling technology. It does not use ozone depleting chemicals (CFCs), hazardous chemicals (NH₃), or greenhouse gases (HCFCs and HFCs). Another key difference between vapour-cycle refrigerators and magnetic refrigerators is the amount of energy loss incurred during the refrigeration cycle. The cooling efficiency in magnetic refrigerators working with gadolinium was shown [1] to reach 60% of the theoretical limit, compared to only about 40% in the best gas-compression refrigerators. This higher energy efficiency will also result in a reduced CO₂ release. Current research aims at new magnetic materials displaying larger MCEs, which then can be operated in fields of about 2T or less and can be generated by permanent magnets. In this paper, we shall discuss the properties of those materials where current research is concentrated on.

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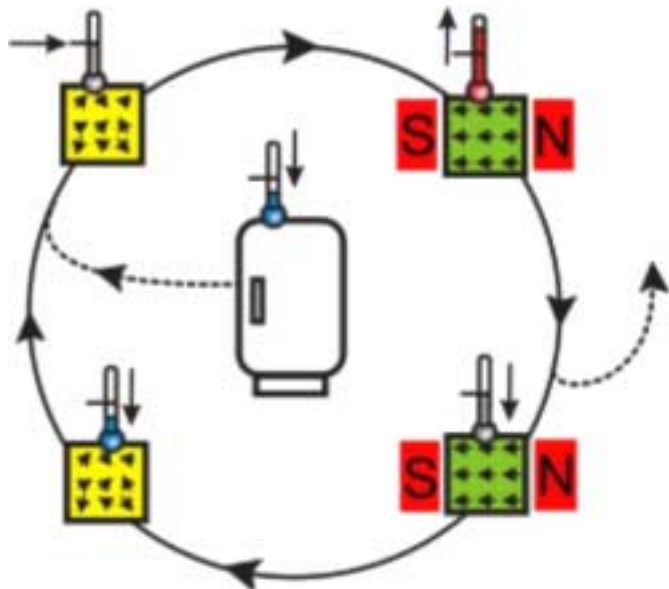


Fig. 1. Schematic representation of a magnetic-refrigeration cycle, that transports heat from the heat load to the ambient.

2. $\text{Gd}_5(\text{Ge,Si})_4$ and related compounds

Though the MCE was first discovered in simple iron [2], for years research on magnetocaloric materials was concentrated on rare earth and their compounds. Following the discovery of a sub-room temperature giant-MCE in the ternary compound $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$ ($0.3 \leq x \leq 0.5$) [3], there is a strongly increased interest from both fundamental and practical points of view to study the MCE in these materials [4,5]. The most prominent feature of these compounds is that they undergo a first-order structural and magnetic phase transition, which leads to a giant magnetic field-induced entropy change, across their ordering temperature. We here, therefore, will discuss to some extent the structural properties of these compounds. At low temperatures for all x $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$ adopts an orthorhombic Gd_5Si_4 -type structure (Pnma) and the ground state is ferromagnetic [6]. However, at room temperature depending on x , three different crystallographic phases are observed. For $x > 0.55$ the aforementioned Gd_5Si_4 structure is stable, for $x < 0.3$ the materials adopt the Sm_5Ge_4 -type structure with the same space group (Pnma) but a different atomic arrangement and a somewhat larger volume, finally in between these two structure types the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ type with space group (P112₁/a) is formed, which has an intermediate volume. The latter structure type is stable only below about 570 K where again the orthorhombic Gd_5Si_4 -type structure is formed in a first-order phase transition [7].

As one may guess, the three structure types are closely related (see Fig. 2) [8]; the unit cells contain four formula units and essentially only differ in the mutual arrangement of identical building blocks which are either connected by two, one or no covalent-like Si–Ge bonds, resulting in successively increasing unit-cell volumes. The giant MCE is

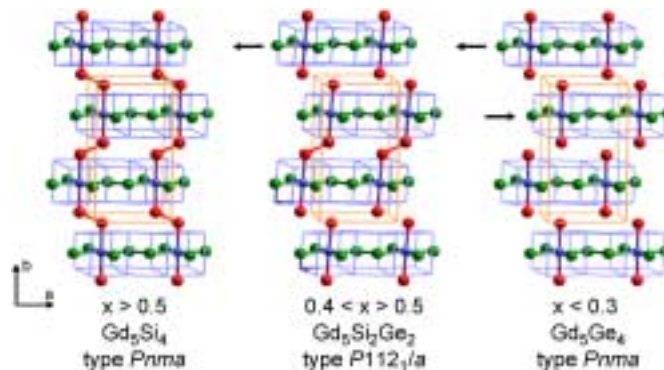


Fig. 2. Room-temperature crystal structures of the pseudo-binary phase diagram $\text{Gd}_5\text{Ge}_4\text{—Gd}_5\text{Si}_4$ after [8].

observed for the compounds that exhibit a simultaneous paramagnetic to ferromagnetic and structural phase transition that can be either induced by a change in temperature, applied magnetic field or applied pressure [9,10]. The fact that the structural and magnetic transitions are simultaneous is somewhat accidental as the exchange energy is of the same order of magnitude as the thermal energy at the structural phase transition. The electrical resistivity and magneto resistance of $\text{Gd}_5\text{Ge}_2\text{Si}_2$ also shows unusual behaviour, indicating a strong coupling between electronic structure and lattice. For several compounds of the series, next to a cusp like anomaly in the temperature dependence of the resistivity, a very large magneto resistance effect is reported [11–14].

In view of building a refrigerator based on $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$, there are a few points to consider. The largest MCE is observed considerably below room temperature, while a real refrigerator should expel heat at least at about 320 K. Because the structural transition is connected with sliding of building blocks, impurities especially at the sliding interface can play an important role. The thermal hysteresis and the size of the MCE connected with the first-order phase transition strongly depend on the quality of the starting materials and the sample preparation [15]. For the compounds $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$ with x , around 0.5 small amounts of impurities like Al, Bi, C, Co, Cu, Ga, Mn, O or Sn may suppress the formation of the monoclinic structure near room temperature. These alloys then show only a phase transition of second order at somewhat higher temperature but with a lower MCE [7,16–18]. The only impurity that appears to enhance the MCE and increases the magnetic ordering temperature is so far Pb [19]. This sensitivity to impurities like carbon, oxygen and iron strongly influences the production costs of the materials that may hamper broad-scale application. Next to the thermal and field hysteresis, the magneto-structural transition in $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$ appears to be rather sluggish [20,21]. This will also influence the optimal operation frequency of a magnetic refrigerator and the efficiency. An aspect that is hardly ever taken into consideration is the availability of the components.

Other $R_5(\text{Si,Ge})_4$ compounds are also found to form in the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure and when the structural transformation coincides with the magnetic ordering transition a large MCE is observed. This is most strikingly evident in the experiments of Morellon et al. [22] on $\text{Tb}_5\text{Si}_2\text{Ge}_2$ where the two transitions were forced to coincide by application of hydrostatic pressure, which results in a strong enhancement of the magnetic entropy change at the ordering temperature. The magnetic ordering temperatures of other $R_5(\text{Si,Ge})_4$ compounds are all lower than for the Gd compound as expected. For cooling applications below liquid nitrogen temperatures, some of these compounds may be interesting.

3. $\text{La}(\text{Fe,Si})_{13}$ and related compounds

Another interesting type of materials are the rare-earth transition-metal compounds crystallizing in the cubic NaZn_{13} type of structure. LaCo_{13} is the only binary compound, from the 45 possible combinations of a rare-earth and iron, cobalt or nickel, that exists in this structure. It was shown that with an addition of at least 10% Si or Al, this structure can also be stabilized with iron and nickel [23]. The NaZn_{13} structure contains two different Zn sites. The Na atoms at 8a and Zn^{I} atoms at 8b form a simple CsCl type of structure. Each Zn^{I} atom is surrounded by an icosahedron of 12 Zn^{II} atoms at the 96i site. In $\text{La}(\text{Fe,Si})_{13}$, La goes on the 8a site, the 8b site is fully occupied by Fe and the 96i site is shared by Fe and Si. The iron-rich compounds $\text{La}(\text{Fe,Si})_{13}$ show typical invar behaviour, with magnetic ordering temperatures around 200 K that increase to 262 K with lower iron content [24]. Thus, though the magnetic moment is diluted and also decreases per Fe atom, the magnetic ordering temperature increases. Around 200 K, the magnetic-ordering transition is found to be also distinctly visible in the electrical resistivity, where a chromium-like cusp in the temperature dependence is observed. In contrast to $\text{Gd}_5\text{Ge}_2\text{Si}_2$, this phase transition is not accompanied by a structural change, thus above and below T_c the material is cubic. Recently, because of the extremely sharp magnetic ordering transition, the (La,Fe,-Si,Al) system was reinvestigated by several research groups and a large MCE was reported [25–27]. The largest effects are observed for the compounds that show a field- or temperature-induced phase transition of first order. Unfortunately, these large effects only occur up to about 210 K as the magnetic sublattice becomes more and more diluted. Almost single-phase samples are reported when, instead of normal arc melting, rapid quenching by melt spinning and subsequent annealing is employed [28–30]. Samples prepared in this way also show a very large MCE. To increase the total magnetic moment partial substitution of Ce for La has been successful [31]. This substitution however, leads next to an enhanced MCE, to a lower magnetic ordering temperature and a broader thermal hysteresis. To increase the magnetic ordering temperature without losing too much magnetic moment, one may

replace some Fe by other magnetic transition metals. Because the isostructural compound LaCo_{13} has a very high critical temperature substitution of Co for Fe is widely studied. The compounds $\text{La}(\text{Fe,Co})_{13-x}\text{Al}_x$ and $\text{La}(\text{Fe,Co})_{13-x}\text{Si}_x$ with $x \approx 1.1$ and thus a very high transition-metal content, show a considerable MCE near room temperature [32–35]. This is achieved with only a few percent of Co and the Co content can easily be varied to tune the critical temperature to the desired value. It should be mentioned however that near room temperature the values for the entropy change steeply drop.

The lattice expansion due to the addition of three hydrogen atoms per formula unit is about 4.5%. The critical temperature can be increased to up to 450 K, the average magnetic moment per Fe increases from 2.0 to up to $2.2 \mu_B$ and the field- or temperature-induced phase transition is found to be of first order for all hydrogen concentrations. This all results for a certain Si percentage in an almost constant value of the magnetic entropy change per mass unit over a broad temperature span see Fig 3.

From the materials cost point of view, the $\text{La}(\text{Fe,Si})_{13}$ type of alloys appear to be very attractive. La is the cheapest from the rare-earth series and both Fe and Si are available in large amounts. The processing will be a little more elaborate than for a simple metal alloy but this can be optimized. For the use in a magnetic refrigerator next to the magnetocaloric properties also mechanical properties and chemical stability may be of importance. The hydrogenation process of rare-earth transition-metal compounds always produces granular material due to the strong lattice expansion. In the case of the cubic NaZn_{13} type of structure, this does not seem to be the case. At the phase transition in $\text{La}(\text{Fe,Si})_{13}$ type of alloys also a volume change of 1.5% is observed [37]. If this volume change is performed very frequently, the material will definitely become very brittle and probably break in even smaller grains. This can have distinct influence on the corrosion

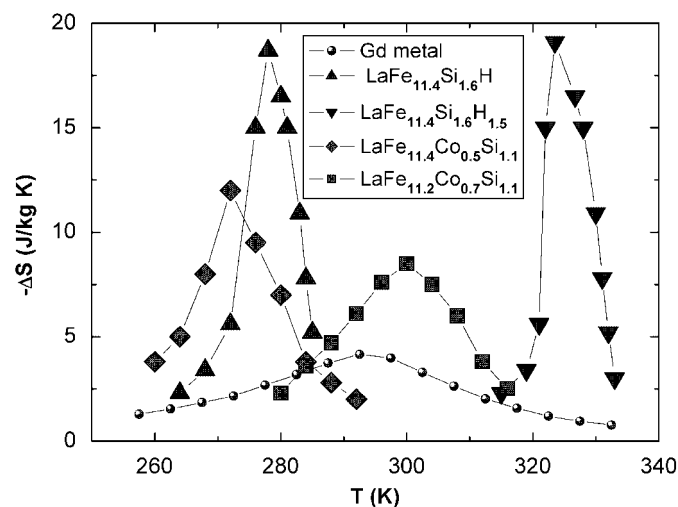


Fig. 3. Magnetic-entropy change for different LaFe_{13} based samples at a field change of 2 T [33,36].

resistance of the material and thus on the lifetime of a refrigerator. The suitability of this material definitely needs to be tested.

4. MnAs-based compounds

MnAs exist similar to $Gd_5Ge_2Si_2$ in two distinct crystallographic structures [38]. At low and high temperature, the hexagonal NiAs structure is found and for a narrow temperature range 307–393 K, the orthorhombic MnP structure exists. The high-temperature transition in the paramagnetic region is of second order. The low-temperature transition is a combined structural and ferro-paramagnetic transition of first order with large thermal hysteresis. The change in volume at this transition amounts to 2.2% [39]. The transition from paramagnetic to ferromagnetic occurs at 307 K, the reverse transition from ferromagnetic to paramagnetic occurs at 317 K. Very large magnetic entropy changes are observed in this transition [40,41]. Similar to the application of pressure [42,43] substitution of Sb for As leads to lowering of T_c [44,45], 25% of Sb gives an transition temperature of 225 K. However, the thermal hysteresis is affected quite differently by hydrostatic pressure or Sb substitution. In Mn(As,Sb), the hysteresis is strongly reduced and at 5% Sb it is reduced to about 1 K. In the concentration range 5–40% of Sb, T_c can be tuned between 220 and 320 K without losing much of the magnetic entropy change [46,47]. Direct measurements of the temperature change confirm a ΔT of 2K/T [48]. On the other hand, MnAs under pressure shows an extremely large magnetic entropy change [49] in conjunction with large hysteresis.

The materials costs of MnAs are quite low, processing of As containing alloys is, however, complicated due to the biological activity of As. In the MnAs alloy, the As is covalently bound to the Mn and would not be easily released into the environment. However, this should be experimentally verified, especially because in an alloy frequently second phases form that may be less stable. The change in volume in Mn(As,Sb) is still 0.7% which may result in aging after frequent cycling of the material.

5. Heusler alloys

Heusler alloys frequently undergo a martensitic transition between the martensitic and the austenitic phase which is generally temperature induced and of first order. Ni_2MnGa orders ferromagnetic with a Curie temperature of 376 K, and a magnetic moment of $4.17 \mu_B$, which is largely confined to the Mn atoms and with a small moment of about $0.3 \mu_B$ associated with the Ni atoms [50]. As may be expected from its cubic structure, the parent phase has a low magneto-crystalline anisotropy energy ($H_a = 0.15$ T). However, in its martensitic phase the compound is exhibiting a much larger anisotropy ($H_a = 0.8$ T). The martensitic transformation temperature is near 220 K. This martensitic transformation temperature can be easily

varied to around room temperature by modifying the composition of the alloy from the stoichiometric one. The low-temperature phase evolves from the parent phase by a diffusionless, displacive transformation leading to a tetragonal structure, $a = b = 5.90 \text{ \AA}$, $c = 5.44 \text{ \AA}$. A martensitic phase generally accommodates the strain associated with the transformation (this is 6.56% along c for Ni_2MnGa) by the formation of twin variants. This means that a cubic crystallite splits up in two tetragonal crystallites sharing one contact plane. These twins pack together in compatible orientations to minimize the strain energy (much the same as the magnetization of a ferromagnet may take on different orientations by breaking up into domains to minimize the magneto-static energy). Alignment of these twin variants by the motion of twin boundaries can result in large macroscopic strains. In the tetragonal phase with its much higher magnetic anisotropy, an applied magnetic field can induce a change in strain why these materials may be used as actuators. Next to this ferromagnetic shape memory effect, very close to the martensitic transition temperature, one observes a large change in magnetization for low applied magnetic fields. This change in magnetization is also related to the magneto crystalline anisotropy. This change in magnetization is resulting in a moderate magnetic entropy change of a few J/molK, which is enhanced when measured on a single crystal [51,52]. When the composition in this material is tuned in a way that the magnetic and structural transformation occurs at the same temperature, the largest magnetic entropy changes are observed [53–55]. Recently in the Heusler alloy $NiMnSn$, a large inverse MCE was reported [56], this effect is related to the increase of magnetization with increasing temperature over the martensitic transition temperature. Substitution of Co for Ni leads to an increase of the transition temperature close to room temperature.

6. Fe_2P -based compounds

The magnetic phase diagram for the system $MnFeP$ – $MnFeAs$ [57] shows a rich variety of crystallographic and magnetic phases. The most striking feature is the fact that for As concentrations between 30% and 65%, the hexagonal Fe_2P type of structure is stable and the ferromagnetic order is accompanied by a discontinuous change of volume. While the total magnetic moment is not affected by changes of the composition, the Curie temperature increases from about 150 K to well above room temperature. We reinvestigated this part of the phase diagram [58,59] and investigated possibilities to partially replace the As [60–62].

Polycrystalline samples can be synthesised starting from the binary Fe_2P and $FeAs_2$ compounds, Mn chips and P powder (red) mixed in the appropriate proportions by ball milling under a protective atmosphere. After this mechanical alloying process, one obtains amorphous powder. To obtain dense material of the crystalline phase, the powders are pressed to pellets wrapped in Mo foil and sealed in quartz

tubes under an argon atmosphere. These are heated at 1273 K for 1 h, followed by a homogenization process at 923 K for 50 h and finally by slow cooling to ambient conditions. The powder X-ray diffraction patterns show that the compound crystallises in the hexagonal Fe_2P -type structure. In this structure the Mn atoms occupy the 3(g) sites, the Fe atoms occupy the 3(f) sites and the P and the As atoms occupy 2(c) and 1(b) sites statistically [63]. From the broadening of the X-ray diffraction reflections, the average grain size is estimated to be about 100 nm [64].

From the magnetization curve at 5 K, the saturation magnetisation was determined as $3.9 \mu_{\text{B}}/\text{f.u.}$ This high magnetization originates from the parallel alignment of the Mn and Fe moments, though the moments of Mn are much larger than those of Fe [57]. Variation of the Mn/Fe ratio may also be used to further improve the MCE. Recently, we have observed a surprisingly large MCE in the compound $\text{MnFeP}_{0.5}\text{As}_{0.3}\text{Si}_{0.2}$ at room temperature [65]. After replacing all As, a considerable large MCE is still observed for $\text{MnFe}(\text{P},\text{Si},\text{Ge})$ [66].

The magnetic-entropy change of different $\text{MnFe}(\text{P},\text{As},\text{Si},\text{Ge})$ alloys is shown in Fig. 4. The origin of the large magnetic-entropy change should be attributed to the

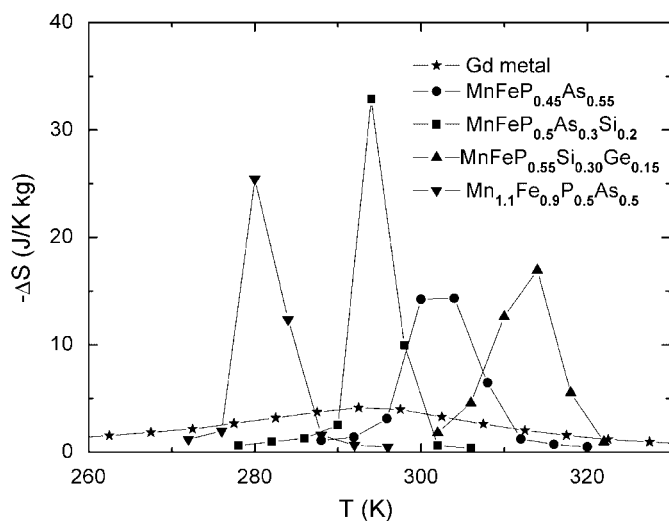


Fig. 4. Magnetic-entropy changes of Fe_2P -type compounds at magnetic field changes of 2 T [64–67].

comparatively high 3d moments and the rapid change of the magnetisation in the field-induced magnetic phase transition. In rare-earth materials, the magnetic moment fully develops only at low temperatures and, therefore, the entropy change near room temperature is only a fraction of their potential. In 3d compounds, the strong magneto-crystalline coupling results in competing intra- and inter-atomic interactions and leads to a modification of metal–metal distances which may change the iron and manganese magnetic moment and favours the spin ordering.

The large MCE observed in Fe_2P -based compounds originates from a field-induced first-order magnetic phase transition. The magnetisation is reversible in temperature and in alternating magnetic field. The magnetic ordering temperature of these compounds is tuneable over a wide temperature interval (200–450 K). The excellent magnetocaloric features of the compounds of the type $\text{MnFe}(\text{P},\text{Si},\text{Ge},\text{As})$, in addition to the very low material costs, make it an attractive candidate material for a commercial magnetic refrigerator. However, same as for MnAs alloys it should be verified that materials containing As do not release this to the environment. The fact that the magneto-elastic phase transition is rather a change of c/a than a change of volume, makes it feasible that this alloy even in polycrystalline form will not experience severe aging effects after frequent magnetic cycling.

7. Comparison of different materials and outlook

The MCEs for field changes of 2 T are summarized in Table 1. It is obvious that above room temperature, a few transition-metal-based alloys perform the best. If one takes into account the fact that ΔT also depends on the specific heat of the compound [68] these alloys are still favourable not only from the cost point of view. This makes them likely candidates for use as magnetic refrigerant materials above room temperature. However, below room temperature a number of rare-earth compounds perform better and for these materials a thorough cost vs. performance analysis will be needed.

The main parameters of the various materials are summarized in Table 1 which allows a fast comparison.

Table 1
Comparison of different potential magnetocaloric materials

Material	Temperature range (K)	ΔS (2T) (J/kg K)	ΔT (2T) (K)	Cost (€/kg)	Avail (t)	Density (t/m^3)
Gd	270–310	5	5.8d	20	1000	7.9
$\text{Gd}_5\text{Ge}_2\text{Si}_2$	150–290	27	6.6d	60	140	7.5
$\text{La}(\text{Fe},\text{Si})\text{H}$	180–320	19	7c	8	22,000	7.1
MnAs	220–320	32	4.1d	10	ul	6.8
MnNiGa	310–350	15	2c	10	60	8.2
$\text{MnFe}(\text{P},\text{As})$	150–450	32	6d	7	ul	7.3

Gd is included as reference material. 'd' means direct measurement 'c' is calculated from a combination of measurements. The costs may strongly fluctuate due to market demands and quality of starting materials. Availability is based on the world mineral production data from USGS.gov, ul means there are no limitations for industrial production.

Because of the limited availability, the Gd, Ge and Ga containing materials will be restricted to niche markets. At present, it is not clear which material will really get to the stage of real-life applications and one may expect that still other materials will be developed. Though it is already feasible that for applications with limited temperature span and a cooling power in the kW range like air conditioning, commercial competitive magnetic refrigerators are quite possible, it is not yet obvious, which of the above-mentioned materials shall be employed. Currently, most attention is paid to the pure magnetocaloric properties and materials costs. In the near future also other properties like corrosion resistance, mechanical properties, heat conductivity, electrical resistivity and environmental impact should be addressed.

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