Magnetocalorics and magnetism in MnFe(P, Si, Ge) materials
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Chapter 4

MnFe(P, Si, Ge) compounds

4.1 Structure, magnetism and magnetocaloric properties of MnFe(P, Si, Ge) compounds

4.1.1 Introduction

In recent years, a significant number of new materials with large MCE have been found, such as the rare-earth (R) Laves phases (RM$_2$ with M = Al, Co or Ni), Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$, MnAs$_{1-x}$Sb$_x$, MnFeP$_{1-x}$As$_x$, LaFe$_{13-x}$Si$_x$ and their hydrides, and the manganites (R$_{1-x}$M$_x$MnO$_3$, with M = Ca, Sr or Ba) [1-5]. Among these materials, Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds with (0.2 $\leq$ x $\leq$ 0.5) [6] and MnFeP$_{1-x}$As$_x$ compounds with (0.15 $\leq$ x $\leq$ 0.65) [7-10] are the most prominent ones.

Gadolinium and its alloys are the best readily available materials today for magnetic refrigeration near room temperature. Gadolinium undergoes a second-order magnetic phase transition which does not involve magnetic and/or thermal hysteresis, and its alloys Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ undergo a combined first-order structural and magnetic phase transition, which leads to a giant magnetic-field-induced entropy change, in the vicinity of their ordering temperatures.

Regarding MnFeP$_{1-x}$As$_x$ and related compounds [11-14], their structural and magnetic properties are strongly related to a first-order magnetic phase transition which leads to a giant magnetic-field-induced entropy change, across their ordering temperatures. In addition, the Curie temperatures of MnFeP$_{1-x}$As$_x$ compounds can be
tuned between about 170 K and 330 K by changing the P/As ratio between about 1.5 and 0.5 without losing the large MCE. Also, the giant MCE in these compounds is reversible. However, Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ and MnFeP$_{1-x}$As$_x$ compounds also have some disadvantages since Gd is rather expensive and slightly soluble in water and As is a toxic element. Our motivation is to find materials that exhibit a large MCE for cooling applications at room-temperature but also are relatively cheap and non-toxic. In this chapter, we investigate the MCEs in MnFe(P, Si, Ge) compounds.

4.1.2 Sample preparation

MnFe(P, Si, Ge) compounds were synthesized by a mechanically activated solid-diffusion method. The starting materials, pure Mn, Si, Ge chips (purity 99.9%), red-P (purity 99.9%) and the binary compound Fe$_2$P (purity 99.5%), were ball milled under vacuum (about 10$^{-7}$ mbar) in a vibrating-ball mill. During the milling process, solid-state reactions are initiated through repeated deformation and fracture of the powder particles. In order to obtain homogeneous samples, 5 g of the starting materials were ball milled up to 200 hours. After milling, the powder was pressed into pellets and sealed in quartz ampoules in Ar atmosphere of 100-200 mbar. Then, the ampoules were heated up at 1100$^0$C for 5-40 hours, followed by annealing at 550-850$^0$C for 50 hours. Finally, they were slowly cooled down to room temperature. In the whole process, the heating and cooling rate is 180$^0$C per hour.

4.1.3 Results and discussion

4.1.3.1 Structural properties

Figure 4.1 shows the powder x-ray diffraction (XRD) patterns of MnFe(P$_{0.89-x}$Si$_x$)Ge$_{0.11}$ compounds, with nominal composition x = 0.19, 0.22, 0.26, 0.30 and 0.33, measured at room temperature. The XRD patterns show that all samples crystallize in the hexagonal Fe$_2$P-type of structure (space group $\bar{P}6_2m$). It is seen that the compounds contain a small amount of second phase which has been identified as cubic Fe$_2$MnSi (space group $Fm\bar{3}m$). The arrow indicates a reflection of the impurity phase. The fraction of this phase increases with increasing Si content. The (3 0 0), (2 1 1) and (0 0 2) reflections almost coincide.
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Figure 4.1: Powder XRD patterns of MnFe(P_{0.89-x}Si_x)Ge_{0.11} compounds with x = 0.19, 0.22, 0.26, 0.30 and 0.33, measured at room temperature.

A schematic drawing of the hexagonal Fe\textsubscript{2}P-type of structure is shown in Fig. 4.2. In this structure, the Mn atoms occupy the 3g sites, the Fe atoms the 3f sites and the P, Ge and Si atoms the 1b and 2c sites, with preference of Ge for the 2c sites and of Si for 1b sites. Although the atomic size of Ge (1.25 Å) is somewhat larger and that of Si (1.10 Å) is a bit smaller than that of As (1.15 Å), the structure does not change when As is totally replaced by Ge and Si in the MnFeP_{1-x}As\_x system. The density $\rho$ of MnFeP_{0.63}Si_{0.26}Ge_{0.11} was estimated using

$$\rho = \frac{M}{V},$$

where M is the mass of one unit cell, and V is the unit-cell volume which is calculated based on the lattice parameters \(a\) and \(c\). The resulting density of MnFeP_{0.63}Si_{0.26}Ge_{0.11} is $\rho = 6.7$ g/cm\textsuperscript{3} which is comparable with the density of bulk Gd ($\rho = 7.9$ g/cm\textsuperscript{3}) [15,16].
Figure 4.2: Schematic representation of the crystal structure of MnFe(P,Si,Ge)

Figure 4.3: EPMA image of MnFeP$_{0.63}$Si$_{0.26}$Ge$_{0.11}$
Figure 4.3 shows an electron probe microanalysis (EPMA) image of MnFeP\textsubscript{0.63}Si\textsubscript{0.26}Ge\textsubscript{0.11}. The energy of the electron beam was 20 kV. In the image, the black area with white shadow represents holes, which account for about 10% of the sample surface. The white area without shadow represents a second phase, which also accounts for about 10% of the sample. A composition analysis carried out on the main phase of the MnFeP\textsubscript{0.70}Si\textsubscript{0.19}Ge\textsubscript{0.11}, MnFeP\textsubscript{0.67}Si\textsubscript{0.22}Ge\textsubscript{0.11}, and MnFeP\textsubscript{0.63}Si\textsubscript{0.26}Ge\textsubscript{0.11} compounds, indicates that the real compositions of the main phase are Mn\textsubscript{1.06}Fe\textsubscript{0.96}P\textsubscript{0.75}Si\textsubscript{0.13}Ge\textsubscript{0.10}, Mn\textsubscript{1.04}Fe\textsubscript{0.98}P\textsubscript{0.76}Si\textsubscript{0.13}Ge\textsubscript{0.09}, and Mn\textsubscript{1.05}Fe\textsubscript{0.98}P\textsubscript{0.67}Si\textsubscript{0.19}Ge\textsubscript{0.11}, respectively. It is seen that the real composition is different from the nominal one. We found excess Mn and P in the main phase of each sample whereas there was less Fe and Si. Accordingly, the second phase was also analyzed, and more Fe and Si were found in the second phase of the samples. So, the difference between the real and the nominal composition is understandable. Because the sample is not homogeneous, Fe and Si go to the second phase. This causes a lack of Fe and Si in the main phase of the sample, leading to a difference in the real composition. Moreover, we found that the resulting composition is very sensitive to the starting materials and to the method of preparation such as ball-milling time, starting-material mass, sintering and annealing conditions. If the quality of the starting material is good, and the milling time is sufficient, and if a proper heat treatment is given, the resulting sample is more homogeneous.

4.1.3.2 Crystallite size investigation

From Fig. 4.3, the average crystallite size in the MnFeP\textsubscript{0.63}Si\textsubscript{0.26}Ge\textsubscript{0.11} sample is estimated to be about 100 nm. Besides this, the crystallite size of this sample was also calculated from the XRD pattern using the Scherrer equation:

\[
d = \frac{k \lambda}{B \cos \theta},
\]

where \(d\) is the crystallite size in the sample, \(k\) is a shape factor (for spheres \(k = 0.89\), for cubes \(k = 0.83\)–0.91, for tetrahedrons \(k = 0.73\)–1.03, and for octahedrons \(k = 0.82\)–0.94), \(\lambda\) is the wavelength (for Cu-K\(_\alpha\) radiation \(\lambda = 1.54\) Å), \(\theta\) is the position of the
strongest reflection, $B$ is the width at half maximum of the strongest reflection corrected for instrument resolution.

The derived crystallite size is $d = 90$ nm, which is in quite good agreement with the value estimated from the EPMA image ($d = 100$ nm).

**Figure 4.4:** Investigated part of the XRD pattern of $\text{MnFeP}_{0.63}\text{Si}_{0.26}\text{Ge}_{0.11}$

**Table 4.1:** Crystallite size in $\text{MnFeP}_{0.63}\text{Si}_{0.26}\text{Ge}_{0.11}$, sintered at $1100^\circ C$ for 5 hours, followed by different annealing temperatures from $550^\circ C$ to $850^\circ C$ for 50 hours or without annealing, then cooled down to ambient temperature

<table>
<thead>
<tr>
<th>Heat-treatment conditions</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1100^\circ C / 5\ h + \text{cool down}$</td>
<td>86</td>
</tr>
<tr>
<td>$1100^\circ C / 5\ h + 550^\circ C / 50\ h + \text{cool down}$</td>
<td>89</td>
</tr>
<tr>
<td>$1100^\circ C / 5\ h + 650^\circ C / 50\ h + \text{cool down}$</td>
<td>90</td>
</tr>
<tr>
<td>$1100^\circ C / 5\ h + 750^\circ C / 50\ h + \text{cool down}$</td>
<td>104</td>
</tr>
<tr>
<td>$1100^\circ C / 5\ h + 850^\circ C / 50\ h + \text{cool down}$</td>
<td>110</td>
</tr>
</tbody>
</table>
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Shown in Fig. 4.4 is part of the XRD pattern of \( MnFeP_{0.63}Si_{0.26}Ge_{0.11} \), sintered at 1100 \(^\circ\)C for 5 hours, followed by annealing at 850 \(^\circ\)C for 50 hours, then cooled down to ambient temperature. The dependence of the crystallite size on the annealing temperature was investigated. XRD was performed on five \( MnFeP_{0.63}Si_{0.26}Ge_{0.11} \) samples, all with the same composition and the same sintering condition but different annealing temperatures as listed in Table 4.1. The crystallite size was found to be annealing-temperature dependent; the higher the annealing temperature, the larger the crystallite size. Samples that have not been annealed have smaller crystallite size than the annealed samples.

4.1.3.3 Magnetic properties

Figure 4.5 shows the magnetic-field dependence of the magnetization of \( MnFeP_{0.63}Si_{0.26}Ge_{0.11} \) at 5 K. The compound is FM at 5 K with measured saturation magnetic moment 4.22 \( \mu_B/\text{f.u.} \). The field dependence of the magnetization of the compounds with \( x = 0.19, 0.22, 0.30, 0.33 \) was also measured. The M-B curves show that all compounds are FM at 5 K and that the observed magnetic moments are in the range 3.9-4.3 \( \mu_B/\text{f.u.} \). These values are consistent with the spontaneous magnetic moments (about 4 \( \mu_B/\text{f.u.} \)) reported for MnFe(P,As) compounds [13].

![Figure 4.5: Field dependence of the magnetization of MnFeP\(_{0.63}Si_{0.26}Ge_{0.11}\) at 5 K](image_url)
In Fig. 4.6, the temperature dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$ is presented. The measurement was carried out in the following way: first the magnetization was measured with decreasing temperature on the as-prepared sample from 350 to 150 K (curve (a)). After this, the measurement was continued with increasing temperature from 150 to 350 K (curve (b)). Finally, measurements were performed with decreasing temperature from 350 to 150 K (curve (c)). In the first cooling process, a virgin state is observed with the lowest paramagnetic (PM) - FM phase-transition temperature occurring at $T_{C1} = 225$ K. This virgin state is unique, and its origin is not yet understood well. However, a more careful study can be found in [14].

![Figure 4.6: Temperature dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$, (a) first cooling of the as-prepared sample, (b) subsequent heating, (c) subsequent cooling, the lines are guides to the eye.](image)

In the subsequent heating process, a FM-PM phase transition temperature is found at $T_{C2} = 288$ K, which is the highest phase-transition temperature. In the second cooling process, the phase-transition temperature is observed at $T_{C3} = 270$ K, which is different from the two transition temperatures mentioned above. The magnetic transition shows a clear thermal hysteresis of 18 K as evidence of a first-order magnetic phase transition. The thermal hysteresis between the transitions observed in the first heating and the second cooling process for all investigated MnFe(P$_{0.89-x}$Si$_x$)Ge$_{0.11}$ samples is in the range 15 - 22 K.
Figure 4.7: Temperature dependence of the magnetization of MnFeP_{0.59}Si_{0.30}Ge_{0.1}*, measured during successive cycles of cooling and heating at 0.05 T

In order to have more samples for studying, a second 5 g batch of MnFeP_{0.59}Si_{0.30}Ge_{0.1} has been prepared. This sample is called MnFeP_{0.59}Si_{0.30}Ge_{0.1}*. Figure 4.7 shows the temperature dependence of the magnetization of MnFeP_{0.59}Si_{0.30}Ge_{0.1}*, measured during successive cycles of cooling and heating at 0.05 T. A clear thermal hysteresis and thermal-history dependence of the magnetic phase transition can be observed. Upon cooling the as-prepared sample for the first time, a sharp increase in magnetization indicates a PM to FM phase transition at 223 K. On increasing the temperature, the FM to PM phase transition occurs at about 286 K. When the temperature is decreased for a second time, the magnetic ordering temperature is about 268 K, which is much higher than that (223 K) in the virgin state. Compared with the previous sample, MnFeP_{0.59}Si_{0.30}Ge_{0.1} (*) has T_{C1} = 223 K, T_{C2} = 286 K, and T_{C3} = 268 K, these values are 2 K lower than those for the sample prepared at the first time. Other properties, such as the thermal hysteresis, the saturation magnetization at 5 K and the sharpness of the magnetic-phase transitions are the same as for the MnFeP_{0.59}Si_{0.30}Ge_{0.1} sample. It means that the compound can be prepared in an almost reproducible way. The FM-PM phase-transition temperature and the magnetization are relatively stable at the subsequent heating and cooling cycles.
Measurements of the temperature dependence of the magnetization of MnFeP<sub>0.59</sub>Si<sub>0.30</sub>Ge<sub>0.11</sub> were carried out in constant fields of 1, 2, 3, 4, and 5 T. In Fig. 4.8, we see that the magnetization adopts higher values with increasing magnetic field and that the magnetic-phase-transition temperature increases with increasing field. The transition temperatures upon heating are 289.5, 291.1, 293.2, 295.6, and 298.5 K in magnetic fields of 1, 2, 3, 4, and 5 T, respectively. A thermal hysteresis of about 18 K is quite stable under the magnetic-field changes.

Figure 4.9 shows the magnetic-phase diagram of MnFeP<sub>0.59</sub>Si<sub>0.30</sub>Ge<sub>0.11</sub> constructed from the magnetization loops in Fig. 4.8. The filled squares are the values of $T_C$ on cooling and the dashed squares are the $T_C$ values on heating. The two straight lines are the linear fits of these data. The distance between these two lines shows a thermal hysteresis of about 18 K. We observed that the Curie temperature increases with increasing applied field with an average rate of 2.2 K/T. This rate is much lower than 4.4 K/T for Gd<sub>5</sub>Si<sub>1.7</sub>Ge<sub>2.3</sub> and 3.3 K/T for MnFeP<sub>0.45</sub>As<sub>0.55</sub>. [13].
4.1.3.4 Relation between lattice parameters and Curie temperature

The relation between the lattice parameters $a$ and $c$ and the Curie temperature has been investigated. In order to obtain accurate values of the lattice parameters, silicon powder was added as a standard, mixed together with MnFe(P$_{0.89-x}$Si$_x$)Ge$_{0.11}$ powder for XRD measurements at room temperature. The Curie temperatures were derived from the magnetization data.

Figure 4.10 shows that the dependencies of the parameters $a$ and $c$, the $c/a$ ratio, and the Curie temperature on the Si content are non-linear. For instance, with increasing Si concentration from 0.19 to 0.26, there is an increase of $a$ and a decrease of $c$. However, for further increase of the Si concentration from 0.26 to 0.33, a decrease of $a$ and an increase of $c$ is observed. The parameter $a$ has its maximum value when the Si concentration is 0.26 where the parameter $c$ has a minimum (see Figs. 4.10 a and b). The dependence of the $c/a$ ratio on the Si concentration is similar to the dependence of the parameter $c$ on the Si concentration (see Figs. 4.10 c and b). $T_C$ reaches its highest value when the parameter $a$ also reaches its maximum, while $c$ reaches a minimum value.
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Figure 4.10: Lattice parameters $a$ and $c$, $c/a$ ratio, and Curie temperature as a function of silicon content for $\text{MnFe}(P_{0.89-x}Si_x)\text{Ge}_{0.11}$ compounds. The lines are guides to the eye.

Table 4.2: Lattice parameters $a$ and $c$, $c/a$ ratio and magnetic-ordering temperature ($T_C$) of $\text{MnFeP}_{0.89-x}\text{Si}_x\text{Ge}_{0.11}$ compounds.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>6.010</td>
<td>3.471</td>
<td>0.577</td>
<td>240</td>
</tr>
<tr>
<td>0.22</td>
<td>6.028</td>
<td>3.459</td>
<td>0.574</td>
<td>270</td>
</tr>
<tr>
<td>0.26</td>
<td>6.040</td>
<td>3.424</td>
<td>0.567</td>
<td>292</td>
</tr>
<tr>
<td>0.30</td>
<td>6.035</td>
<td>3.458</td>
<td>0.573</td>
<td>288</td>
</tr>
<tr>
<td>0.33</td>
<td>6.030</td>
<td>3.469</td>
<td>0.575</td>
<td>260</td>
</tr>
</tbody>
</table>

Figures 4.10 b and d show that $T_C$ increases as the parameter $c$ decreases. This might be understood bearing in mind that when the parameter $c$ decreases, the Fe-Fe layer distance also decreases, leading to a stronger exchange interaction between
adjacent Fe-layers, so that $T_C$ will be higher. The non-linear dependence of $T_C$ on the Si concentration is in good agreement with other results \[18\].

It can be seen in Table 4.2 that the Curie temperature, which is also the temperature where the maximum isothermal magnetic-entropy change occurs, can be tuned by the Si concentration. However, the dependence of the Curie temperature on the Si concentration is extremely strong and non-linear. The most suitable $T_C$ for room-temperature magnetic-refrigeration application is observed for the compounds with $x = 0.26$ and 0.30. The $c/a$ ratio is inverse proportional to the Curie temperature: $T_C$ has a maximum value of 292 K for $x = 0.26$ while $c/a$ has a minimum value at this composition.

### 4.1.3.5 Magnetocaloric effect

The magnetization of a sample is usually measured as follows: Taking MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$ as an example, starting at a temperature in the FM state, at 276 K, a magnetic isotherm is measured with increasing magnetic field. After the measurement, the temperature is increased from 276 to 280 K where the next magnetic isotherm is measured. This is repeated with a 4 K temperature step up to 292 K, covering the whole magnetic-phase-transition region. This way of measurement is called the “normal method”, in contrast with the “new method” of measuring magnetic isotherms of samples with a large thermal hysteresis, which we will discuss later.

Figure 4.11 shows the magnetic isotherms of MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$, measured in the vicinity of the Curie temperature with increasing and subsequently with decreasing magnetic field. The measurements were carried out by the “normal method”. A gradual decrease of the magnetization with temperature increasing from 276 to 292 K is observed. Up to 5 T, no field-induced magnetic transition is observed, but a small magnetic hysteresis between the curves measured with increasing and subsequent decreasing field is present at 280, 284, and 288 K. This hysteresis is expected for first-order magnetic phase transitions. In contrast with MnFe(P$_{1-x}$As$_x$) and Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds, we do not observe a field-induced transition for fields up to 5 T in all samples. But the large change of magnetization with temperature near the phase transition results in large MCE values.
**Figure 4.11:** Magnetic isotherms of \( \text{MnFeP}_{0.59}\text{Si}_{0.30}\text{Ge}_{0.11} \), measured in the vicinity of the Curie temperature with increasing and subsequent decreasing magnetic field. The measurement was carried out following the “normal method”.

In Fig. 4.12, the magnetic isotherms of \( \text{MnFeP}_{0.89-x}\text{Si}_x\text{Ge}_{0.11} \) compounds are displayed, measured in the vicinity of the Curie temperature with increasing temperature and magnetic field. All measurements were performed with increasing temperature, according to the normal method. All samples show a large change of magnetization with temperature near the transition. From the isothermal magnetization measurements, the isothermal magnetic-entropies were derived using the Maxwell relations.
Figure 4.12: Magnetic isotherms of $\text{MnFeP}_{0.89-x}\text{Si}_x\text{Ge}_{0.11}$ measured in the vicinity of the Curie temperature with increasing temperature and magnetic field. The measurements were carried out following the “normal method”.

Figure 4.13: Isothermal magnetic-entropy changes in $\text{MnFeP}_{0.89-x}\text{Si}_x\text{Ge}_{0.11}$ compounds with $x = 0.22, 0.26, 0.30,$ and $0.33,$ for magnetic-field changes of 0-2 T (lower curves) and 0-5 T (upper curves).
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In Fig. 4.13 are, the magnetic-entropy change -\( \Delta S_m \) is presented for MnFe\(_{0.89-x}\)S\(_x\)Si\(_x\)Ge\(_{0.11}\) compounds, as derived from magnetization measurements according to the “normal method”. All compounds show appreciable peaks when subjected to magnetic field changes from 0 to 2 T and from 0 to 5 T. The -\( \Delta S_m \) values for 0 – 2 T and for 0 – 5 T field change are listed in Table 4.3.

However, the magnetic-entropy change derived from the magnetization obtained following the “normal method” brings a problem. The problem arises because of the large thermal hysteresis, which directly affects the history dependence of the magnetic response of the first-order transition. So far, there have been a lot of arguments about the correct determination of the isothermal magnetic-entropy change from magnetic measurements carried out on materials with the first-order magnetic phase transition [19-21]. To avoid the hysteresis problem, we have recently developed a new method of measuring magnetic isotherms of these compounds [22]. We argue that the Maxwell relations are valid but experiments need to be carried out with great care, and the history dependence of the magnetic response of the first-order transition should be considered when planning the experiment. By means of this new method, the isothermal magnetic-entropy changes can be derived more accurately with the Maxwell relation. We found that the way to treat the history of the samples correctly is to measure the isothermal magnetization by cooling the samples from the PM state to the target temperature for each of the magnetic isotherms. This we call the “new method”.

Figure 4.14 shows magnetization isotherms of MnFe\(_{0.89-x}\)S\(_x\)Si\(_x\)Ge\(_{0.11}\). We observe S-shaped magnetization curves for all compounds in the vicinity of the magnetic-phase-transition temperature, corresponding to a magnetic field-induced transition which is similar to that reported for MnFe\(_{1-x}\)As\(_x\) compounds. Let us make a comparison between the magnetic isotherms, measured by the normal method shown in the Fig. 4.12 and those measured by the new method shown in the Fig. 4.14. Surprisingly, there is a field-induced magnetic phase transition in the curves measured by the new method. What is the reason for this?

It can be understood as follows: In the sample which has a first-order magnetic-phase transition, and exhibits very large thermal hysteresis, when the measurements are performed by the normal method, the first measurement (the first magnetization curve) starts mainly in the FM state. After this measurement, the
portion of the FM state has increased and, from that point on, we find a larger FM contribution than there should actually be present. Therefore, in the next measurement (the next magnetization curve) there is a strong memory of the FM state, and when the field-induced transition is not a pronounced one, it is barely observed. In contrast, when the magnetic isotherms are measured by the new method, after each measurement, the sample is brought to the PM state. By doing this, the memory of each previous measurement is erased, so that we observe the correct fraction of FM and PM state, and then the field-induced transition is observed.

**Figure 4.14:** Magnetic isotherms of $\text{MnFeP}_{0.89-x}\text{Si}_x\text{Ge}_{0.11}$, measured in the vicinity of the Curie temperature with increasing temperature and magnetic field. The measurements were carried out following the “new method”.
In Fig. 4.15, the magnetic-entropy changes are presented for some selected compounds, derived from the magnetization data which have been measured with the “new method”. All compounds show pronounced peaks when subjected to field changes. The \(-\Delta S_m\) values for 0 – 2 T and 0 – 5 T field changes are listed in Table 4.3.

**Figure 4.15:** Isothermal magnetic-entropy changes in MnFe(P_{0.89-x}Si_{x})Ge_{0.11} compounds with x = 0.22, 0.26, 0.30, and 0.33, for magnetic field changes of 0-1 T (lowest curves), 0-2, 0-3 0-4, and 0-5 T (upper curves)

Although the shape of the magnetic isotherms looks different when the measurements were carried out following the normal and the new method, a large magnetization change under the temperature changes is still observed in all compounds. The derived magnetic-entropy changes are large and the values are not much different between these two methods. This observation is different from what was found for Mn_{0.99}Cu_{0.01}As and MnFeP_{0.8}Ge_{0.2} where the MCE values derived by the new method are less than half of those derived by the normal method [22]. This is
because in the MnFe$P_{0.89-x}Si_xGe_{0.11}$ compounds, the magnetic-phase transition is much broader than in Mn$_{0.99}$Cu$_{0.01}$As and MnFeP$_{0.8}$Ge$_{0.2}$. For the latter two compounds step-like magnetic isotherms are observed which is not observed for the MnFe$P_{0.89-x}Si_xGe_{0.11}$ compounds.

In Table 4.3, the magnetic ordering temperature measured at 0.05 T, thermal hysteresis, and isothermal magnetic-entropy change for a field change from 0 to 2 T and from 0 to 5 T for the MnFe$P_{0.89-x}Si_xGe_{0.11}$ compounds are summarized. We found a large MCE in all samples near room temperature which is of importance for magnetic-cooling application. The magnetic-entropy change in MnFe$P_{0.89-x}Si_xGe_{0.11}$ compounds near room temperature is larger than in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds and about the same as in MnFe(P$_{1-x}$As$_x$) compounds.

<table>
<thead>
<tr>
<th>x</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_{hys}$ (K)</th>
<th>$-\Delta S_m$ (J/kg$^{-1}$K$^{-1}$)</th>
<th>$-\Delta S_m$ (J/kg$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>&quot;normal method&quot;</td>
<td>&quot;new method&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta B = 0-2$ T</td>
<td>$\Delta B = 0-5$ T</td>
</tr>
<tr>
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<td>22</td>
<td>14.0</td>
<td>38.5</td>
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<td>15.6</td>
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</tr>
<tr>
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<td>18</td>
<td>13.9</td>
<td>39.1</td>
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<tr>
<td>0.33</td>
<td>260</td>
<td>20</td>
<td>13.1</td>
<td>36.4</td>
</tr>
</tbody>
</table>

4.1.3.6 Heat capacity
Specific-heat measurements were performed in the temperature range from 20-320 K in a home-built set-up. The accuracy of the measurement is better than 1 % in the whole temperature range. Figure 4.16 shows the temperature dependence of the specific heat of MnFe$P_{0.59}Si_{0.39}Ge_{0.11}$, measured with increasing temperature in zero field.
Figure 4.16: Temperature dependence of the specific heat of $\text{MnFeP}_{0.59}\text{Si}_{0.30}\text{Ge}_{0.11}$, measured in zero field with increasing temperature. The inset shows the temperature dependence of the total entropy, derived from the specific-heat data.

The peak position corresponds to a Curie temperature of about 286 K, which is slightly smaller than the value of $T_C$ obtained from the magnetic measurement (288 K) at 0.05 T. The sharpness and the relatively large amplitude of the peak are both evidence of a first-order phase transition. The temperature dependence of the total entropy ($S$) in zero field was obtained by means of the formula:

$$ S(T) = S(0) + \int_0^T \frac{C_p(T')}{T'} dT', $$

taking $S(0) = 0$.

The inset of Fig. 4.16 shows the temperature dependence of the total entropy, derived from the specific-heat data. There is a change of the total entropy at the transition indicating that there is a change in the magnetic entropy at the transition that contributes to the total entropy change.
4.1.3.7 Transport properties
We have investigated the magnetic phase transitions and magnetocaloric properties of MnFe(P,Si,Ge) compounds by means of magnetic measurements [17, 23]. We have found large MCE values at a large range of working temperatures from about 250 K up to above 300 K. This temperature range is of great importance for magnetic-cooling applications. Further study of these compounds is needed. Besides the magnetocaloric properties, the electrical and heat conductivity are of utmost importance. Here, we present the electrical transport properties of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$.

![Figure 4.17: Field dependence of the magnetization of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$, measured on the virgin sample with decreasing temperature from 220-190 K](image)

Figure 4.17 shows the field dependence of the magnetization of a virgin sample at different temperatures. The measurement was carried out at a few temperatures decreasing from 220-190 K and, at each temperature, the curve was measured with increasing field from 0-5 T, except at 200 K where the measurement was done with both increasing and subsequently decreasing field. A linear field dependence of the magnetization is observed at temperatures higher than 205 K, showing PM states. When the temperature is decreased to 200 K, a sharp change in
the magnetization can be observed with increasing field at about 4 T. However, a similar change cannot be observed with decreasing field, except for a kink at about 4.4 T. Such behavior is not observed at lower temperatures. The magnetization curves at temperatures below 199 K show the FM state. From the results above, we can see that not only the temperature but also the magnetic field can induce an irreversible change in magnetization.

![Graph](image)

**Figure 4.18:** Temperature dependence of the resistivity of \( \text{MnFeP}_{0.67} \text{Si}_{0.22} \text{Ge}_{0.11} \), measured on the virgin sample at zero field and at a field of 3 T

In order to investigate the magneto-transport behavior in the virgin state, another virgin sample was used to investigate the temperature dependence of the resistivity in an applied field of 3 T. In Fig. 4.18, the temperature dependence of the resistivity of \( \text{MnFeP}_{0.67} \text{Si}_{0.22} \text{Ge}_{0.11} \) is shown in 0 and 3 T. The transition temperature has clearly shifted from 190 K to 203 K for magnetic fields of 0 and 3 T, respectively. It means that the average increase rate of the ordering temperature of the virgin sample is 4.3 K/T. Together with the shift of the transition temperature to a higher value, the resistivity also increases from 2500 \( \mu \Omega \text{cm} \) to 4360 \( \mu \Omega \text{cm} \) in 3 T, indicating that cracks are formed during the transition, causing an increase of the resistivity.
In Fig. 4.19 is the field dependence of the resistivity of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$, measured on the virgin sample at 250 K and 200 K. At 250 K, there is no clear change in the field dependence of the resistivity, but when the temperature is decreased to 200 K, with increasing field, a huge increase in the resistivity can be observed near the critical field ($B_c$) of about 1 T. When the field is decreased, the resistivity remains high, indicating an irreversible change in the resistivity with field. However, some changes in the resistivity can still be detected near the critical field (see the inset of Fig. 4.19).

Figure 4.19: Field dependence of the resistivity of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$, measured on a virgin sample at 250 K and 200 K. The inset presents the resistivity at 200 K in the range from 4570 to 4680 $\mu\Omega$ cm, measured with decreasing field.

In Fig. 4.20, the temperature dependence of the resistivity of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$ is shown in zero field. In order to compare the magnetic and the transport properties of this compound, the resistivity measurements were performed including also three steps. First, a measurement was carried out with decreasing temperature on the as-prepared sample. After this, a measurement was performed with increasing temperature and, finally, a measurement was performed with decreasing temperature on the once-cooled sample.
Chapter 4: MnFe(P, Si, Ge) compounds

Figure 4.20: Temperature dependence of the resistivity of \( \text{MnFeP}_{0.67}\text{Si}_{0.22}\text{Ge}_{0.11} \) at zero field.

Figure 4.21: Temperature dependence of the magnetization of \( \text{MnFeP}_{0.67}\text{Si}_{0.22}\text{Ge}_{0.11} \), measured at a magnetic field of 0.05 T. (1) first cooling of the as-prepared sample, (2) subsequent heating, (3) subsequent cooling.
We observed an extremely sharp transition at 190 K, where the electrical resistivity increases from about 300 $\mu\Omega$cm to 2500 $\mu\Omega$cm. Below this transition temperature, the resistivity is constant and above the transition it decreases slowly with decreasing temperature and has metallic character. The transition at 190 K is associated with the virgin effect observed in the magnetic measurement (Fig. 4.21). On a subsequent temperature increase, the resistivity increases slowly and a maximum value around 3755 $\mu\Omega$cm is observed. Then, the resistivity decreases abruptly showing a transition at 268 K.

This transition corresponds to the transition at $T_{C2}$ in Fig. 4.21 and indicates a strong coupling between spin, charge and lattice in the compound. Above this transition, the resistivity slowly decreases until the temperature reaches 300 K. When the measurement was performed with subsequent decreasing temperature, there is a magnetic transition at 248 K corresponding to the transition at $T_{C3}$ in the magnetization measurement. The resistivity increases dramatically in a narrow temperature range and then recovers the metal-like temperature dependence. The resistivity becomes much larger after this cooling process. Similar results have been observed in Fe$_{0.75}$Mn$_{1.35}$As [24] and ZnNMn$_3$ [25].

In the MnFe(P,Si,Ge) system, there are magnetic interactions between Mn-Mn, Mn-Fe, and Fe-Fe moments. The magnetoelastic phase transition can be associated with the Mn-Fe and Fe-Fe distances, which are related to the $a$ and $c$ lattice parameters [26]. The change in $T_C$ is associated with a change in the $c/a$ ratio. Correspondingly, after the first cycle of cooling and warming the PM-FM phase-transition temperature increases due to the irreversible change in lattice parameters and the thermal hysteresis decreases due to the smaller grain size, which results in the virgin effect.

After several cycles of cooling and warming processes, the microcracks in the sample are saturated. Figure 4.22 shows the temperature dependence of the resistivity of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$, measured at 5 T with increasing and subsequent decreasing temperature. The measurement was performed on the sample after three cycles of cooling and warming. The curves shown in Fig. 4.22 indicate that a 5 T magnetic field suppresses spin fluctuations, stabilizes the FM state and increases the PM-FM phase-transition temperature to higher temperatures.
Figure 4.22: Temperature dependence of the resistivity of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$, measured at 5 T with increasing and subsequent decreasing temperature.

Figure 4.23 represents the field dependence of the magnetoresistance (MR) for MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$ at different temperatures, in which MR is given by:

$$MR = \frac{(\rho_H - \rho_0)}{\rho_0} \times 100\%$$

We observed small values of MR at 280 and 285 K under a magnetic-field change, but a significant value as large as $MR = 28\%$ is observed at 270 K in a 5 T applied field. The magnetoresistance increases with increasing applied field.
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In conclusion, we have observed an agreement of the magnetic-phase transition temperatures in the magnetic and electrical-resistivity measurements. The transition at $T_{C1}$ is the sharpest, and $T_{C1}$ is much lower than $T_{C2}$ and $T_{C3}$. There is an unusual thermal history of the magnetic phase transition, the so-called virgin behavior. The virgin behavior is due to an irreversible change in lattice parameters at the transition. The lattice parameter change implies a volume change. The magnetization curves show that on cooling the as-prepared sample for the first time, a PM-FM phase transition is observed at 188 K. Subsequently increasing the temperature, the FM-PM phase transition occurs at about 270 K and upon a second decrease of the temperature, the magnetic-ordering temperature is at about 250 K, but the phase-transition temperatures and the magnetization are relatively stable at further heating and cooling cycles. However, a difference is observed in the electrical-resistivity measurements. The resistivities become higher with cycling. The irreversible change in resistivity is associated with electron scattering on cracks, defects and dislocations which are due to the formation of micro-cracks induced by the sharp change of lattice parameters during the magnetic phase transition. Moreover, we observed thermal hysteresis in both the magnetic and the electrical-resistivity measurements.

Figure 4.23: Field dependence of the magneto-resistance (MR) of MnFeP$_{0.67}$Si$_{0.22}$Ge$_{0.11}$ at 270, 275, 280 and 285 K

In conclusion, we have observed an agreement of the magnetic-phase transition temperatures in the magnetic and electrical-resistivity measurements. The transition at $T_{C1}$ is the sharpest, and $T_{C1}$ is much lower than $T_{C2}$ and $T_{C3}$. There is an unusual thermal history of the magnetic phase transition, the so-called virgin behavior. The virgin behavior is due to an irreversible change in lattice parameters at the transition. The lattice parameter change implies a volume change. The magnetization curves show that on cooling the as-prepared sample for the first time, a PM-FM phase transition is observed at 188 K. Subsequently increasing the temperature, the FM-PM phase transition occurs at about 270 K and upon a second decrease of the temperature, the magnetic-ordering temperature is at about 250 K, but the phase-transition temperatures and the magnetization are relatively stable at further heating and cooling cycles. However, a difference is observed in the electrical-resistivity measurements. The resistivities become higher with cycling. The irreversible change in resistivity is associated with electron scattering on cracks, defects and dislocations which are due to the formation of micro-cracks induced by the sharp change of lattice parameters during the magnetic phase transition. Moreover, we observed thermal hysteresis in both the magnetic and the electrical-resistivity measurements.
4.1.4 Conclusions

We have studied the structural, magnetic and magnetocaloric properties of MnFe(P,Si,Ge) compounds. The structural properties of the compounds were determined by XRD at room temperature which shows that all investigated compounds crystallize in the hexagonal Fe$_2$P-type structure with space group $P6_2m$. The (3 0 0), (2 1 1) and (0 0 2) reflections almost coincide, which indicates that all samples are PM at room temperature. The homogeneity and stoichiometry of the compounds were checked by EPMA, with results that are in a good agreement with the XRD results. It is very difficult to obtain a single phase MnFe(P,Si,Ge) sample by ball milling. However, the amount of second phase can be limited by reducing the silicon concentration.

The crystallite sizes of the samples were derived using the Scherrer equation, and are in the range from 90 to 110 nm. The crystallite size was found to depend on the annealing-temperature: the higher the annealing temperature, the larger the crystallite size. Magnetization measurements show that all investigated MnFe(P,Si,Ge) compounds are in the FM state at low temperature. With increasing temperature, the compounds undergo a FM-PM phase transition and the Curie temperatures are found tunable over a wide temperature interval covering the room-temperature range. In good agreement with MnFeP$_{1-x}$As$_x$ and Gd$_5$Si$_{1.7}$Ge$_{2.3}$ compounds, the Curie temperature of the MnFe(P,Si,Ge) compounds is found to be magnetic-field dependent: $T_C$ increases with increasing applied magnetic field with an average rate of 2.2 K/T. Above the magnetic-ordering temperature, the compounds are in the PM state, which is in a good agreement with the XRD results. In the FM state, the spontaneous magnetic moments are in the range 3.9-4.3 $\mu_B$/f.u. These values are consistent with the spontaneous magnetic moments (about 4 $\mu_B$/f.u) observed for the MnFe(P,As) compounds [13]. The magnetic moments at low temperature originate from the spin moments of the 3d electrons of the Mn and Fe atoms. Specific-heat measurements carried out on MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$ show a first-order FM-PM phase transition. The MCE derived from the magnetization data shows that this effect in the MnFe(P, Si, Ge) compounds is equally large as in Gd-based and MnFeP$_{1-x}$As$_x$ compounds. This means that we have succeeded in completely replacing As by (Ge, Si) in the latter compounds without losing the favorable magnetic properties. We have observed large MCEs in all investigated compounds. It is shown that, for first-
order magnetic-phase transition compounds, when the magnetization measurements are performed with the appropriate so-called “new method”, the real isothermal magnetic-entropy changes can be obtained by using the Maxwell relation. The upshot is that we have found relatively low-cost and non-toxic materials for room-temperature-cooling application. The magnetic, transport and magneto-transport properties of $\text{MnFeP}_{0.67}\text{Si}_{0.22}\text{Ge}_{0.11}$ have been investigated. The irreversible change in the lattice parameters results in thermal-history behavior associated with the magnetic phase transition, which indicates a strong dependence of the exchange interaction on the separation between the magnetic atoms. With increasing number of heating and cooling cycles, the electrical resistivity shifts to higher values due to the formation of microcracks induced by the sharp lattice-parameter change during the magnetic phase transition. The origin of this irreversible transport behavior is the reduction of the mean-free path of the charge carriers, associated with electron scattering on cracks, defects and dislocations. Both the temperature and the magnetic field can induce irreversible changes in resistivity and in magnetization. A significant positive magnetoresistance, as large as 28%, is observed at 270 K in an applied field of 5 T.
4.2 Influence of Si and Ge on the magnetic and magnetocaloric properties of MnFe(P, Si, Ge) compounds

4.2.1 Introduction

We have found large MCEs and favourable magnetic properties for low-cost and non-toxic MnFe(P, Si, Ge) compounds. One interesting characteristic of these compounds is the non-linear dependence of the Curie temperature ($T_C$) on the Si concentration. This dependence is associated with the change of the lattice parameters $a$ and $c$, and their $c/a$ ratio. Compounds with a larger parameter $a$ and smaller $c/a$ ratio have higher $T_C$. It is clear that Si and Ge atoms play an important role in the magnetic and magnetocaloric properties of the MnFe(P, Si, Ge) compounds. In this section, we study the effect of Si and Ge on the magnetic phase transition, thermal hysteresis and magnetocaloric properties of these materials. Our study shows that the thermal hysteresis can be smaller for certain Ge contents and some Si/Ge ratios. In addition, the magnetic-phase-transition temperature can be tuned in the room-temperature range without losing the giant magnetocaloric properties.

4.2.2 MnFeP$_{0.59}$Si$_{0.41-x}$Ge$_x$ compounds

To investigate the influence of Ge concentration and Si/Ge ratio on the physical properties of MnFe(P, Si, Ge) compounds, a study of MnFeP$_{0.59}$Si$_{0.41-x}$Ge$_x$ compounds with nominal compositions $x = 0.03$, 0.07, 0.11, and 0.15 was carried out. In this series, all compounds have the same P concentration but different Ge and Si concentrations.

4.2.2.1 Structural properties

In Fig. 4.24 powder XRD patterns of MnFeP$_{0.59}$Si$_{0.41-x}$Ge$_x$ compounds with nominal composition $x = 0.03$, 0.07, 0.11, and 0.15 are displayed, measured at room temperature. It is clear that all samples crystallize in the hexagonal Fe$_2$P-type structure, space group $p\bar{6}m$. The extra reflection at $2\theta = 45^\circ$ shows that all compounds contain a small amount of second phase.
Figure 4.24: Powder XRD patterns of MnFeP\textsubscript{0.59}Si\textsubscript{0.41-x}Ge\textsubscript{x} compounds, measured at room temperature.
From the position of the additional reflection, the second phase has been identified as cubic $\text{Fe}_2\text{MnSi}$ (space group $\text{Fm3m}$), which is in agreement with the impurity found in the $\text{MnFe}(\text{P}_{0.89-x}\text{Si}_x)\text{Ge}_{0.11}$ compounds. The fraction of second phase is smaller in the sample with $x = 0.07$ than in the other samples.

![Graph showing lattice parameters a and c as a function of Ge content for $\text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x$ compounds at room temperature. The lines are linear fits to the observed values.](image)

**Figure 4.25**: Lattice parameters $a$ and $c$ as a function of Ge content of $\text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x$ compounds at room temperature. The lines are linear fits to the observed values.

Figure 4.25 presents the parameters $a$ and $c$ as a function of Ge content for $\text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x$ compounds. The values were derived from XRD measurements at room temperature which were carried out on powder samples mixed with Si powder. An increase of the Ge content leads to a linear expansion of the $a$ axis and to a linear reduction of the $c$ axis. However, from the slopes of the straight lines in Fig. 4.25, one can conclude that upon increasing Ge content, the rate of the expansion of the $a$ axis is slower than the reduction of the $c$ axis. For instance, for $x$ increasing from 0.03 up to 0.15, $a$ increases by 0.77% and $c$ decreases by 1.93%.

### 4.2.2.2 Magnetic properties

In Fig. 4.26 the magnetic field dependence of the magnetization for the $\text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x$ compounds is presented, measured at 5 K. It can be seen that all compounds are FM at 5 K, and that all magnetization curves look very similar. The
lowest magnetic moment at 5 K is found for the compound with $x = 0.03$ which contains less Ge than the others. The measured spontaneous magnetic moments of all compounds are about $4 \mu_B/f.u.$

![Figure 4.26: Field dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.41-x}$Ge$_x$ compounds with $x = 0.03, 0.07, 0.11$ and $0.15$, measured at 5 K](image)

In Fig. 4.27, the temperature dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.41-x}$Ge$_x$ compounds in a field of $0.05$ T is shown. The measurements were carried out independently on each sample with increasing temperature from $150$ K up to above $320$ K where all samples are in the PM state. In good agreement with the magnetization versus magnetic field curves shown in Fig. 4.26, the lowest magnetization at low field was found for the sample with the lowest Ge concentration $x = 0.03$. The magnetization increases with increasing Ge concentration, the curves are shifted to higher temperatures and the phase transition becomes sharper when the Ge concentration increases.
Figure 4.27: Temperature dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.30}$Ge$_{0.11}$ compounds, measured with increasing temperature in a field of 0.05 T

Figure 4.28: Temperature dependence of the magnetization of MnFeP$_{0.59}$Si$_{0.41}$Ge$_{0.11}$ compounds, measured with increasing and decreasing temperature
Figure 4.28 shows the magnetization loop of the compound with \( x = 0.11 \). This measurement was carried out on the sample after removing the virgin state. The magnetic transition exhibits pronounced thermal hysteresis between the heating and the cooling curve. This thermal hysteresis and the abrupt change of the magnetization are characteristics of a first-order phase transition. We found that, with increasing Ge concentration, the thermal hysteresis becomes smaller and that the FM-PM phase transition becomes sharper. The observed values of the thermal hysteresis are 40, 27, 20 and 16 K for the compounds with \( x = 0.03, 0.07, 0.11 \) and 0.15, respectively. The Curie temperatures have been derived from magnetization measurements with increasing temperature in a field of 0.05 T. The \( T_C \) values are proportional to the Ge concentration which may be correlated with the linear increase of the lattice parameter \( a \) with increasing Ge concentration.

### 4.2.2.3 Magnetocaloric effect

In Table 4.4 are the Si/Ge ratio, \( T_C \), \( \Delta T_{hys} \) and \( -\Delta S_m \) of the \( \text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x \) compounds are presented for a field change from 0 to 2 T. The compound with \( x = 0.03 \) has a small MCE, as a result of the broad magnetic phase transition and the small change of the magnetization upon the field change. When the Ge content increases, the isothermal magnetic-entropy change also increases and MCE values of 14 (J/kgK) are achieved under a field change of 2 T for the compound with \( x = 0.15 \). It shows that the MCE for \( x = 0.11 \) and \( x = 0.15 \) near room temperature is about the same as for \( \text{MnFeP}_{1-x}\text{As}_x \) compounds [5,7,8]. The high MCE is associated with a smaller Si/Ge ratio.

Table 4.4: Si/Ge ratio, magnetic ordering temperature (\( T_C \)), thermal hysteresis (\( \Delta T_{hys} \)) and isothermal magnetic-entropy change (\( -\Delta S_m \)) for \( \text{MnFeP}_{0.59}\text{Si}_{0.41-x}\text{Ge}_x \) compounds. The asterisk indicates that the value has been derived from a magnetization measurement carried out by means of the normal method (described in section 4.1.3.5)

<table>
<thead>
<tr>
<th>( x )</th>
<th>Si/Ge</th>
<th>( T_C ) (K)</th>
<th>( \Delta T_{hys} ) (K)</th>
<th>( -\Delta S_m ) (J/kgK) at 2 T</th>
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</thead>
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<tr>
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<td>small</td>
</tr>
<tr>
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<td>280</td>
<td>27</td>
<td>6 *</td>
</tr>
<tr>
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<td>286</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>0.15</td>
<td>1.73</td>
<td>288</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>
4.2.3 MnFeP₀.₆₇Si₀.₃₃₋ₓGeₓ compounds

In order to provide more evidence of the influence of the Ge concentration on the magnetic and magnetocaloric properties of MnFe(P, Si, Ge) compounds, a second series of samples with different Ge concentration was studied. However, in this series the P concentration is fixed at a higher value (67% P). In Table 4.5, the magnetic-ordering temperatures, thermal hysteresis and isothermal magnetic-entropy changes of MnFeP₀.₆₇Si₀.₃₃₋ₓGeₓ compounds are shown for a field change from 0 to 2 T. The compounds with x = 0.15 has the smallest thermal hysteresis, 14 K, and a value of - ∆Sₘ = 19 J/kgK was obtained for a 2 T magnetic/field change. These results are in good agreement with the results for MnFeP₀.₅₉Si₀.₄₁₋ₓGeₓ compounds. That is, Tₐ increases with increasing Ge content, the thermal hysteresis becomes smaller and the isothermal magnetic-entropy change becomes larger when the Ge content is increased.

<table>
<thead>
<tr>
<th>x</th>
<th>Tₐ (K)</th>
<th>∆Tₜₖₚₜ (K)</th>
<th>- ∆Sₘ (J/kgK) at 2 T</th>
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</thead>
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<td>0.07</td>
<td>235</td>
<td>32</td>
<td>19</td>
</tr>
<tr>
<td>0.11</td>
<td>268</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>0.15</td>
<td>297</td>
<td>14</td>
<td>19</td>
</tr>
</tbody>
</table>

4.2.4 MnFeP₀.₈₅₋ₓSiₓGe₀.₁₅ compounds

The motivation to study MnFeP₀.₈₅₋ₓSiₓGe₀.₁₅ compounds is to investigate the influence of Si on the magnetic and magnetocaloric properties of the MnFe(P, Si, Ge) compounds. In this series, the concentration of Ge was fixed at 15 % and the P/Si ratio was varied. This Ge concentration is highest of all compounds investigated in this thesis.

Figure 4.29 shows the powder XRD pattern of MnFeP₀.₅₅Si₀.₃₀Ge₀.₁₅, measured at room temperature. It shows that the compound crystallizes in the hexagonal Fe₂P-type of structure, with space group P̅6₃m. However, for MnFeP₀.₅₅Si₀.₃₀Ge₀.₁₅, the
(300), (211) and (002) reflections are separated, indicating a FM state at room temperature, the separation obviously being caused by magnetostriction in the ordered state. The separated reflections are also observed in MnFeP_{0.67}Si_{0.18}Ge_{0.15}.

![Powder XRD patterns](image)

**Figure 4.29:** Powder XRD patterns of MnFeP_{0.55}Si_{0.30}Ge_{0.15}, measured at room temperature.

![Field dependence of magnetization](image)

**Figure 4.30:** Field dependence of the magnetization of MnFeP_{0.55}Si_{0.30}Ge_{0.15} at 5 K

Plotted in Fig. 4.30, the magnetic field dependence of the magnetization at 5 K is presented for MnFeP_{0.55}Si_{0.30}Ge_{0.15}. The compound is FM at 5 K and the measured
spontaneous magnetic moment is 4.13 \( \mu_B/\text{f.u.} \). The values for \( y = 0.26 \) and \( y = 0.18 \) are 4.10 and 3.90 \( \mu_B/\text{f.u.} \), respectively. These values are consistent with those for the MnFeP\textsubscript{0.59}Si\textsubscript{0.41-x}Ge\textsubscript{x} and MnFeP\textsubscript{0.67}Si\textsubscript{0.33-x}Ge\textsubscript{x} compounds.

![Figure 4.31: Temperature dependence of the magnetization of MnFeP\textsubscript{0.55}Si\textsubscript{0.30}Ge\textsubscript{0.15}, measured at 0.05 T with increasing and decreasing temperature.](image)

**Table 4.6:** Magnetic-ordering temperature (\( T_C \)), thermal hysteresis (\( \Delta T_{\text{hys}} \)) and isothermal magnetic-entropy change (\( -\Delta S_m \)) for field changes from 0 to 2 T and from 0 to 5 T of MnFeP\textsubscript{0.85-y}Si\textsubscript{y}Ge\textsubscript{0.15}

<table>
<thead>
<tr>
<th>( y )</th>
<th>( T_C ) (K)</th>
<th>( \Delta T_{\text{hys}} ) (K)</th>
<th>( -\Delta S_m ) (J/kgK) at 2 T</th>
<th>( -\Delta S_m ) (J/kgK) at 5 T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>297</td>
<td>14</td>
<td>19</td>
<td>48</td>
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<tr>
<td>0.26</td>
<td>288</td>
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<td>35</td>
</tr>
<tr>
<td>0.30</td>
<td>316</td>
<td>9</td>
<td>16</td>
<td>41</td>
</tr>
</tbody>
</table>

In Fig. 4.31, the temperature dependence of the magnetization of MnFeP\textsubscript{0.55}Si\textsubscript{0.30}Ge\textsubscript{0.15} is shown, measured at 0.05 T with increasing and decreasing temperature. The measurement was carried out on the sample after removal of the virgin state. A first-order magnetic phase transition is observed with a much smaller
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thermal hysteresis of 9 K. The sharp magnetic phase transition promises a large value of magnetic/entropy change (see Table 4.6).

Figure 4.32 shows the magnetic isotherms of MnFeP$_{0.55}$Si$_{0.30}$Ge$_{0.15}$ in the vicinity of the phase transition, measured with increasing and decreasing field. The magnetization process shows that there is a field-induced magnetic phase transition from a PM to a FM state at the phase-transition temperature. The field hysteresis indicates a first-order field-induced transition. The sample exhibits a large magnetization change in the applied magnetic field.

![Figure 4.32](image)

**Figure 4.32:** Magnetic-field dependence of the magnetization of MnFeP$_{0.55}$Si$_{0.30}$Ge$_{0.15}$, measured with increasing and decreasing field in the vicinity of the phase transition

The isothermal magnetic-entropy changes for MnFeP$_{0.85-y}$Si$_{y}$Ge$_{0.15}$ compounds are presented in Fig. 4.33. The compounds show large peaks when subjected to a 2 and 5 T field change. The maximum $-\Delta S_m$ values are listed in Table 4.6. Compared with MnFeP$_{0.89-x}$Si$_{x}$Ge$_{0.11}$ compounds, the isothermal magnetic-entropy changes of the MnFeP$_{0.85-y}$Si$_{y}$Ge$_{0.15}$ compounds are larger. It proves that a higher Ge concentration leads to a sharper magnetic phase transition and, therefore, to a larger magnetic/-entropy change.
4.2.5  MnFeSi$_{0.30}$P$_{0.70-z}$Ge$_z$ compounds

In Fig. 4.34, the temperature dependence of the magnetization of MnFeSi$_{0.30}$P$_{0.70-z}$Ge$_z$ compounds with $z = 0.07$, 0.11, and 0.15 is shown, measured with increasing and decreasing temperature in a magnetic field of 0.05 T. All samples show a large thermal hysteresis, with values 35, 20 and 9 K for $z = 0.07$, 0.11 and 0.15, respectively. The thermal hysteresis becomes much smaller and the magnetic phase transition becomes much sharper when the Ge concentration is higher. Also, the magnetization in the FM state is larger for higher Ge concentration.

In Table 4.7, the magnetic-ordering temperatures, thermal hysteresis and isothermal magnetic-entropy change for a field change from 0 to 2 T are shown for MnFeSi$_{0.30}$P$_{0.70-z}$Ge$_z$ compounds. We observed that, when $T_C$ increases, the thermal...
hysteresis becomes smaller and the isothermal magnetic-entropy changes become larger with increasing Ge content.

![Figure 4.34: Temperature dependence of the magnetization of MnFeSi\(_{0.30}\)P\(_{0.70-z}\)Ge\(_z\) compounds, measured with increasing and decreasing temperature in a magnetic field of 0.05 T](image)

**Figure 4.34:** Temperature dependence of the magnetization of MnFeSi\(_{0.30}\)P\(_{0.70-z}\)Ge\(_z\) compounds, measured with increasing and decreasing temperature in a magnetic field of 0.05 T

**Table 4.7:** Magnetic/ordering temperature (T\(_C\)), thermal hysteresis (\(\Delta T_{hys}\)) and isothermal magnetic-entropy change (-\(\Delta S_m\)) of MnFeSi\(_{0.30}\)P\(_{0.70-z}\)Ge\(_z\) compounds. The asterisk indicates that the value has been derived from a magnetization measurement carried out by means of the normal method (described in section 4.1.3.5)

<table>
<thead>
<tr>
<th>(z)</th>
<th>T(_C) (K)</th>
<th>(\Delta T_{hys}) (K)</th>
<th>-(\Delta S_m) (J/kgK) at 2 T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>250</td>
<td>35</td>
<td>3 *</td>
</tr>
<tr>
<td>0.11</td>
<td>286</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>0.15</td>
<td>316</td>
<td>9</td>
<td>16</td>
</tr>
</tbody>
</table>

Recently, Song et al. have made an assessment of the magnetic-entropy change in MnFeSi\(_{0.25}\)P\(_{0.75}\)Ge\(_x\) compounds with \(x = 0.08, 0.1, \) and 0.12 [27]. The magnetic and magnetocaloric properties found in the MnFeSi\(_{0.30}\)P\(_{0.70-z}\)Ge\(_z\) compounds are consistent with those reported for MnFeSi\(_{0.25}\)P\(_{0.75}\)Ge\(_x\) compounds. For example,
the Curie temperatures of the MnFeSi$_{0.25}$P$_{0.75}$Ge$_x$ compounds are 275, 293, and 323 K for $x = 0.08, 0.1$ and $0.12$, respectively. The magnetic-entropy changes are about 25 J/kgK for all the samples when subjected to a magnetic-field change from 0 to 2 T. These values are higher than those observed in the MnFeSi$_{0.30}$P$_{0.70-z}$Ge$_z$ compounds with $z = 0.07, 0.11$, and $0.15$. This is not surprising since the Si contents of these two compounds are different. Moreover, the MCE values of the MnFeSi$_{0.25}$P$_{0.75}$Ge$_x$ compounds were derived from magnetization measurements with a small temperature step of 1 K, while the MCE values of the MnFeSi$_{0.30}$P$_{0.70-z}$Ge$_z$ compounds were derived from magnetization measurements with a step of 4 K.

4.2.6 Discussion and conclusions

Here, we will discuss the properties of the MnFe(P,Si,Ge) compounds and the influence of Si and Ge on the magnetic and magnetocaloric properties of the compounds. XRD was carried out on all samples, and the results show that all compounds crystallize in the hexagonal Fe$_2$P-type of structure with space group $P\bar{6}m$. In this structure, the Mn atoms occupy the 3g sites, the Fe atoms the 3f sites and the P, Ge, Si atoms occupy the 1b and 2c sites, with preference of Ge for the 2c sites and of Si for 1b sites[xx]. At low temperatures, the investigated compounds are in the FM state. With increasing temperature, all compounds undergo a first-order magnetic phase transition from the FM to the PM state. They also exhibit a virgin state with a much lower transition temperature than the Curie temperature found with increasing temperature. The spontaneous magnetic moments of these compounds at 5 K are in the range from 3.9 to 4.2 $\mu_B$/f.u., which is in good agreement with the magnetic moments found for the MnFeP$_{1-x}$As$_x$ compounds.

Table 4.8 presents the Si/Ge ratio, magnetic/ordering temperature ($T_C$), thermal hysteresis ($\Delta T_{hys}$) and isothermal magnetic-entropy change ($-\Delta S_m$) for a field change from 0 to 2 T for some selected MnFe(P,Si,Ge) compounds with different Si/Ge ratios.

It is seen that the Curie temperatures are in the range 235 - 316 K, covering room temperature. If the P concentration is fixed, $T_C$ increases rapidly with increasing Ge concentration (compounds 3-6) and (compounds 9-11). The Si/Ge ratio plays an important role in increasing $T_C$, improving the thermal hysteresis and enhancing the isothermal magnetic-entropy change of the compounds. The thermal hysteresis of the (Si,Ge)-based compounds can be quite large, but is controllable since it depends on
the Ge concentration. It is seen that the thermal hysteresis becomes smaller and the magnetic phase transition becomes sharper with increasing Ge concentration. The smallest thermal hysteresis is observed in the sample with smaller Si/Ge ratio or higher Ge concentration. Recent work shows that the thermal hysteresis can be reduced remarkably by increasing the Mn concentration; especially in ribbon samples without Si, the thermal hysteresis can be reduced to 1 K [28].

Table 4.8: Si/Ge ratio, magnetic-ordering temperature ($T_C$), thermal hysteresis ($\Delta T_{hys}$) and isothermal magnetic-entropy change ($-\Delta S_m$) for a field change from 0 to 2 T for the MnFe(P, Si, Ge) compounds. The asterisk indicates that the value has been derived from a magnetization measurement carried out by means of the normal method (described in section 4.1.3.5)

<table>
<thead>
<tr>
<th>No</th>
<th>P</th>
<th>Si</th>
<th>Ge</th>
<th>Si/Ge</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_{hys}$ (K)</th>
<th>$-\Delta S_m$ (J kg$^{-1}$ K$^{-1}$) at 2 T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.55</td>
<td>0.3</td>
<td>0.15</td>
<td>2.00</td>
<td>316</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>0.56</td>
<td>0.33</td>
<td>0.11</td>
<td>3.00</td>
<td>260</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>0.59</td>
<td>0.26</td>
<td>0.15</td>
<td>1.73</td>
<td>288</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>0.59</td>
<td>0.3</td>
<td>0.11</td>
<td>2.73</td>
<td>286</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>0.59</td>
<td>0.34</td>
<td>0.07</td>
<td>4.86</td>
<td>280</td>
<td>27</td>
<td>6 *</td>
</tr>
<tr>
<td>6</td>
<td>0.59</td>
<td>0.38</td>
<td>0.03</td>
<td>12.67</td>
<td>252</td>
<td>40</td>
<td>small</td>
</tr>
<tr>
<td>7</td>
<td>0.63</td>
<td>0.26</td>
<td>0.11</td>
<td>2.36</td>
<td>292</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>0.63</td>
<td>0.3</td>
<td>0.07</td>
<td>4.29</td>
<td>250</td>
<td>35</td>
<td>3 *</td>
</tr>
<tr>
<td>9</td>
<td>0.67</td>
<td>0.18</td>
<td>0.15</td>
<td>1.20</td>
<td>297</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>0.67</td>
<td>0.22</td>
<td>0.11</td>
<td>2.00</td>
<td>268</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>0.67</td>
<td>0.26</td>
<td>0.07</td>
<td>3.71</td>
<td>235</td>
<td>32</td>
<td>2 *</td>
</tr>
</tbody>
</table>

The MCE in MnFe(P, Si, Ge) compounds is equally large as in MnFe(P, As) compounds but, when the Ge concentration is reduced to nearly zero, the MCE collapses. However, when Ge is eliminated and the Si concentration is between 40 and 60 %, the MCE recovers with values between 7 and 30 J kg$^{-1}$ K$^{-1}$ at a 2 T field change. This will be discussed in detail in chapter 6 of this thesis.

In order to have a better overview of the thermal hysteresis and the Curie temperature of all MnFe(P, Si, Ge) compounds, a schematic diagram is presented in Fig. 4.35. Each chimney carries a number from 1 to 11 that corresponds to the number
Chapter 4: *MnFe(P, Si, Ge) compounds*

of the compound in Table 4.8. The position of the chimney represents the concentrations of P, Si, and Ge. Each chimney consists of two parts, a bottom part and a top part. The height of the bottom part represents the thermal hysteresis and the height of the top part the Curie temperature.

![Diagram](image)

**Figure 4.35:** Schematic diagram that illustrates systematically the Curie temperatures and thermal hysteresis of MnFe(P, Si, Ge) compounds

It is clear that compounds with larger Ge concentrations (compounds 1, 3, and 9) have higher $T_C$ and smaller $\Delta T_{hys}$ values than the others. $\Delta T_{hys}$ is larger in the area where the compounds 3, 8, 5, and 11 are located, indicating that samples with smaller Ge concentration than about 7% have larger thermal hysteresis.

In conclusion, we have prepared a number of MnFe(P, Si, Ge) compounds and have investigated the influence of Si, Ge, and their ratio on the structure, magnetic and magnetocaloric properties of these compounds. Si and Ge substitution affect the magnetic and magnetocaloric properties of the MnFe(P, Si, Ge) compounds quite differently. For instance, $T_C$ is proportional to the Ge concentration in MnFeP$_{0.50}$Si$_{0.41-x}$Ge$_x$ and in MnFeP$_{0.60}$Si$_{0.33-x}$Ge$_x$ compounds. On the other hand, in MnFeP$_{0.85-y}$Si$_y$Ge$_{0.15}$ compounds, the dependence of $T_C$ on the Si concentration was found to be
extremely strong but non-linear. This is in good agreement with our previous results [18,23]. Generally, the $T_c$ dependence of all samples correlates with changes of the lattice parameters $a$ and $c$. $T_c$ is higher in samples with larger parameter $a$ and smaller parameter $c$. We have achieved a large MCE, spanning a large range of working temperatures from about 235 up to 316 K. This temperature range is of crucial importance for magnetic/cooling applications. The thermal hysteresis is reduced with increasing Ge concentration.

References

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[27] L. Song, G.F. Wang, O. Tegus, D.T. Cam Thanh, E. Brück and K.H.J. Buschow, “An assessment of magnetic entropy change in MnFeSi0.25P0.75-\(x\)Ge\(x\)”, (to be submitted)