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MAGNETOCALORIC REFRIGERATION AT AMBIENT TEMPERATURE

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Abstract. Modern society relies on readily available refrigeration. Magnetic refrigeration has three prominent advantages compared to compressor-based refrigeration. First there are no harmful gasses 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 paper we compare different materials, however, concentrating on transition metal containing compounds, as we expect that the limited availability of Rare-earth elements will hamper the industrial applicability. Because fundamental aspects of MCE are not so widely discussed we also give some theoretical considerations.

Keywords: magnetic refrigeration, transition metal compounds, magnetic entropy

1. Introduction

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. Therefore, magnetic refrigeration is an environmentally friendly cooling technology. It does not use ozone depleting chemicals (CFCs), hazardous chemicals (NH_3), 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 has been shown (Zimm et al. 1998) 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 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.

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 (Tishin 1999). 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, 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 increases the temperature span of the refrigerator, in comparison with the temperature change in a single cycle, all demonstrators nowadays are based on the active magnetic regenerator design (Barclay et al. 1981).

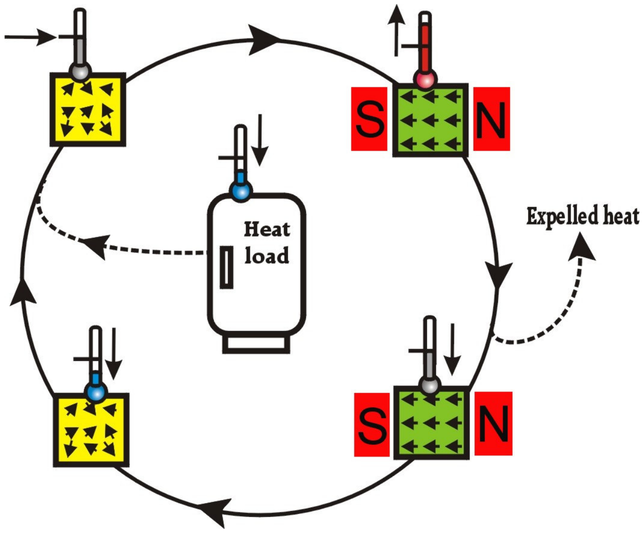

Figure 1 Schematic representation of a magnetic-refrigeration cycle, which transports heat from the heat load to the ambient. Left and right depict material in low and high magnetic field, respectively.

2. Theoretical considerations

When a material is magnetized in an applied magnetic field, the entropy associated with the magnetic degrees of freedom, the so called magnetic entropy S_m, is changed as the field changes the magnetic order of the material. Under adiabatic conditions, ΔS_m must be compensated by an equal but opposite change of the entropy associated with the lattice, resulting in a change in temperature of the material. This temperature change ΔT_{ad}, is usually called the magnetocaloric effect. It is related to the magnetic properties of the material through the thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B . \qquad (1)$$

For magnetization measurements made at discrete temperature- and field-intervals, ΔS_m can be calculated by means of

$$\Delta S_m(T,B) = \sum_i \frac{M_{i+1}(T_{i+1},B) - M_i(T_i,B)}{T_{i+1} - T_i} \Delta B \quad , (2)$$

where $M_{i+1}(T_{i+1},B)$ and $M_i(T_i,B)$ represent the values of the magnetization in a magnetic field B at the temperatures T_{i+1} and T_i , respectively. On the other hand, the magnetic entropy change can be obtained more directly from a calorimetric measurement of the field dependence of the heat capacity and subsequent integration:

$$\Delta S_m(T,B) = \int_0^T \frac{C(T',B) - C(T',0)}{T'} dT' \ , \qquad (3)$$

where *C(T, B)* and *C(T, 0)* are the values of the heat capacity measured in a field B and in zero field, respectively. It has been confirmed that the values of $\Delta S_m(T,B)$ derived from the magnetization measurement coincide with the values from calorimetric measurement (Gschneidner et al. 1999; Tegus et al. 2002c).

The adiabatic temperature change can be derived either by monitoring the temperature of the material during a field sweep, so called direct measurement, or by using the experimentally measured or theoretically predicted magnetization and heat capacity and integrating numerically

$$\Delta T_{ad}(T,B) = -\int_0^B \frac{T}{C(T,B')} \left(\frac{\partial M}{\partial T} \right)_B dB' \,. \quad (4)$$

Obviously, the MCE is large when $\left(\frac{\partial M}{\partial T} \right)_B$ is large and *C(T,B)* is small at the same temperature. This condition is true for paramagnetic materials near zero Kelvin where the magnetic susceptibility diverges and the heat capacity approaches zero. This is the reason why the first realization of magnetic refrigeration worked at very low temperatures (Giauque et al. 1933). As we are interested in effects at higher temperatures, the heat capacity is generally quite large, of the order of the Dulong Petit rule; C~3NR with N the number of atoms and R the molar gas constant. Therefore, we should concentrate on finding a large change in magnetization at the relevant temperature. Since $\left(\frac{\partial M}{\partial T} \right)_B$ peaks at the magnetic ordering temperature, a large MCE is expected close to this magnetic phase-transition and the effect may be further maximized, when the order-parameter of the phase transition changes strongly within a narrow temperature-interval. The latter is true for phase transitions of first order.

Most magnetic phase-transitions are of second order, there exist two theoretical models that under certain conditions account for first order phase-transition, the model of itinerant electron metamagnets and the Bean-Rodbell model(Bean et al. 1962; Moriya et al. 1977). In the former, spin fluctuations are treated in a Landau-Ginzburg type of approach. Bean and Rodbell postulate a strong volume dependence of the critical temperature and find, for a certain range of parameters, a local minimum in the Gibb’s free energy. These models are currently used to describe the unusual magnetic response of several possible magnetic refrigerants that will be discussed below(Yamada et al. 2003; von Ranke et al. 2004a; von Ranke et al. 2004b; Tegus et al. 2005b).

In view of applications the interest in first order transitions is directly related to the fact that a relatively small applied magnetic field can induce a strong change in entropy because it includes a certain amount of latent heat. However, with any first order transition, also thermal- or field-hysteresis is occurring which for applications should be small. The latent heat associated with the first order magnetic phase-transition can also improve the performance of the active magnetic refrigerator regenerator (Russek et al. 2006).

3. Magnetocaloric materials

Though the MCE was first discovered in simple iron(Warburg 1881), 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 $Gd_5(Ge_{1-x}Si_x)_4$ ($0.3 \leq x \leq 0.5$)(Pecharsky et al. 1997b), there is a strongly increased interest from both fundamental and practical points of view to study the MCE in these materials (Choe et al. 2000; Morellon et al. 2000). There exists a long list of recent publications on Gd5(Ge, Si)4 and related compounds. For this we would like to refer the reader to a recent review of Geschneidner et al. (Gschneidner et al. 2005b). 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. Many interesting physical phenomena have been observed in these compounds (Morellon et al. 1998a; Pecharsky et al. 2002; Pecharsky et al. 2003b; Morellon et al. 2004a; Mozharivskyj et al. 2005)including unusual magnetoresistance (Morellon et al. 1998b; Levin et al. 2001; Morellon et al. 2001; Tang et al. 2004).

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(Pecharsky et al. 2003a). 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(Pecharsky et al. 1997a; Provenzano et al. 2004; Mozharivskyj et al. 2005). This sensitivity to impurities like carbon, oxygen and iron strongly influences the production costs of the materials which may hamper broad-scale application. The only impurities known so far to enhance the magnetocaloric effect and increases the magnetic ordering temperature are Pb, Sn (Li et al. 2006; Zhuang et al. 2006). 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 (Giguere et al. 1999; Gschneidner et al. 2000). This will also influence the optimal operation-frequency of a magnetic refrigerator and the efficiency.

Other $R_5(Si,Ge)_4$ compounds are also found to form in the monoclinic $Gd_5Si_2Ge_2$ type structure and when the structural transformation coincides with the magnetic ordering transition a large magnetocaloric effect is observed. This is most strikingly evidenced in the experiments of Morellon et al (Morellon et al. 2004b) on $Tb_5Si_2Ge_2$ 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 $R_5(Si,Ge)_4$ compounds are all lower than for the Gd compound as expected from De Gennes law. For cooling applications below liquid nitrogen temperatures some of these compounds may be interesting.

3.1. La(Fe,Si)$_{13}$ and related compounds

An 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, resulting in an alloy that contains by weight almost 80% transition elements (Kripyakevich et al. 1968). 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 (Palstra et al. 1983). 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 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 magnetocaloric effect was reported (Hu et al. 2000; Hu et al. 2001b; Fujieda et al. 2002). 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. 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(Liu et al. 2004c; Gutfleisch et al. 2005; Liu et al. 2005). Samples prepared in this way also show a very large magnetocaloric effect. To increase the magnetic ordering temperature without loosing 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 $La(Fe,Co)_{13-x}Al_x$ and $La(Fe,Co)_{13-x}Si_x$ with $x \approx 1.1$ and thus a very high transition-metal content, show a considerable magnetocaloric effect near room temperature (Hu et al. 2001a; Shen et al. 2004; Hu et al. 2005b; Proveti et al. 2005). 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 fact that the alloys with the highest Fe content have an antiferromagnetic ground-state indicates that antiferromagnetic direct exchange-interaction plays an important role in these compounds. Taking into account that this occurs at a very high Fe density, one may expect that expansion of the lattice will lead to an increase in ferromagnetic exchange. In rare-earth transition-metal compounds this can be achieved by hydrogenation, or introduction of other small atoms like B, C or N. A very strong lattice expansion (< 9%) and increase of T_C to almost 900 K is observed when nitrogen is used as interstitial element in La(Fe, Al)$_{13}$(Liu et al. 1995). Alloys with low aluminum content are found to accommodate up to 3 nitrogen atoms per formula unit. However, careful structural analysis showed that the interstitial atoms are located at 24 d sites between the icosahedrons formed by Fe^{II}, thus the Fe-Fe separation does hardly change and the strong increase in Tc should rather be attributed to changes in the electronic structure than changes in interatomic distances (Moze et al. 1999; Moze et al. 2000). The effect of interstitial nitrogen on the magnetocaloric properties is not studied yet. One may however expect that it is considerably reduced because the magnetic moments are reduced and the phase transition appears to be broadened. The latter however can be due to the fact that most samples studied so far are not fully homogeneous. Finally it should be mentioned that the authors of all studies on nitrogenated samples report the occurrence of considerable amounts of α Fe as impurity phase. Carbon as interstitial atom also leads to an increase in critical temperature (Chen et al. 2003; Shcherbakova et al. 2003; Liu et al. 2004a; Liu et al. 2004b; Wang et al. 2004). Similar to the nitrogen interstitials the Fe magnetic moments are reduced and for 0.5 carbon atoms per formula unit the phase transition becomes of second order with a much lower magnetic entropy change.

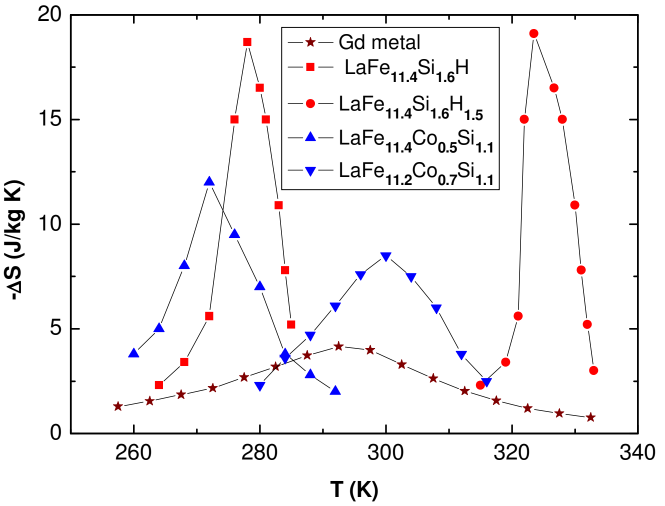

Figure 2 Magnetic-entropy change for different LaFe$_{13}$ based samples at a field change of 2 T (Fujita et al. 2003; Hu et al. 2005a).

Hydrogen is the most promising interstitial element. In contrast to the above mentioned interstitial atoms, interstitial hydrogen not only increases the critical temperature but also leads to an increase in magnetic moment (Irisawa et al. 2001; Fujieda et al. 2002; Fujita et al. 2003; Fujieda et al. 2004; Nikitin et al. 2004; Mandal et al. 2005). 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 μ_B to up to 2.2 μ_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. 2.

Obviously the question arises what causes the distinct differences resulting from different interstitial elements. The lower lattice expansion observed for hydrogen is consistent with the smaller volume of hydrogen compared with carbon or nitrogen. Unfortunately there are no electronic band-structure calculations available for these compounds but from general arguments we may discuss the observations. The lattice expansion, common to all interstitial alloys, leads to a narrowing of the Fe d-states and thus results in an increase in critical temperature and moment. On the other hand Fe d states may hybridize stronger with C or N p-states than with H s-states and it is well known that hybridization leads to an reduced moment (Qi et al. 1994). Because the interstitial sites are surrounded by a large fraction of Fe this effect is stronger than the former increase and thus leads for C and N interstitials to a net loss of moment. However, concerning the position of the interstitials, one would then expect that the reduction in moment would be stronger at Fe^{II} sites rather than at Fe^{I} sites, which is opposite to the observations from neutron diffraction (Moze et al. 2000). Obviously the interplay of exchange interaction and moment formation is more complex in these materials.

From the materials cost point of view the $La(Fe,Si)_{13}$ 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 produces always 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 $La(Fe,Si)_{13}$ type of alloys also a volume change of 1.5% is observed(Wang et al. 2003). 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.

3.2. MnAs based compounds

MnAs exist similar to $Gd_5Ge_2Si_2$ in two distinct crystallographic structures (Pytlik et al. 1985). 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%(Fjellvag et al. 1984). The transition from paramagnetic to ferromagnetic occurs at 307K, the reverse transition from ferromagnetic to paramagnetic occurs at 317K. As depicted in fig. 3, very large magnetic entropy changes are observed in this transition (Wada et al. 2001; Kuhrt et al. `1985). Similar to the application of pressure (Menyuk et al. 1969; Yamada et al. 2002) substitution of Sb for As leads to lowering of T_c (Wada et al. 2002; Wada et al. 2003), 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 to 40% of Sb T_C can be tuned between 220 and 320 K without loosing much of the magnetic entropy change (Morikawa et al. 2004; Wada et al. 2005a). Direct measurements of the temperature change confirm a ΔT of 2K/T (Wada et al. 2005b). On the other hand MnAs under pressure shows an extremely large magnetic entropy change (Gama et al. 2004; von Ranke et al. 2006) 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.

3.3. 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 μ_B, which is largely confined to the Mn atoms and with a small moment of about 0.3 μ_B associated with the Ni atoms(Webster et al. 1984). 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 Å, c=5.44 Å. 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(Hu et al. 2001c; Marcos et al. 2002). 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 (Kuo et al. 2005; Long et al. 2005; Zhou et al. 2005).

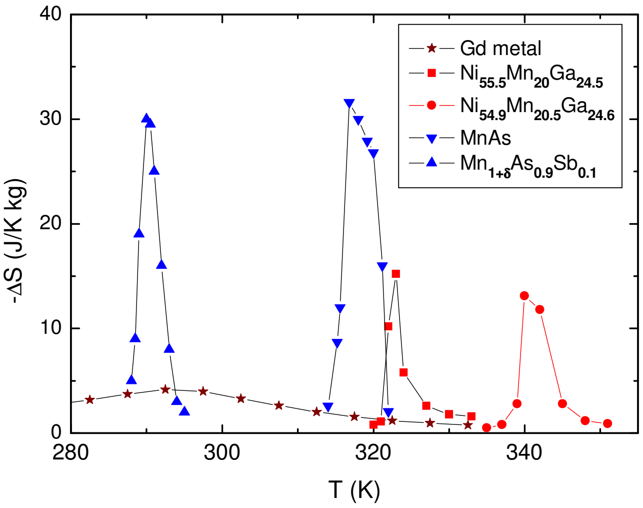

Figure 3 Magnetic-entropy change for MnAs and $Mn_{1+\delta}As_{0.9}Sb_{0.1}$(Wada et al. 2005a) and two NiMnGa(Long et al. 2005) alloys at a field change of 2 T.

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.

3.4. Fe_2P based compounds

The binary intermetallic compound Fe_2P can be considered as the parent alloy for an interesting type of materials. This compound crystallizes in the hexagonal non centre-symmetric Fe_2P 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 μ_B whereas the moment on the 3f sites is about 1 μ_B (Fujii et al. (1979)). The Curie temperature of this compound is 216 K and the magnetic transition is of first order (Fujii et al. (1977)). 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 (Kadomatsu et al. 1985). Substitution of As, B or Si into the P sublattice results in an increase of the Curie temperature (Jernberg et al. 1984), 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 μ_B. To stabilize the Fe_2P-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 (Beckmann et al. 1991) 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 (Tegus et al. 2002b; Brück et al. 2003; Bruck et al. 2005) and investigated possibilities to partially replace the As (Tegus et al. 2003; Tegus et al. 2005a; Zhang et al. 2005).

Polycrystalline samples can be synthesised starting from the binary Fe_2P, $MnAs_2$ 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 wrapt in Mo foil and sealed in quartz tubes under an argon atmosphere. These are heated at 1273 K for 1 hour, followed by a homogenisation process at 923 K for 50 hours 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 (Bacmann et al. 1994). From the broadening of the X-ray diffraction reflections, the average grain size is estimated to be about 100 nm (Tegus et al. 2002a).

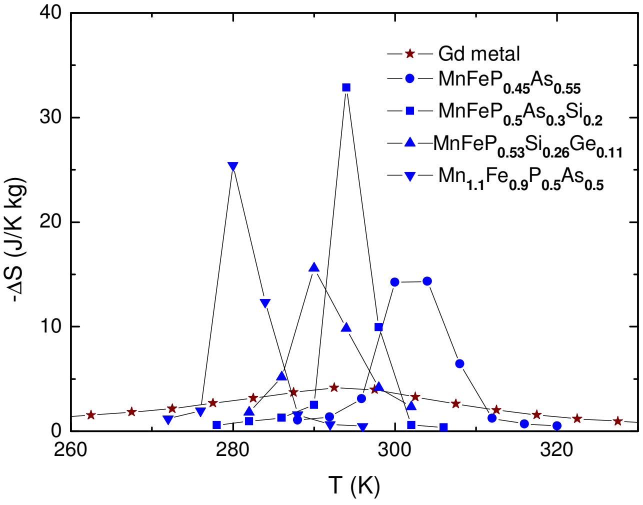

Figure 4 Magnetic-entropy changes of Fe_2P type compounds at magnetic field changes of 2 T(Tegus et al. 2002a; Tegus et al. 2004; Cam Thanh et al. 2006; Dagula et al. 2006).

Recently, we have observed a surprisingly large magnetocaloric effect in the compound $MnFeP_{0.5}As_{0.3}$ $Si_{0.2}$ at room temperature (Dagula et al. 2006). After replacing all As a considerable large magnetocaloric effect is still observed for MnFe(P,Si,Ge) (Cam Thanh et al. 2006).

We calculate the magnetic-entropy changes, ΔS_m, from magnetisation data by means of the equation 2. The results for several compounds are shown in fig. 4. The calculated maximum values of the magnetic entropy change are 14.5 J/kg K, 25.4 J/kg K and 32.9 J/kg K for a field change from 0 to 2 T. The maximum magnetic entropy in 3d materials depends on the spin moment S. Because there are two magnetic ions per formula unit, one has $S_m = 2R\ln(2S+1)$, where R is the universal gas constant. From the saturation magnetic moment, we estimate the average S value of the magnetic ions to be equal to S = 1 thus S_m = 18.3 J/mol K = 117 J/kg K, which is about 3.5 times larger than the value obtained from the magnetisation measurements. The origin of the large magnetic-entropy change should be attributed to the 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.

Bearing in mind the use of these materials in magnetic refrigerators, next to the magnetocaloric properties also the electrical and heat conductivity is of utmost importance. There is hardly any information on the electrical-transport properties of these alloys. The electrical resistance can also be useful for a more detailed investigation of the magnetic phase transition because it is very sensitive to changes in the interactions between magnetic ions. The availability of electrical-resistance data would make it possible to compare the critical magnetic fields derived from magnetic and electrical measurements and to understand the role of the electron-phonon and electron-magnon interactions in the magnetic phase transitions. The temperature dependence of the electrical resistance of $MnFeP_{0.55}As_{0.45}$, measured during cooling of a sample of $MnFeP_{0.55}As_{0.45}$, exhibits an anomaly T_{cr} = 231 K. Below T_{cr}, the electrical resistance increases with increasing temperature and has metallic character but, above T_{cr}, it decreases dramatically in a narrow temperature range and then recovers the metal-like dependence on temperature. The total contribution from both the electron-phonon scattering and the electron-magnon scattering in the paramagnetic (PM) phase is smaller than in the ferromagnetic (FM) phase which is contrary to normal ferromagnetic metallic materials. It is interesting to note that the transition at T_{cr} is accompanied by a change in the c/a ratio (Beckmann et al. 1991), which may lead to a change in the Fermi-surface topology and may affect the electron-phonon scattering. Preliminary band-structure calculations indicate a strong shift of the Fermi level associated with the phase-transition (Samolyuk et al. 2005).

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 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.

4. Refrigerator designs

Refrigerator design is an art on itself and as being not a specialist in this field, here I only want to mention a few aspects of this. The first magnetic refrigerator prototype or better demonstrator operating at room temperature utilized superconducting magnets and linear translation(Zimm et al. 1998). With an applied magnetic field of 5 tesla a cooling power of 600 W was realized with a charge of 3 kg of Gd spheres. Two equally sized cups containing the Gd spheres were reciprocating in and out of the high-field region, respectively. Nowadays there exist many magnetic refrigerators designed by different groups that operate near room temperature and utilize permanent magnets as field source. The first rotary magnetic refrigerator was built in Barcelona, Spain (Bohigas et al. 2000) utilizing permanent rod-magnets arranged on both sides of the magnetocaloric material (Gd metal foil) with in the gap a magnetic induction of 0.3 Teslal. An interesting permanent magnet design is a so called permanent-magnet array (PMA). A PMA based on the Halbach rotation theorem has been designed and constructed by Lee et al. (Lee et al. 2002) for a rotary-magnetic refrigeration system. The magnetic field generated by this PMA was over 3 tesla with an air gap of 5.8 mm. In a rotary design either the refrigerant or the magnet may be moving, the later was demonstrated in a collaboration project of Chubu electric company and Toshiba. The main advantage of moving the magnet instead of the AMRR is, that the connections between the heat exchangers and the AMRR do not change. Thus one avoids the need of sliding seals, which will increase the reliability of the device(Okamura et al. 2006). A modular system employing double channel micro heat-exchangers and rotating magnets with up to 1.9 tesla in a 20mm air gap has been presented by the company Cooltech Applications(Vasile et al. 2006). Steven Russek has recently discussed the costs of an air conditioner with a cooling power of 10.5kW based on magnetic refrigeration(Russek et al. 2006). Starting with a few challenging assumptions he comes to the conclusion that the magnet costs are the main constraint to achieve competing production costs. However, the assumption of a cycle frequency of 10 Hz nowadays at least appears unrealistic but advanced porous gradient material AMRR's may make this feasible. On the technology side of the development clearly many challenges remain to be solved.

5. Comparison of different materials and outlook

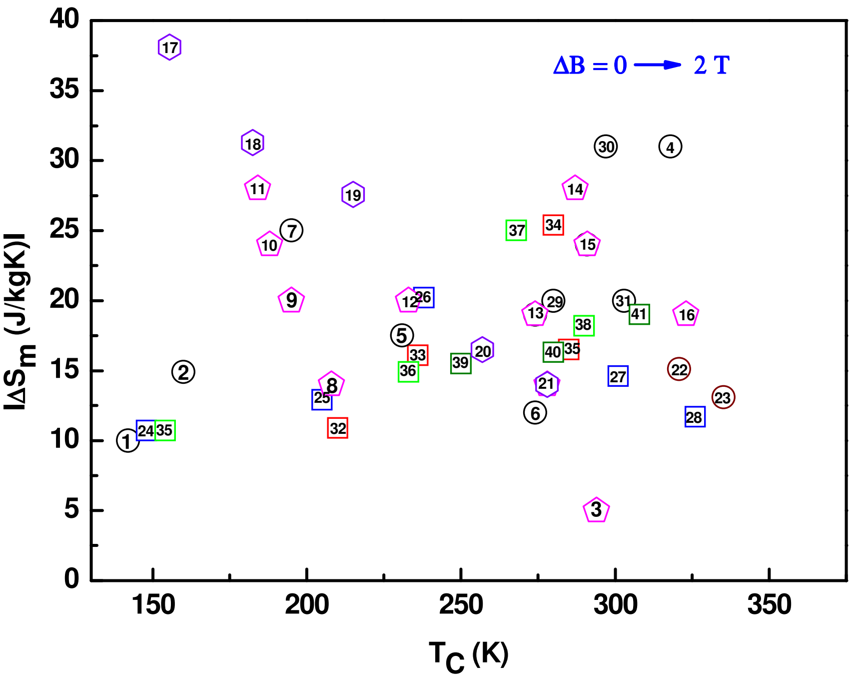

Figure 5 Maximal observed entropy-change of various materials at magnetic field changes of 2 T. 1 $DyCo_2$ (Gschneidner et al. 2005a), 2 Mn_3GaC (Tohei et al. 2003), 3 Gd (Dan'kov et al. 1998), 4 MnAs (Wada et al. 2003), 5 $MnAs_{0.75}Sb_{0.25}$ (Wada et al. 2003), 6 $LaFe_{11.2}Co_{0.7}Si_{1.1}$ (Hu et al. 2002),7 $LaFe_{11.8}Si_{1.2}$ (melt-spun) (Gutfleisch et al. 2005), 8 $La(Fe_{0.877}Si_{0.123})_{13}$ (Fujita et al. 2003), 9 $La(Fe_{0.880}Si_{0.120})_{13}$ (Fujita et al. 2003), 10 $La(Fe_{0.890}Si_{0.110})_{13}$ (Fujita et al. 2003), 11 $La(Fe_{0.90}Si_{0.10})_{13}$ (Fujita et al. 2003), 12 $La(Fe_{0.88}Si_{0.12})_{13}H_{0.5}$ (Fujita et al. 2003), 13 $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ (Fujita et al. 2003), 14 $LaFe_{11.7}Si_{1.3}H_{1.1}$ (Fujita et al. 2003), 15 $LaFe_{11.57}Si_{1.43}H_{1.3}$ (Fujita et al. 2003), 16 $La(Fe_{0.88}Si_{0.12})H_{1.5}$ (Fujita et al. 2003), 17 $Gd_5(Si_{0.25}Ge_{0.75})_4$ (Casanova I Fernandez 2004), 18 $Gd_5(Si_{0.30}Ge_{0.70})_4$ (Casanova I Fernandez 2004), 19 $Gd_5(Si_{0.365}Ge_{0.635})_4$ (Casanova I Fernandez 2004), 20 $Gd_5(Si_{0.45}Ge_{0.55})_4$ (Casanova I Fernandez 2004), 21 $Gd_5(Si_{0.45}Ge_{0.55})_4$ (Casanova I Fernandez 2004), 22 $Ni_{55.5}Mn_{20}Ga_{24.5}$ (Long et al. 2005), 23 $Ni_{54.9}Mn_{20.5}Ga_{24.6}$ (Long et al. 2005), 24 $MnFeP_{0.75}As_{0.25}$ (Tegus et al. 2002b), 25 $MnFeP_{0.65}As_{0.35}$ (Tegus et al. 2002b), 26 $MnFeP_{0.55}As_{0.45}$ (Tegus et al. 2002b), 27 $MnFeP_{0.45}As_{0.55}$ (Tegus et al. 2002b), 28 $MnFeP_{0.35}As_{0.65}$ (Tegus et al. 2002b), 29 $MnFeP_{0.5}As_{0.4}Si_{0.1}$ (Dagula et al. 2006), 30 $MnFeP_{0.5}As_{0.3}Si_{0.2}$ (Dagula et al. 2006), 31 $MnFeP_{0.5}As_{0.2}Si_{0.3}$ (Dagula et al. 2006), 32 $Mn_{1.3}Fe_{0.7}P_{0.5}As_{0.5}$ (Brück et al. 2003), 33 $Mn_{1.2}Fe_{0.8}P_{0.5}As_{0.5}$ (Brück et al. 2003), 34 $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}$ (Brück et al. 2003), 35 $Mn_{1.1}Fe_{0.9}P_{0.7}As_{0.3}$ (Brück et al. 2003), 36 $Mn_{1.1}Fe_{0.9}P_{0.7}As_{0.25}Ge_{0.05}$ (Tegus et al. 2005a), 37 $Mn_{1.1}Fe_{0.9}P_{0.7}As_{0.2}Ge_{0.1}$ (Tegus et al. 2005a), 38 $Mn_{1.1}Fe_{0.9}P_{0.7}As_{0.15}Ge_{0.15}$ (Tegus et al. 2005a), 39 $Mn_{1.1}Fe_{0.9}P_{0.80}Ge_{0.20}$ (Dagula et al. 2005), 40 $Mn_{1.1}Fe_{0.9}P_{0.78}Ge_{0.22}$ (Dagula et al. 2005), 41 $Mn_{1.1}Fe_{0.9}P_{0.77}Ge_{0.23}$ (Dagula et al. 2005).

The MCEs for field changes of 2 T are summarized in fig. 5. 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 (Pecharsky et al. 2001) these alloys are still favorable 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.

Material	T range K	ΔS(2T) J/kg K	ΔT(2T) K	Cost €/kg	Avail t	Limiting ingredient	Density t/m^3
Gd	270-310	5	5.8^d	20	1000	Gd	7.9
$Gd_5Ge_2Si_2$	150-290	27	6.6^d	60	140	Ge	7.5
La(Fe,Si)H	180-330	19	7^c	8	22000	La	7.1
MnAs	220-320	32	4.1^d	10	ul	none	6.8
MnNiGa	310-350	15	2^c	10	60	Ga	8.2
MnFe(P,As)	150-450	32	6^d	7	ul	none	7.3

Table 1: Comparison of different potential magnetocaloric materials. 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.

The main parameters of the various materials are also summarized in tab. 1 which allows a fast comparison. At present it is not clear which material will really get to the stage of real life applications. 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.

Taking into account the different requirements for magnetic refrigerants, it may be stated, that the ideal magnetic refrigerant should at least contain 80% transition metals with a large magnetic moment like Fe or Mn. In addition to this it should contain some cheap p-metal like Al or Si that can be used to tune the working point of the material. This material should then exhibit a magnetic ordering-transition of first order. Be workable as steel, with a corrosion resistance like stainless steel and a high electrical resistance. From that point of view one may get the impression that magnetic refrigeration is going to experience a similar future as the past 20 years of fuel cells. However, magnetic refrigeration is already currently much further developed. The gap to market is less severe because the refrigerators and heat pumps will consist of mainly the same parts as today's technology except of the compressor.

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