

## Introduction to magnetic refrigeration

E. Brück

Van der Waals–Zeeman Instituut, Universiteit van Amsterdam, Valckenierstr. 65, 1018  
XE Amsterdam, The Netherlands

Magnetic refrigeration, based on the magnetocaloric effect (MCE), has recently received increased attention as an 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 cooling of the material below 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. The cycle described here is very similar to the vapour compression refrigeration cycle: on compression the temperature of a gas increases, in the condenser this heat is expelled to the environment and on expansion the gas cools below ambient temperature and can take up heat from the environment. In contrast to a compression cycle the magnetic refrigeration cycle can be performed quasi static which results in the possibility to operate close to Carnot efficiency.

Therefore, magnetic refrigeration is an environmentally friendly cooling technology. It does not use ozone depleting chemicals (CFCs), hazardous chemicals ( $\text{NH}_3$ ), or greenhouse gases (HCFCs and HFCs). The difference between vapour-cycle refrigerators and magnetic refrigerators manifests itself also is the amount of energy loss incurred during the refrigeration cycle. From thermodynamics it appears feasible to construct magnetic refrigerators that have very high Carnot efficiency compared to conventional vapour pressure refrigerators [1, 2]. This higher energy efficiency will also result in a reduced  $\text{CO}_2$  release. Current research aims at new magnetic materials displaying larger magnetocaloric effects, which then can be operated in fields of about 2 T or less, that can be generated by permanent magnets.

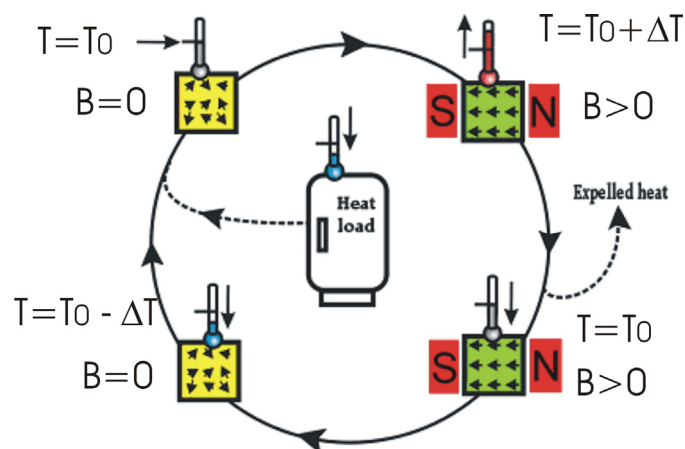


Figure 1 Schematic representation of a magnetic-refrigeration cycle, which transports heat from the heat load to the ambient. Left and right depict material in low and high magnetic field, respectively.

The heating and cooling described above is proportional to the change of magnetization and the applied magnetic field. This is the reason that, until recently, research in magnetic refrigeration was almost exclusively conducted on super-paramagnetic materials and on rare-earth compounds [3]. For room-temperature applications like refrigerators and air-conditioners, compounds containing manganese or iron should be a good alternative. Manganese and iron are transition metals with high abundance. Also, there exist in contrast to rare-earth compounds, an almost unlimited number of manganese and iron compounds with critical temperatures near room temperature. However, the magnetic moment of manganese generally is only about half the size of heavy rare-earth elements and the magnetic moment of iron is even less. Enhancement of the caloric effects associated with magnetic moment alignment may be achieved through the induction of a first order phase-transition or better a very rapid change of magnetisation at the critical temperature, which will bring along a much higher efficiency of the magnetic refrigerator. In combination with currently available permanent magnets [4], based on modern Rare-Earth Transition-metal compounds [5], this opens the path to the development of small-scale magnetic refrigerators, which no more rely on rather costly and service-intensive superconducting magnets. Another prominent advantage of magnetocaloric refrigerators is that the cooling power can be varied by scaling from milliwatt to a few hundred watts or even kilowatts. To increase the temperature span of the refrigerator, in comparison with the temperature change in a single cycle, all demonstrators or prototypes nowadays are based on the active magnetic regenerator design [6].

### **Gd<sub>5</sub>Ge<sub>2</sub>Si<sub>2</sub> type compounds**

Following the discovery of a sub-room temperature giant-MCE in the ternary compound Gd<sub>5</sub>(Ge<sub>1-x</sub>Si<sub>x</sub>)<sub>4</sub> (0.3 ≤ x ≤ 0.5) [7], there is a strongly increased interest from both fundamental and practical points of view to study the MCE in these materials [8, 9]. 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 Gd<sub>5</sub>(Ge<sub>1-x</sub>Si<sub>x</sub>)<sub>4</sub> adopts an orthorhombic Gd<sub>5</sub>Si<sub>4</sub>-type structure (Pnma) and the ground state is ferromagnetic [10]. However, at room temperature depending on x three different crystallographic phases are observed. For x > 0.55 the aforementioned Gd<sub>5</sub>Si<sub>4</sub> structure is stable, for x < 0.3 the materials adopt the Sm<sub>5</sub>Ge<sub>4</sub>-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 Gd<sub>5</sub>Si<sub>2</sub>Ge<sub>2</sub> type with space group (P112<sub>1</sub>/a) is formed, which has an intermediate volume. The latter structure type is stable only below about 570K where again the orthorhombic Gd<sub>5</sub>Si<sub>4</sub>-type structure is formed in a first-order phase transition [11]. As one may guess, the three structure types are closely related; 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 magnetocaloric effect is 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 [12, 13]. In contrast to most magnetic systems the ferromagnetic phase has a 0.4% smaller volume than the paramagnetic phase which results in an increase of T<sub>c</sub> on application of pressure with about 3K/kbar. The structural change at the phase transition brings along also a very large magneto-elastic effect and the electrical resistivity behaves anomalous. The strong coupling between lattice degrees of freedom and magnetic and electronic properties is rather

unexpected, because the magnetic moment in Gd originates from spherical symmetric s-states that in contrast to other rare-earth elements hardly couple with the lattice. First principle electronic structure calculations in atomic sphere and local-density approximation with spin-orbit coupling added variationally, could reproduce some distinct features of the phase transition [14]. Total energy calculations for the two phases show different temperature dependences and the structural change occurs at the temperature where the energies are equal. There appears a distinct difference in effective exchange-coupling parameter for the monoclinic and orthorhombic phase, respectively. This difference could directly be related to the change of the Fermi-level in the structural transition. Thus 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  $Gd_5Ge_2Si_2$  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 magnetoresistance effect is reported[15-18].

In view of building a refrigerator based on  $Gd_5(Ge_{1-x}Si_x)_4$ , there are a few points to consider. The largest magnetocaloric effect is observed considerably below room temperature, while a real refrigerator should expel heat at least at about 320K. 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 magnetocaloric effect connected with the first-order phase transition strongly depend on the quality of the starting materials and the sample preparation[19]. For the compounds  $Gd_5(Ge_{1-x}Si_x)_4$  with x around 0.5 small amounts of impurities 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 magnetocaloric effect[11, 20, 21]. This sensitivity to impurities like carbon, oxygen and iron strongly influences the production costs of the materials which may hamper broad-scale application. Next to the thermal and field hysteresis the magneto-structural transition in  $Gd_5(Ge_{1-x}Si_x)_4$  appears to be rather sluggish[22, 23]. This will also influence the optimal operation-frequency of a magnetic refrigerator and the efficiency.

### **La(Fe,Si)<sub>13</sub> and related compounds**

Another interesting type of materials are 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 an rare-earth and iron, cobalt or nickel, that exists in this structure. It has been shown that with an addition of at least 10% Si or Al this structure can also be stabilized with iron and nickel[24]. 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  $La(Fe,Si)_{13}$  La goes on the 8 a site, the 8b site is fully occupied by Fe and the 96i site is shared by Fe and Si. The iron rich compounds  $La(Fe,Si)_{13}$  show typical invar behavior, with magnetic ordering temperatures around 200K that increase to 262K with lower iron content[25]. Thus, though the magnetic moment is diluted and also decreases per Fe atom, the magnetic ordering temperature increases. Around 200K 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  $Gd_5Ge_2Si_2$  this phasetransition 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 magnetocaloric effect was reported[26-28]. The largest effects are observed for the compounds that show a field-

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. When using standard melting techniques, preparation of homogeneous single-phase samples appears to be rather difficult especially for alloys with high transition metal content. Almost single phase samples are reported when, instead of normal arc melting, rapid quenching by melt spinning and subsequent annealing is employed[29-31]. Samples prepared in this way also show a very large magnetocaloric effect. 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  $\text{LaCo}_{13}$  has a very high critical temperature substitution of Co for Fe is widely studied. The compounds  $\text{La}(\text{Fe},\text{Co})_{13-x}\text{Al}_x$  and  $\text{La}(\text{Fe},\text{Co})_{13-x}\text{Si}_x$  with  $x \approx 1.1$  and thus a very high transition-metal content, show a considerable magnetocaloric effect 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.

Hydrogen is the most promising interstitial element. In contrast to other interstitial atoms, interstitial hydrogen not only increases the critical temperature but also leads to an increase in magnetic moment[27, 36-40]. 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 450K, the average magnetic moment per Fe increases from  $2.0 \mu_B$  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.

From the materials cost point of view the  $\text{La}(\text{Fe},\text{Si})_{13}$  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 produces always granular material due to the strong lattice expansion. In the case of the cubic  $\text{NaZn}_{13}$  type of structure this does not seem to be the case. At the phase transition in  $\text{La}(\text{Fe},\text{Si})_{13}$  type of alloys also a volume change of 1.5% is observed[41]. 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 resistance of the material and thus on the lifetime of a refrigerator. The suitability of this material definitely needs to be tested.

### **MnAs based compounds**

MnAs exist similar to  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  in two distinct crystallographic structures[42]. At low and high temperature the hexagonal NiAs structure is found and for a narrow temperature range 307 K to 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%[43]. The transition from paramagnetic to ferromagnetic occurs at 307K, the reverse transition from ferromagnetic to paramagnetic occurs at 317K. Very large magnetic entropy changes are observed in this transition[44, 45]. Similar to the application of pressure[46, 47] substitution of Sb for As leads to lowering of  $T_c$ [48, 49], 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  $\text{Mn}(\text{As},\text{Sb})$  the hysteresis is strongly reduced and at 5%

Sb it is reduced to about 1 K. In the concentration range 5 to 40% of Sb  $T_C$  can be tuned between 220 and 320 K without losing much of the magnetic entropy change[50, 51]. Direct measurements of the temperature change confirm a  $\Delta T$  of  $2K/T$ [52]. On the other hand MnAs under pressure shows an extremely large magnetic entropy change[53] 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.

### **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[54]. As may be expected from its cubic structure, the parent phase has a low magnetocrystalline 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 magnetocrystalline 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[55, 56]. 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[57-59].

For magnetocaloric applications the extremely large length changes in the martensitic transition will definitely result in aging effects. It is well known for the magnetic shape-memory alloys that only single crystals can be frequently cycled while polycrystalline materials spontaneously powderize after several cycles.

### **Fe<sub>2</sub>P based compounds**

The binary intermetallic compound Fe<sub>2</sub>P can be considered as the parent alloy for an interesting type of materials. This compound crystallizes in the hexagonal non centre-symmetric Fe<sub>2</sub>P type structure with space group P $\bar{6}$ 2m. In this structure Fe and P occupy four different crystallographic sites, Fe occupies the 3g and 3f sites and P the 1b and 2c sites. Thus one has a stacking of alternating P-rich and P-poor layers. Neutron diffraction revealed that the magnetic moment of Fe on the 3g sites is about 2  $\mu_B$  whereas the moment on the 3f sites is about 1  $\mu_B$  [60]. The Curie temperature of this compound is 216 K and the magnetic transition is of first order [61]. The magnetic-ordering transition from the paramagnetic state to the ferromagnetic state is accompanied by a discontinuous change of the volume of 0.05%. Thus, the ferromagnetic state has a higher volume than the paramagnetic one. This phase transition is found to be extremely sensitive to changes in pressure or magnetic field. Application of pressure first reduces the Curie temperature and at pressures exceeding 5 kbar antiferromagnetic ordering preceding the ferromagnetic ordering is observed [62]. Substitution of As, B or Si into the P sublattice results in an increase of the Curie temperature [63], which can easily be lifted to above room temperature for As or Si concentrations of 10% or by 4% of B. Substitution of Mn for Fe on the 3g sites further increases the magnetic moment to about 4  $\mu_B$ . To stabilize the Fe<sub>2</sub>P-type of structure, simultaneously to the Mn substitution also part of the P should be replaced.

The most extensively studied series of alloys is of the type MnFe(P,As). The magnetic phase diagram for the system MnFeP-MnFeAs [64] 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<sub>2</sub>P 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 [65, 66] and investigated possibilities to partially replace the As [67-69].

The large MCE observed in Fe<sub>2</sub>P 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 K to 450K). The excellent magnetocaloric features of the compounds of the type MnFe(P,Si,Ge,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.

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