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“Investigations in the aluminium rich part of the ternary phase diagram Al—Fe—Ge“

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Declaration of Authorship

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- I have acknowledged all main sources of help.

- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

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Chapter 1

Introduction

Intermetallic compounds of transition metals and aluminium exhibit various superior characteristics. Regarding their density, mechanical properties and resistance against corrosion at elevated temperatures, they were often found to be advantageous. Of special interest are iron aluminides in respect of cost efficiency; furthermore, they are having a weight reduction of up to 30% compared to steel alloys and a reliable resistance against oxidising and sulfidising environments, which is due to the formation of a protective Al₂O₃ layer (e.g. [1, 2]). Intermetallics of transition metals and triels or tetrels (TM–X where X = Al, Ga, Si, Ge) are also known to often exhibit unusual magnetic properties (e.g. [3, 4]).

In previous investigations of Al–TM–X (X = tetrel) ternary phase diagrams, the aluminium rich part was often found to contain various stable and metastable ternary phases (e.g. [5]). Al-Fe-Si, for instance, is reported to possess twelve intermetallic phases [6, 7]; similar is reported for ternary systems as Al–Mn–Si (ten intermetallic phases [8]), Al–Ni–Si (six intermetallic phases [9]) or Al–Co–Si (seven intermetallic phases [10]). These phases are of potential interest in aluminium industry, where their appearance should be avoided. However, new ternary compounds in this composition range may also have new and advantageous properties, so their synthesis and characterisation is of high potential interest.

Ternary systems of Al–TM–Si were already studied extensively in many cases. Due to the closely parallel physical properties of Si and Ge, similar results regarding the number of phases and their properties (e.g. Al–Fe–Si: brittle, hard ternary and high corrosion resistance) are expected. Therefore, the up to now almost unknown phase diagram Al–Fe–Ge was investigated in an exploratory approach, with respect to phase equilibria and structural properties of the ternary phases. The Al rich part of the system Al–Fe–Ge, was studied in four vertical sections at 10, 23, 40 and 60 at.% Fe and two partial isothermal sections at 400 °C as well as at 800 °C, in order to understand changes in equilibrium as a function of temperature and composition. Structural features of several new intermetallic compounds were studied by single crystal and powder X-ray diffraction.
Chapter 2

Literature review

2.1 Basic materials

2.1.1 Al

Amongst metals, aluminium is the most common element. Its mass content in lithosphere is approximately 7.96 to 8.41 w% [12]. Due to its chemically high affinity to oxygen aluminium never occurs native, but as oxides. Typical oxidic and hydroxidic compounds are Al₂O₃ (corundum), Al(OH)₃ (gibbsite) and AlO(OH) (boehmite). Feldspar and mica, which are common aluminosilicates, are parent materials to clays and bauxites. Also AlF₃ (aluminium fluoride) and some of its alkaline metal derivatives (e.g. Na₃[AlF₆] - cryolite) are reported to occur in nature.

Red bauxite, which contains 20 – 25 % Fe₂O₃ and 1 – 5 % SiO₂, serves as industrial feedstock for alumina production in the Bayer process. During this process, the grained bauxite is stirred for up to eight hours at 140 – 250 °C and 5 – 7 bar in 35 – 38 % sodium hydroxide, Na[Al(OH)₄] is produced. The residue, which is called red mud, is filtered and deposited, whilst the filtrate is cooled and diluted to precipitate Al(OH)₃. Afterwards the hydroxide is annealed at 1200 – 1300 °C to yield α-Al₂O₃. In the Hall-Héroult-process the Al₂O₃ is dissolved in crylite at an eutectic mixture (Tm = 935 °C). The mixture is then subjected to a fused salt electrolysis with 3 – 5 V direct current passing through the bath. The dense liquid aluminium serves here

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</tr>
<tr>
<td>Atomic mass (g·mol⁻¹)</td>
</tr>
<tr>
<td>Covalent radius (pm)</td>
</tr>
<tr>
<td>Melting point (°C)</td>
</tr>
<tr>
<td>Density (g·cm⁻³)</td>
</tr>
</tbody>
</table>
### Table 2.2: Properties of iron [11]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>26</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Ar] 3d⁶ 4s²</td>
</tr>
<tr>
<td>Classification</td>
<td>8th, iron group</td>
</tr>
<tr>
<td>Atomic mass (g·mol⁻¹)</td>
<td>55.847</td>
</tr>
<tr>
<td>Covalent radius (pm)</td>
<td>126</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1535</td>
</tr>
<tr>
<td>Density (g·cm⁻³)</td>
<td>7.873</td>
</tr>
</tbody>
</table>

As cathode, while the oxygen reduces the carbon block anodes to form pure carbon dioxide.

Aluminium is a ductile paramagnetic metal which crystallises face centered cubic (cF4) and has Fm̅3m as structure type and is reported to have a Mohs hardness of 2.75 [13]. Its specific electrical conductivity is two third of the conductivity of copper. One high pressure modification above 217 GPa is known to crystallise in a hexagonal close packed crystal structure [14]. Above 380 GPa a body-centered cubic structure is predicted by density functional theory calculations [12, 15].

Aluminium is usually trivalent and by this gets oxidised under significant heat development by most non-metals. Intermetallic phases are known to form with almost all metals. Bulk aluminium is stable against further corrosion due to its persistent oxide layer. Reactions with non-oxidising acids (e.g. HCl), in contrast to oxidising acids (e.g. HNO₃), appear to be a dissolution of aluminium under hydrogen evolution. In alkaline solutions and strong acids no protective Al(OH)₃-layer is created, as it is in water and weak acids.

#### 2.1.2 Fe

With a weight fraction of 4.32 to 4.58 w% [12], iron is the second most abundant metal in lithosphere. It may occur in the vast majority of cases as oxides, sulphides and carbonates rather than native. Fe₂O₃ (magnetite), Fe₃O₄ (hematite), Fe₂O₃·xH₂O (bog iron), FeS₂ (pyrite) and FeCO₃ (siderite), which is also found in Eisenerz (Austria), are of significant economic importance. Notable is the high nuclear binding energy of the isotope Fe-56 of 8.8 MeV. It is one of the tightest bond nuclei and possesses the highest binding energy per nucleon.

By utilisation of the Boudouard reaction, the oxidic iron ore is reduced in three steps to yield pig iron together with liquid slag, which is formed by limestone and silica. Since pig iron still contains several percent of impurities like carbon, silicon, manganese, phosphorus and sulphur it possesses some undesirable features such as brittleness. By the use of oxygen steelmaking oxygen is blown onto the molten pig
iron until the desired impurity content is reached. The oxidation of the impurities
to slag ensures that the steel reheat during the process.

The ductile and silver-white appearing iron is exhibiting three enantiotropic mod-
fications. The body-centered cubic $\alpha$-Fe ($Im\bar{3}m$ – ferrite), the face-centered cubic
$\gamma$-Fe ($Fm\bar{3}m$ – austenite) and the body-centered cubic $\delta$-Fe ($Im\bar{3}m$). At a Curie-
temperature of 768 °C [11] the ferromagnetic feature disappears in favour for a para-
magnetic one. One high pressure modification above 10 GPa is verified [16]. $\varepsilon$-Fe has a hexagonal close packed crystal structure of the Mg-type ($hP2$). Pure iron has a
specific electrical conductivity of $1.03 \times 10^7$ S*m, which is roughly one sixth of that of
copper [11]. Its Mohs hardness is 4.0 [17].

Iron forms an oxidic protective layer on its surface, which prevents reactions
with dry air, pure water, lyes and concentrated HNO$_3$ and H$_2$SO$_4$. In diluted non-
oxidising acids it is dissolved under subsequent hydrogen evolution. In a wet and
carbon dioxide containing environment it is oxidised to FeO(OH) (vulgo: rust). Most compounds formed by iron are in +2 or +3 oxidation state, but also oxidation
states up to +6 and -2 are known.

2.1.3 Ge

Germanium can be found in many minerals and is therefore a relatively common
metalloid. Nevertheless, weight fractions between 1.25 and 1.6 ppm are rarely ex-
ceeded in lithosphere [18, 19]. Its native form is usually as germanates and sul-
phides, which generally are accompanied by tin or copper compounds. Typical
examples are Cu$_6$FeGe$_2$S$_8$ (germanite) as well as Ag$_8$GeS$_6$ (argyrodite) which is iso-
morphous to Ag$_8$SnS$_6$ (canfieldite).

| Atomic number | 32 |
| Electron configuration | $[\text{Ar}] 3d^{10} 4s^2 4p^2$ |
| Classification | 14$^{th}$, carbon group |
| Atomic mass (g*mol$^{-1}$) | 72.61 |
| Covalent radius (pm) | 122 |
| Melting point (°C) | 937.4 |
| Density (g*cm$^{-3}$) | 5.323 |

Flue gas that is rich in GeO$_2$ is a by-product of zinc production. It is recovered
from roasting of (Zn,Cu)S (sphalerite). In the first step thereafter the mixture of
GeO$_2$ and ZnO is dissolved in H$_2$SO$_4$ and converted to GeCl$_4$ and ZnCl$_2$ by addition
of HCl of Cl$_2$. In the second step the GeCl$_4$ can be removed by distillation due to
its low boiling point. After hydrolysation the GeO$_2$ is reduced with hydrogen or
carbon to obtain germanium. Further purification is possible by application of a zone melting process.

At standard pressure germanium crystallises in its $\alpha$-modification, a diamond cubic crystal structure ($cF8$) with $Fd\bar{3}m$ as space group. In this allotropic form it is a brittle and grey-silver semi-conductor with a Mohs hardness of 6.0 [20]. Above 12 GPa the electrical conducting $\beta$-modification in $\beta$-Sn-structure is stable. Furthermore certain metastable modifications are reported as well as amorphous germanium. Due to its higher coordination number (e.g. eight instead of four) in the liquid state germanium possesses a negative thermal expansion in the process of melting.

At ambient temperature germanium is stable against oxidation. Above $250^\circ C$ it oxidises to $\text{GeO}_2$ similarly as it is in oxidising acids. In non-oxidising acids and dilute alkali almost no dissolution occurs. Its oxidation states are usually +4 or +2, but also values of +3 and some negative as -4 (e.g. $\text{GeH}_4$) are observed [18].

2.2 Binary subsystems

2.2.1 Al–Fe

The phase diagram Al–Fe is of significant importance in a broad field of theoretical and commercial applications [21]. Little data on phase equilibria at lower temperatures are known, albeit the Al–Fe phase diagram was investigated extensively since decades; first approaches were executed in 1922 by Kurnakow et al. [22] and 1927 by Gwyer and Phillips [23]. Nine phases are known to be present in the Al–Fe system (table 2.4).

In the region with high Fe content various order-disorder transitions are reported. These are second order or first order transition ordering processes; namely $\alpha$-Fe (A2) $\leftrightarrow$ AlFe (B2) and AlFe (B2) $\leftrightarrow$ AlFe$_3$ (D0$_3$). Additionally, AlFe is reported to have three subdivisions of different defect ordering: B2’, B2(h) and B2(l). Those phenomena, however, are not entirely understood up to now. Furthermore, at low temperatures a K1 and a K2 region are reported by some authors [24, 25] (compare figure 2.1 and figure 2.2), which appear to form only on certain impurity levels and heat-treatment history [26]. The ferro-/paramagnetic transition in AlFe$_3$ decreases linearly, whilst the Curie temperature profile in $\alpha$-Fe it is decreasing in a non-linear manner. A $\gamma$-loop exists until several at.% of Al.

In the region with low Fe content four stable phases are known. The $\varepsilon$-phase in the central part decomposes in an eutectoid reaction at temperatures higher than $1080^\circ C$, which caused difficulties in structure determination. Albeit a stabilisation
2.2. Binary subsystems

Figure 2.1: Al–Fe binary phase diagram, which is based on assessment and CAPLHAD calculations of Sundman et al. [21]; dot-dashed lines indicate magnetic transitions at Curie temperature; dashed lines label not well determined solubility lines; there are two invariant reactions at 1153 very close to each other, which cannot be resolved in this picture;

to lower temperatures by addition of 5 at.% Cr, Mo or Ti is possible, the Cu₅Zn₈ type structure of undoped ε was recently confirmed by neutron diffraction [27, 28].

Al₂Fe was referred to be of a P1 structure. Re-determination in 2010 concluded in a space group of higher symmetry with PT and a derivation from the YPd₂Si structure [29]. In experiments also executed in 2010 the temperature dependence of lattice parameters in P1 space group is given [27] (table 2.4).

Next to the low temperature modification of Al₃Fe, in some references also referred as Al₁₃Fe₄, in space group C2/m [30], a high temperature metastable modification is reported [31, 32]. By splat-cooling a displacive polymorphic phase transformation was observed. This gives rise to multiple twinning with decagonal pseudosymmetry, which was observed in planes (100) and (001) in the low temperature modification. Several additional metastable (Al₆Fe, Al₅Fe₂ and AlmFe) and quasicrystalline (Al₅Fe₂₀ and Al₃Fe) phases are known to exist [33-36]. High pressure
Phase diagrams are reported to form in the unary systems, but not the binary phase diagram.

Furthermore, this phase melts congruent and exhibits a slightly higher melting point than Al$_2$Fe and Al$_3$Fe. Unfortunately, all three possess a melting point very close to each other, which causes severe difficulties in phase diagram determination. Especially the type of decomposition reaction of Al$_3$Fe is controversial (Table 2.5). Du et al. [37] propose congruent melting of Al$_3$Fe and an eutectic reaction between Al$_2$Fe and Al$_3$Fe in their calculations, whereas many other authors suggest a peritectic decomposition [21, 26, 35, 36]. Therefore, the peritectic case and the very recent phase diagram of Turcharin et al. (Figure 2.2), which includes the solubility ranges for all binary phases, was used in this investigation. The more recent phase diagram assessed by Turcharin et al. [35] was used in for further investigation on the ternary phase diagram Al–Fe–Ge.
Table 2.4: Phases in Al–Fe phase diagram; not given compositions were estimated by the author and written in brackets;

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. (at.% Fe)</th>
<th>Comp. (at.% Fe)</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Structure type</th>
<th>Strukturbericht des.</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>(α-Fe)</td>
<td>~55–100</td>
<td>55–100</td>
<td>cl2</td>
<td>Im3m</td>
<td>W</td>
<td>A2</td>
<td>[21]</td>
</tr>
<tr>
<td>(γ-Fe)</td>
<td>98.7–100</td>
<td>(~98–100)</td>
<td>cF4</td>
<td>Fm3m</td>
<td>Cu</td>
<td>Al</td>
<td>[21]</td>
</tr>
<tr>
<td>AlFe</td>
<td>~45–76.7</td>
<td>~47–76.5</td>
<td>P8</td>
<td>Pm3m</td>
<td>CsCl</td>
<td>B2</td>
<td>[21]</td>
</tr>
<tr>
<td>AlFe3</td>
<td>~66–~77</td>
<td>(~63.2–~76.5)</td>
<td>cF16</td>
<td>Fm3m</td>
<td>BiF3</td>
<td>D03</td>
<td>[21]</td>
</tr>
<tr>
<td>ε</td>
<td>~35–~42</td>
<td>~35.5–~40</td>
<td>cI52</td>
<td>I43m</td>
<td>Cu5Zn8</td>
<td>D82</td>
<td>[21, 27, 28]</td>
</tr>
<tr>
<td>Al2Fe</td>
<td>33.1–34</td>
<td>~33.5–~34</td>
<td>aP18</td>
<td>P1</td>
<td>FeAl2</td>
<td>…</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>aP19</td>
<td>PT</td>
<td>FeAl2</td>
<td>…</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al2Fe</td>
<td>27–30</td>
<td>~28–~33</td>
<td>oS15</td>
<td>Cmcm</td>
<td>Fe2Al5</td>
<td>not given</td>
<td>[39]</td>
</tr>
<tr>
<td>Al3Fe</td>
<td>23.4–25.5</td>
<td>23.4–~25</td>
<td>mC102</td>
<td>C2/m</td>
<td>Fe4Al13</td>
<td>…</td>
<td>[21, 30]</td>
</tr>
<tr>
<td>(Al)</td>
<td>~0</td>
<td>99.975–100</td>
<td>cF4</td>
<td>Fm3m</td>
<td>Cu</td>
<td>A1</td>
<td>[21]</td>
</tr>
</tbody>
</table>
Table 2.5: A comparison of the composition and temperatures of invariant reactions in the Al–Fe phase diagram; controversial reactions are denoted by italics [21, 26, 35-37, 40];

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction type</th>
<th>Composition (at.% Fe)</th>
<th>Composition (at.% Fe)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature</td>
<td></td>
<td>[26, 35]</td>
<td>[36, 40]</td>
<td>[35]</td>
</tr>
<tr>
<td>L ↔ α-Fe</td>
<td>congruent</td>
<td>~90</td>
<td>not given</td>
<td>1540 ± 1</td>
</tr>
<tr>
<td>α-Fe ↔ AlFe</td>
<td>critical</td>
<td>55</td>
<td>1318</td>
<td>1318 ± 1</td>
</tr>
<tr>
<td>L + AlFe ↔ ε</td>
<td>peritectic</td>
<td>~40 48 40.6</td>
<td>48.4 42.6</td>
<td>1231 1222</td>
</tr>
<tr>
<td>L ↔ Al₅Fe₂</td>
<td>congruent</td>
<td>29 28.6</td>
<td>1157</td>
<td>1154 1158.1</td>
</tr>
<tr>
<td>L ↔ ε + Al₅Fe₂</td>
<td>eutectic</td>
<td>31.5 35.5 31.6</td>
<td>36.6 28.6</td>
<td>1155 1154</td>
</tr>
<tr>
<td>L ↔ Al₅Fe</td>
<td>congruent</td>
<td>not given</td>
<td>not given</td>
<td>1155.4</td>
</tr>
<tr>
<td>L ↔ Al₅Fe₂ + Al₃Fe</td>
<td>eutectic</td>
<td>not given</td>
<td>not given</td>
<td>1154.7</td>
</tr>
<tr>
<td>L + Al₅Fe₂ ↔ Al₃Fe</td>
<td>peritectic</td>
<td>~25 ~28 ~25 24.2</td>
<td>28.6 24.7</td>
<td>1149 1146 1149 ± 1</td>
</tr>
<tr>
<td>ε + Al₅Fe₂ ↔ Al₂Fe</td>
<td>peritectic</td>
<td>~36 ~33 ~33.5</td>
<td>28.6 33.3</td>
<td>1146 1153 1153.0</td>
</tr>
<tr>
<td>ε ↔ FeAl + Al₂Fe</td>
<td>eutectic</td>
<td>~40 ~47 ~40.4</td>
<td>46.2 33.3</td>
<td>1095 1089 1095 ± 1</td>
</tr>
<tr>
<td>L ↔ Al₃Fe + (Al)</td>
<td>eutectic</td>
<td>0.9 23.4 0.9</td>
<td>23.7 0</td>
<td>655 654 654</td>
</tr>
<tr>
<td>α-Fe ↔ AlFe</td>
<td>critical</td>
<td>76.5 not given</td>
<td>not given</td>
<td>612</td>
</tr>
<tr>
<td>AlFe ↔ AlFe₃</td>
<td>critical</td>
<td>73.5 not given</td>
<td>545</td>
<td>545 ± 2</td>
</tr>
</tbody>
</table>
2.2. Binary subsystems

2.2.2 Al–Ge

The binary phase diagram of aluminium and germanium is a simple eutectic system. Three phases are present: (Al); the liquid, L; (Ge). First approaches on the phase diagram were executed by Kroll in 1926 [41] as well as Stöhr and Klemm in 1939 [42]. Further thermodynamic key data was collected by Glazov in 1962 [43], Wilder in 1966 [44] and Batalin and Beloborodova in 1968 [45]. Initial critical assessments were performed by Ansara et al. [46] and McAllister and Murray [47]. Re-evaluations utilising Redlich-Kister polynomial models of Srikanth et al. [48] and Islam et al. [49] were based on more recent STGE data and phase equilibria information.

![Figure 2.3: Al–Ge phase diagram redrawn based on assessment and CAPHAD calculations of Islam et al. [49]](image_url)

Despite extensive studies, due to its significance in semiconductor industry, the eutectic temperature is still ambiguous. While Eslami et al. [50] measured an invariant reaction at $417 \pm 3 \, ^\circ\text{C}$ in an electromotive force study, values range from $415.5 \pm 1 \, ^\circ\text{C}$ [51] to $424 \, ^\circ\text{C}$ [42] in different observations. Also, the eutectic point was shifted to a higher aluminium content in more recent studies, as visible in table 2.6.
The solid solubilities are well examined on the aluminium rich side, whilst on the germanium rich side fewer data exists [49].

Four metastable phases are reported to exist between 30 and 51 at.% Ge [53-55]. A monoclinic ($P2_1/c$), a rhombohedral ($R3c$), a hexagonal ($P6/mmm$) and an orthorhombic ($Pbca$) phase crystallise under non-equilibrium conditions. The metastable equilibria only appear between $\alpha$-Al and the metastable phases, but not with $\beta$-Ge. The presence of suitable nucleation sites is just as redounding as the extent of undercooling of the liquid. High pressure metastable phases of Al–Ge are superconducting [56-58]; therefore, also the pressure dependence of the system was investigated several times. Minamino et al. [59] created three isobaric sections (0.1 MPa, 2.2 GPa and 2.6 GPa). An extension of solubility of aluminium from 2.59 to 6.76 at.% Ge and the constant value of germanium at about 1.5 at.% Al are stated to be in good agreement with thermodynamic data. Earlier investigations of Soma et al. [60], which were performed up to 10 GPa showed a similar behaviour by reaching a solubility of more than 22 at.% Ge in Al.

Islam et al.’s assessment [49] (figure 2.3) was used for the investigations in the Al–Fe–Ge phase diagram, as it combines the experimental and CAPLHAD data of various authors and is the most recent assessment on this topic.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Literature</th>
<th>Composition (at.% Ge)</th>
<th>Temperature (°C)</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L ↔ (Al) + (Ge)</td>
<td>[47]</td>
<td>28.4 ± 1.0</td>
<td>2.0 ± 0.5</td>
<td>98.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>[48]</td>
<td>28.0</td>
<td>2.56</td>
<td>98.74</td>
</tr>
<tr>
<td></td>
<td>[49]</td>
<td>27.33</td>
<td>not given</td>
<td></td>
</tr>
<tr>
<td>L ↔ Al</td>
<td>[47]</td>
<td>0</td>
<td>660.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[48]</td>
<td>0</td>
<td>660.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[49]</td>
<td>0</td>
<td>660.85</td>
<td></td>
</tr>
<tr>
<td>L ↔ Ge</td>
<td>[47]</td>
<td>100</td>
<td>938.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[48]</td>
<td>100</td>
<td>938.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[49]</td>
<td>100</td>
<td>938.85</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2.7: Crystal structure data for Al–Ge phase diagram [48, 52]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (at.% Ge)</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Structure type</th>
<th>Strukturbericht designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Al)</td>
<td>0–2.56</td>
<td>cF4</td>
<td>Fm$\bar{3}$m</td>
<td>Cu</td>
<td>A1</td>
</tr>
<tr>
<td>(Ge)</td>
<td>98.74–100</td>
<td>cF8</td>
<td>Fd$\bar{3}$m</td>
<td>C (diamond)</td>
<td>A4</td>
</tr>
</tbody>
</table>
2.2.3 Fe–Ge

First experiments were carried out in 1940 by Ruttewit and Masing [61]. Two different phase diagrams are described in literature. One was created by Richardson through chemical vapour deposition in 1967 [62]. It was confirmed by Bosholm et al. by chemical vapour deposition experiments in 2001 [63] (figure 2.4). The other one was revised by Kato from various available data sources in 1993 [64] and reassessed by Okamoto in 2008 [65]. Seven intermetallic phases (figure 2.5) are known to be stable under equilibrium conditions in the phase diagram Fe–Ge. The main differences between both available phase diagrams are the number of phases, the solubility ranges of the phases $\beta$ and $\eta$ as well as the type of decomposition reaction of FeGe$_2$ (table 2.8 and table 2.9).

![Figure 2.4: Adapted phase diagram Fe–Ge; created by Richardson [62] in 1967 and redrawn by Bosholm et al. [63] in 2001; dotted lines mark structural phase transitions; dot-dashed lines indicate magnetic transitions at Curie temperature; dashed lines label not well determined solubility lines.](image)

Considering the solubility ranges of the phases, the Fe rich part exhibits broad solid solutions whereas in the Ge rich part stoichiometric line phases dominate. The
Figure 2.5: Fe–Ge assessed by Okamoto [65] in 2008; dot-dashed lines indicate magnetic transitions at Curie temperature; long dashed lines label order-disorder transitions; dotted lines mark structural transitions; the transition $\alpha_1 \leftrightarrow \alpha_2$ is a transition of higher order, although not indicated in the phase diagram;

Fe rich part possesses similarities to the Al–Fe phase diagram, discussed earlier, regarding order-disorder transitions (namely $\alpha$-Fe (A2) $\leftrightarrow \alpha_1$ (B2) and $\alpha_1$ (B2) $\leftrightarrow \alpha_2$ (D0$_3$)), the magnetic transition at Curie temperature, and a solubility of Ge in $\gamma$-Fe of several percent in shape of a $\gamma$-loop.

The phases $\epsilon$ and FeGe are reported to exhibit two respectively three polymorphs. Whereas, the cubic modification of FeGe has the highest density in the system [66]. The precise transition temperatures are given in table 2.9.

The chimney ladder Nowotny phase Fe$_2$Ge$_3$ was detected by Gerasimov and Pavlov in 2000 by mechanical alloying of the pure elements [67]. Due to the kinetic inhibition during the transformation in the eutectoid reaction of FeGe$_2$ $\leftrightarrow$ Fe$_2$Ge$_3$ + (Ge) it was not found earlier. Further investigations in 2014 by Li et al. revealed a slight deviation from the ideal stoichiometric composition and stated the formula FeGe$_{1.52}$ [68]. Understandably, the phase FeGe$_{1.52}$ is missing in the Richardson phase diagram due to its recent discovery.
In the central part of the phase diagram two closely related phases are reported. Due to various designations (e.g. Fe$_{1.75}$Ge, Fe$_{2-x}$Ge, Fe$_{13}$Ge$_8$, Fe$_5$Ge$_3$ and Fe$_3$Ge$_2$) for β and η used by different authors, a distinction between them is a rather challenging endeavour. As visible in table 2.10, Pd$_{13}$Tl$_9$, NiAs and Ni$_2$In are possible structure types for β and η [65, 69]; but also the non B8-typ structures as Co$_2$Ge and CoGe have been suggested [70]. Furthermore, a fast formation within 15 minutes of sintering [71] and Curie temperature at 212 ± 2°C were reported for β [72]. A relationship between the monoclinic phase Fe$_6$Ge$_5$ and B8-type structures was investigated by Larsson et al. [73]. Additional discussions related to β and η as well as their relationship to B8-type structures will be discussed later (chapter 5). Neither a high pressure nor a metastable phase are reported to exist in the Fe–Ge phase diagram.

The phase diagram of Okamoto (figure 2.5) was chosen as basis on further investigations due to up-to-dateness. Only on the transition temperatures of the FeGe polymorphs this study refers to Bosholms’ phase diagram (as indicated in table 2.8).
Table 2.8: Invariant reactions according to the Okamoto Fe–Ge phase diagram [65]; not given data was estimated by the author and indicated by brackets;

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition (at.% Ge)</th>
<th>Temperature (°C)</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\alpha\text{-Fe}) \leftrightarrow \alpha_1)</td>
<td>18.7</td>
<td>(1240)</td>
<td>critical</td>
</tr>
<tr>
<td>(L \leftrightarrow \beta)</td>
<td>37.5</td>
<td>1170</td>
<td>congruent</td>
</tr>
<tr>
<td>(\alpha_1 + \beta \leftrightarrow \varepsilon)</td>
<td>29.4</td>
<td>1122</td>
<td>peritectic</td>
</tr>
<tr>
<td>(L \leftrightarrow \beta + \alpha_1)</td>
<td>30.3</td>
<td>1105</td>
<td>eutectic</td>
</tr>
<tr>
<td>(L + \beta \leftrightarrow \eta)</td>
<td>57</td>
<td>928</td>
<td>peritectic</td>
</tr>
<tr>
<td>(L + \alpha_2 \leftrightarrow \varepsilon)</td>
<td>17.5</td>
<td>(905)</td>
<td>peritectic</td>
</tr>
<tr>
<td>(L + \eta \leftrightarrow \text{FeGe}_2)</td>
<td>68</td>
<td>840</td>
<td>peritectic</td>
</tr>
<tr>
<td>(L \leftrightarrow \text{FeGe}_2 + \text{Ge})</td>
<td>70</td>
<td>838</td>
<td>eutectic</td>
</tr>
<tr>
<td>(\eta + \text{FeGe}_2 \leftrightarrow \text{FeGe (mon.)})</td>
<td>43.5</td>
<td>748</td>
<td>peritectic</td>
</tr>
<tr>
<td>(\text{FeGe (mon.)} \leftrightarrow \text{FeGe (hex.)})</td>
<td>50</td>
<td>(740)</td>
<td>congruent</td>
</tr>
<tr>
<td>(\varepsilon \leftrightarrow \varepsilon')</td>
<td>23.7-25.5</td>
<td>(700)</td>
<td>congruent</td>
</tr>
<tr>
<td>(\text{FeGe(hex.)} \leftrightarrow \text{FeGe(cub.)})</td>
<td>50</td>
<td>(630)</td>
<td>congruent</td>
</tr>
<tr>
<td>(\eta + \text{FeGe (cub.)} \leftrightarrow \text{Fe}_6\text{Ge}_5)</td>
<td>43.5</td>
<td>(600)</td>
<td>peritectic</td>
</tr>
<tr>
<td>(\text{FeGe}_2 + \text{FeGe(cub.)} \leftrightarrow \text{Fe}_2\text{Ge}_3)</td>
<td>50</td>
<td>600 or 60</td>
<td>580</td>
</tr>
<tr>
<td>(\text{FeGe}_2 \leftrightarrow \text{Fe}_2\text{Ge}_3 + \text{(Ge)})</td>
<td>60.3 or 60</td>
<td>530</td>
<td>eutectic</td>
</tr>
<tr>
<td>(\eta \leftrightarrow \text{Fe}_6\text{Ge}_5 + \beta)</td>
<td>42.8</td>
<td>525</td>
<td>eutectic</td>
</tr>
<tr>
<td>(\varepsilon' \leftrightarrow \beta + \alpha_1)</td>
<td>24.8</td>
<td>400</td>
<td>eutectic</td>
</tr>
</tbody>
</table>
Table 2.9: Invariant reactions according to the Richardson Fe–Ge phase diagram [62]; not given data was estimated by the author and indicated by brackets;

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition (at.% Ge)</th>
<th>Temperature (°C)</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(α-Fe) ↔ α1</td>
<td>20</td>
<td>(1260)</td>
<td>critical</td>
</tr>
<tr>
<td>α1 + β ↔ ε</td>
<td>19.9 33.8 25.2</td>
<td>(1180)</td>
<td>peritectic</td>
</tr>
<tr>
<td>L ↔ β</td>
<td>38.6</td>
<td>1170</td>
<td>congruent</td>
</tr>
<tr>
<td>L ↔ β + α1</td>
<td>32.3 33.5 20</td>
<td>1130</td>
<td>eutectic</td>
</tr>
<tr>
<td>L + β ↔ η</td>
<td>51 42.6 42.8</td>
<td>1000</td>
<td>peritectic</td>
</tr>
<tr>
<td>L ↔ FeGe₂</td>
<td>66.7</td>
<td>866</td>
<td>congruent</td>
</tr>
<tr>
<td>L ↔ FeGe₂ + Ge</td>
<td>77.6 66.7 100</td>
<td>860</td>
<td>eutectic</td>
</tr>
<tr>
<td>L ↔ FeGe₂ + η</td>
<td>64.2 66.7 45.8</td>
<td>835</td>
<td>eutectic</td>
</tr>
<tr>
<td>η + FeGe₂ ↔ FeGe (mon.)</td>
<td>42.5 66.7 50</td>
<td>750</td>
<td>peritectic</td>
</tr>
<tr>
<td>FeGe (mon.) ↔ FeGe (hex.)</td>
<td>50</td>
<td>740</td>
<td>congruent</td>
</tr>
<tr>
<td>η + FeGe (hex.) ↔ Fe₅₆Ge₅</td>
<td>42.2 50 45.5</td>
<td>(738)</td>
<td>peritectic</td>
</tr>
<tr>
<td>ε ↔ ε’</td>
<td>24-26 700</td>
<td>700</td>
<td>congruent</td>
</tr>
<tr>
<td>FeGe(hex.) ↔ FeGe(cub.)</td>
<td>50</td>
<td>630</td>
<td>congruent</td>
</tr>
<tr>
<td>η ↔ Fe₅₆Ge₅ + β</td>
<td>40 45.5 38.8</td>
<td>(520)</td>
<td>eutectic</td>
</tr>
<tr>
<td>ε’ ↔ β + α1</td>
<td>25.2 37 19</td>
<td>400</td>
<td>eutectic</td>
</tr>
</tbody>
</table>
Table 2.10: Crystal structure data for phases in Fe–Ge phase diagram; Compositions of the phase diagram assessed by Richardson [62] were estimated by the author; discrepancies between references citing each other were observed (indicated bold);

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. (at.% Ge) [62]</th>
<th>Comp. (at.% Ge) [65]</th>
<th>Pearson sym.</th>
<th>Space group</th>
<th>Structure type</th>
<th>Strukturbericht</th>
<th>Lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(α-Fe)</td>
<td>0–20</td>
<td>0–17.5</td>
<td>cI2</td>
<td>Im-3m</td>
<td>W</td>
<td>A2</td>
<td>[65]</td>
</tr>
<tr>
<td>(γ-Fe)</td>
<td>0–2.5</td>
<td>0–3.4</td>
<td>cF4</td>
<td>Fm3m</td>
<td>Cu</td>
<td>A1</td>
<td>[65]</td>
</tr>
<tr>
<td>α1</td>
<td>11.5–20</td>
<td>10–22</td>
<td>cP2</td>
<td>Pm3m</td>
<td>CsCl</td>
<td>B2</td>
<td>[65]</td>
</tr>
<tr>
<td>α2</td>
<td>not given</td>
<td>15.2–21.5</td>
<td>cF16</td>
<td>Fm3m</td>
<td>BiF3</td>
<td>D03</td>
<td>[65]</td>
</tr>
<tr>
<td>ε</td>
<td>24.2–26.2</td>
<td>23.7–25.7</td>
<td>hP8</td>
<td>P63/mmm</td>
<td>Ni2Sn</td>
<td>D019</td>
<td>[65]</td>
</tr>
<tr>
<td>ε’</td>
<td>24.2–26.2</td>
<td>23.7–25.7</td>
<td>cP4</td>
<td>Pm3m</td>
<td>AuCu3</td>
<td>L12</td>
<td>[65]</td>
</tr>
<tr>
<td>β</td>
<td>33.5–42.6</td>
<td>33.5–41</td>
<td>h..</td>
<td>P3m1</td>
<td>Pd13Tl9</td>
<td>[69, 74]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>h..</td>
<td>P63/mmc</td>
<td>Co2Ge</td>
<td>[69, 70]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hP6</td>
<td>P63/mmc</td>
<td>Ni2In</td>
<td>B82</td>
<td>[69, 72]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hP4</td>
<td>P63/mmm</td>
<td>NiAs</td>
<td>B81</td>
<td>[65]</td>
</tr>
<tr>
<td>η</td>
<td>39.6–45.8</td>
<td>40.8–43.5</td>
<td>hP21</td>
<td>P63/mmc</td>
<td>CoGe</td>
<td>[70]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>h..</td>
<td>NiAs</td>
<td></td>
<td></td>
<td>[69, 70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hP6</td>
<td>P63/mmc</td>
<td>Ni2In</td>
<td>B82</td>
<td>[65]</td>
</tr>
<tr>
<td>Fe₆Ge₅</td>
<td>45.5</td>
<td>45.5</td>
<td>mS44</td>
<td>C2/m</td>
<td>Fe₆Ge₅</td>
<td>[75]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>...</td>
<td>C2/m</td>
<td>...</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>FeGe</td>
<td>50</td>
<td>50</td>
<td>mC16</td>
<td>C2/m</td>
<td>CoGe</td>
<td>...</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hP6</td>
<td>P6/mmm</td>
<td>CoSn</td>
<td>B35</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>cP8</td>
<td>P213</td>
<td>FeSi</td>
<td>B20</td>
<td>[65]</td>
</tr>
<tr>
<td>Fe₂Ge₃</td>
<td>not given</td>
<td>60</td>
<td>tP20</td>
<td>P4c2</td>
<td>Ru₂Sn₃</td>
<td>...</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.3</td>
<td>tP20</td>
<td>P4c2</td>
<td>Ru₂Sn₃</td>
<td>...</td>
<td>[68]</td>
</tr>
<tr>
<td>FeGe₂</td>
<td>66.7</td>
<td>66.7</td>
<td>tI12</td>
<td>I4/mcm</td>
<td>Al₄Cu</td>
<td>C16</td>
<td>[65]</td>
</tr>
<tr>
<td>(Ge)</td>
<td>100</td>
<td>100</td>
<td>cF8</td>
<td>Fd3m</td>
<td>C (diamond)</td>
<td>A4</td>
<td>[65]</td>
</tr>
</tbody>
</table>
2.3 Ternary phase diagram Al–Fe–Ge

A couple of studies have been performed in the ternary system Al–Fe–Ge. Of these, several concern thermodynamic properties and metallic glass formation. Due to repulsive interactions in Al–Ge and strongly attractive in Fe–Ge they differ from usual transition metal metal-metalloid type alloys [76].

Substitutional impurities in Fe were studied by Akdeniz and Mekhrabov stating a decreasing activity coefficient of Al in $\alpha$-Fe$_{0.95}$(Al/Ge)$_{0.05}$ resulting in thinner Al–Fe intermetallic diffusion layers [77].

In investigations by Gruzin et al. [78], Athanassiadis et al. [79] and Golovin et al. [80, 81] an improved D0$_3$-type ordering, compared to B2-type, was reported for Al–Fe–Ge alloys. This effect is due to the repulsive interaction between Al and Ge atoms in AlFe and AlFe$_3$. The repulsive interaction, however, is also the reason, that no ferromagnetic Heusler type alloys of composition AlFe$_2$Ge can be found. This circumstance and the rising transition temperature of the order-disorder transition $\text{B2} \leftrightarrow \text{D0}_3$ is visible in figure 2.6.

![Figure 2.6: Vertical section at 75 at.% Fe [78, 94]](image-url)
Five partial isothermal sections from the Fe rich corner are reported. Two of them are sections at 600 °C, but created by the same authors Kozakai et al. [82, 83]. The more recent version (figure 2.7) shows no miscibility gap in the α2 phase region, compared to the older version. The α2 phase, which is the structurally corresponding analogue to the binary AlFe3 phase, is already stabilised by approximately 2.5 at.% Ge. A section at 700 °C drawn by the same author exhibits similar features (figure 2.8). The section at 400 °C was created by Schmid-Fetzer (figure 2.9) [84]. Unfortunately the Fe–Ge binary phase α2 was not considered during phase diagram evaluation. The fifth isothermal section is a non-equilibrium one (figure 2.10). Though it was retrieved from Ravhagan [85], its origin is uncertain, since the literature of Elyutin et al. [86] was not available. In the case it originates from Elyutin et al. the samples were annealed for one hour and then slowly cooled (20 K/min) to room temperature at a speed of 20 K/min [84].

![Figure 2.7: More recent partial isothermal section at 600 °C taken from Ravhagan [93]; created by Kozukai et al. [82]](image-url)
2.3. Ternary phase diagram Al–Fe–Ge

Estimations about the glass forming tendency (GFT) were found to be in a region containing less than 50 at.% Ge and between 10 and 60 at.% Fe [87]. The achievement of super-cooling is difficult in amorphous alloys of the Al–Fe–Ge system and amorphous alloys yielded by melt-spinning processes tend to change greatly with composition [76, 88-90].

On ternary structures, only three references are known. Inoue et al. [76] reported on four amorphous ternary structures in the section of high Al content, which were obtained by melt spinning. They matched several other amorphous Al–Ge–TM (TM = V, Cr, Mn, Co, Ni) systems by their compositions of \( \text{Al}_{90-x}\text{Fe}_{10}\text{Ge}_x \) (\( x \approx 14 \) and 47) as well as \( \text{Al}_{75-x}\text{Fe}_x\text{Ge}_{25} \) (\( x \approx 7 \) and 23). No information on the according crystal structures was given. Another metastable phase of monoclinic structure was reported by Fadeeva et al. at 56 at.% Fe [91]. It is formed out of Fe(Al,Ge) solid solution at temperatures of 520 to 580 °C and decomposes peritectically into the

![Figure 2.8: Partial isothermal section at 700 °C taken from Ravhagan [93]; created by Kozakai et al. [82]](image-url)
Chapter 2. Literature review

Figure 2.9: Partial isothermal section of Fe rich side of Al–Fe–Ge at 400°C by Schmid-Fetzer [84]; short dashed lines label uncertain phase boundaries; dotted lines indicate higher order transitions; unfortunately α1, but not α2 was considered in the evaluation;

equilibrium phases \( \text{Al}_{1-x} \text{Fe}_x \text{Ge}_x \), \( \text{Fe}_6 \text{Ge}_5 \) and \( \eta \) above 850°C. Kubalova et al. found a monoclinic phase of composition \( \text{Al}_2 \text{Fe}_6 \text{Ge}_3 \) and Pearson symmetry (\( mC44/8 \)) to be stable up to a peritectic decomposition at 750 to 850°C [92]. The reported lattice parameters (\( a = 0.9896 \) nm, \( b = 0.7931 \) nm, \( c = 0.7679 \) nm, \( \beta = 108.68 \) with a R-value of 3.77) were determined by means of the Nelson–Riley method. Both authors used mechanical alloying for their investigations. The reported composition corresponds well to the binary phase \( \text{Fe}_6 \text{Ge}_5 \) and thus the lattice parameters exhibit similarities. The atomic positions were refined from powder XRD patterns. The 24 8j, 4i, 4h and 4f positions are attributed to Fe, whilst the remaining 20 atomic positions are mix-filled (Al/Ge). Furthermore, they stated a low symmetry structure of Fe(Al,Ge) below 750°C.
2.3. Ternary phase diagram Al–Fe–Ge

Figure 2.10: slowly cooled from 860°C to 27°C; taken from Ravhagan [85], but presumably originated from Elyutin et al. [86]
Chapter 3

Theroretical background

3.1 Phase diagrams

A phase is a uniform material of homogenous state of matter, of certain chemical composition and structure. It possesses distinct physical properties and a specific atomic arrangement in solid state. It is a fact that these phases are separable under mechanical influence in the majority of cases.

Regarding an unary phase diagram polymorphic phase changes might occur next to changes of the state of matter, when altering the variables pressure and/or temperature. As already discussed in chapter 2, iron for instance possesses several polymorphic forms; each exhibiting its individual properties and crystal structure. Thus iron is called to be an allotropic element.

Adding a certain number of elements so-called binary, ternary or even quaternary phase diagrams are created. These represent the phase relationships of the elements and often compounds under equilibrium conditions in form of geometrically finite phase fields. When different phases are in thermodynamic equilibrium, as it is frequently the case, it is a so-termed heterogeneous equilibrium. At thermodynamic equilibrium the Gibbs free energy \((G; J^{\text{mol}^{-1}})\) reaches a minimum.

\[ (G)_{T,p, x_1\ldots x_j} = \min \]

The state of the system may be potted, in a so called phase diagram, which as a function of independent state variables that can be intensive (e.g. pressure, temperature) or extensive (e.g. mole fraction). Metastable equilibria usually are not represented in phase diagrams, unless distinctly labelled. Nevertheless, in some cases pseudo-equilibria are included for mainly practical reasons. For instance \(\text{Fe}_3\text{C}\) (cementite) possesses an extremely slow rate of decomposition and is therefore often included in the C-Fe phase diagram. This proceeding is not scientifically sound, but useful for practical purposes [95].
The Gibbs’ phase rule expresses the number of degrees of freedom \( v \) for a system of a certain number of components \( n \), containing a certain number of phases \( p \).

\[
v = c + 2 - p
\]

The rule might be reduced to following, when keeping one of the intensive properties, i.e. pressure or temperature, constant:

\[
v' = c + 1 - p
\]

The phase field rule is independent of the kind of used diagram (e.g. potential phase diagrams) and applicable for phase diagrams of higher order. The dimensionality of a geometrical phase field \( d \) is related to the number of axis in the diagram \( r \) (equals \( c+1 \)) and the number of phases. Thus it is mandatory to possess information about the exact component number to make a statement on sectioning.

\[
d = r + 1 - p
\]

In a binary system, a four-phase point, would be achieved in the case of \( d < 0 \), which is rarely the case.

The so-called MPL (Masing, Palatnik and Landau) boundary rule is the application of the phase field rule in three dimensional space. When crossing a phase boundary a number of phases emerge and vanish in adjacent fields (\( D^+ \) and \( D^- \)). This phenomenon is dependent on the number of axis \( r \) and the dimensionality of the boundary \( b \).

\[
D^+ + D^- = r - b
\]

For greater convenience certain boundaries are termed to mark their distinct features; the liquidus, between liquid and liquid-solid two phase field; the solidus, between the solid phase and the liquid-solid two phase field; the solvus, between a solid solution and a field of two (or more) solid phases.

Utilising the lever rule in multicomponent systems, molar compositions \( A_m^\alpha \) and their relative sizes \( f_\beta \) of are accessible easily for each subsystem, by knowledge of the average molar content \( A_m^{av} \).

\[
f_\beta = \frac{A_m^\beta - A_m^\alpha}{A_m^{av} - A_m^\alpha}
\]
An extension on systems of higher order is trivial.

\[ A_{m}^{av} = f_{n}^{0} + f_{n}^{\beta} + f_{n}^{\gamma} + \cdots \]

A phase transformation is the life cycle of an occurring phase transition. However, the usage of these terms is often less consistent in literature. Next to the mentioned allotropic transformations in unary systems, other transformations are possible in phase diagrams of higher order. A distinction between invariant or sharp transformations \((d=0)\) and non-invariant or gradual transformations \((d>0)\) has to be made. For sharp transformations in the binary eutectic (E-type) and peritectic transformations (P-type) can occur, whereas, in the ternary a class II four-phase transformation reaction (U-type) is possible in addition to E- and P-type reactions.

For phase transitions, first (discontinuous) and second order transitions (continuous) are distinguished for theoretical reasons. The driving forces are the change of any internal variable. On the one hand different arrangements lead to order-disorder transitions and were already depicted in chapter [2]. On the other hand, displacive transitions are possible, where the configurational entropy remains constant whereas the structure deformation is decreased. There is no two-phase field between one phase fields in case of a second order transition reaction; this fact is often emphasized in phase diagrams by dashed lines and an apostrophe [96].

### 3.2 Methods for isothermal characterisation

By utilisation of various methods, annealed and quenched samples can be investigated in order to collect data on the phases and the associated phase boundaries at selected temperatures.

#### 3.2.1 X-ray single crystal diffraction

X-ray diffraction is the main method in structure determination. It is based on the diffraction of an electromagnetic wave by a lattice of periodic electron density. X-rays generated by Cu and Mo (rare cases Cr, Fe and Ag) are typically applied for investigations on crystalline substances.

Focusing an electron beam, generated by a heated tungsten cathode at a high voltage, on one of the above mentioned anode materials, induces two effects. On the one hand the electrons are slowed down in the Coulomb field of the core, as consequence yielding a white background radiation according to Plank’s rule and Kramer’s rule. On the other hand, inbound electrons eject electrons from the core
Chapter 3. Theoretical background

orbitals. Re-occupation from outer orbitals is allowed under the condition of \( \Delta l = \pm 1 \). A characteristic radiation is emitted that follows Mosley’s law. Its wavelength is proportional to the energy difference of the involved orbitals and the intensity is dependent on the transition probability. The most probable characteristic emissions emerge from the L–K and the M–K orbital transitions; they are denoted as \( K_{\alpha 1} \) and \( K_{\alpha 2} \) or as \( K_{\beta 1} \) and \( K_{\beta 2} \) respectively, after Siegbahn’s notation. For proper elimination of the unwanted white radiation and the interfering \( K_{\beta} \)-duplet, a monochromatic filter is induced in the light path, which is usually an element one atomic number lower than the anode material (e.g. Ni in case of Cu), or a thin single crystal of graphite, quartz or Ge is used as monochromator.

According to Bragg’s law, a periodic lattice that features an interplanar distance \( d \) close to the wavelength of an incoming electromagnetic beam \( \lambda \), exhibits an interference effect. Whether this interference effect is of constructive or destructive character is depended on the scattering angle \( \theta \).

\[
2 \times d \times \sin \theta = n \times \lambda
\]

Macroscopically it appears to be a reflection on a plane and by that is called diffraction plane. Since the order of reflection \( n \) can be only integer, discrete “reflexes” for long range periodicity are expected.

In three-dimensional space a decomposition in three separate one-dimensional structures is auxiliary. All three Laue equations have to be complied with for the incident beam (angle: \( \mu \)) and an outbound reflection (angle: \( \nu \)), to yield a virtual atomic plane of reflection that is denoted by Miller indices.

\[
a \times (\cos \mu_a - \cos \mu_a) = n_1 \times \lambda \\
b \times (\cos \mu_b - \cos \mu_b) = n_2 \times \lambda \\
c \times (\cos \mu_c - \cos \mu_c) = n_3 \times \lambda
\]

The reciprocal space is a convenient tool for indicating all possible reflexes in a known unit cell. Furthermore, it is utilised in Ewald’s sphere for diffraction experiments to address all possible reflexes. A reflex that complies with Bragg’s law will hit the sphere of radius \( 1/\lambda \) at a certain reciprocal distance \( d^* \) and a scattering angle \( \theta \). The intensity \( I_{hkl} \) of each reflex is proportional to the squared structure factor \( F_{hkl} \). Additionally, it is dependent on a scaling factor \( k \), the Lorenz-polarization correction that often includes geometric correction factors of the device \( L_p \), the multiplicity of the plane \( H \) and some further factors such as an absorption coefficient \( A \).
\[ I_{hkl} \propto |F_{hkl}|^2 \]

\[ I_{hkl} = k * |F_{hkl}|^2 * L_p * H * A * \cdots \]

Each structure factor is composed of the sum of all phase shifted atomic scattering factors \((f_i)\), which represents the magnitude of scattering of a wave by a single atom. Atomic displacement parameters \((B)\), such as temperature movement, are included in this angle and wavelength dependent factor.

\[ F_{hkl} = \sum_i f_i * e^{2\pi i (hx_i + kx_i + lx_i)} \]

\[ f_i = f_0 * e^{-B * \sin^2 \theta \lambda} \]

Various methods for single crystal diffraction are available, of which the four circle goniometer is the nowadays most commonly used in structure determination. Its fundamental principle of a rotation around four individual angles \((\omega, \theta, \chi, \kappa, \phi)\), are adapted in two different variants, each having its distinct advantages and disadvantages; the Eulerian geometry and the Kappa geometry.

After careful positioning of the single crystal, which is mounted on a glass capillary, a preliminary image is recorded. It is utilised to determine the unit cell, its parameters and the relative orientation in regard to goniometer axis. This orientation matrix is usually generated by automatic reflex indexation and least-square refinement programmes (refer to next subsection). It is the basis for the calculation of all occurring reflexes that are individually measured in further experiments and by this prone to errors such as superstructures or twinning. The measurement of the individual peaks is executed with a certain redundancy for high peaks to eliminate the possibility of decomposition of the crystal.

CCD-detectors and image plates are cost-effective ways to detect and digitalise the signals. The problem with any available detection system is that only the intensity, but not the phase can be measured, which is referred to as “phase problem”. It has to be solved by direct methods or the Patterson summation in order to obtain a coherent picture of the crystal structure [97-101].

### 3.2.2 X-ray powder diffraction and Rietveld refinement

Albeit applying the same physical principles as single crystal diffraction, powder diffraction is not the method of choice in structure determination. Nevertheless, it
is a superb technique for phase identification due to its convenience in specimen preparation and possibility of multi-phase analysis, since it reduces the reflexes on Ewald’s sphere by two dimensions.

Nowadays, two established techniques are used, depending on the desired mode. Both utilise similar X-ray sources, collimator slits and base on the Rowland cycle for pseudo-focusing. In some cases monochromatisation optics are utilised.

On the one hand, the Bragg-Brentano geometry for powder diffractometers applies a reflecting or transition mode and is available in $\theta/\theta$– geometry (source and detector moving) and $\theta/2\theta$– geometry (sample and detector moving). Modern Si-strip detectors are a fast way to detect powder pattern, by combination of several small Si-strips. Energy dispersive “solid state” detectors are applied in case of strong X-ray fluorescence (e.g. Fe in case of Cu-radiation) and are based on electron-hole pair formation.

On the other hand, the Guinier type camera is used, which is capable of realising the geometry of the Rowland circle in two ways; the transmission mode as well as the reflection mode. Its main advantages are the simultaneous measurement of the whole pattern and the use of an image plate, which has a favourable noise to background ratio [99-102].

Manual indexation of multi-phase patterns is a difficult task due to possible overlap of peaks. Structure refinement with Rietveld method adds up all contributions to one point, instead of calculating individual structure factors for each peak. Therefore, foreknowledge on the structure of all contributing phases is mandatory. Furthermore, large unit cells and low symmetry unit cells are aggravating factors that limit the application.

Comparison of calculated ($y_{Ci}$) and observed intensities ($y_{Oi}$) of each point in the pattern by a least square algorithm is the key part of Rietveld refinement. Due to background noise, a weight factor ($w_i$) is introduced in each calculation. The weighted R-factor ($R_{wp}$) is the measure for the congruence of the calculated and observed pattern, but best results are obtained by additional manual inspection of the “difference plot”.

\[
\chi^2_i = \frac{\sum_i w_i \ast (y_{oi} - y_{ci})^2}{\sum_i w_i \ast y_{oi}}
\]

\[
R_{wp} = \sqrt{\frac{\sum_i w_i \ast |(y_{oi} - y_{ci})|^2}{\sum_i w_i \ast y_{oi}^2}}
\]

Next to qualitative and semi-quantitative composition of the sample as well as crystallographic information, additional valuable data such as crystallite sizes, preferred orientation, texture, amorphous content or residual stress can be gathered in
3.2. Methods for isothermal characterisation

3.2.3 Optical microscopy

The established method of light microscopy is a perfect complement to electron microscopy for microstructure determination, since best results can be obtained by an examination at a magnification that is stepwise increased. Valuable information about the physical as well as in some cases chemical properties of the constituents are provided by inspection in several examination modes. A careful preparation of the specimen is mandatory.

A common starting point is the bright-field illumination mode, for which a paralleled light beam is shone perpendicular on the sample surface. The reflected fraction of the light is then paralleled again and observed through an eyepiece. The underlying mechanism is that any slanted surface reflects a smaller fraction in direction of the eyepiece compared to a perpendicular surface and as a consequence any roughness will appear darker.

An inverted scheme is applied in dark-field illumination. The light beam is shone on the surface at a low angle. When the beam hits an edge it is diffracted out of the optical path. Thus only light that is produced by diffuse scattering contributes to the resulting image. The product is usually a reverse image to the bright-field image. The examination of a metallurgical sample in dark-field is a proper method to inspect the grade of polishing, as scratches, cracks and holes appear bright, while perfectly flat surfaces are dark.

For polycrystalline materials of different constituents a polarised light examination is an integral part of the procedure to differentiate and identify the phases, detect the grain structure and reveal a possible preferred orientation. Two polarisers are placed in the light path, which have a plane of polarization perpendicular to each other, to ensure a complete extinction in optically isotropic materials as well as in optically anisotropic materials that are plane-polarised parallel in regard to the first polariser. Unfortunately, polarising filters are imperfect, resulting in incomplete extinction. A pseudocolour image may be obtained utilising a half-wave plate. Recent developments in phase identification, such as the electron micro probe analysyer, led to a less frequent utilisation.

Employing a modification of the setup above by a Wollaston prism, topographic details and the relative hardness of the constituents become observable. The difference interference contrast (DIC) is utilising the phase difference that is a result of the different path lengths the light has to travel when there are small differences in

powder refinements [97, 99, 102].
height. Via movement of the two birefringent crystals the relative height difference and as a consequence the colour and brightness are alternated.

A lot of information is obtained in optical microscopy. Typically the thermal history, the amount of phases, their crystallisation sequence and reaction types are accessible, next to their grain sizes. In some cases even precipitating phases, segregation and twinning is visible.

An often useful extension to the fundamental technique of optical microscopy is chemical etching. It is capable to enhance the gain of knowledge about the microstructure, by revealing features such as subgrain networks and dislocations [100, 103-105].

### 3.2.4 Scanning electron microscopy and microprobe analysis

Resolution limits in optical microscopy compel users to employ electron beams in preference to visible light, due to wavelengths that are shortened by several orders of magnitude. This versatile technique allows not only topographic and microstructural observations down to the nanometre scale, but, by utilising other types of signals that are emitted from the specimen, a characterisation of the material is possible too.

In order to produce a highly focused electron beam, an elaborate apparatus is needed. The electron gun follows similar principles as the X-ray tubes that were already discussed. An acceleration voltage of up to 50 kV is applied between a ring anode and a cathode, which can be a tungsten or, for higher brightness, a LaB$_6$ filament. In order to restrict the diameter of the electron beam and reduce the anodic voltage needed, a Wehnelt cylinder is introduced, which limits the effective emitting area by negative potential relative to the cathode. Further reduction from the emitted 50 µm down to the final spot size of the demagnified image on the surface is usually obtained by three magnetic electron lenses and interjacent apertures. By altering the size of the spot that is scanned across the sample, the magnification is varied. In order to prevent a burn out of the filament, high vacuum is required. Furthermore, high vacuum aids in minimising losses of the electron beam as a result of scattering.

The interaction of a well-focused electron beam with a material leads to several effects of different lateral resolution and depth of penetration. Inelastic scattering, which occurs at the outer atomic electrons and exhibits energy losses of up to 50 eV per scattering event, and elastic scattering that occurs at the core electrons and at electron energies greater than 50 eV, have to be distinguished. After several elastic scattering events that modify the electron trajectory by an angle greater than 90°,
which is strongly dependent on the atomic number, these backscattered electrons (BE) are detected by a scintillation counter. The same detection device is utilised for secondary electron (SE) detection, which are ejected by the incident beam or backscattered electrons from conduction orbitals of the sample. These low energy electrons are used for topographic observations, since they are almost independent of the atomic number. Next to non-radiative mechanisms (e.g. phonon generation, current absorption), also radiative mechanisms (e.g. Auger electrons, characteristic X-rays, X-ray fluorescence, cathodoluminescence) provide information in abundance that can be detected by various spectroscopy methods.

Employing the characteristic X-ray generation, which only prerequisites an incident electron energy greater than the critical excitation energy, the electron micro probe analyser (EMPA) is the presumably most important tool for qualitative and quantitative analysis of a metallic specimen. Two dispersive detection systems are used; energy-dispersive (EDX) and wavelength-dispersive X-ray spectroscopy (WDX). The former is usually based on a silicon drift detector, a “solid state” detector which records the whole spectrum (energy against counts) at the same time and therefore has high count rates. The latter is based on a goniometer that counts a single wavelength at a time using a scintillation counter. Hence it has longer measuring times, when measuring the whole spectrum (wavelength against intensity), but exhibits better spectral resolution and lower detection limits.

Any quantitative result needs to be standardised with respect to matrix corrections in order to be reliable. The measured intensities for each element (I) are corrected depended on the atomic number (Z), the absorption (A) and the X-ray fluorescence (F), to yield a weight fraction (w) [103, 106-108].

$$\frac{w_i}{w_{i-\text{Std.}}} = \{ZAF\}_i * \frac{I_i}{I_{i-\text{Std.}}}$$

### 3.3 Dynamic methods for characterisation

#### 3.3.1 Differential thermal analysis

Each phase transition requires (endothermic) or provides heat (exothermic), due to enthalpy changes. Differential thermal analysis (DTA) is a technique where these phase transitions can be monitored as a function of temperature.

A sample and a reference are subjected to a temperature programme in two identical inert crucibles (e.g. Al₂O₃) until the sample is fully molten. In many cases, inert gas (e.g. Ar) is used to avoid oxidation of the sample. The resulting temperature
difference between sample and reference is measured by two thermocouples at the bottom of the crucibles.

The resulting plots (reference temperature against temperature difference) are evaluated for effect types, which can be distinguished by shape. The invariant effect (F=0) is of steep asymmetrical appearance and occurs at a fixed temperature, whereas the non-invariant reaction (F>0) can have various shapes and takes place in a temperature interval. Deviations from these ideal shapes are due to delayed heat transfers. Furthermore, supercooling is often a problem encountered, when cooling curves are analysed.

A combination of DTA with gravimetric measurements are often helpful, since they provide valuable information about changes in mass as a function of temperature, thus oxidation, reduction and crystal water can be identified and quantified [95, 104, 109].
Chapter 4

Experimental

4.1 Sample preparation

According to advance information (chapter 2) no useful investigation grid could be established for the exploratory research. Therefore, some slowly cooled samples were synthesised in order to yield a rough concept for a further investigation scheme of isotherms and isopleths.

4.1.1 Basic materials

All binary and ternary samples were weight in utilising a semi-micro balance (Sartorius research, R200D) according to the table 4.1 and figure 4.1 to an accuracy of ±0.5 mg and a total sample mass of 800 mg. As basic materials, following high purity elements were used:

- Al slug, 3.175 mm x 6.35 mm, 99.999 %, Alfa Aesar
- Fe sheet, 99.9 %, vacuum cast
- Ge pieces, 3 – 9 mm, 99.999 %, Alfa Aesar
Table 4.1: All sample compositions that were weighed out as well as the according temperature treatments;

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4.1.2 Arc furnace

All samples were molten up to three times in an electric arc furnace (Johanna Otto GmbH, MAM1) under Ar atmosphere (Messer, Ar 5.0, >99.999 vol.%) and using Zr as getter material. The losses in weight were checked after each melting cycle and are negligible.

The apparatus is based on a vacuum chamber, a Th doped W needle as anode and a water cooled Cu plate with cavities in it as cathode. The specimen accompanied by an oxygen affine getter material are placed in individual cavities. After several evacuate-refill cycles with Ar, high voltage is applied onto the electrodes. A short circuit is created by touching a W tip that is mounted on the Cu plate, which ionises the Ar. The resulting Ar plasma attains temperatures up to 3000 °C and is adjustable by current variation.
Pre-melting of the getter removes any residual oxygen from the chamber and is a convenient leakproofness test. After every melting cycle, which is completed by entire melting of the whole sample, the specimen are turned upside down to achieve a better homogenisation in the pellet.

### 4.1.3 Equilibration

All pellets containing Al were placed inside an Al$_2$O$_3$ crucible in order to prevent any reaction of Al with SiO$_2$. These crucibles as well as samples without Al content were molten into evacuated (9*10$^{-6}$ bar) quartz glass tubes utilising a H$_2$/O$_2$ welding equipment.

After all samples were screened for leakage they were annealed in a muffle furnace (1100 / 1300 $^\circ$C Nabertherm) for 12 days to 4 months. Either a slow cooling programme or annealing at constant temperature of 400 $^\circ$C,600 $^\circ$C or 800 $^\circ$C was chosen (table [4.1]). In order to conserve thermodynamic conditions after annealing, all samples were quenched in cold water. Due to an additional insulating layer, to be more precise the Al$_2$O$_3$ crucible, a quick cooling of the specimen was deferred.

Several not well equilibrated samples were powdered using a WC mortar or an agate mortar in case of magnetic samples. 200 to 300 mg of powder were pressed for three minutes at 20 kN in a hydraulic press (Larzep, EC10.13). The resulting pellets (6 mm in diameter) were sealed in quartz glass tubes and annealed again as described above.

### 4.1.4 Embedding

Before embedding, all samples were divided into quarters either by crushing or in case of ductile samples, by cutting (Buehler, low speed saw). One quarter was embedded into electrically conducting phenolic hot mounting resin with a carbon filler (Struers, PolyFast). For this, the resin was heated to 180 $^\circ$C at a pressure of 15 kN. After six minutes the block was chilled by water for three minutes, preserving the pressure of 15 kN (Struers, LaboPress-1).

The block of resin was mounted on a grinding and polishing machine (Struers, LaboPol - 6). A smooth and flat surface was obtained by grinding with SiC abrasive paper of increasing grit size (240 to 1200). To shine the sample surfaces Al$_2$O$_3$ powder of 1 $\mu$m grain size (Buehler, Micropolish II) was employed. Dark-field microscopy was used to check the progress.
Chapter 4. Experimental

4.2 Measurements

4.2.1 X-ray powder diffraction

One quarter of the annealed sample pellets was powdered using a WC mortar or an agate mortar (in case of magnetic samples). The powders were mounted on Si single crystal sample holders using petrolatum.

In order to obtain a qualitative and quantitative overview of the sample constituents, X-ray powder diffraction (XRD) patterns were measured on a Bragg-Brentano pseudo-focusing goniometer in $\theta/2\theta$ arrangement (Bruker, D8 ADVANCE). A Ni filter was used for monochromatisation of the Cu-$K_{\alpha}$ beam. For the purpose of an irradiation area independent of the illumination angle, a variable aperture was used. The acceleration voltage and current of the X-Ray tube were adjusted dependent on the two possible detectors.

For critical measurements of samples having high Fe content and by that high X-ray fluorescence, an energy dispersive measurement (SolX) was used. Each sample was measured for four hours at an acceleration voltage of 40 kV and current of 50 mA. In all other cases the Si strip based high speed detection system (Lynxeye) was used with a measuring time of one hour and an X-ray generation at 40 kV / 40 mA. All evaluations and Rietveld refinements were carried out utilising Topas software (Bruker, Topas 3).

4.2.2 X-ray single crystal diffraction

New ternary phases were investigated on a four-cycle single crystal diffractometer in kappa geometry (Nonius, Kappa CCD). Therefore one quarter of the annealed pellet was crushed and ideally equilateral single crystals of size 100 x 100 x 100 $\mu$m were selected with a stereo microscope (Zeiss Stemi 2000-C). After mounting them on a glass capillary they were irradiated by a collimated graphite-monochromatised Mo-K$\alpha$ beam. A CCD detector was used to register all reflections in $2\theta$ of the least-square refined unit cell. Structure determination was carried out using SHELX-97 software.
4.2.3 Optical microscopy

An evaluation of the microstructure of the embedded and polished samples was performed with a binocular reflected-light microscope (Zeiss, Axiotech 100). Bright-field and dark-field images were taken. Furthermore, difference interference contrast images and polarisation images of rotations till $180^\circ$ were used for microstructural investigations.

4.2.4 Scanning electron microscopy and microprobe analysis

The Zeiss Supra 55 VP environmental scanning electron microscope (ESEM) was used for further microstructural examinations as well as for quantitative evaluations. Therefore, a SE detector, a BSE detector and an EDX detector were utilised. Calibration of the EDX detector was carried out using Co. Furthermore, the pure elements of Al, Fe and Ge were used as standard materials for calibrating the characteristic X-ray lines. In order to obtain reliable results, at least three individual spots were measured for each observed phase. The investigations were executed at an acceleration voltage of 20 kV and a beam current of 10 nA for the field emission cathode [110].

4.2.5 Differential thermal analysis

![Temperature profile in DTA measurements](image)

**Figure 4.2:** Temperature profile in DTA measurements

In order to construct the vertical sections and investigate phase transition temperatures of the ternary phases, DTA was carried out. Therefore, one piece of roughly 50 mg was placed in a 100 µl $\text{Al}_2\text{O}_3$ crucible and heated above the estimated melting point in two cycles at an absolute temperature variation of 5 K per minute (figure...
4.2 and table 4.2). Constant inert gas (Messer, Ar 5.0, >99.999 vol.%) flow and an evacuation-refill cycle at the outset protected the specimen from oxidation. Furthermore, mass changes were documented by weighing back all samples.

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<th>Sample</th>
<th>$T_{\text{min}}$ [$^\circ\text{C}$]</th>
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A calibration of the TG-DTA apparatus (Setaram, SETSYS Evolution TGA & DTA 2400) was done beforehand using the melting temperatures of Cu, Ni and Sn. The temperature was measured with a type-S thermocouple (Pt10Rh-Pt), which is limited to a maximum temperature of 1600 $^\circ\text{C}$.

4.2.6 Solid-liquid diffusion couple

A solid-liquid diffusion couple was created to investigate the reaction paths and reaction sequence between the Al–Ge eutectic and pure Fe. A polished piece of Al–Ge eutectic mixture was placed on a polished Fe sheet. Due to complications in the first trial, which were probably due to the passivation layer of Al$_2$O$_3$, the Al–Ge eutectic mixture was welded onto the Fe sheet by a short heating cycle in arc furnace. This specimen was placed in a tube furnace for wetting experiments and heated under inert gas atmosphere (Messer, Ar 5.0, >99.999 vol.%) to 470 $^\circ\text{C}$ for 180 minutes. A CCD camera permitted monitoring of the melting procedure. After cutting and embedding, the specimen was examined in ESEM.
Chapter 5

Results

The prepared samples, their mean compositions and their lattice parameters, can be found in several individual tables in the according subsections. The presumable liquid phase as well as encountered problems were specially indicated. Some samples exhibit more phases than allowed in thermodynamic equilibrium; those phases, which were only found in traces were marked. As the crystal structures of $\tau_6$ and $\tau_8$ are unknown, they could not be included into the refinement of powder X-ray diffraction patterns. In some cases two mean compositions are given, because two distinct sets of compositions were measured in the investigation by electron microprobe analysis. Al$_5$Fe$_2$ caused problems in Rietveld refinement of several samples, as not one, but two significantly different data sets of Al$_5$Fe$_2$ were needed to fit the patterns. This might be a sign of coexistence of two different modifications of Al$_5$Fe$_2$ in these samples. No conclusive solution for this problem was found upto now.

For preinvestigation several samples were cooled slowly, in order to exhibit the approximate compositions of the unknown ternary phases (table 5.1). This knowledge served as foundation for further investigations in this ternary system.
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Note: $\tau_5$ indicates the phase fraction for the angular distribution of the X-ray peaks.
5.1 Re-evaluation of the β- and η-phase in Fe–Ge

As already indicated in chapter 2, the phase diagram Fe–Ge exhibits, same as Co–Ge and Ni–Ge, various B8-type related structures, which are discussed controversially in literature. Hence a careful investigation on the structures, lattice parameters and phase boundaries was carried out between 34.0 and 45.0 at.% Ge at 800°C (figure 5.1 and table 5.2).

**Figure 5.1:** The weighed out nominal composition and number of phases in comparison to the binary phase diagram Fe–Ge by assessed Okamoto [65]
Table 5.2: Samples prepared in the binary system Fe-Ge; mean compositions determined by electron micro-probe analysis and semi quantitative compositions as well as lattice parameters determined by powder X-ray diffractometry of all samples; superscripts mark the presumable liquid (L), traces (T), an uncertain predominance of one composition in one phase (P), more than one phase in order to fit pattern in Rietveld refinement (R) and unknown crystal structures (*).

<table>
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<tr>
<th>sample (at.% Al/Fe/Ge)</th>
<th>phase</th>
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<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
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<th>composition [at.%)</th>
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Table 5.2 – continued from previous page

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<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
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<td>-</td>
<td>34.0</td>
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5.1. Re-evaluation of the $\beta$- and $\eta$-phase in Fe–Ge

The $\eta$-phase was of special interest due to little available concurrent data. Single crystal diffractometry of a suited crystal of sample E19 (table 5.3) yielded a slightly different structure model as described by Malaman et al. in 1980 [70]. Strong displacement parameters and shortened Fe3–Ge1 bonds were observed for the original model on Ge1 position during structure refinement, yielding large R values. A shift of the Ge1 site from a fully occupied 2($d$) to a 6($h$) Wyckoff position that is located slightly off the $\bar{6}$ axis and is occupied by one third solved this question (table 5.4 and figure 5.2). Since the Fe3 site is only partially occupied, the structure can be interpreted as following (figure 5.3); the vacant position of the Fe3 site attracts the Ge1 to leave the ideal 2($d$) position causing elongated Fe3–Ge1 bonds (table 5.5) that fit prior estimations.

| Table 5.3: Single crystal structure data of the $\eta$-phase |
|----------------|------------------|
| Sample          | E19              |
| Phase notation  | $\eta$           |
| Compound        | Fe$_{7-x}$Ge$_{4+y}$ |
| $x \approx 1.10$, $y \approx 0.04$ | Fe$_{13}$Ge$_8$ |
| Structure type  | hP26             |
| Pearson symbol  | hP26             |
| 7.9783(10)      | 4.9920(8)        |
| c [Å]           | $P6_3/mmc$ (no. 194) |
| 275.2 / 2       |                    |
| $\rho_{calc}$ [g cm$^{-3}$] / $\mu$(Mo$K_{\alpha}$) [mm$^{-1}$] | 7.70 / 37.3 |
| range of data collection (±h ±k ±l) [°] | 3 < 20 < 70 |
| number of images / scan time [s/°] | 524 / 150 |
| rotation angle per image | 2° |
| distinct $\omega$-angles for $\varphi$-scans mode | 11 |
| measured reflections | 4438 |
| unique reflections (n) / reflections with $F_o > 4\sigma(F_o)$ | 259 / 251 |
| $R_{int} = \sum |F_o^2 - F_c^2(mean)|/\sum F_o^2$ | 0.038 |
| $F_v = F_c k[1 + 0.001F_c^2\lambda^3/sin(2\theta)]^{-1/4}$ | 0.0084(10) |
| $R1 = \sum (|F_o^2| - |F_c^2|)^2/\sum F_o$ (observed / all reflections) | 0.020 / 0.021 |
| $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$ | 0.055 |
| $GooF = [\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ | 1.24 |
| weighting parameters a / b | 0.025 / 0.86 |
| max $\Delta / \sigma$ / number of variable parameters (p) | < 0.001 / 24 |
| final difference Fourier map [eÅ$^{-3}$] | -1.37 to +1.85 |
TABLE 5.4: sites, fractional atomic coordinates and displacement parameters of the phase η; the anisotropic displacement parameters are defined as: $\exp \left[ -2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j \right]$;

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<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eqiv}/U_{iso}$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
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<td>1/4</td>
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5.1. Re-evaluation of the $\beta$- and $\eta$-phase in Fe–Ge

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Returning to the discussion of the $\beta$-phase, it remains uncertain, whether the $\beta$-phase is found to be short range ordered as described by Malaman et al. [70], because the results almost do not differentiate, when a shift of the 2(c) and to 2(d) to a 6(h) position is executed. Their weighted R values were comparable (e.g. sample E9p: $R_{wp}$-shifted = 1.750 and $R_{wp}$-unshifted = 1.771). Since shortened Fe₁—Ge₁ bonds seem to demand this shift as it is the case with the $\eta$-phase all powder X-ray refinements were executed with the shifted version, although a shift could not be ascertained. All powder patterns containing the $\beta$-phase showed some systematic deviations concerning the intensity distribution; only h1k reflections were affected (e.g. the 012 peak was calculated too low, whereas the 110 reflection was calculated too high; refer to figure 5.4) and up to now, this behaviour is not understood.

Concerning phase boundaries, several difficulties were encountered during measurements. Uncertainties whether all samples could be equilibrated in twelve days and problems in refinement of powder diffraction patterns led to the decision to anneal powder pills (chapter 4) of all samples for additional seven days. Furthermore, metallographic preparations were disturbed by the brittleness of all samples and
due to a very narrow two phase field no satisfying phase contrast could be achieved in ESEM observations. Nevertheless, two additional properties were exploited for phase boundary determination. On the one hand samples E16 to E23 showed no magnetic features when mortaring in contrast to samples E1 to E15, which indicates that the two phase field of $\beta$ and $\eta$-phase stretches out till E15 on one side. This observation was confirmed by powder diffraction data, which revealed sample E13 as the other side of the two phase field. After refining the lattice parameters and site occupations of all powered diffraction patterns, a plot of the nominal (figure 5.5) and measured (figure 5.6) concentration against the relationship $c/a$ (in case of $\eta$ $c/2a$ respectively) was created, which is characteristic for B8-type phases. The single phase field of $\eta$ was found to exist between 41.3 and 43.8 at.% Ge (measured: 40.9 and 43.7 at.% Ge), when extrapolating the trend lines and analysing the points of discontinuity. The single phase field of $\beta$ stretches out between 35.5 and 40.1 at.% Ge (measured:35.4 and 39.9 at.% Ge). Furthermore, the lattice parameters of $\beta$ were found to change not linearly according to Vegard’s law, but vary by two linear regression lines of a significant deviation at 38.3 at.% Ge (measured: 36.7 at.% Ge) in slope. The cause if this effect is unclear, as the compositions of 38 at.% Ge does not mark a special point in the phase field. One might speculate that this supports the
assumption, in which \( \beta \) has no pure Ni\(_3\)In structure, but a disordered variant of it (as proposed by Malaman et al. in 1980 [70]). In this case the point of discontinuity could correspond to the loss in short range ordering and, therefore, the change in Wyckoff position. Figure 5.1 compares the binary phase diagram Fe–Ge by assessed Okamoto [65] to the number of phases found in samples of this study. The agreement was found to be good, however, slight shifts of the phase fields to higher Fe contents are possible in the light of the current result.

5.2 Partial isothermal sections

5.2.1 Partial isothermal section at 800 °C

Figure 5.7 shows a partial isothermal section at 800 °C. This section is based on samples given in table 5.6. Eleven intermetallic phases and the liquid are present in this part. The position of the liquid was estimated by liquidus temperatures determined in DTA experiments and is therefore not accurate. The liquid stretches out deep into the ternary phase field and expands not straightforward from the eutectic composition, but at about 50 at.% Ge, which is in contrast to the Al–Fe–Si system.

A relatively low solubility of Al and Fe in Ge was expected from the respective binary phase diagrams (below 1 at.% Al at 800 °C and effectively no solubility for Fe). Electron micro probe analysis showed values of up to 5 at.% (Al,Fe) in Ge. This
is probably due to precipitation of Fe and/or interference of neighbouring phases in the electron micro probe analysis results, thus the values were fixed to an expectancy value. Apart from AlFe, solubilities of Ge in Al–Fe binary phases were up to 9.3 at.% Ge. In contrast, the Fe–Ge binary phases exhibited solubilities up to 11.9 at.% Al. The stable ternary phases had broad homogeneity ranges based on Al/Ge substitution. The Fe content was effectively constant within the error of measurement, except for $\tau_3$.

In the Fe rich part, broad solid solutions of the AlFe and the $\eta$-phase can be found. Albeit the $\beta$-phase possesses a higher melting point and a broader solubility range in the binary Fe–Ge phase diagram than the $\eta$-phase, the $\eta$-phase was found to be favourably stabilised in the ternary isothermal section at 800 °C. In both cases, there is not only a substitution by Al and Ge, but also a slight stabilisation to higher Fe contents.

The cubic polymorph of FeGe, which originates from the binary phase diagram Fe–Ge, was found to be stabilised up to higher temperatures by addition of Al. At 800 °C its range of existance was found to be from 7.7 to 12.5 at.% Al. An analogous stabilisation of the recently discovered FeGe$_{1.52}$ was not observed. No ternary intermetallic phase can be reported above Ge contents of 50 at.%.
5.2. Partial isothermal sections

**Figure 5.5**: Development of the fraction of lattice parameters $c/a$ (and for better comparison $c/2a$ respectively) against the weighed out composition; squares mark single phase fields; crosses indicate two phase fields; two phase fields were assumed to be at a constant lattice parameter ratio; the values of the two phase field of $\beta$ and $\eta$-phase is not plotted, as the lattice parameters of the phases were almost indistinguishable in Rietveld refinement.

Unfortunately, several samples (e.g. C1 and C2) contained traces of the low temperature phase $\tau_6$, which presumably evolved during quenching procedure. This is accounted for by slow cooling rates were due to the additional thermal insulation caused by the alumina crucibles.
FIGURE 5.6: Development of the fraction of lattice parameters $c/a$ (and for better comparison $c/2a$ respectively) against the measured composition; squares mark single phase fields; crosses indicate two phase fields; two phase fields were assumed to be at a constant lattice parameter ratio; the values of the two phase field of $\beta$ and $\eta$-phase is not plotted, as the lattice parameters of the phases were almost indistinguishable in Rietveld refinement.
5.2. Partial isothermal sections

![Partial isothermal section diagram](image)

**Figure 5.7**: Partial isothermal section at 800 °C; mean phase compositions measured by electron micro probe analysis are indicated by dots; dashed lines indicate uncertain or assumed three phase fields.
Table 5.6: Samples annealed at 800 °C; mean compositions determined by electron micro-probe analysis and semi-quantitative compositions as well as lattice parameters determined by powder X-ray diffractometry of all samples annealed at 800 °C; superscripts mark the presumable liquid (L), traces (T), an uncertain predominance of one composition in one phase (P), more than one phase in order to fit pattern in Rietveld refinement (R) and unknown crystal structures (*).

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5.2. Partial isothermal sections

5.2.2 Partial isothermal section at 400 °C

In the partial isothermal section at 400 °C, 15 phases were found. The binary phase FeGe$_{1.52}$ was assumed to exist, but not observed. At this temperature no liquid was found to be present. Some difficulties were encountered during construction of this partial isothermal section; the most plausible equilibrium is shown figure [5.7]. Several samples (table [5.7]) exhibited more phases than possible at equilibrium conditions. This especially applies for samples of high Fe content notwithstanding the long annealing time. Samples K5 and K6 showed three-phase fields, which were not in agreement with each other. A verification of the adjacent ternary phase field by X-ray powder diffraction was not possible in several cases due to the lack of data regarding the crystal structures of $\tau_6$ and $\tau_8$.

Figure 5.8: Partial isothermal section at 400 °C; mean phase compositions measured by electron micro probe analysis are indicated by dots; dashed lines indicate uncertain or assumed phases and three phase fields; the value for AlFe at high Fe content was taken from literature (figure 2.9) [84]
Chapter 5. Results

Same as for the partial isothermal section at 800 °C, the solid solutions are mainly caused by Al/Ge substitution. Al shows almost no Fe or Ge content as expected. Electron micro probe analysis yielded higher solubilities of Al and Fe in Ge. Same as in the isothermal section at 800 °C, the value was fixed to a reasonable value. The binary phases, apart from AlFe, exhibit intermixing of Al and Ge up to 12 at.%. AlFe was assumed to stretch out in a parabolic manner to fit the partial isothermal section shown in chapter 2 [84]. By addition of Al, FeGe$_2$ is stabilised to lower temperatures than the binary decomposition temperature of 530 °C. The phase FeGe$_{1.52}$, however, was not observed, which is presumably due to the sample positions.

The new ternary phases in this section are: $\tau_5$, $\tau_6$, $\tau_7$ and $\tau_8$. Above Ge contents of 50 at.%, no ternary intermetallic phases were measured. The ternary phases $\tau_6$, $\tau_7$ and $\tau_8$, which were not observed under equilibrium conditions at 800 °C, showed no extension within the measurement error; this is in contrast to phases below 60 at.% Al. The extend of the solid solution in the $\tau_4$ phase is uncertain due to a lack in data, but it may be comparable to the solubility range observed at 800 °C. The unusual shape of the $\tau_3$ phase is retained also at 400 °C. A vanishing of $\tau_2$ in favour of $\tau_5$ was observed. The phases occur at the same composition, but have different crystal structures. This phase shows, next to Al/Ge intermixing, a higher variability of the Fe content, at high Ge contents. In samples I3 and I4 additional peaks in the powder diffraction pattern as well as an unknown composition in sample I3 (29 at.% Fe, 38 at.% Fe, 33 at.% Ge) may be an evidence for one further unknown phase. This phase, however, was not included in the isothermal section, as it was a single observation only.

5.2.3 Samples at 600 °C

Due to the small amount of samples prepared (table 5.8), no partial isothermal section at 600 °C could be proposed. The main results for the samples annealed at 600 °C may be summarised as follows:

- As for the section at 400 °C, $\tau_5$ replaces the high temperature phase $\tau_2$.
- A significant quantity of $\tau_8$ was found in equilibrium with liquid and $\tau_1$. 
Table 5.7: Samples annealed at 400 °C; mean compositions determined by electron micro-probe analysis and semi-quantitative compositions as well as lattice parameters determined by powder X-ray diffractometry of all samples annealed at 400 °C; superscripts mark the presumable liquid (L), traces (T), an uncertain predominance of one composition in one phase (P), more than one phase in order to fit pattern in Rietveld refinement (R) and unknown crystal structures (*).

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<th>a [Å]</th>
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<td>38.5</td>
<td>6.222</td>
<td>-</td>
<td>9.721</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45.4 17.1 37.5</td>
</tr>
<tr>
<td>Al$_5$Fe$_2$T</td>
<td>3.8</td>
<td>7.661</td>
<td>6.387</td>
<td>4.264</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59.6 29.9 10.5</td>
</tr>
<tr>
<td>$\tau_5^T$</td>
<td>33.9</td>
<td>3.944</td>
<td>-</td>
<td>11.232</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33.7 32.4 33.9</td>
</tr>
<tr>
<td>K5 Ge</td>
<td>23.8</td>
<td>5.661</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5   2.1 95.4</td>
</tr>
<tr>
<td>(30/23/47)</td>
<td>26.7</td>
<td>6.224</td>
<td>-</td>
<td>9.718</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45.7 16.8 37.5</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>49.5</td>
<td>3.954</td>
<td>-</td>
<td>11.171</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30.9 33.1 35.9</td>
</tr>
<tr>
<td>K6 Ge</td>
<td>32.8</td>
<td>5.660</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.1   1.6 96.2</td>
</tr>
<tr>
<td>(23/23/54)</td>
<td>10.8</td>
<td>6.225</td>
<td>-</td>
<td>9.717</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45.7 17.0 37.3</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>56.5</td>
<td>3.966</td>
<td>-</td>
<td>11.108</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25.2 33.2 41.6</td>
</tr>
<tr>
<td>K7 Ge</td>
<td>32.9</td>
<td>5.657</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3   4.4 93.3</td>
</tr>
<tr>
<td>(12/23/65)</td>
<td>6.1</td>
<td>5.931</td>
<td>-</td>
<td>4.916</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.4 32.9 55.7</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>61.0</td>
<td>3.996</td>
<td>-</td>
<td>10.976</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.3 31.4 48.3</td>
</tr>
</tbody>
</table>
### Table 5.8: Samples annealed at 600 °C; mean compositions determined by electron micro-probe analysis and semi quantitative compositions as well as lattice parameters determined by powder X-ray diffractometry of all samples annealed at 600 °C; superscripts mark the presumable liquid (Li), traces (Ti), an uncertain predominance of one composition in one phase (Pi), more than one phase in order to fit pattern in Rietveld refinement (R) and unknown crystal structures (*).

<table>
<thead>
<tr>
<th>sample fraction</th>
<th>phase</th>
<th>composition [at.%]</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Al</th>
<th>Fe</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>(at.% Al/Fe/Ge)</td>
<td></td>
<td></td>
<td>55.3</td>
<td>15.483</td>
<td>8.093</td>
<td>12.470</td>
<td>-</td>
<td>107.699</td>
<td>-</td>
<td>75.0</td>
<td>23.6</td>
</tr>
<tr>
<td>F2</td>
<td>Al₂Fe</td>
<td>τ₁</td>
<td>44.7</td>
<td>6.266</td>
<td>-</td>
<td>9.619</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>55.5</td>
<td>16.9</td>
</tr>
<tr>
<td>(67/22/11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>F6</td>
<td>Ge</td>
<td>τ₅</td>
<td>32.5</td>
<td>5.660</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>31.6</td>
<td>32.7</td>
</tr>
<tr>
<td>(24/25/51)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.6</td>
<td>0.5</td>
</tr>
<tr>
<td>F8</td>
<td>Geₐ</td>
<td>τ₆*</td>
<td>5.4</td>
<td>4.052</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>96.7</td>
<td>0.1</td>
</tr>
<tr>
<td>(55/9/36)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>65.4</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>τ₇</td>
<td>12.0</td>
<td>20.860</td>
<td>6.263</td>
<td>6.260</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67.5</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>τ₁</td>
<td>51.6</td>
<td>6.259</td>
<td>-</td>
<td>9.631</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>54.2</td>
<td>16.4</td>
</tr>
</tbody>
</table>
5.3 Solid-liquid diffusion couple

The reaction zone of the diffusion couple experiment at 470 °C is shown in figure 5.9 (phases are listed in table 5.9). Comparing the central part of the contact zone and the edges, a high amount of Al₃Fe at the edge is evident. This incident is probably due to the pre-melting in the arc furnace, yielding Al₃Fe at the high temperature of reaction. Next to it a layer of τ₈ was found, which almost vanishes in the centre, in contrast to Al₃Fe. τ₅ was only observed in the central part of the contact zone. Grains of τ₆ with diameters up to 40 µm were observed all over the eutectic mixture part of the sample in high quantities. τ₁ and τ₇, however, was not detected, which could be due to the short annealing time. It has to be mentioned, that the observed sequence of phases does not correspond to a regular reaction sequence. Longer annealing time would be necessary to solve this problem.

| Table 5.9: Mean compositions determined by electron micro-probe analysis and semi quantitative compositions as well as lattice parameters determined by powder X-ray diffractometry of the solid-liquid diffusion couple |
|----------------------------------|---|---|---|
| sample (at.% Al/Fe/Ge) | phase | composition [at.%] | |
| | | Al | Fe | Ge |
| F1 | τ₆ | 66.6 | 7.0 | 26.3 |
| diff. | τ₈ | 71.6 | 9.7 | 18.7 |
| couple | τ₇ | 71.2 | 26.3 | 2.5 |
| (72/0/28) | τ₁ | 47.2 | 17.4 | 35.4 |

5.4 New ternary compounds

Suitable single crystals were extracted from five different samples (A3, A8, D2, F12 and H10). Three phases (τ₅, τ₆ and τ₈) could not be identified utilising single crystal X-ray diffraction. For τ₅, a proposal on the crystal structure could be made after indexation, careful comparison with existing structure types and refinement of powder diffraction patterns.

5.4.1 Al₃FeGe₂ (τ₁)

X-ray powder patterns in different ternary samples indicated a ternary structure τ₁ Al₃₊ₓFeGe₂₋ₓ (-0.36 ≤ x ≤ 0.22), which is isotypic to Al₃FeSi₂ [6] and has Ga₅Pd as structure type [111, 112]. The atomic coordinates and lattice parameters of Al₃FeSi₂ were found to be a suitable starting point for further structural refinements using
single crystal diffractometry. All crystallographic data of $\tau_1$, which was found to be in space group $I4/mcm$ and has $I124$ as Pearson symbol, are given in table 5.10. The measured composition of sample A3 (47.3 at.% Al, 16.9 at.% Fe, 35.8 at.% Ge and therefore: $\text{Al}_{2.8}\text{FeGe}_{2.1}$), which was determined by electron micro-probe analysis, and the refined composition of the single crystal ($\text{Al}_{3-x}\text{FeGe}_{2+x}$ with $x \approx 0.15$) were found to be in good agreement.

**Table 5.10: Single crystal structure data of the $\tau_1$-phase**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase notation</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>Compound</td>
<td>$\text{Al}<em>{3-x}\text{FeGe}</em>{2+x}$, $x \approx 0.15$</td>
</tr>
<tr>
<td>Structure type</td>
<td>Ga$_5$Pd</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>$I124$</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>6.2303(11)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>9.710(2)</td>
</tr>
<tr>
<td>space group</td>
<td>$I4/mcm$ (no. 140)</td>
</tr>
<tr>
<td>$V$ [Å$^3$] / $Z$</td>
<td>376.9 / 4</td>
</tr>
<tr>
<td>$\rho_{calc}$ [g cm$^{-3}$] / $\mu$(MoK$\alpha$) [mm$^{-1}$]</td>
<td>4.97 / 20.1</td>
</tr>
<tr>
<td>crystal dimensions (µm)</td>
<td>70x85x90</td>
</tr>
<tr>
<td>range of data collection (±h ±k ±l) [°]</td>
<td>3 &lt; 2θ &lt; 70</td>
</tr>
<tr>
<td>number of images / scan time [s / °]</td>
<td>510 / 110</td>
</tr>
<tr>
<td>rotation angle per image</td>
<td>2°</td>
</tr>
<tr>
<td>distinct $\omega$-angles for $\varphi$-scans mode</td>
<td>10</td>
</tr>
<tr>
<td>measured reflections</td>
<td>2560</td>
</tr>
<tr>
<td>unique reflections (n) / reflections with $F_o &gt; 4\sigma(F_o)$</td>
<td>246 / 240</td>
</tr>
<tr>
<td>$R_{int} = \sum</td>
<td>F_o^2 - F_c^2</td>
</tr>
<tr>
<td>extinction parameter $k$: $F_o^2 = F_c^2 [1 + 0.001 F_c^2 \lambda^2 / \sin(2\theta)]^{-1/4}$</td>
<td>0.0140(10)</td>
</tr>
<tr>
<td>$R1 = \sum (</td>
<td></td>
</tr>
<tr>
<td>$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$</td>
<td>0.038</td>
</tr>
<tr>
<td>$Goof = {\sum [w(F_o^2 - F_c^2)^2] / (n-p)}^{1/2}$</td>
<td>1.17</td>
</tr>
<tr>
<td>weighting parameters a / b</td>
<td>0.021 / 0.44</td>
</tr>
<tr>
<td>max $\Delta / \sigma$ / number of variable parameters (p)</td>
<td>&lt; 0.001 / 14</td>
</tr>
<tr>
<td>final difference Fourier map [eÅ$^{-3}$]</td>
<td>-0.62 to +0.51</td>
</tr>
</tbody>
</table>

The sites 4(a) and 4(c) are fully occupied by Fe and Al respectively, whereas the 16(l) site shows mixed occupation of Al and Ge. The ratio in the measured single crystal was found to be 0.46(2) to 0.54(2), so approximately one half.
5.4. New ternary compounds

**Figure 5.9**: Solid-liquid diffusion couple at 470 °C; top: side part of the contact zone; bottom: central part of the contact zone;
Table 5.11: sites, fractional atomic coordinates and displacement parameters of the phase $\tau_1$; the anisotropic displacement parameters are defined as: 
\[ e^{x p \left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j\right]}; \]

<table>
<thead>
<tr>
<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{\text{equiv}} / U_{\text{iso}}$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{23}$</th>
<th>$U_{13}$</th>
<th>$U_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe$_{1.0}$</td>
<td>4(a)</td>
<td>422</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>0.00629(13)</td>
<td>0.00616(15)</td>
<td>0</td>
<td>0.00655(19)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>Al$_{1.0}$</td>
<td>4(c)</td>
<td>4/m</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01018(19)</td>
<td>0.0117(3)</td>
<td>0</td>
<td>0.0070(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>Al0.46(2)Ge0.54(2)</td>
<td>16(l)</td>
<td>..m</td>
<td>0.15205(3)</td>
<td>1/2+x</td>
<td>0.14193(3)</td>
<td>0.01015(12)</td>
<td>0.00900(13)</td>
<td>0</td>
<td>0.01243(16)</td>
<td>0.00038(5)</td>
<td>0</td>
<td>0.00159(6)</td>
</tr>
</tbody>
</table>
The structure can be described by one of the two following well proportioned coordination polyhedra. The fully occupied Fe 4(α) Wyckoff position is coordinated by a mixed position of Al/Ge to feature a square antiprism. This antiprism is bicapped by Al (figure 5.10). The Al 4(γ) position, on the other hand, is coordinated by a bi-capped square prism (figure 5.11). Both feature coordination number of 10, align in direction [001] by corner connection and are edge connected in the (001) plane. No interatomic bond lengths were observed to be shortened (table 5.12). As Ga₅Pd is related to Al₂Cu, which is homotypical to CuMg₂, a close relationship between τ₁ and τ₂ is evident.

![Figure 5.10: Fe coordination polyhedra of the τ₁-phase in [100] direction](image)

The lattice parameters of τ₁ behave according to Vegard’s law to variations in concentration by a linear manner. By increasing Al content the unit cell is clinched, resulting in a shortened c and elongated a parameter (figure 5.12 and figure 5.13 plot all samples that were found to include τ₁). Therefore, the volume is slightly increased by addition of Al, from a mean volume of 375.9 Å³ at 45 at.% Al to 377.4 Å³ at 55 at.% Al. The deviations in Fe content were found to be not the reason for the observed scattering of data.
Table 5.12: bond lengths in the phase $\tau_1$; undersized interatomic distances are given by dotted lines ($\cdots$);

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe—Al</td>
<td>2.4274(5)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe—M</td>
<td>2.5881(4)</td>
<td>8x</td>
</tr>
<tr>
<td>Al—Fe</td>
<td>2.4274(5)</td>
<td>2x</td>
</tr>
<tr>
<td>Al—M</td>
<td>2.7379(4)</td>
<td>8x</td>
</tr>
<tr>
<td>M—Fe</td>
<td>2.5881(4)</td>
<td>2x</td>
</tr>
<tr>
<td>M—M</td>
<td>2.6794(7)</td>
<td></td>
</tr>
<tr>
<td>M—Al</td>
<td>2.7379(4)</td>
<td>2x</td>
</tr>
<tr>
<td>M—M</td>
<td>2.7562(8)</td>
<td></td>
</tr>
<tr>
<td>M—M</td>
<td>2.8274(6)</td>
<td></td>
</tr>
</tbody>
</table>

5.4.2 AlFeGe ($\tau_2$)

The $\tau_2$ phase $\text{Al}_{1+x}\text{FeGe}_{1-x}$ ($-0.41 \leq x \leq 0.38$) was found to be isotypic to FeGaGe [113] from X-ray powder diffraction pattern. It is the ternary variant of the CuMg$_2$ structure type [112, 114, 115]. FeGaGe was used as starting point, from which a single crystal structure refinement was executed. All crystallographic data of $\tau_2$, which was found to be in space group $Fdd\bar{d}$ and has $oF48$ as Pearson symbol, are given in table 5.13. The measured composition of sample A8 (39.9 at.% Al, 33.0 at.% Fe, 27.1 at.% Ge and therefore: $\text{Al}_{1.2}\text{FeGe}_{0.8}$), which was determined by electron microprobe analysis, and the refined composition of the single crystal ($\text{Al}_{1+x}\text{FeGe}_{1-x}$ with $x \approx 0.16$) were found to be in good agreement.

Three sites are occupied in this crystal structure; one 16(e) and two 16(g) sites. Fe fully occupies one of the two 16(g) Wyckoff positions. The other two sites are mixed occupied by Al and Ge with a deviation in stoichiometry towards Al. The occupation numbers of these two sites are similar to each other, exhibiting an Al surplus of 0.56(2) and 0.60(2) respectively (table 5.14). This is in contradiction to findings of Malaman et al. [113], who refined the crystal structure of FeGaGe with equal site occupation factors for the mixed positions of Ga/Ge.
### Table 5.13: Single crystal structure data of the τ₂-phase; origin choice 2 was used

<table>
<thead>
<tr>
<th>Sample</th>
<th>A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase notation</td>
<td>τ₂</td>
</tr>
<tr>
<td>Compound</td>
<td>Al₁₋ₓFeGe₁₋ₓ</td>
</tr>
<tr>
<td>x ≈ 0.16</td>
<td></td>
</tr>
<tr>
<td>Structure type</td>
<td>CuMg₂</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>oF48</td>
</tr>
<tr>
<td>a [Å]</td>
<td>8.627(2)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>4.9139(8)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>16.369(3)</td>
</tr>
<tr>
<td>space group</td>
<td>Fddd (no. 70)</td>
</tr>
<tr>
<td>V [Å³] / Z</td>
<td>693.9 / 16</td>
</tr>
<tr>
<td>ρ calc [g cm⁻³] / µ(MoKα) [mm⁻¹]</td>
<td>5.67 / 22.9</td>
</tr>
<tr>
<td>crystal dimensions (µm)</td>
<td>70x85x95</td>
</tr>
<tr>
<td>range of data collection (±h ±k ±l) [°]</td>
<td>3 &lt; 2θ &lt; 70</td>
</tr>
<tr>
<td>number of images / scan time [s/°]</td>
<td>478 / 110</td>
</tr>
<tr>
<td>rotation angle per image</td>
<td>2°</td>
</tr>
<tr>
<td>distinct ω-angles for φ-scans mode</td>
<td>10</td>
</tr>
<tr>
<td>measured reflections</td>
<td>2526</td>
</tr>
<tr>
<td>unique reflections (n) / reflections with F₀ &gt; 4σ(F₀)</td>
<td>380 / 323</td>
</tr>
<tr>
<td>Rint = ∑</td>
<td>F₀²</td>
</tr>
<tr>
<td>extinction parameter k:</td>
<td></td>
</tr>
<tr>
<td>F_c² = F_c[k[1 + 0.001F_c²/λ³/sin(2θ)]⁻¹/⁴]</td>
<td>0.0275(10)</td>
</tr>
<tr>
<td>wR² = [ ∑ w(F₀² − F_c²)² / ∑ wF₀² ]¹/²</td>
<td>0.053</td>
</tr>
<tr>
<td>GooF = { ∑ w(F₀² − F_c²)² / (n − p) }¹/²</td>
<td>1.20</td>
</tr>
<tr>
<td>weighting parameters a / b</td>
<td>0.022 / 4.46</td>
</tr>
<tr>
<td>max Δ/σ / number of variable parameters (p)</td>
<td>&lt; 0.001 / 21</td>
</tr>
<tr>
<td>final difference Fourier map [eÅ⁻³]</td>
<td>-1.09 to +1.13</td>
</tr>
</tbody>
</table>
Figure 5.11: Al coordination polyhedra of the $\tau_1$-phase in [100] direction
5.4. New ternary compounds

**Figure 5.12:** Variation of the lattice parameter $a$ with the composition in the $\tau_1$-phase.

**Figure 5.13:** Variation of the lattice parameter $c$ with the composition in the $\tau_1$-phase.
Table 5.14: sites, fractional atomic coordinates and displacement parameters of the phase $\tau_2$; the anisotropic displacement parameters are defined as: $exp \left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j \right]$;

<table>
<thead>
<tr>
<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{\text{equiv}} / U_{\text{iso}}$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe$_{1.0}$</td>
<td>16(g) .2</td>
<td>1/8</td>
<td>1/8</td>
<td>0.25275(2)</td>
<td>0.00714(16)</td>
<td>0.0068(2)</td>
<td>0.0059(2)</td>
<td>0.0088(2)</td>
<td>0</td>
<td>0</td>
<td>0.00054(14)</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>Al$<em>{0.546(2)}$Ge$</em>{0.454(2)}$</td>
<td>16(e) .2</td>
<td>0.28517(5)</td>
<td>1/8</td>
<td>1/8</td>
<td>0.01118(19)</td>
<td>0.0119(3)</td>
<td>0.0122(3)</td>
<td>0.0094(2)</td>
<td>0.00164(18)</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>Al$<em>{0.60(2)}$Ge$</em>{0.40(2)}$</td>
<td>16(g) .2</td>
<td>1/8</td>
<td>1/8</td>
<td>0.54102(3)</td>
<td>0.0124(2)</td>
<td>0.0106(3)</td>
<td>0.0071(3)</td>
<td>0.0194(3)</td>
<td>0</td>
<td>0</td>
<td>-0.00012(19)</td>
<td></td>
</tr>
</tbody>
</table>
Coordination polyhedra present in this structure are based on the same motive as in \( \tau_1 \). The fully occupied Fe 16(g) Wyckoff position is coordinated by the mixed position of Al/Ge to feature a square antiprism. This antiprism is bi-capped by the adjacent Fe 16(g) (figure 5.14 and figure 5.15), to feature coordination number of 10 and a small asymmetry. Compared to \( \tau_1 \), which aligns all polyhedra in direction [001], \( \tau_2 \) aligns them in an alternating manner along [110] and [110], to enclose an angle of 60°. Furthermore, a relationship of the Al\(_2\)Cu type FeGe\(_2\) and the \( \tau_2 \) phase is evident for above stated reasons (same as for \( \tau_1 \) the antiprismatic Fe polyhedra are all aligned in direction [001]). No interatomic bond lengths are shorter as expected (table 5.15).

### Table 5.15: Bond lengths in the phase \( \tau_2 \); undersized interatomic distances are given by dotted lines (· · ·);

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe—M1</td>
<td>2.4727(4)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe—Fe</td>
<td>2.4837(2)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe—M1</td>
<td>2.5064(5)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe—M2</td>
<td>2.5593(3)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe—M2</td>
<td>2.5599(3)</td>
<td>2x</td>
</tr>
<tr>
<td>M1—Fe</td>
<td>2.4727(4)</td>
<td>2x</td>
</tr>
<tr>
<td>M1—Fe</td>
<td>2.5064(5)</td>
<td>2x</td>
</tr>
<tr>
<td>M1—M1</td>
<td>2.7637(10)</td>
<td>2x</td>
</tr>
<tr>
<td>M1—M1</td>
<td>2.9049(6)</td>
<td>2x</td>
</tr>
<tr>
<td>M2—Fe</td>
<td>2.5593(3)</td>
<td>4x</td>
</tr>
<tr>
<td>M2—M2</td>
<td>2.7494(11)</td>
<td></td>
</tr>
<tr>
<td>M2—M1</td>
<td>2.8221(5)</td>
<td>2x</td>
</tr>
<tr>
<td>M2—M1</td>
<td>3.0814(6)</td>
<td>2x</td>
</tr>
</tbody>
</table>

Varying the lattice parameters of \( \tau_2 \) with composition, an increase of the lattice parameter \( c \) is correlated linearly to an increase in Al content (figure 5.16), whereas \( a \) and \( b \) exhibit saturation effects (figure 5.17 and figure 5.18). Between 30 and 35 at.% of Al, which is presumably the stoichiometric composition of 33.3 at.% of Al, a switch in lattice parameter shortening is observed.

### 5.4.3 Al\(_8\)Fe\(_9\)Ge\(_4\) (\( \tau_3 \))

X-ray powder pattern refinement yielded a structure isotypic to Fe\(_3\)Ga\(_4\) [116, 117], for the \( \tau_3 \) phase Al\(_{7+x}\)Fe\(_{9+y}\)Ge\(_{5-x}\) (-0.24 \( \leq \) \( x \) \( \leq \) 1.14 and -0.27 \( \leq \) \( y \)). All crystallographic data of \( \tau_3 \), which was found to be in space group \( C2/m \) and has \( mS42 \) as Pearson symbol, are given in table 5.16. The refined lattice parameters, but not the
composition, fit the monoclinic phase (Pearson symmetry: \textit{mc44/8}) that was reported by Kobalova et al. [92]. The measured composition of sample D2 (33.8 at.% Al, 42.9 at.% Fe, 23.3 at.% Ge and therefore: Al_{7.0}Fe_{9}Ge_{5.0}), which was determined by electron micro-probe analysis, and the refined composition of the single crystal (Al_{7-x}Fe_{9}Ge_{5+x} with x \approx 0.06) were found to be in acceptable agreement.

<table>
<thead>
<tr>
<th>Table 5.16: Single crystal structure data of the (\tau_3)-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td><strong>Phase notation</strong></td>
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<tr>
<td><strong>Compound</strong></td>
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<tr>
<td><strong>Structure type</strong></td>
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<tr>
<td><strong>Pearson symbol</strong></td>
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<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>(a) [Å]</strong></td>
</tr>
<tr>
<td><strong>(b) [Å]</strong></td>
</tr>
<tr>
<td><strong>(c) [Å]</strong></td>
</tr>
<tr>
<td><strong>(\beta) [°]</strong></td>
</tr>
<tr>
<td><strong>(V) [Å^{3}] / (Z)</strong></td>
</tr>
<tr>
<td><strong>(\rho_{calc}) [g cm^{-3}] / (\mu)(MoK\textsubscript{\textgreek{a}}) [mm^{-1}]</strong></td>
</tr>
<tr>
<td><strong>Crystal dimensions (µm)</strong></td>
</tr>
<tr>
<td><strong>Range of data collection (±h ±k ±l) [°]</strong></td>
</tr>
<tr>
<td><strong>Number of images / scan time [s/°]</strong></td>
</tr>
<tr>
<td><strong>Rotation angle per image</strong></td>
</tr>
<tr>
<td><strong>Number of distinct (\omega)-angles for (\varphi)-scans mode</strong></td>
</tr>
<tr>
<td><strong>Number of measured reflections</strong></td>
</tr>
<tr>
<td><strong>Number of unique reflections ((n) / \text{reflections with } F_o &gt; 4\sigma(F_o))</strong></td>
</tr>
<tr>
<td>**(R_{int}=\frac{\sum</td>
</tr>
<tr>
<td><strong>Extinction parameter k:</strong></td>
</tr>
<tr>
<td>**(R_1=\frac{\sum(</td>
</tr>
<tr>
<td><strong>(wr2=\frac{\sum w(F_o^2-F_c^2)^2}{\sum wF_o^4}^{1/2})</strong></td>
</tr>
<tr>
<td><strong>(GooF={\sum[w(F_o^2-F_c^2)]/{n-p}}^{1/2})</strong></td>
</tr>
<tr>
<td>**Max (</td>
</tr>
<tr>
<td>**Final difference Fourier map [eÅ^{-3}])</td>
</tr>
</tbody>
</table>

Of the eight sites four are fully occupied by Fe; the 2(\(a\)), two of the 4(\(i\)) and one 8(\(j\)). In the remaining mixed occupied sites a preferred occupation is observed. Ge predominantly occupies the 4(\(i\)) Wyckoff positions, whereas Al is outweighing Ge in the 8(\(j\)) sites (table 5.17).
Figure 5.14: Fe coordination polyhedra of the $\tau_2$-phase in [001] direction; M1 is visible in the front and on the rear side of the coordination polyhedra.
Figure 5.15: Fe coordination polyhedra of the $\tau_2$-phase in [110] direction.
5.4. New ternary compounds

\textbf{FIGURE 5.16}: Variation of the lattice parameter $c$ with the composition in the $\tau_2$-phase

\textbf{FIGURE 5.17}: Variation of the lattice parameter $a$ with the composition in the $\tau_2$-phase
FIGURE 5.18: Variation of the lattice parameter $b$ with the composition in the $\tau_2$-phase
Table 5.17: sites, fractional atomic coordinates and displacement parameters of the phase $\tau_{3b}$; the anisotropic displacement parameters are defined as: $exp \left[ -2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* b_i b_j \right]$;

<table>
<thead>
<tr>
<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{equiv}$/Uiso</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>Fe1.0</td>
<td>2(a)</td>
<td>2/m</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00728(8)</td>
<td>0.00678(16)</td>
<td>0.00745(18)</td>
<td>0.00758(18)</td>
<td>0</td>
<td>0.00223(14)</td>
<td>0</td>
</tr>
<tr>
<td>Fe2</td>
<td>Fe1.0</td>
<td>4(i)</td>
<td>m</td>
<td>0.48966(3)</td>
<td>0</td>
<td>0.30425(4)</td>
<td>0.00799(7)</td>
<td>0.00717(12)</td>
<td>0.00874(14)</td>
<td>0.00810(14)</td>
<td>0</td>
<td>0.00247(10)</td>
<td>0</td>
</tr>
<tr>
<td>Fe3</td>
<td>Fe1.0</td>
<td>4(i)</td>
<td>m</td>
<td>0.22204(3)</td>
<td>0</td>
<td>0.62044(4)</td>
<td>0.00760(7)</td>
<td>0.00747(12)</td>
<td>0.00708(13)</td>
<td>0.00744(13)</td>
<td>0</td>
<td>0.00119(10)</td>
<td>0</td>
</tr>
<tr>
<td>Fe4</td>
<td>Fe1.0</td>
<td>8(j)</td>
<td>1</td>
<td>0.13338(2)</td>
<td>0.20638(3)</td>
<td>-0.15789(3)</td>
<td>0.00836(6)</td>
<td>0.00779(9)</td>
<td>0.00871(11)</td>
<td>0.00863(10)</td>
<td>-0.00024(7)</td>
<td>0.00267(7)</td>
<td>-0.00067(7)</td>
</tr>
<tr>
<td>M1</td>
<td>Al0.129Ge0.871(1)</td>
<td>4(i)</td>
<td>m</td>
<td>0.26063(2)</td>
<td>0</td>
<td>0.08132(3)</td>
<td>0.01034(8)</td>
<td>0.00898(11)</td>
<td>0.00800(12)</td>
<td>0.01155(13)</td>
<td>0</td>
<td>-0.00032(8)</td>
<td>0</td>
</tr>
<tr>
<td>M2</td>
<td>Al0.035Ge0.965(2)</td>
<td>4(i)</td>
<td>m</td>
<td>0.03907(2)</td>
<td>0</td>
<td>0.33668(3)</td>
<td>0.01055(7)</td>
<td>0.01198(11)</td>
<td>0.00921(12)</td>
<td>0.00767(11)</td>
<td>0</td>
<td>-0.00057(8)</td>
<td>0</td>
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<tr>
<td>M3</td>
<td>Al0.915Ge0.085(1)</td>
<td>8(j)</td>
<td>1</td>
<td>0.61154(4)</td>
<td>0.20036(6)</td>
<td>0.15025(6)</td>
<td>0.01026(13)</td>
<td>0.00800(18)</td>
<td>0.0119(2)</td>
<td>0.0110(2)</td>
<td>0.00321(15)</td>
<td>0.00315(14)</td>
<td>0.00156(13)</td>
</tr>
<tr>
<td>M4</td>
<td>Al0.738Ge0.26(2)</td>
<td>8(j)</td>
<td>1</td>
<td>0.35395(3)</td>
<td>0.18517(4)</td>
<td>0.43528(4)</td>
<td>0.00928(10)</td>
<td>0.00985(14)</td>
<td>0.00967(16)</td>
<td>0.00928(16)</td>
<td>0.00224(10)</td>
<td>0.00438(11)</td>
<td>0.00314(10)</td>
</tr>
</tbody>
</table>
The structure of the $\tau_3$ phase can be described by alternating puckered Ge rich (figure 5.19) and flat Al rich layers of atoms (figure 5.20) in (101) plane. The former exhibits pentagonal patterns, whilst the latter is, according to Malaman et al. [75], of a distorted hexagonal structure. Alternatively two types of pentagonal structures are visible in plane (403) (figure 5.21); one of M coordinated by Fe and one vice versa with alternating occupation of the Fe in central position. Only one well-proportioned coordination polyhedra can be found in $\tau_3$. The Fe1 2(a) Wyckoff position possesses icosahedral structure motives of coordination number 12 (figure 5.22), other coordination polyhedra were found to be not well-proportioned. The interatomic distances of the first coordination sphere are of expected values (table 5.18).
Figure 5.19: The (101) plane of \( \tau_3 \) at \( y \approx 0 \)
Figure 5.20: The (101) plane of $\tau_3$ at $y = 1/4$
Figure 5.21: A cut in plane (403) of the $\tau_3$-phase
FIGURE 5.22: The coordination polyhedron of the Fe1 site in the $\tau_3$-phase viewed in direction [001]
Table 5.18: bond lengths in the phase $\tau_3$; undersized interatomic distances are given by dotted lines ($\cdots$);

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.5169(6)</td>
<td>2x</td>
<td>M1—Fe2</td>
<td>2.4306(7)</td>
<td></td>
</tr>
<tr>
<td>Fe1—M2</td>
<td>2.5539(5)</td>
<td>2x</td>
<td>M1—Fe4</td>
<td>2.4511(4)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe1—Fe4</td>
<td>2.6206(4)</td>
<td>4x</td>
<td>M1—Fe4</td>
<td>2.4695(4)</td>
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</tr>
<tr>
<td>Fe1—M3</td>
<td>2.6342(5)</td>
<td>4x</td>
<td>M1—Fe1</td>
<td>2.5169(6)</td>
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</tr>
<tr>
<td>Fe2—M1</td>
<td>2.4306(7)</td>
<td></td>
<td>M1—M3</td>
<td>2.8644(6)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe2—M4</td>
<td>2.4812(6)</td>
<td>2x</td>
<td>M1—M3</td>
<td>2.9635(6)</td>
<td>2x</td>
</tr>
<tr>
<td>Fe2—M3</td>
<td>2.4957(5)</td>
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</tr>
<tr>
<td>Fe2—M4</td>
<td>2.5086(5)</td>
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<td>M2—Fe4</td>
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</tr>
<tr>
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<td></td>
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<tr>
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<tr>
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<tr>
<td>Fe3—M4</td>
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<td>2x</td>
<td>M3—Fe4</td>
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<tr>
<td>Fe3—Fe4</td>
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Continued on next page
Table 5.18 – continued from previous page

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<td>2.9121(6)</td>
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<td>M4—Fe2</td>
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<td>M4—Fe3</td>
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<tr>
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<td></td>
<td>M4—Fe4</td>
<td>2.5210(5)</td>
<td></td>
</tr>
<tr>
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<td></td>
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<td>2.5555(5)</td>
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<td>M4—M4</td>
<td>2.6153(7)</td>
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<tr>
<td>Fe4—Fe2</td>
<td>2.6235(4)</td>
<td></td>
<td>M4—M4</td>
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<tr>
<td>Fe4—Fe3</td>
<td>2.6950(4)</td>
<td></td>
<td>M4—M4</td>
<td>2.8219(8)</td>
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<td></td>
<td></td>
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</tbody>
</table>
5.4. New ternary compounds

A comparison of the related Fe₆Ge₅ type structure and two modifications of FeGe (the hexagonal and the monoclinic), was done by Malaman et al. [75]. On the one hand there are layers that exhibit pentagonal patterns in \( \tau_3 \) (figure 5.19) as well as the above mentioned phases. In case of \( \tau_3 \), these patterns are built up by Al/Ge that coordinate Fe sites. There is an additional motive of a hole, which is coordinated by four Al/Ge and one Fe atoms in case of \( \tau_3 \) or three Al/Ge and two Fe in case of Fe₆Ge₅. On the other hand there are layers of distorted hexagonal patterns (as in figure 5.20). These are built up by pairs of Fe, M₃ and M₄, as if the chains of Fe that are found in all three resembling phases were completely removed by lowering the Fe content.

5.4.4 \( \text{Al}_{2.98}\text{Fe}_{11.59}\text{Ge}_{7.47} (\tau_4) \)

The phase \( \tau_4 \), which was found to be different from Fe₆Ge₅ in powder X-ray diffraction refinements, caused severe problems in single crystal X-ray diffraction refinements, as the reflection intensities suggested the centrosymmetric crystal structure in the executed statistical analysis. The extinction symbol yielded in this chase was C-c-. All attempts to refine the crystal structure in the underlying space group \( \text{Cmcm} \) failed. As a consequence, the acentric sub-space-groups \( \text{Cmc}_2 \) and \( \text{C}2mc \), according to Bärnighausen-tree, were attempted; the former was successful. Unfortunately, unstable refinements were encountered, as several elements of the correlation matrix were close to 1.0. Observations of special values of various sites, which were not caused by the underlying space group symmetry, led the decision to utilize constraints. Further constraints were applied between \( x \), \( y \), and \( z \) as well as the displacement parameters of distinct sites that were found to be related (table 5.20). In the final stage of the refinements these constrains resulted in only insignificantly increased R values, but satisfying converging of the refinement. Tests on twining, yielded twin components of 0.46(4) : 0.54. All crystallographic data of \( \tau_4 \), which was found to be in space group \( \text{Cmc}_2 \) and has \( \sigma\text{C180} \) as Pearson symbol, are given in table 5.19. The solubility ranges between \( x \leq 0.2 \), \( y \leq 0.15 \) and \( z \leq 0.43 \) for \( \text{Al}_{2.98+x}\text{Fe}_{11.59-y}\text{Ge}_{7.47-z} \).

The new structure type exhibits 32 individual sites, which are all either 4(\( a \)) or 8(\( b \)) Wyckoff positions and fully occupied. Due to the complexity of the crystal structure it was not possible to differentiate between occupations lower than one and mixed sites. However, the calculated single crystal composition (\( \text{Al}_{2.98}\text{Fe}_{11.59}\text{Ge}_{7.47} \)) was close to the composition detected in electron micro probe analysis (sample D2: 14.9 at.% Al, 51.3 at.% Fe, 33.8 at.% Ge and therefore: \( \text{Al}_{3.0}\text{Fe}_{11.4}\text{Ge}_{7.5} \)). The mixed
sites are occupied by Al and Ge. Three different categories of Ge contents were observed:

1. Ge outweighing Al by a content larger than 80 at.% Ge
2. an almost equal mixture of Al and Ge from 48 to 52 at.% Ge
3. Ge contents lower than 26 at.% Ge

### Table 5.19: Single crystal structure data of the \( \tau_4 \)-phase

<table>
<thead>
<tr>
<th>Sample</th>
<th>F12</th>
<th>( \tau_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase notation</td>
<td>Al&lt;sub&gt;2.98&lt;/sub&gt;Fe&lt;sub&gt;11.59&lt;/sub&gt;Ge&lt;sub&gt;7.47&lt;/sub&gt;</td>
<td>new structure</td>
</tr>
<tr>
<td>Compound</td>
<td>new structure</td>
<td></td>
</tr>
<tr>
<td>Structure type</td>
<td>oC180</td>
<td></td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>Cmc2&lt;sub&gt;1&lt;/sub&gt; (no. 36)</td>
<td></td>
</tr>
<tr>
<td>space group</td>
<td>Cmc2&lt;sub&gt;1&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>( a ) [Å]</td>
<td>7.9120(10)</td>
<td></td>
</tr>
<tr>
<td>( b ) [Å]</td>
<td>19.786(3)</td>
<td></td>
</tr>
<tr>
<td>( c ) [Å]</td>
<td>14.7692(3)</td>
<td></td>
</tr>
<tr>
<td>( V ) [Å&lt;sup&gt;3&lt;/sup&gt;] / Z</td>
<td>2312.4 / 8</td>
<td></td>
</tr>
<tr>
<td>( \rho_{calc} ) [g cm&lt;sup&gt;-3&lt;/sup&gt;] / ( \mu ) (MoK&lt;sub&gt;a&lt;/sub&gt;) [mm&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>7.29 / 33.3</td>
<td></td>
</tr>
<tr>
<td>Range of data collection (±h ±k ±l) [°]</td>
<td>3 &lt; 2θ &lt; 70</td>
<td></td>
</tr>
<tr>
<td>Number of images / scan time [s/°]</td>
<td>773 / 270</td>
<td></td>
</tr>
<tr>
<td>Rotation angle per image</td>
<td>2°</td>
<td></td>
</tr>
<tr>
<td>Distinct ( \omega )-angles for ( \varphi )-scans mode</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Measured reflections</td>
<td>18508</td>
<td></td>
</tr>
<tr>
<td>Unique reflections (n) / reflections with ( F_o &gt; 4\sigma(F_o) )</td>
<td>5328 / 3343</td>
<td></td>
</tr>
<tr>
<td>( R_{int} = \sum</td>
<td>F_o^2 - F_c^2(\text{mean})</td>
<td>/\sum F_o^2 )</td>
</tr>
<tr>
<td>Extinction parameter k:</td>
<td>( F_c^* = F_c k [1 + 0.001F_c^2 \lambda^2 / \sin(2\theta)]^{-1/4} )</td>
<td></td>
</tr>
<tr>
<td>( R_1 = \sum (</td>
<td>F_o^2</td>
<td>-</td>
</tr>
<tr>
<td>( wR_2 = \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 )</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>( Goof = { \sum [w(F_o^2 - F_c^2)^2] / (n - p) }^{1/2} )</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Weighting parameters a / b</td>
<td>0.022 / 39.7</td>
<td></td>
</tr>
<tr>
<td>Max ( \Delta / \sigma ) / Number of variable parameters (p)</td>
<td>&lt;0.001 / 180</td>
<td></td>
</tr>
<tr>
<td>Final difference Fourier map [eÅ&lt;sup&gt;-3&lt;/sup&gt;]</td>
<td>-2.56 to +3.02</td>
<td></td>
</tr>
</tbody>
</table>
Parameters are defined as: 
\[ \exp \left[ -2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j \right] \]; stars (*) indicate constrained values, which do not result from the space group symmetry Cmc21.

### Table 5.20: sites, fractional atomic coordinates and displacement parameters of the phase \( t_4 \); the anisotropic displacement parameters are defined as:

<table>
<thead>
<tr>
<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq/\langle a \rangle</th>
<th>Ueq/\langle b \rangle</th>
<th>Ueq/\langle c \rangle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.60267(17)</td>
<td>0.43333(5)</td>
<td>0.0097(8)</td>
<td>0.0035(19)</td>
<td>0.0075(15)</td>
</tr>
<tr>
<td>Fe2</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.09464(4)</td>
<td>0.60421(3)</td>
<td>0.0089(8)</td>
<td>0.012(2)</td>
<td>0.0097(15)</td>
</tr>
<tr>
<td>Fe3</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.12915(6)</td>
<td>1/4*</td>
<td>0.0126(2)</td>
<td>0.0114(6)</td>
<td>0.0121(5)</td>
</tr>
<tr>
<td>Fe4</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.31450(4)</td>
<td>1/2-a(FE2)</td>
<td>0.0066(8)</td>
<td>0.0062(2)</td>
<td>0.0084(15)</td>
</tr>
<tr>
<td>Fe5</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.31450(4)</td>
<td>-a(FE2)</td>
<td>0.0034(9)</td>
<td>0.0102(2)</td>
<td>0.0131(9)</td>
</tr>
<tr>
<td>Fe6</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.49181(3)</td>
<td>0.54887(5)</td>
<td>0.0053(7)</td>
<td>0.0061(6)</td>
<td>0.0065(14)</td>
</tr>
<tr>
<td>Fe7</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.49086(6)</td>
<td>1/4*</td>
<td>0.0095(2)</td>
<td>0.0061(5)</td>
<td>0.0125(9)</td>
</tr>
<tr>
<td>Fe8</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>1/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe9</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>1/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe10</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>3/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe11</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>3/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe12</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>3/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe13</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>3/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Fe14</td>
<td>5(f)</td>
<td>1</td>
<td></td>
<td>1/4*</td>
<td>3/8*</td>
<td>0*</td>
<td>0.0070(16)</td>
<td>0.0081(4)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Ge1</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.19697(16)</td>
<td>-0.04607(4)</td>
<td>0.0077(8)</td>
<td>0.0062(14)</td>
<td>0.0087(12)</td>
</tr>
<tr>
<td>Ge2</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.19697(16)</td>
<td>-0.04607(4)</td>
<td>0.0077(8)</td>
<td>0.0062(14)</td>
<td>0.0087(12)</td>
</tr>
<tr>
<td>Ge3</td>
<td>w.</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.30568(4)</td>
<td>-y(Ge1)</td>
<td>0.0114(7)</td>
<td>0.0120(11)</td>
<td>0.0112(8)</td>
</tr>
<tr>
<td>M1</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>-y(FE1)</td>
<td>1/2-z(FE1)</td>
<td>0.0125(7)</td>
<td>0.0139(4)</td>
<td>0.0197(4)</td>
</tr>
<tr>
<td>M2</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.1243(6)</td>
<td>3/4*</td>
<td>0.0102(3)</td>
<td>0.0098(4)</td>
<td>0.0110(4)</td>
</tr>
<tr>
<td>M3</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.00743(8)</td>
<td>1/4*</td>
<td>0.0128(3)</td>
<td>0.0137(9)</td>
<td>0.0120(9)</td>
</tr>
<tr>
<td>M4</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.00743(8)</td>
<td>1/4*</td>
<td>0.0128(3)</td>
<td>0.0137(9)</td>
<td>0.0120(9)</td>
</tr>
<tr>
<td>M5</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M6</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M7</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M8</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M9</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M10</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.317(3)</td>
<td>0.173(9)</td>
<td>0.009(5)</td>
<td>0.010(4)</td>
<td>0.009(5)</td>
</tr>
<tr>
<td>M11</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.1942(4)</td>
<td>y(Ge1)</td>
<td>0.1442(3)</td>
<td>0.011(2)</td>
<td>0.014(2)</td>
</tr>
<tr>
<td>M12</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.1942(4)</td>
<td>y(Ge1)</td>
<td>0.1442(3)</td>
<td>0.011(2)</td>
<td>0.014(2)</td>
</tr>
<tr>
<td>M13</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.1942(4)</td>
<td>-y(M12)</td>
<td>0.0142(3)</td>
<td>0.011(2)</td>
<td>0.014(2)</td>
</tr>
<tr>
<td>M14</td>
<td>Ge106259/Al1312</td>
<td>4(e)</td>
<td></td>
<td>0</td>
<td>0.1942(4)</td>
<td>-y(M12)</td>
<td>0.0142(3)</td>
<td>0.011(2)</td>
<td>0.014(2)</td>
</tr>
</tbody>
</table>

5.4. New ternary compounds
Chapter 5. Results

The vicinal relationship as well as the almost doubled lattice parameters of $\tau_4$, demand a discussion of the relationship of Fe$_6$Ge$_5$ and $\tau_4$. The structure of $\tau_4$ consists of flat and puckered layers as they are observed in Fe$_6$Ge$_5$ too. The puckered layer consists of a pseudo-hexagonal pattern ($y \approx 1/4$) (figure 5.24). Only low substitutions of Ge by Al are visible. Fully occupied Fe sites are aligned in rows, whereas the Ge and Ge rich mixed sites are aligned together with Fe in an alternating manner. This layout is equivalent to Fe$_6$Ge$_5$. The flat layers exhibit pentagonal patterns (figure 5.23), which resemble those observed in Fe$_6$Ge$_5$. On the first glance differences are only in the sequence of empty and filled pentagons, but the central atoms of that pentagons as well as the coordinating atoms disagree. Additionally, regarding the distances of interatomic bonds (table 5.21), the addition of Al elongates bonds along the $c$ axis, but not the $b$ axis. Therefore, bonds, which appear to be already in the second coordination sphere are indicated by dashed bonds. As Fe$_6$Ge$_5$ is related to FeGe [75] and the new ternary phase $\tau_3$, a similar comparison between $\tau_3$ and $\tau_4$ is possible. No visually pleasant coordination polyhedra can be reported.

**Figure 5.23:** Plane (101) $y \approx 0$; for better readability the sites of mixed occupation are denoted by “MhGe” (Ge content larger than 80 at.% Ge), “MmGe” (average Ge content of 48 to 52 at.% Ge) and “MiGe” (Ge content lower than 26 at.% Ge); dashed interatomic bonds are presumably in the second coordination sphere;
Figure 5.24: Plane (101) $y = 1/4$; for better readability the sites of mixed occupation are denoted by “MhGe” (Ge content larger than 80 at.% Ge), “MmGe” (average Ge content of 48 to 52 at.% Ge) and “MI Ge” (Ge content lower than 26 at.% Ge); dashed interatomic bonds are presumably in the second coordination sphere;
TABLE 5.21: bond lengths in the phase $\tau_4$; undersized interatomic distances are given by dotted lines (· · ·);

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
<th>bond</th>
<th>length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1—Fe14</td>
<td>2.4689(7)</td>
<td>2x</td>
<td>Fe15—M1</td>
<td>2.4689(7)</td>
</tr>
<tr>
<td>Fe1—Fe8</td>
<td>2.4773(7)</td>
<td>2x</td>
<td>Fe15—M10</td>
<td>2.5190(6)</td>
</tr>
<tr>
<td>Fe1—Fe2</td>
<td>2.5296(10)</td>
<td></td>
<td>Fe15—M12</td>
<td>2.5255(8)</td>
</tr>
<tr>
<td>Fe1—Fe10</td>
<td>2.5536(4)</td>
<td>2x</td>
<td>Fe15—Ge3</td>
<td>2.5354(8)</td>
</tr>
<tr>
<td>Fe1—M4</td>
<td>2.6261(10)</td>
<td></td>
<td>Fe15—Fe6</td>
<td>2.5530(7)</td>
</tr>
<tr>
<td>Fe1—M3</td>
<td>2.9032(10)</td>
<td></td>
<td>Fe15—Fe14</td>
<td>2.6027(8)</td>
</tr>
<tr>
<td>Fe1—Fe3</td>
<td>3.0319(9)</td>
<td></td>
<td>Fe15—Fe9</td>
<td>2.6632(5)</td>
</tr>
<tr>
<td>Fe1—Ge2</td>
<td>3.0708(7)</td>
<td></td>
<td>Fe15—M3</td>
<td>2.6703(9)</td>
</tr>
<tr>
<td>Fe1—M1</td>
<td>3.0919(11)</td>
<td></td>
<td>Fe15—Fe3</td>
<td>2.7147(8)</td>
</tr>
<tr>
<td>Fe2—M2</td>
<td>2.4116(7)</td>
<td></td>
<td>Fe15—Fe8</td>
<td>2.7236(5)</td>
</tr>
<tr>
<td>Fe2—Ge3</td>
<td>2.4501(4)</td>
<td>2x</td>
<td>Fe15—Fe7</td>
<td>2.7597(8)</td>
</tr>
<tr>
<td>Fe2—Fe1</td>
<td>2.5296(10)</td>
<td></td>
<td>Ge1—Fe13</td>
<td>2.3984(3)</td>
</tr>
<tr>
<td>Fe2—Ge2</td>
<td>2.5479(9)</td>
<td></td>
<td>Ge1—Fe13</td>
<td>2.3984(3)</td>
</tr>
</tbody>
</table>
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| Fe2—M3        | 2.6363(11) |              | Ge1—Fe12     | 2.5055(6)  | 2x
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<td>M12—Fe13</td>
<td>2.4645(5)</td>
<td></td>
</tr>
<tr>
<td>Fe14—M10</td>
<td>2.5190(6)</td>
<td></td>
<td>M12—Fe9</td>
<td>2.5271(5)</td>
<td></td>
</tr>
<tr>
<td>Fe14—M14</td>
<td>2.5255(8)</td>
<td></td>
<td>M12—Fe3</td>
<td>2.5325(7)</td>
<td></td>
</tr>
<tr>
<td>Fe14—M13</td>
<td>2.5354(8)</td>
<td></td>
<td>M12—M6</td>
<td>3.0511(7)</td>
<td></td>
</tr>
<tr>
<td>Fe14—M11</td>
<td>2.5530(7)</td>
<td></td>
<td>M12—M7</td>
<td>3.081(5)</td>
<td></td>
</tr>
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</table>

Continued on next page
<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
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<tr>
<td>Fe14—Fe15</td>
<td>2.6027(8)</td>
<td></td>
<td>M13—Fe7,Fe8</td>
<td>2.4549(5)</td>
<td></td>
</tr>
<tr>
<td>Fe14—Fe10</td>
<td>2.6631(5)</td>
<td></td>
<td>M13—Fe9</td>
<td>2.4920(5)</td>
<td></td>
</tr>
<tr>
<td>Fe14—M3</td>
<td>2.6703(9)</td>
<td></td>
<td>M13—Fe14</td>
<td>2.5354(8)</td>
<td></td>
</tr>
<tr>
<td>Fe14—Fe3</td>
<td>2.7147(8)</td>
<td></td>
<td>M13—Fe12</td>
<td>2.5564(8)</td>
<td></td>
</tr>
<tr>
<td>Fe14—Fe8</td>
<td>2.7237(5)</td>
<td></td>
<td>M13—M9</td>
<td>2.6313(11)</td>
<td></td>
</tr>
<tr>
<td>Fe14—Fe7</td>
<td>2.7597(8)</td>
<td></td>
<td>M14—Fe4</td>
<td>2.4526(4)</td>
<td></td>
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<td>2.4645(5)</td>
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<td></td>
<td></td>
<td></td>
<td>M14—M5</td>
<td>2.5114(4)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>M14—Fe12,Fe14</td>
<td>2.5225(7)</td>
<td></td>
</tr>
<tr>
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<td>M14—Fe10</td>
<td>2.5272(5)</td>
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<td>M14—Fe3</td>
<td>2.5325(7)</td>
<td></td>
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<td></td>
<td></td>
<td>M14—M6</td>
<td>3.0511(7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M14—M8</td>
<td>3.0623(6)</td>
<td></td>
</tr>
</tbody>
</table>
5.4.5 AlFeGe (τ₅)

Electron micro probe analysis showed a phase of equal composition to τ₂, but with the difference of a smaller phase field (Al₁₊ₓFeGe₁₋ₓ with -0.15 ≤ x ≤ 0.01). Nevertheless, X-ray diffraction pattern showed no matching peak profiles to the τ₂ phase. Therefore a low temperature modification of the τ₂ phase is assumed. It could not be investigated by single crystal diffractometry, due to twinning and insufficient crystal size (figure 5.25). As an approach to structure refinement, all unknown peaks were indexed and refined, to finally yield several possible solutions regarding the Bravais lattice and cell metrics. Careful comparison of existing structure types utilising the inorganic crystal structure database FindIt [118], and the unknown peak pattern (figure 5.26) narrowed down the possible structures onto the La₂Sb type (table 5.22), which is in space group I₄/mmm and has tI12 as Pearson symbol. One of the 4(e) positions is fully occupied by Fe. The remaining 4(c) and 4(e) Wyckoff positions are mixed occupied by Al and Ge, albeit with a small predominance of Ge in sample K7 (table 5.23). This, however, leads to the desired stoichiometric composition of roughly AlFeGe. The measured composition of sample K7 (20.3 at.% Al, 31.4 at.% Fe, 48.3 at.% Ge and therefore: Al₀.₉FeGe₁.₁), which was determined by electron micro-probe analysis, and the refined composition of the powder diffraction pattern (Al₁₊ₓFeGe₁₋ₓ with x ≈ 0.15) were found to be in fair agreement. As the calculated composition is still within the phase field it was considered as sufficient.

<table>
<thead>
<tr>
<th>Dataset</th>
<th>K7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notation</td>
<td>τ₅</td>
</tr>
<tr>
<td>Compound</td>
<td>Al₁₊ₓFeGe₁₋ₓ</td>
</tr>
<tr>
<td>Structure type</td>
<td>La₂Sb</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>tI12</td>
</tr>
<tr>
<td>a [Å]</td>
<td>3.9963</td>
</tr>
<tr>
<td>c [Å]</td>
<td>10.9759</td>
</tr>
<tr>
<td>space group</td>
<td>I₄/mmm (no. 139)</td>
</tr>
<tr>
<td>V [Å³] / Z</td>
<td>175.3</td>
</tr>
</tbody>
</table>

The proposed structure of τ₅ is build up by triplet layers. Those however, are consisting of two layers of alternating Fe respectively Al/Ge M2 sites and one complete layer of mixed Al/Ge M1 sites in between. The M1 site spans square prisms of Fe and M2 as coordination polyhedra. These polyhedra have a coordination number of eight (figure 5.27) and are tilted by 45 degrees with respect to the unit cell. Coordination polyhedra presided by Fe or M2 are square pyramidal and therefore
Table 5.23: Sites, occupation, temperature displacement factors and fractional atomic coordinates of the phase \( \tau_5 \), determined by powder X-ray diffraction;

<table>
<thead>
<tr>
<th>site</th>
<th>occupation</th>
<th>multiplicity</th>
<th>symmetry</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe(_{1.0})</td>
<td>4(e)</td>
<td>4( mm )</td>
<td>0</td>
<td>0</td>
<td>0.36240</td>
<td>2.072</td>
</tr>
<tr>
<td>M1</td>
<td>Al(<em>{0.4414})Ge(</em>{0.5586})</td>
<td>4(c)</td>
<td>3( m2 )</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>2.382</td>
</tr>
<tr>
<td>M2</td>
<td>Al(<em>{0.4117})Ge(</em>{0.5883})</td>
<td>4(e)</td>
<td>4( mm )</td>
<td>0</td>
<td>0</td>
<td>0.13426</td>
<td>1.337</td>
</tr>
</tbody>
</table>

of coordination number five. The top of the pyramids are the opposite of the central site (so Fe in case of a M2 central atom and vice versa), whereas the base of the pyramids are built up by M1.

Comparing \( \tau_2 \) phase and the \( \tau_5 \) phase, the flat layers of only Al/Ge mixed positions (M1) and the puckered layers of alternating Fe and Al/Ge (M2) sites in plane \((110)\) are in common. Furthermore, a tetrahedral coordination of Fe around M1 is visible in both structures, whereas the tetrahedral coordination of M2 around M1 is not existent in the first coordination shell of \( \tau_2 \). Regarding the interatomic distances, the layers of the hexagonal \((\tau_2)\) respectively quadratic \((\tau_5)\) arranged mixed positions exhibit almost equilateral distances of 2.88 Å and 2.85 Å respectively 2.83 Å. In contrast, the distances in the puckered layers are subjected to changes. The interatomic bond distances of Fe atoms to M2 increase from 2.55 Å and 2.60 Å to 2.83 Å. Distances of matched pairs (Fe—Fe and M2—M2) in the same layer elongate and are by that greater than the first coordination sphere (3.75 Å and 3.80 Å in \( \tau_5 \)). Due to the “missing layer” of M1 in \( \tau_5 \), elongated Fe—M2 bonds can form. No bonds were found to be undersized (table 5.24).

Table 5.24: Bond lengths in the phase \( \tau_5 \); undersized interatomic distances are given by dotted lines (· · ·);

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe—M2</td>
<td>2.5040</td>
<td></td>
</tr>
<tr>
<td>Fe—M1</td>
<td>2.5047</td>
<td>4x</td>
</tr>
<tr>
<td>Fe—M2</td>
<td>2.8260</td>
<td>4x</td>
</tr>
<tr>
<td>Fe—Fe</td>
<td>3.0206</td>
<td></td>
</tr>
<tr>
<td>M1—M2</td>
<td>2.4828</td>
<td>4x</td>
</tr>
<tr>
<td>M1—Fe</td>
<td>2.5047</td>
<td>4x</td>
</tr>
<tr>
<td>M1—M1</td>
<td>2.8258</td>
<td>2x</td>
</tr>
<tr>
<td>M2—M2</td>
<td>2.4828</td>
<td></td>
</tr>
<tr>
<td>M2—Fe</td>
<td>2.5040</td>
<td></td>
</tr>
<tr>
<td>M2—Fe</td>
<td>2.8260</td>
<td>4x</td>
</tr>
<tr>
<td>M2—M1</td>
<td>2.9472</td>
<td>4x</td>
</tr>
</tbody>
</table>
No severe deviations from Vegard’s law in lattice parameters $a$ and $c$ were observed (figure 5.28 and figure 5.29). An increase in Al content leads to an elongated $c$ and a decreased $a$ lattice parameter. Refinements of the occupation of the $4(e)$ mixed site were unsatisfying in some cases. This was reflected in the site occupation, which appeared to have a strong surplus of Al in the samples of lower Al content (samples: A5, F16, K5). This surplus could not be refined down to the expectancy value, hence the value was fixed to the composition measured by electron micro probe analysis in further refinements.

The La$_2$Sb type structure is known to be superconducting. Therefore, further investigations regarding the magnetic behaviour and electrical properties of the related $\tau_5$ structure would be of interest. Furthermore, an investigation on a possible homologous phase in the phase diagram Fe–Ga–Ge would be of interest.

### 5.4.6 $\tau_6$

The phase $\tau_6$, which possesses a mean composition of 70.4 at.% Al, 9.5 at.% Fe, 20.1 at.% Ge, was found in several samples (e.g. C1, C2) annealed at 800 °C. It was located in a thin layer between $\tau_1$ and the liquid phase. Therefore, and due to slow cooling rates in those samples, this phase was not evaluated as an equilibrium phase at 800 °C. Albeit an extensive annealing duration at 400 °C, only small crystallite sizes were observed in the relevant samples (figure 5.30). Hence, no successful single crystal diffraction was carried out. No satisfying proposal on the crystal structure could be developed by powder diffraction patterns. Powder patterns of several evaluated samples, exhibited broad peaks at an angle of $2\theta \approx 40.5^\circ$ and $46.5^\circ$, indicating insufficient crystal quality. Sample F15, which featured sharper peaks, suggested a body-centred orthorhombic cell that possesses of lattice parameters $a = 6.89$ Å, $b = 7.95$ Å, $c = 8.77$ Å. This structural information fits in other samples too, but could not be identified by homologous structures of equal lattice parameter. Nevertheless, the phase was found to be polarising in optical microscopy and thus certainly is of non-cubic structure type.

Larger amounts of $\tau_6$ were observed in the solid-liquid diffusion couple at 470 °C. The possibility that the phase $\tau_6$ is metastable, as suggested by Inoue et al. [76], could be eliminated by the liquid-solid diffusion couple experiment and the slowly cooled sample F15.

### 5.4.7 Al$_{8.08}$Fe$_2$Ge$_{2.52}$ ($\tau_7$)

The $\tau_7$ phase Al$_{8+x}$Fe$_2$Ge$_{2+y}$ ($0.08 \leq x \leq 0.35$ and $0.44 \leq y \leq 0.52$) exhibits similarities to Al$_{4.35}$FeSi with respect to lattice parameters. The crystal system of that phase
is controversially discussed in literature, whether it is tetragonal, orthorhombic or monoclinic. Moreover, the angle $\beta$ of the monoclinic variant, being between $90^\circ$ and $91^\circ$, and a doubled $c$ lattice parameter are under discussion [119, 120]. Utilising synchrotron, X-ray and electron based diffraction methods, Hansen et al. [119] investigated stacking faults of a tetragonal sub-unit, in order to explain the doubled $c$ axis. They reported on diffuse streaks and additional spots indicating super structure formation.

A careful comparison for the two possible structural options of the $\tau_7$ phase in X-ray powder diffraction pattern (figure [5.31], indicated the orthorhombic structure type. Additional reflexes as well as splitting of several reflexes in the monoclinic case could not be confirmed. Also, the single crystal data yielded no hints for monoclinic distortion, but a pseudo-tetragonal cell of space group Cmce that possesses seven sites. The measured composition of sample H10 (66.9 at.% Al, 15.5 at.% Fe,

| Table 5.25: Single crystal structure data of the $\tau_7$-phase |
| Sample | H10 |
| Phase notation | $\tau_7$ |
| Compound | $\text{Al}_{8+x}\text{Fe}_2\text{Ge}_{2+y}$ |
| Structure type | new structure |
| Pearson symbol | oC84 |
| $a$ [Å] | 20.6871(4) |
| $b$ [Å] | 6.269(2) |
| $c$ [Å] | 6.271(2) |
| space group | Cmce (Cmca; no. 64) |
| $V$ [Å$^3$] / $Z$ | 820.5 / 2 |
| $\rho_{\text{calc}}$ [g cm$^{-3}$] / $\mu(\text{MoK}\alpha)$ [mm$^{-1}$] | 4.21 / 13.3 |
| range of data collection ($\pm h \pm k \pm l$) [°] | 3 < $2\theta$ < 70 |
| number of images / scan time [s/°] | 602 / 200 |
| rotation angle per image | 2° |
| distinct $\omega$-angles for $\phi$-scans mode | 11 |
| measured reflections | 6267 |
| unique reflections (n) / reflections with $F_o > 4\sigma(F_o)$ | 926 / 802 |
| $R_{\text{int}} = \sum |F_o^2 - F_c^2(\text{mean})|/\sum F_o^2$ | 0.046 |
| extinction parameter $k$: $F_c^* = F_c k [1 + 0.001 F_c^2 \lambda^2/\sin(2\theta)]^{-1/4}$ | 0.0013(3) |
| $R1 = \sum (|F_o^2| - |F_c^2|)^2/\sum F_o^2$ (observed / all reflections) | 0.022 / 0.028 |
| $wR2 = \sum w(F_o^2 - F_c^2)^2/\sum wF_o^4$ | 0.062 |
| $GooF = \{\sum [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ | 1.16 |
| weighting parameters a / b | 0.029 / 0.98 |
| max $\Delta/\sigma$ / number of variable parameters (p) | < 0.001 / 58 |
| final difference Fourier map [eÅ$^{-3}$] | -0.91 to +0.77 |
17.7 at.% Ge and therefore: $\text{Al}_{8.3}\text{Fe}_2\text{Ge}_{2.5}$, which was determined by electron microprobe analysis, and the refined composition of the single crystal ($\text{Al}_{8.4+}\text{Fe}_2\text{Ge}_{2+y}$ with $x \approx 0.08$ and $y \approx 0.68$) were found to be in acceptable agreement.

The observed differences are probably due problems with three of the 16(g) Al sites, which are not fully occupied. The same incident applies for the 16(g) Ge site. The remaining three sites are fully occupied by Fe (8(d)), Al (4(a)) as well as by Al and Ge mixed (8(d)) with a predominance of Al (table 5.26).

Direct methods and succeeding difference Fourier summations were utilised to solve the crystal structure. Taking account of twinning (twin matrix 1 0 0 / 0 0 1 / 0 1 0) with twin components $0.76 \approx 0.24(6)$, R-values were further improved. As a matter of fact the streaks, which were already described by Hansen et al. [119], were detected also in the phase $\tau_7$. It gives rise the questions, whether superstructures of tetragonal building blocks, which were observed for $\text{Al}_{4.5}\text{FeSi}$, exist also in case of $\tau_7$ and if the tetragonal structure type is obtainable by different crystal pulling techniques.

The structure (figure 5.32 and figure 5.33) consists of five layers; a sheet of fully occupied Al1 positions, a puckered layer of M that is mixed occupied Al and Ge as well as a triple layer of which two consist of partial occupied Ge, Al2, Al3 and Al4 sites that coordinate a fully occupied Fe site. Interatomic bond distances between the partial occupied sites Ge and Al3 as well as Al2 and Al4 are shortened (table 5.27). The Fe coordination sphere is furthermore capped by Al1 and M. Hence it can be described by a slightly distorted double-capped octagonal prism of coordination number 18. For the Al1 position an equivalent coordination polyhedra can be found, except for the capping that is composed of Fe in both cases. The M site possesses a coordination number of 13. The base of the coordination figure consists of a square, the top of an octagon of Al2 and Al4. Additionally Fe caps the octagonal motive. In contrast, $\text{Al}_{4.5}\text{FeSi}$ is reported to exhibit no splitting in partially occupied positions and thus Fe is coordinated a by bi-capped square antiprism.
Figure 5.25: Sample K5: top: optical microscopy polarisation contrast; middle: optical microscopy bright field; bottom: SEM BE detector; the dotted single phase region of $\tau_5$ is of very fine grained nature (grain sizes less than 10 µm)
5.4. New ternary compounds

**FIGURE 5.26:** X-ray powder diffraction pattern of sample K7; Peak pattern of Ge (green), FeGe₂ (magenta) and the presumable low temperature modification of AlFeGe (τ₅) (black) exhibit a good fit;
Figure 5.27: $\tau_5$ viewed in [010] direction;
5.4. New ternary compounds

Figure 5.28: Variation of the lattice parameter $a$ with the composition in the $\tau_5$ phase; the samples I1, I2 and one of the compositions (Al/Fe/Ge = 30.6/33.2/36.2 at.%) of A5 were not included, due to the low content of the $\tau_5$ phase.

Figure 5.29: Variation of the lattice parameter $c$ with the composition in the $\tau_5$ phase; the samples I1, I2 and one of the compositions (Al/Fe/Ge = 30.6/33.2/36.2 at.%) of A5 were not included, due to the low content of the $\tau_5$ phase.
Figure 5.30: Sample H3; crystal sizes up to 20 µm for the τ₆ phase were observed.
5.4. New ternary compounds

Figure 5.31: X-ray powder diffraction pattern of sample H10; the sample contains Ge (black), Al$_{8.08}$Fe$_2$Ge$_{2.52}$ ($\tau_7$) (green) and $\tau_6$ (not indicated due to lack of structure data); comparing the two possible symmetry options of $\tau_7$ (orthorhombic in green and monoclinic in magenta), the phase is obviously Cmca.
Table 5.26: Sites, fractional atomic coordinates and displacement parameters of the phase $\tau_7$; the anisotropic displacement parameters are defined as: $exp \left[ -2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j \right]$;

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupation</th>
<th>Multiplicity</th>
<th>Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eqiv}$ / $U_{iso}$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>Fe1.0</td>
<td>8(d)</td>
<td>2.</td>
<td>0.115127(14)</td>
<td>0</td>
<td>0</td>
<td>0.00616(11)</td>
<td>0.00507(16)</td>
<td>0.0067(2)</td>
<td>0.0061(2)</td>
<td>-0.0002(2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al1</td>
<td>Al1.0</td>
<td>4(d)</td>
<td>2/m</td>
<td>0.23218(3)</td>
<td>0</td>
<td>0</td>
<td>0.0106(2)</td>
<td>0.0062(4)</td>
<td>0.0127(7)</td>
<td>0.0127(7)</td>
<td>0.0002(7)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>Al0.472(Ge0.128(5))</td>
<td>8(d)</td>
<td>2.</td>
<td>0.23218(3)</td>
<td>0</td>
<td>0</td>
<td>0.0106(2)</td>
<td>0.0062(4)</td>
<td>0.0127(7)</td>
<td>0.0127(7)</td>
<td>0.0002(7)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al2</td>
<td>Al1.833(4)</td>
<td>16(g)</td>
<td>1</td>
<td>0.16122(4)</td>
<td>0.1667(15)</td>
<td>0.33347(16)</td>
<td>0.0134(2)</td>
<td>0.0147(3)</td>
<td>0.0130(5)</td>
<td>0.0125(5)</td>
<td>-0.0037(2)</td>
<td>-0.0037(2)</td>
<td>0.0039(3)</td>
</tr>
<tr>
<td>Al3</td>
<td>Al1.334(4)</td>
<td>16(g)</td>
<td>1</td>
<td>0.0634(4)</td>
<td>0.1469(4)</td>
<td>0.3550(3)</td>
<td>0.0054(5)</td>
<td>0.0069(4)</td>
<td>0.0104(5)</td>
<td>0.0026(4)</td>
<td>0.0000(4)</td>
<td>0.0000(4)</td>
<td>0.0000(7)</td>
</tr>
<tr>
<td>Al4</td>
<td>Al0.666(4)</td>
<td>16(g)</td>
<td>1</td>
<td>0.16125(14)</td>
<td>0.3329(7)</td>
<td>0.1669(7)</td>
<td>0.0099(10)</td>
<td>0.0077(14)</td>
<td>0.014(3)</td>
<td>0.008(2)</td>
<td>-0.0031(10)</td>
<td>-0.0033(10)</td>
<td>-0.016(15)</td>
</tr>
<tr>
<td>Ge</td>
<td>Ge0.5071(15)</td>
<td>16(g)</td>
<td>1</td>
<td>0.065788(15)</td>
<td>0.35256(9)</td>
<td>0.14713(8)</td>
<td>0.01018(11)</td>
<td>0.01065(15)</td>
<td>0.0096(3)</td>
<td>0.0030(3)</td>
<td>-0.00017(10)</td>
<td>-0.00023(14)</td>
<td>0.00012(14)</td>
</tr>
</tbody>
</table>
5.4.8 $\tau_8$

The phase $\tau_8$ of an approximate composition $\text{Al}_{14}\text{Fe}_2\text{Ge}_4$, was found in samples annealed at 800 °C and 400 °C, as well as slowly cooled samples in small amounts (figure 5.30). Since only small amounts were formed in all relevant samples, no suitable single crystals could be isolated. Indexation of the powder X-ray diffraction pattern was not possible due to the low contents and by this small intensities. $\tau_8$ was found to be polarising in optical microscopy and therefore belongs to a non-cubic space group. Whether this phase is only metastable (as the composition proposed by Inoue et al. [76]) or stabilised by oxygen could not be determined.

5.5 Isopleths

Interpreted Isopleths in a ternary system can be only drawn after a full evaluation of the corresponding reaction scheme. In the current course, much more experimental input would be required to reach this goal:

- evaluation of the primary crystallisation fields
- preparation of additional samples in order to determine the missing isothermal equilibria
- additional key experiments with DTA to test the first hypothesis on the reaction scheme

All this is work in progress, so an interpretation of DTA results in the four investigated isopleths (at 10, 23, 40 and 60 at.% Fe) can not be given. However, the thermal effects found in the DTA experiments are shown in figure 5.34, figure 5.35, figure 5.36 and figure 5.37 together with a rough extrapolation of the liquidus curve, which
### Table 5.27: bond lengths in the phase $\tau_7$; undersized interatomic distances are given by dotted lines (· · ·);

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was also used to evaluate the extent of the liquid phase in the isothermal section at 800°C.
Figure 5.34: Uninterpreted isopleth located at 10 at.% Fe content
FIGURE 5.35: Uninterpreted isopleth located at 23 at.% Fe content
Figure 5.36: Uninterpreted isopleth located at 40 at.% Fe content
Figure 5.37: Uninterpreted isopleth located at 60 at.% Fe content
Chapter 6

Summary

In this thesis, the Fe poor part of the ternary Al–Fe–Ge system was investigated with special attention to the existence of new ternary compounds, which were expected in analogy to the related Al–Fe–Si system.

Previous investigations in literature on the ternary system Al–Fe–Ge were scarce. Isothermal sections are reported in literature only at Fe contents above 50 at.\% on the Al side and 72 at.\% on the Ge side of the ternary phase diagram. Several phases, most of them being metastable, were already reported in this system. The according crystal structures were either not given in literature or refined from powder X-ray diffraction patterns. Furthermore, the binary phase diagram Fe–Ge was discussed controversially in literature. Therefore, the critical section of the $\beta$- and $\eta$-phase was reinvestigated in this thesis.

Including the reinvestigated $\eta$-phase in the binary Fe–Ge system, six new structures determined by single crystal X-ray diffractometry could be reported. One additional phase was investigated by powder X-ray diffractometry and a structure proposal, which fits all associated powder X-ray diffraction patterns was presented. Two structures ($\tau_6$ and $\tau_8$), which were reported to be amorphous, could not be properly investigated due to a lack in suitable single crystals and their close vicinity. However, one of them ($\tau_6$) yielded an orthorhombic or monoclinic cell, after indexing of the sharp peaks exhibited in the powder patterns. These two structures and the phase $\tau_7$, which shows signs of domains or superstructures, require further investigations.

The structural motives of the new ternary phases were presented to be related to those featured in the Fe–Ge binary phase diagram. On the one hand tetragonal and pseudo-tetragonal structural features of FeGe$_2$ dominated the phase diagram below 35 at.\% Fe. On the other hand pseudo-hexagonal structural features were discussed to be related to Fe$_6$Ge$_5$ and FeGe between 35 and 55 at.\% Fe.

Two isothermal sections, which are located at 400 $^\circ$C and 800 $^\circ$C were developed in the course of this thesis. A stabilisation to higher temperatures of the cubic polymorph of FeGe was observed. Due to the complexity of the phase diagram in the Al
rich part, further investigations are needed in order to yield a proper suggestion on the isopleths as well as to present a liquidus projection.

Additional investigations on the magnetic properties of all phases, but especially on the possible superconductivity of the phase \( \tau_5 \) seem promising, as literature reports on extraordinary magnetic properties in TM–X (X = Al, Ga, Si, Ge) systems.
Chapter 7

Zusammenfassung


Es konnte gezeigt werden, dass strukturelle Beziehungen der neuen ternären Phasen vornehmlich aus dem binären Phasendiagramm Fe–Ge herrühren. Während
bei Fe-Gehalten unter 35 at.% Fe, die tetragonalen und pseudo-tetragonalen strukturellen Merkmale der FeGe₂ Phase dominieren, wurde gezeigt dass bei Fe-Gehalten zwischen 35 und 55 at.% Fe, die pseudo-hexagonalen Merkmale mit den Phasen Fe₆Ge₅ und FeGe in Verbindung gebracht werden können.

Im Zuge dieser Arbeit wurden Isotherme Schnitte bei 400 °C und 800 °C erarbeiteten. Eine Stabilisierung des kubischen Polymorph von FeGe, hin zu höheren Temperaturen, wurde beobachtet. Auf Grund der Komplexität im Al reichen Teil des Phasendiagramms, sind weitere Untersuchungen notwendig, um die Isopleten sowie eine Liquidusprojektion mit hinreichender Sicherheit beschreiben zu können.

Eine Untersuchung der magnetischen Eigenschaften aller Phasen, ins besonders mit Hinblick auf die mögliche Supraleitfähigkeit der Phase τ₅ scheinen vielversprechend, da in der einschlägigen Literatur außerordentliche magnetische Eigenschaften in Systemen der Art TM–X (X = Al, Ga, Si, Ge) beschrieben werden.
Chapter 8

References


27. Stein, F., Vogel, S. C., Eumann, M. Palm, M. Determination of the crystal structure of the e phase in the Fe–Al system by high-temperature neutron diffraction. Intermetallics 18, 150-156 (2010).


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