Magnetotransport and magnetocaloric effects in intermetallic compounds
Duijn, H.G.M.

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Chapter 8
Magnetic properties of Gd₅(Ge₅Si₄) compounds

8.1 Introduction

During the last decade, a continuous increase of interest has arisen in magnetic refrigeration as an alternative technology for the traditional gas-compression/expansion technique in use today. As the gas-compression/expansion technique approaches its technical limitations in energy efficiency, and because of environmental concerns, magnetic refrigeration in the room-temperature range promises significant improvements. The development of the magnetic-refrigeration technology requires basic research on the exploration and characterisation of new magnetic refrigerant materials as well as on the design of new magnetic-refrigeration devices. For a review on the recent progress and future needs of magnetic refrigeration, we refer to an article of Pecharsky and Gschneidner [8.1].

The technology of magnetic refrigeration utilises the magnetocaloric effect, which is the heating or cooling of magnetic materials due to a varying magnetic field. For practical applications, materials with a large magnetocaloric effect are needed to improve the energy efficiency. Recently, an extraordinarily large magnetocaloric effect has been discovered in the compound Gd₅(Ge₀.⁵Si₀.⁵)₄ [8.2]. This compound belongs to the pseudobinary system Gd₅(Ge₁-xSi₄)x₄, in which the magnetic properties change from antiferromagnetic to ferromagnetic with increasing Si content x. The magnetic phase diagram of the system Gd₅(Ge₁-xSi₄)x₄ as reported in ref. 8.3 is shown in figure 8.1. For 0.25 ≤ x ≤ 0.5, the originally orthorhombic structure undergoes a monoclinic distortion, which brings about a different magnetic behaviour of the alloy. Originally, it was believed [8.4] that, for 0.25 ≤ x ≤ 0.50, Gd₅(Ge₁-xSi₄)x₄ orders magnetically in two steps. Upon cooling the compounds order ferromagnetically, the ordering temperature increasing linearly from 125 K for x = 0.25 to 300 K for x = 0.50. About 20 K below the ordering temperature, the compound undergoes a first-order phase transition to another ferromagnetic structure, that is accompanied with the so-called giant magnetocaloric effect. As in the present work we are interested in the resistance effects at magnetic order-order transitions, we have started an investigation of the magnetic and transport properties of the system Gd₅(Ge₁-xSi₄)x₄ with 0.25 ≤ x ≤ 0.50. During the course of the investigation it became apparent that Gd₅(Ge₁-xSi₄)x₄ with 0.25 ≤ x ≤ 0.50...
does not order in two steps, but undergoes only one, first-order magnetic phase transition that is accompanied by a structural phase transition [8.5]. The previously found upper transition is attributed to an impurity phase.

In this chapter, we investigate the physical properties of the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$. For a first characterisation, we prepared three polycrystalline batches of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ with nominal Si contents of $x = 0.25$, 0.43 and 0.50. These compounds were investigated by means of magnetisation measurements. Furthermore, a single-crystalline sample with $x = 0.40$ was prepared. Part of the single crystal was powdered in order to investigate the structural properties as a function of temperature by means of X-ray diffraction. Additionally, the results of magnetisation and electrical-resistivity measurements along the three principal axes are reported. The entropy change associated with the magnetic/structural phase transition is calculated from the magnetisation data using a thermodynamic Maxwell relation. Finally, the anisotropy observed in magnetisation is discussed in relation to the results of symmetry considerations with the theory of group representations.

8.2 Experimental

Polycrystalline Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ samples with a nominal Si content of $x = 0.25$, 0.43 and 0.50 were prepared by arc-melting the pure starting materials in a water-cooled copper crucible in a continuously Ti-gettered Ar atmosphere. The batches were turned over and
remelted twice to achieve good homogeneity. The purity of the Gd starting material was 3 N,
while the Ge and Si starting materials were 7 N pure. The samples were wrapped in Ta foil
and annealed in water-free quartz ampoules at 1000 °C for five days in an Ar atmosphere of
150 mbar. The homogeneity and stoichiometry of the batches were checked by means of
electron-probe micro-analysis (EPMA). All three samples contain about 10 vol. % second
phase with the approximate composition Gd₅(Ge, Si)₃.

Furthermore, a single crystal was grown by means of the travelling-floating-zone
method in an adapted NEC double ellipsoidal image furnace. The feed, with nominal
composition Gd₅Ge₂.₄₀Si₁.₆₃, had an excess of 2 at. % Si to compensate for evaporation of Si
during the growth. The crystal was grown under an Ar atmosphere of 900 mbar with a speed
of 3 mm/h. The feed and seed were counter-rotated at rates of 22 and 31 rpm, respectively.
The as-grown single crystal, with a cylindrical shape of 4 mm and a length of 5 cm, was
checked on composition, homogeneity and single-crystallinity by means of EPMA and X-ray
Laue backscattering. At the edge of the crystal, a band of about 0.5 mm contains grains of a
secondary phase, having the approximate composition GdGe₀.₅Si₀.₅. The bulk of the crystal is
homogeneous, having about 3 at. % excess of Gd. One should, however, bear in mind the
rather limited accuracy of the EPMA analysis for the light element Si. The Si content changes
along the growth direction of the crystal from \( x = 0.355 \) at about 2 cm below the top to
\( x = 0.386 \) at the top of the crystal. The expected change in ordering temperature due to the
increasing Si content, deduced from the phase diagram given in figure 8.1, is about 20 K for
the two above-mentioned Si concentrations.

Laue X-ray photographs showed reasonable diffraction spots, the proper monoclinic
symmetry was observed over the whole length of the crystal. The growth direction was found
to be about 25° tilted from the \( c \) direction. The single crystal was cut by means of spark
erosion into bars with typical dimensions of \( 1 \times 1 \times 4 \text{ mm}^3 \) along the three principal axes. On
these samples, the magnetisation was measured between 5 and 350 K in magnetic fields up to
5 T, using a SQUID magnetometer. Next, the magnetisation at 4.2 K was measured up to 15 T in a home-built extraction magnetometer. Electrical-resistivity measurements on these samples failed because the samples displayed cracking at the structural phase transition. Therefore, part of the single crystal was first annealed for 7 days at 1000 °C, and then cut into bars. Resistivity measurements on the annealed samples turned out to be successful. However, EPMA showed that the annealed batch contains two impurity phases with the approximate compositions Gd$_5$(Ge$_{0.75}$Si$_{0.25}$)$_3$ and GdGe$_{0.5}$Si$_{0.5}$. As can be seen in figure 8.2, the impurity phases form as striped precipitates that are perpendicular to each other. The bulk of the annealed Gd$_5$(Ge$_{1.3}$Si$_{1.4}$)$_4$ crystal is homogeneous, having again about 3 at.% excess of Gd and a change in Si content along the growth direction of the crystal from $x = 0.356$ to 0.363.

8.3 Structural properties

The structural properties of the compounds Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ have already been reported over thirty years ago [8.6; 8.7]. Both compounds crystallise in the same orthorhombic Sm$_3$Ge$_4$-type of structure (space group No. 62; Pnma). This crystal structure has three independent 4c sites at positions (x, 0.25, z) and three independent 8d sites at positions...
Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ compounds

Figure 8.4. X-ray-diffraction data of Gd$_5$(Ge$_{0.50}$Si$_{0.50}$)$_4$ taken at room temperature.

(x, y, z). Gd occupies one 4c site and two 8d sites, while Si/Ge occupy two 4c sites and one 8d site. A study of the room-temperature crystallographic properties of the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ over the whole composition range has been performed by Pecharsky and Gschneidner [8.4]. For $0.25 \leq x \leq 0.5$, the originally orthorhombic structure undergoes a monoclinic distortion to space group P 2$_1$/c (No. 14). The crystal structures of Gd$_5$Si$_4$, Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ and Gd$_5$Ge$_4$ as reported in ref. 8.4 are shown in figure 8.3. The crystal structure in the monoclinic space group P 2$_1$/c has nine independent 4e sites with positions (x, y, z), five of which are occupied by Gd and four of which are occupied by Ge/Si.

The X-ray-diffraction spectrum measured on the Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ sample is given in figure 8.4. The spectrum has been analysed by means of the Rietveld refinement procedure, using the atom positions of the Gd and Ge/Si atoms as given in ref. 8.4, and keeping them fixed. The refined unit-cell parameters are in good agreement with those reported in ref. 8.4.

X-ray-diffraction spectra measured at several temperatures on a powdered sample of the Gd$_5$Ge$_{2.6}$Si$_{1.4}$ single crystal are given in figure 8.5. Again, the room-temperature spectrum can be indexed with the monoclinic space group P 2$_1$/c, the refined unit-cell parameters being $a = 7.590(1)$ Å, $b = 14.771(1)$ Å, $c = 7.762(1)$ Å and $\gamma = 93.04(1)$°. With decreasing temperature, the measured diffractograms show large differences among them, indicating the presence of a structural phase transition. Some reflections that change as a function of temperature are marked with arrows in figure 8.5. The pattern measured at 5 K can be indexed with the orthorhombic space group $Pnma$, the refined unit-cell parameters being $a = 7.522(3)$ Å, $b = 14.760(6)$ Å and $c = 7.792(4)$ Å. The X-ray-diffraction spectra measured at temperatures between 224 and 150 K, gradually change from the monoclinic to the orthorhombic structure, indicating the structural phase transition to occur over a broad temperature range. To compare the crystallographic phase transition with the magnetic phase
transition, the temperature dependence of the magnetisation of a free-powder sample was measured. The results are given in figure 8.6. The magnetic ordering is smeared out over a broad temperature range. For comparison, the magnetisation of a bulk piece of the single crystal is displayed in figure 8.6, too. The single crystal displays a rather sharp transition. Hence, we believe due to the powderisation of the sample the crystalline perfection of the sample is reduced and strain is introduced, yielding less pronounced magnetic and structural properties.
8.4 Application of the theory of group representations

In order to understand the magnetic properties of the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds, we have applied the theory of group representations, as introduced in section 2.3. In principle, this approach yields the magnetic structures allowed by symmetry. The applicability of group theory to Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ is limited, however, as it primarily describes magnetic structures that order through a second-order phase transition, in which one symmetry is broken (see section 2.3), while the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ has a first-order structural/magnetic phase transition. Still, we believe the symmetry analysis with the theory of group representations is instructive for the interpretation of the (anisotropic) magnetic properties observed (see section 8.5). Because of their size the tables in this section are given in appendix B.

The group under consideration is the orthorhombic space group P nma. The eight symmetry operations $P_g$ ($g = 1$ to 8) of space group P nma, obtained from the generators listed in the book of Miller and Love [8.8], are given in table B.1. Note that the generators are different from the ones listed in the generally used "International tables for crystallography" [8.9], resulting in a different order of the symmetry operations. As the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds with $0.25 \leq x \leq 0.50$, are assumed to order ferromagnetically (wave vector $q = 0$), the group to consider consists of all eight symmetry operations. The irreducible representations are again obtained from the generators listed in ref. 8.8, and are given in table B.2.
The effects of the symmetry operations on the components of the magnetic moments at the 4c and 8d sites are listed in tables B.3 and B.4, respectively. Note that for both crystallographic sites, the magnetic moments along the three different crystallographic directions are decoupled, i.e.: there is no symmetry operation that projects a magnetic moment from one crystallographic direction onto another. This leads us to take the following starting functions \( f \) for the two crystallographic sites:

\[
\begin{align*}
    f_{4c} &= \{1(A, B, C); 2(0, 0, 0); 3(0, 0, 0); 4(0, 0, 0)\} \\
    f_{8d} &= \{1(D, E, F); 2(0, 0, 0); 3(0, 0, 0); 4(0, 0, 0); 5(0, 0, 0); 6(0, 0, 0); 7(0, 0, 0); 8(0, 0, 0)\}
\end{align*}
\]  

(8.1)

For example, the starting function for the 4c site consists of a moment with size A in the \( a \) direction, size B in the \( b \) direction and size C in the \( c \) direction at atom 1, and no moments at atoms 2, 3 and 4.

We can apply equations 2.33 and 2.34 to the information obtained so far, yielding the basis functions \( f_k^i \) belonging to irreducible representation \( \Gamma^i \). The results are given in table B.5 and B.6 for the 4c and 8d sites, respectively. Thus, both on the 4c and the 8d site several ferromagnetic and (non-)collinear antiferromagnetic structures are allowed by symmetry. The magnetic structures at the 8d site are symmetric for the \( a, b \) and \( c \) axis. For the 4c site, however, magnetic structures exist that are different for the \( b \) axis compared to the \( a \) and \( c \) axes. The origin lies in the confinement of the atom position of the 4c site to \( y = 1/4 \) (and \( 3/4 \)). Note that the Gd atoms in the orthorhombic structure of \( \text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4 \) occupy one 4c site and two independent 8d sites. Hence, the basis functions of a single representation may yield already complex magnetic structures. Furthermore, we recall that the applicability of group theory to \( \text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4 \) is limited due to the first-order origin of the magnetic phase transition. Therefore, the actual magnetic structure may be built up from magnetic structures of different representations.

### 8.5 Magnetic properties

The temperature dependence of the magnetisation of free-powder samples \( \text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4 \) with \( x = 0.25, 0.43 \) and \( 0.50 \) was measured in applied fields of 0.01 and 5 T. The results for the compound \( \text{Gd}_5(\text{Ge}_{0.75}\text{Si}_{0.25})_4 \) are shown in figure 8.7. The magnetic ordering is observed as a pronounced change in magnetisation, indicating that the transition is of first-order. Furthermore, the magnetic behaviour is clearly different from the description of a simple ferromagnet with the Brillouin function. The ordering temperature is determined as the minimum of the first derivative of the thermomagnetic curve measured in 0.01 T. The results are given in table 8.1. With increasing field, the transition temperature increases, indicating ferromagnetic ordering. In the thermomagnetic curve measured in 0.01 T, a small anomaly is perceptible at about 175 K, that is attributed to an impurity phase [8.5].
Figure 8.7. Magnetisation versus temperature of powder Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ that was free to rotate in an applied field of 0.01 T (left axis) and 5 T (right axis). Inset: Inverse magnetisation versus temperature of the $B = 5$ T curve. The solid line is a fit of the Curie-Weiss law.

Table 8.1. Magnetic information of the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_C$ (K)</th>
<th>$\theta_p$ (K)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$/Gd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>260 (5)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.43</td>
<td>220 (5)</td>
<td>186 (3)</td>
<td>8.0 (1)</td>
</tr>
<tr>
<td>0.25</td>
<td>120 (5)</td>
<td>82 (3)</td>
<td>8.5 (1)</td>
</tr>
<tr>
<td>0.40; B/\textit{a}</td>
<td>220 (5)</td>
<td>192 (3)</td>
<td>8.4 (1)</td>
</tr>
<tr>
<td>0.40; B/\textit{b}</td>
<td>220 (5)</td>
<td>187 (3)</td>
<td>8.1 (1)</td>
</tr>
<tr>
<td>0.40; B/\textit{c}</td>
<td>215 (5)</td>
<td>196 (3)</td>
<td>8.4 (1)</td>
</tr>
</tbody>
</table>

The temperature dependence of the inverse magnetisation of Gd$_5$(Ge$_{0.75}$Si$_{0.25}$)$_4$ measured in 5 T is given in the inset of figure 8.7. At temperatures above 150 K, the curve obeys the Curie-Weiss law. The obtained paramagnetic Curie temperatures, $\theta_p$, and the effective magnetic moments, $\mu_{\text{eff}}$, for the several compounds are given in table 8.1. For the compound Gd$_5$(Ge$_{0.50}$Si$_{0.50}$)$_4$, no Curie-Weiss behaviour was observed, as the magnetisation measurements did not extend to sufficiently high temperatures. The measured effective moments are slightly higher than the calculated value of 7.94 $\mu_B$/Gd. Note that the Curie-Weiss behaviour observed in the paramagnetic state describes the magnetic behaviour of the monoclinic phase of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$. Thus, the measured positive paramagnetic Curie temperatures indicate that the monoclinic phase of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ would order ferromagnetically. As the values of the paramagnetic Curie temperatures are comparable to the Curie temperatures, the orthorhombic and monoclinic phases of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ are likely to have similar magnetic properties.
Figure 8.8. Magnetisation versus temperature of single-crystalline Gd$_5$Ge$_{2.4}$Si$_{1.6}$ in magnetic fields of 0.01 T (top) and 5 T (bottom) applied along the three principal axes. Inset: Inverse magnetisation versus temperature of the B = 5 T curves. The solid lines are fits of the Curie-Weiss law.

The temperature dependence of the magnetisation of the Gd$_5$Ge$_{2.4}$Si$_{1.6}$ single crystal measured in magnetic fields of 0.01 and 5 T applied along the a, b and c axes is given in figure 8.8. The magnetisation curves were measured on three samples with slightly different Ge/Si ratios. Hence, the ordering temperatures of the three samples are somewhat different. Similar to the polycrystalline samples, the magnetic ordering is observed as a pronounced
change in magnetisation, indicating that the transition is of first order. Furthermore, the magnetisation curves display anisotropic behaviour, i.e.: the magnetisation measured in a magnetic field of 5 T applied along the $b$ axis is lower than the magnetisation measured in a field of 5 T applied along the $a$ and $c$ axes. In the inset of figure 8.8, the temperature dependence of the inverse magnetisation measured in 5 T is given. Anisotropy of the magnetisation is observed above the ordering temperature, too. The obtained paramagnetic Curie temperatures and effective moments are given in table 8.1. Thus, it seems that the anisotropy of the magnetisation is also present in the monoclinic phase of Gd$_5$Ge$_{2.4}$Si$_{1.6}$.

To further investigate the anisotropic magnetic properties of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ in the orthorhombic phase, the field dependence of the magnetisation was measured at 5 K up to 15 T. The results are presented in figure 8.9. The magnetisation measured along the $a$ and $c$ axis displays simple ferromagnetic behaviour, the spontaneous magnetisation being about 36 μ$_B$/f.u.. This value is in agreement with 35 μ$_B$/f.u. expected for the five Gd atoms per formula unit. In contrast, the magnetisation of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ in a magnetic field applied along the $b$ axis levels off to a lower value, the spontaneous magnetisation being only 30 μ$_B$/f.u.. Upon application of a magnetic field larger than 3 T, the magnetisation gradually increases towards the $a$-axis magnetisation. Thus, it seems that for a magnetic field applied along the $b$ axis, only four of the five Gd atoms per formula unit develop a net magnetic moment along the $b$ axis. Upon application of a magnetic field larger than 3 T, also on the fifth atom a net magnetic moment along the $b$ axis is induced. A discussion of the anisotropic magnetic properties of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ in relation to the results of symmetry considerations is given in section 8.7.

**Figure 8.9.** Magnetic isotherms of single-crystalline Gd$_5$Ge$_{2.4}$Si$_{1.6}$ measured at 5 K in magnetic fields applied along the three principal axes.
The results of an investigation of the magnetic properties of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ around the ordering temperature are given in figure 8.10. At $T < T_C$, the magnetisation curves show simple ferromagnetic behaviour, the spontaneous magnetisation along the $b$ axis being somewhat lower than that along the $a$ and $c$ axis, again. At $T \geq T_C$, the magnetisation isotherms show a field-induced transition, that has a hysteresis of the order of 1 T. At temperatures well above the ordering temperature, the magnetisation increases linearly, which is characteristic for simple paramagnetic behaviour.
Gd$_5$(Ge,Si)$_4$ compounds

Figure 8.11. Magnetic-entropy change of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for a magnetic field change of 5 T calculated from the magnetic isotherms of figure 8.10 using equation 8.3. The closed (open) symbols correspond to magnetisation data taken with increasing (decreasing) magnetic field.

Let us consider the magnetisation curves in figure 8.10 to obtain information on the magnetocaloric effect of Gd$_5$Ge$_{2.4}$Si$_{1.6}$. When a material is magnetised by application of a magnetic field, the entropy associated with the magnetic degrees of freedom, $S_{\text{mag}}$, is changed as the field changes the magnetic order of the material. Under adiabatic conditions, $\Delta S_{\text{mag}}$ must be compensated for by an equal but opposite change of the entropy associated with the lattice, resulting in a change in temperature of the material, $\Delta T_{\text{ad}}$. This temperature change, the magnetocaloric effect, can be related to the magnetic properties of the material through the thermodynamic Maxwell relation

$$\left( \frac{\partial S}{\partial B} \right)_T = \left( \frac{\partial M}{\partial T} \right)_B$$  \hspace{1cm} (8.2)

For magnetisation measurements made at discrete temperature intervals, $\Delta S_{\text{mag}}$ can be approximated by

$$\Delta S_{\text{mag}} \approx \frac{1}{\Delta T} \left[ \int_{B}^{B+\Delta T} M(T,B')dB' - \int_{B}^{B'} M(T,B')dB' \right]$$  \hspace{1cm} (8.3)

which is the area between two magnetic isotherms divided by the temperature difference between the isotherms [8.10]. Analysis of the magnetic isotherms displayed in figure 8.10 using equation 8.3, yields the entropy changes as given in figure 8.11. As the magnetic
isotherms show large hysteresis, the entropy changes have been calculated for both increasing and decreasing magnetic fields. These results, as well as the results for fields applied along the three different crystallographic axes, are comparable. However, due to the limited number of isotherms taken, the estimated entropy changes have limited accuracy.

To determine the entropy change at the magnetic phase transition more accurately, several magnetic isotherms and magnetisation versus temperature curves have been measured on a cubical shaped sample of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ in fields applied along the $a$ axis. The magnetisation versus temperature together with the calculated magnetic-entropy change are

**Figure 8.12.** Top: Magnetisation versus temperature of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for magnetic fields applied along the $a$ axis. Bottom: Magnetic-entropy change of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for a magnetic field change of 5 T calculated from magnetisation versus temperature curves (■) and magnetic isotherms (○). See text for details.
Figure 8.13. Magnetic transition temperatures of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ determined from the magnetisation versus temperature curves given in figure 8.12. The line serves as guide for the eye. The inset shows the schematic B-T phase diagram of Gd$_5$(Ge$_{1+x}$Si$_{1-x}$)$_4$ with $0.25 < x < 0.50$. The arrows indicate the direction of the phase transition.

given in figure 8.12. The open circles in the bottom part of figure 8.12 are obtained with equation 8.3. In figure 8.12, the maximum entropy change occurs at somewhat lower temperature than that in figure 8.11. This is due to a slightly different composition of the samples. The magnetic-entropy change can be determined from the magnetisation-versus-temperature curves by calculating

$$
\Delta S_{\text{mag}} = \int_{0}^{B} \left( \frac{\partial M}{\partial T} \right)_{B'} dB'
$$  \hspace{1cm} (8.4)

The integration from 0 to 5 T has been done with the trapezoidal rule [8.11], using all six magnetisation-versus-temperature curves presented in the top part of figure 8.12. As can be seen in the bottom part of figure 8.12, the magnetic-entropy change calculated with the two different methods compares well, the entropy change amounting to 28 J/kg K at 210 K. Here, we note that the magnetic entropy available to the system due to the $(2J+1)$-fold degeneracy of the ground-state multiplet is $R \ln(2J+1) = 17.3$ J/mol K ($J = 7/2$ for Gd), which is almost a factor of two smaller than the value obtained from magnetisation measurements. (Direct comparison of the above given values is easy, because the molar mass of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ is 1.005 kg.) A discussion on the obtained entropy changes and a comparison to the values reported in literature, is given in section 8.7. For sake of completeness, we note that the adiabatic temperature change, $\Delta T$, can be obtained from the magnetisation curves by
\[
\Delta T = - B \left( \frac{T}{C} \right)_B \left( \frac{\partial M}{\partial T} \right)_B \mathrm{dB}
\]

(8.5)

where C is the specific heat [8.1].

From the thermomagnetic curves in figure 8.12, we have constructed the magnetic phase diagram shown in figure 8.13. The transition temperatures have been determined as the minimum in the temperature derivative of the thermomagnetic curves. The schematic B-T phase diagram given in the inset of figure 8.13 will be discussed in section 8.7.

8.6 Electrical resistance

The temperature dependence of the electrical resistance of Gd$_5$Ge$_2.4$Si$_{1.6}$ was measured on the same samples used for the magnetisation measurements shown in figures 8.8 to 8.10. The lead contacts were soldered to the samples. A typical result of the electrical-resistance measurements is given in the top part of figure 8.14. When passing the magnetic/structural phase transition at about 225 K, the samples displayed cracking, yielding an erratic behaviour of the electrical resistance in this temperature region. The initial room-temperature value of the resistivity is estimated to be 500 to 600 \(\mu\Omega\)cm. However, due to the possibility of cracks being present at room temperature already, this value has a large uncertainty.

In order to reduce stresses and therewith the occurrence of cracking of the samples, part of the single crystal was first annealed for 7 days at 1000 °C, and then cut into bars. To prevent the induction of stresses, the lead contacts were not soldered but were pressed onto the samples. In this way, the resistance measurements on the annealed samples turned out to be more successful. The results of electrical-resistance measurements with the measuring current along the \(a\) axis together with a result of magnetisation measurements, is given in the bottom part of figure 8.14. At about 55 K, the resistance has a pronounced kink and the magnetisation has a small upturn, anomalies that are not present in curves measured on the as-grown Gd$_5$Ge$_2.4$Si$_{1.6}$ crystal. Hence, the anomalies at 55 K are attributed to antiferromagnetic ordering of the impurity phases Gd$_5$(Ge$_{0.75}$Si$_{0.25}$)$_3$ and GdGe$_{0.5}$Si$_{0.5}$, only present in the annealed samples [8.12]. We note that the anomaly in the resistivity is observed in the curves for \(i \parallel a\) and \(c\), but not in the curve for \(i \parallel b\) axis (cf. bottom part figure 8.14 with inset figure 8.15). This is remarkable as the three samples were cut from the same annealed batch, the 'b-axis' sample being obtained from the area in between the 'a' and 'c-axis' sample.

The magnetic/structural phase transition shows up at about 190 K as a strong increase of the resistance with increasing temperature. The observed resistance behaviour at \(T_C\) is clearly different from the anomaly expected for a simple ferromagnetic metal (see figure 2.5), and can be interpreted as being due to changes in band structure. A blow-up of the temperature dependence of the electrical resistance around the transition temperature for the measuring current applied along the three main crystallographic directions is given in figure
Figure 8.14. Top: Electrical resistance versus temperature of as-grown Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for measuring current i applied along the a axis. Bottom left axis: Electrical resistance versus temperature of annealed Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for measuring current i applied along the a axis. Bottom right axis: Magnetisation versus temperature of annealed Gd$_5$Ge$_{2.4}$Si$_{1.6}$ for B // a axis. Both curves in the bottom part were measured with increasing temperature.

8.15. Above T$_C$, the curves measured with increasing temperature have higher resistance than the curves measured with decreasing temperature. We attribute this to microcracks that enter the sample when the sample goes through the transition. The transition temperatures have a hysteresis of about 5 K, confirming the first-order nature of the magnetic/structural transition. The transitions temperatures are somewhat shifted for the three samples, which is due to the slightly different Si contents of the samples. The transition temperature observed in the curve for i // b axis is, as expected, in between the transition temperatures observed in the curves for i // a and c.
The electrical resistance for \( i \parallel b \) axis has a different behaviour than the electrical resistance for \( i \parallel a \) and \( c \). The change in electrical resistance at the phase transition is 20% for \( i \parallel a \) and \( c \), while it is 28% for \( i \parallel b \). Besides, the width of the transition is different, i.e.: the transition is more pronounced for \( i \parallel b \). Furthermore, above \( T_C \) the electrical resistance for \( i \parallel b \) axis is almost temperature independent, while the resistance curves measured with \( i \parallel a \) and \( c \) axes show a significant increase. The question arises whether the deviating behaviour of the electrical resistance for \( i \parallel b \) has the same origin as the anisotropy observed in the magnetic properties or whether it is due to the impurity phases. Note that for the as-grown crystal the electrical resistance for \( i \parallel a \) axis is almost temperature independent above \( T_C \), too (see top part figure 8.14). Moreover, the electrical resistance of several polycrystalline
Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ samples reported in literature [8.13; 8.14] is almost temperature independent above $T_C$, as well. Hence, one may conclude that the anisotropy in electrical resistance is due to the impurity phases. On the other hand, we are convinced that the impurities are also present in the 'b-axis' sample, although they don't show up in the electrical resistivity. We note that the two impurity phases form as striped precipitates that are perpendicular to each other (see figure 8.2). Moreover, it is likely that the precipitates have formed along the principal axes of the bulk phase. Hence, the distribution of the precipitates may be different in the three samples, and may have a different effect on the electrical resistivity.

8.7 Discussion

For $0.25 \leq x \leq 0.50$, the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ has with decreasing temperature a phase transition from a paramagnetic-monoclinic (P-M) phase to a ferromagnetic-orthorhombic (F-O) phase. Judged on the basis of the pronounced behaviour of the magnetisation at the transition temperature and the hysteresis in the temperature dependence of the electrical resistance, we conclude that the phase transition is of first order. Moreover, at temperatures just above the ordering temperature, the P-M to F-O transition can be evoked by the application of a magnetic field. The hysteresis observed in the field dependence of the magnetisation indicates that the field-induced transition is of first order, too. The resulting phase diagram is depicted schematically in the inset of figure 8.13 [8.5; 8.13; 8.14].

The entropy change associated with the phase transition has been calculated from magnetisation data using the thermodynamic Maxwell relation 8.2. The calculated entropy change of maximal 28 J/kg K at 210 K (figure 8.12) is consistent with the results reported in ref. 8.2, which are also based on magnetisation measurements. In ref. 8.2, the entropy change has been calculated for several Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds, and depends strongly on the Si content. Besides, it has been discussed [8.15] that, due to the accumulation of errors in the magnetisation, temperature and magnetic field upon numerical integration, the relative error in $\Delta S_{\text{mag}}$ may amount to 30%.

Several groups have reported on the adiabatic temperature change, $\Delta T_{\text{adv}}$, associated with the P-M to F-O phase transition in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ [8.2; 8.5; 8.16]. The adiabatic temperature change has been determined from magnetisation measurements (equation 8.5), specific-heat measurements and direct measurements. Giguère et al. [8.16] claim that the adiabatic temperature change calculated from heat-capacity data is much overestimated when compared to their direct measurements. Therefore, the validity of the use of the Maxwell relation 8.2 for Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ is questioned. Instead, they claim that the Clausius-Clapeyron equation

$$\left( \frac{\partial B}{\partial T} \right)_p = \frac{|\Delta S|}{|\Delta M|}$$

(8.6)
is valid. In our opinion [8.17], the experimental results obtained by direct measurement of \( \Delta T_{ad} \) obtained by Giguère et al. are based on non-equilibrium experimental data, and therefore, cannot be compared with the values calculated from heat-capacity data. Furthermore, we believe that the Maxwell relation holds, because all available experimental data indicate that the derivatives \( (\partial M/\partial T)_{B} \) and \( (\partial S/\partial B)_{T} \) remain well defined for \( \text{Gd}_{5}(\text{Ge}_{x}\text{Si}_{1-x})_{4} \). In fact, the derivatives would be non-defined only if the first-order phase transition occurs infinitely fast as a function of temperature or magnetic field. Moreover, as the first-order phase transition does not occur infinitely fast, the use of the Clausius-Clapeyron equation 8.6 becomes complicated. The value of \( (\partial B/\partial T)_{p} \) can be determined from the phase diagram (see figure 8.13). However, the data points in figure 8.13 can be obtained by different methods, and may yield a different slope. Similarly, the determination of \( \Delta M \) is not unambiguous. In figure 8.16, we present four different methods to determine \( \Delta M \) from a magnetisation curve. Likewise, one can determine \( \Delta M \) in different ways from the temperature dependence of the magnetisation. Unfortunately, in none of the reports on the magnetocaloric effect in \( \text{Gd}_{5}(\text{Ge}_{x}\text{Si}_{1-x})_{4} \) the method used to determine \( \Delta M \) is explicated. Thus, the application of the Clausius-Clapeyron equation is not unambiguous for a not-ideal first-order phase transition. Note that we do not question the validity of the Clausius-Clapeyron equation to the system \( \text{Gd}_{5}(\text{Ge}_{x}\text{Si}_{1-x})_{4} \).

As can be seen in figure 8.6, the width of the magnetic/structural phase transition and the accompanying change in magnetisation depends on the quality of the sample. As these properties reflect the size of the magnetocaloric effect, the utilisation of (low-quality) \( \text{Gd}_{5}(\text{Ge}_{x}\text{Si}_{1-x})_{4} \) in a magnetic refrigerator may be hampered.
In summary, we have considered three methods to determine the entropy change, $\Delta S_{\text{mag}}$, from magnetisation measurements, which are characterised by equations 8.3, 8.4 and 8.6. The determination of the entropy change, $\Delta S_{\text{mag}}$ (and the adiabatic temperature change $\Delta T_{\text{ad}}$) characterising the magnetocaloric effect is not unambiguous, as the quality of the samples, the measuring technique and the analysis method used may yield considerable deviations. Still, we can conclude that the magnetocaloric effect observed in the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds is 'giant', the entropy change associated with the phase transition being close to or even larger than the upper limit $R \ln(2J+1)$. For example, at room temperature the compound Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ has a larger magnetocaloric effect than pure Gd [8.2], which may be counter-intuitive, as in Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ the number of magnetic Gd atoms has been considerably reduced. However, since the magnetic-ordering transition in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ is accompanied by a crystallographic phase transition, latent heat may give rise to an additional contribution to the magnetocaloric effect.

The latent heat mainly arises from the enthalpy change at the structural phase transition. Closer inspection of the crystal structures of the low-temperature and high-temperature Gd$_5$(Ge$_{0.5}$Si$_{0.5}$)$_4$ phases indicates that the major crystallographic change occurs due to the break-up of covalent-like Si—Si, Si—Ge and Ge—Ge bonds at the transition from the low-temperature orthorhombic to the high-temperature monoclinic phase [8.14]. The monoclinic lattice, therefore, is more loosely bonded compared to the orthorhombic one. The size of the entropy change due to the structural phase transition in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ is not yet known. Since, for instance, the entropy change at the structural phase transition of $\alpha$-Fe to $\gamma$-Fe is comparable to the observed entropy changes, we have confidence that the entropy change connected with the structural phase transition of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ may have a significant contribution [8.18]. Additionally, the phonon spectrum may be modified upon the transition. Hence, the lattice contribution to the specific heat may be somewhat different for the two structures, which can be envisaged as a difference in the Debye temperature for the two structures.

A last remark we make in the discussion on the magnetocaloric effect in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$, addresses a statement made in literature, that the latent heat is not observed in the magnetisation data [8.19]. This misconception apparently arises from the assumption that the structural phase transition has no influence on $\Delta M$. However, as is given by the Clausius-Clapeyron equation 8.6, the entropy change is not only determined by $\Delta M$, but also by $(\partial B/\partial T)_p$. In our opinion, the additional latent heat at the P-M to F-O phase transition is reflected by the slope of the phase line in the phase diagram (figure 8.13).

Let us now discuss the anisotropy observed in the magnetic properties of Gd$_5$Ge$_{2.4}$Si$_{1.6}$. We recall that the magnetisation measured at 5 K in a magnetic field applied along the $a$ and $c$ axes displays simple ferromagnetic behaviour. In contrast, it seems that for a magnetic field applied along the $b$ axis, only four of the five Gd atoms per formula unit develop a magnetic moment along the $b$ axis. Upon application of a magnetic field larger than 3 T also on the fifth Gd atom a net magnetic moment is induced along the $b$ axis. A magnetic field of about 15 T is
needed to make the $a$ axis and $b$ axis magnetisation coincide.

At first sight, the anisotropy in the magnetic properties of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ may appear peculiar, as the orientation of the half-filled $4f$ shell of Gd does not couple directly to the crystalline electric field. A clue on the origin of the anisotropy is given by the results of symmetry considerations. We note that the analysis with the theory of group representations has limited validity, because the magnetic phase transition is of first order and because we don’t know the magnetic propagation vector. Hence, we don’t have enough information to decide in which representation (or combination of representations) the magnetic moments of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ order. As is given in table B.5, there are several magnetic models for which no component of the magnetic moment along the $b$ axis is allowed at the 4$c$ site, while the components of the magnetic moment along $a$ and $c$ may have a non-vanishing size. Furthermore, we note that one of the five Gd atoms per formula unit occupies the 4$c$ site, while the other four Gd atoms per formula unit occupy two non-equivalent 8$d$ sites. Therefore, we are led to the conclusion that, apparently, Gd$_5$Ge$_{2.4}$Si$_{1.6}$ orders in a magnetic structure that is described by a representation (or a combination of representations) in which no component of the magnetic moment along the $b$ axis is allowed at the 4$c$ site. This conclusion generates a lot of questions, the answers to which we can, at the moment, only speculate on. We discuss some aspects below.

The conclusion that a magnetic moment is not allowed along a certain crystallographic direction because of symmetry appears somewhat unsatisfactory. Usually, the anisotropy observed in the magnetisation is described in terms of a consideration between magnetocrystalline anisotropy energy and the Zeeman energy (see for example (Hf,Ta)Fe$_2$, section 4.4). Therefore, one can debate on the interactions that determine the magnetic structure, and on the resulting anisotropy. The magnetic moments in Gd$_5$(Ge$_{1.4}$Si$_{3.4}$) mainly arise from the well-localised $4f$-electron spins of Gd. Due to the $s$-character of the $4f$ electronic shell of Gd, crystalline-electric-field effects are not expected to play an important role. Hence, in our opinion, in the system Gd$_5$(Ge$_{1.4}$Si$_{3.4}$) the (anisotropic) magnetic properties may be determined by exchange interactions. Let us consider a possible exchange mechanism that may give rise to anisotropy. As the $4f$-electron spins of Gd are well localised, these spins can interact indirectly via polarisation of the $5d$-electron spins. The $5d$-electron spins are coupled to the $5d$ orbital moments via spin-orbit coupling. In turn, the $5d$ orbits may be confined to specific directions in the crystal due to the formation of covalent-like bonds with Si/Ge. Then, the $4f$-electron spins are coupled indirectly to a specific direction (or plane) in the crystal. Indeed, in Gd$_5$(Ge$_{1.4}$Si$_{3.4}$) the $5d$-electron spins of Gd appear to be polarised, because the magnetisation measured at 5 K is slightly larger than the expected value (3.6 versus 3.5 $\mu_B$/f.u.). Furthermore, the measured effective magnetic moments are somewhat enhanced compared to their free-atom value (see table 8.1). A detailed investigation of the atomic surroundings of the 4$c$ site and 8$d$ sites is needed to substantiate the given reasoning, i.e.: the surrounding of the 4$c$ site should be anisotropic. In this picture, the anisotropy is due to a competition between the Zeeman energy and an energy corresponding to the breaking of one of the above-given coupling mechanisms.
As the magnetic moments are confined to the Gd atoms and the Gd atoms are part of the lattice, one may argue that, in principle, the resulting magnetic structure has to obey the symmetry of the lattice. Still, it seems unfavourable to have a magnetic moment perpendicular to the applied magnetic field, because no Zeeman energy is gained. Hence, it may be favourable for the magnetic system to decouple from the lattice, i.e.: lower its symmetry. However, as is manifested by the simultaneous crystallographic/magnetic phase transition, in the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ there is a strong coupling between the crystallographic and magnetic structure. Then, as is marked by the magnetisation curve given in figure 8.9, at 5 K a magnetic field of 3 T can overcome the coupling.

Furthermore, one may question why upon the application of a magnetic field the magnetic structure does not transform from its original representation into a representation in which the moments are allowed along the $b$ axis. Here, we note that according to the Landau theory, to each representation belongs a characteristic energy (equation 2.36). Upon the application of a magnetic field, one can envisage that the energies of the representations shift relative to each other. Then, at 5 K a transition from one representation to another representation occurs upon application of a magnetic field of 3 T. In this picture, the origin of the energy corresponding to a representation is not discussed. It is likely, however, that the origin lies in the exchange interactions between the magnetic moments.

Additionally, one may dispute the validity of the symmetry analysis in an applied magnetic field. Upon application of a magnetic field, the time-reversal symmetry is broken, which may require a different approach of the symmetry analysis. On the other hand, if the applied magnetic field is small, one can consider the magnetic field as a perturbation. Then, in first approximation, the zero-field symmetry analysis remains valid and one may question how large a magnetic field is needed to invalidate it. If the applied magnetic field is to be compared with the internal field of the system, a value of 3 T at 5 K seems reasonable. The results of magnetisation measurements (figures 8.8 and 8.10), however, indicate that the field-induced transition shifts to higher field with increasing temperature. As in the simple Weiss model the internal field is proportional to the magnetisation, this behaviour appears non-trivial.

In conclusion, in the system Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ the magnetic and structural properties are intimately related due to a strong magnetoelastic coupling, leading to a simultaneous crystallographic/magnetic phase transition as a function of temperature, magnetic field and pressure. The magnetocaloric effect observed in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ with $0.25 \leq x \leq 0.50$, is 'giant', because at the transition the entropy change has a contribution from both the magnetic moments and the crystal lattice. Due to the strong magnetoelastic coupling present in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$, the symmetry of the lattice imposes confinements upon the magnetic structure, that yield a measurable anisotropy in the magnetic properties. The electrical resistance of Gd$_5$Ge$_{2.4}$Si$_{1.6}$ changes 20 % at the crystallographic/magnetic phase transition, and can be interpreted as being due to changes in the band structure. Finally, the Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ compounds are extremely complex and exciting materials that require much more detailed experimental and theoretical studies before their nature is fully understood.
References