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„The Ni-rich part of the system Al-Ge-Ni
with particular reference to the B8-phases“

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1. Introduction

The investigation of phase diagrams, binary as well as ternary and higher order, is an important task to understand alloy systems. With their help it is possible to predict properties of particular mixing ratios of components and therefore find suitable alloys for various applications.

In the here studied system Al-Ge-Ni one of the predominant phases is the phase with NiAs-type structure (Strukturbericht designation: B8). This structure type is a very common one and present in many alloy systems. As it is composed of main group elements of groups 13-16 in combination with transition elements, a huge variety of compositions with different structural, magnetic and electrical properties is possible and was summarised in an early review of Kjekshus and Pearson [1]. Today there are more than 400 compounds with NiAs-structure known and there will be even more in the future.

The B8 structure is special, not only because of its large distribution, but also because it forms large ranges of homogeneity and forms various superstructures. As already mentioned the general B8 structure ($T_{1\pm x}B$) is composed of a transition element T and a main group element B out of the 13th to 16th group. The basic NiAs structure crystallises in the hexagonal space group $P6_3/mmc$ with the T-atom at the Wyckoff-position $2a$ (0, 0, 0) and the B-atom at $2c$ ($1/3$, $2/3$, $1/4$) (Fig. 1 middle). It also can be described as a hexagonal close-packed lattice of B-atoms, where the T-atoms occupy all the octahedral holes.

Besides the octahedral holes a hexagonal close-packed structure contains also trigonal-bipyramidal holes that correspond to the Wyckoff-position $2d$ ($1/3$, $2/3$, $3/4$). This holes can be occupied by additional T-atoms to form $T_{1+x}B$ structures until this position is completely filled and the Ni_2In ($P6_3/mmc$, Strukturbericht designation: B8₂) structure type (Fig. 1 right) is reached.

On the other hand vacancies at the $2a$ position lead to $T_{1-x}B$ structures. If the vacancies are ordered in every second layer perpendicular to the c-axis the CdI_2 ($P\bar{3}m1$) structure type (Fig. 1 left) is formed. So the composition range of the general NiAs-

structure type reaches from T_2B through the ideal composition of TB to TB_2 , although usually only parts of this broad homogeneity range are found in real alloy systems.

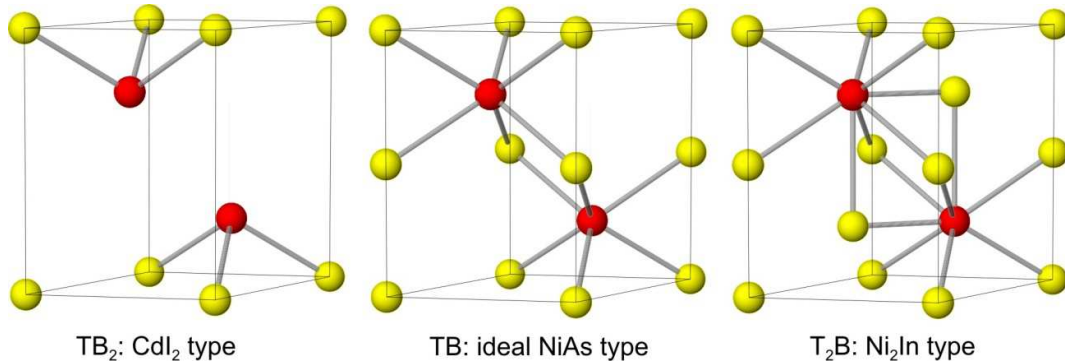


Fig. 1 NiAs and related structures

Based on these general NiAs structure types a variety of superstructures are formed. Such superstructures are often found as low temperature phases in systems with high-temperature NiAs-phases.

Superstructures with a composition of $T_{1-x}B$ are formed by ordering of vacancies at the $2a$ or $2c$ positions in most cases and build hexagonal or monoclinic crystal structures [1, 2]. $T_{1+x}B$ superstructures are usually formed by additional ordering at the $2d$ position, mixing T- and B-positions and many other mechanisms [3, 4]. The latter group also includes the superstructures in the binary Ge-Ni alloy system (ϵ' -Ge₃Ni₅, Ge₁₂Ni₁₉).

This diversity of the NiAs structure type is responsible for its importance in many alloy systems. In particular, the B8 structures of systems containing Al, Ge and Ni are currently under research for applications in contacts for compound semiconductor devices [5, 6], insertion electrodes for lithium-ion batteries [7-10] and joining technologies, such as lead-free soldering [11, 12] or diffusion brazing [13, 14].

But the Al-Ge-Ni system contains more than only the phases with NiAs-type structure. Especially the Ni-rich part of the system is of great interest because of phases that play an important role in the so-called superalloys. Superalloys are materials of complex composition based on chromium or nickel for high-temperature applications. Ni-based superalloys are secondary hardened by addition of aluminium and hence the formation of the gamma prime phase $AlNi_3$. By adding different other materials the properties are adapted to the designated applications.

The major properties of superalloys are their mechanical strength, high temperature creep resistance, oxidation and corrosion resistance. Therefore they are used in gas turbines [15-17] particularly. Other important tasks are coatings [18] and applications for aerospace [19].

To connect such superalloys with other materials diffusion brazing is a common method. Therefore brazing materials, which have a lower melting point but similar structural properties than the substrate, are necessary. Because Ge forms a deep eutectic with Al, it is considered as a melting point depressant element of nickel aluminides.

The current work was performed with the aim to better understand the phase equilibria and structures in the Ni-rich part of the alloy system Al-Ge-Ni. Based on this new fundamental knowledge, the understanding of alloy properties in the Al-Ge-Ni system will be increased and further improvement of higher order systems and complex alloy materials will be possible.

2. Literature review

2.1 Binary subsystems

2.1.1 Al-Ge phase diagram

The assessed Al-Ge phase diagram was published by McAlister and Murray [20] in 1984. It is a simple eutectic system including the liquid, the fcc (Al) solid solution and the diamond cubic (Ge) solid solution shown in Fig. 2. The eutectic temperature lies at 420 ± 4 °C, with the eutectic point at 28.4 at.% Ge. There germanium has a solubility of about 2 at.% in (Al) and vice versa aluminium 1.09 at.% in (Ge). But the authors admit that these data are only based on estimations of Eslami et al. [21] and their thermodynamic calculation, so they claim it to be not fully reliable.

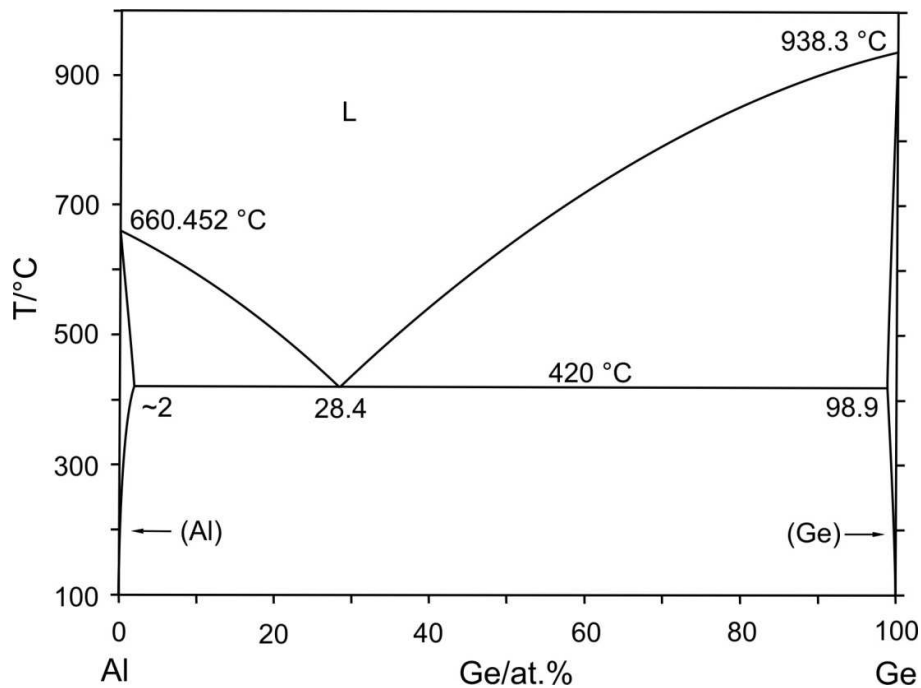


Fig. 2: Al-Ge phase diagram according to McAlister and Murray [20]

In 1996 a re-evaluation of the system was done by Srikanth et al. [22]. They calculated an eutectic temperature of 696.85 K, which is about 4 degrees higher than the previous work stated. Furthermore they enhanced the maximum solubility of germanium in aluminium to 2.56 at.% Ge.

2.1.2 Al-Ni phase diagram

The Al-Ni system was investigated repeatedly. It is a more complex system with different peritectic and eutectic reactions. A first assessment was given in 1990 by Singleton and Nash [23], see Fig. 3.

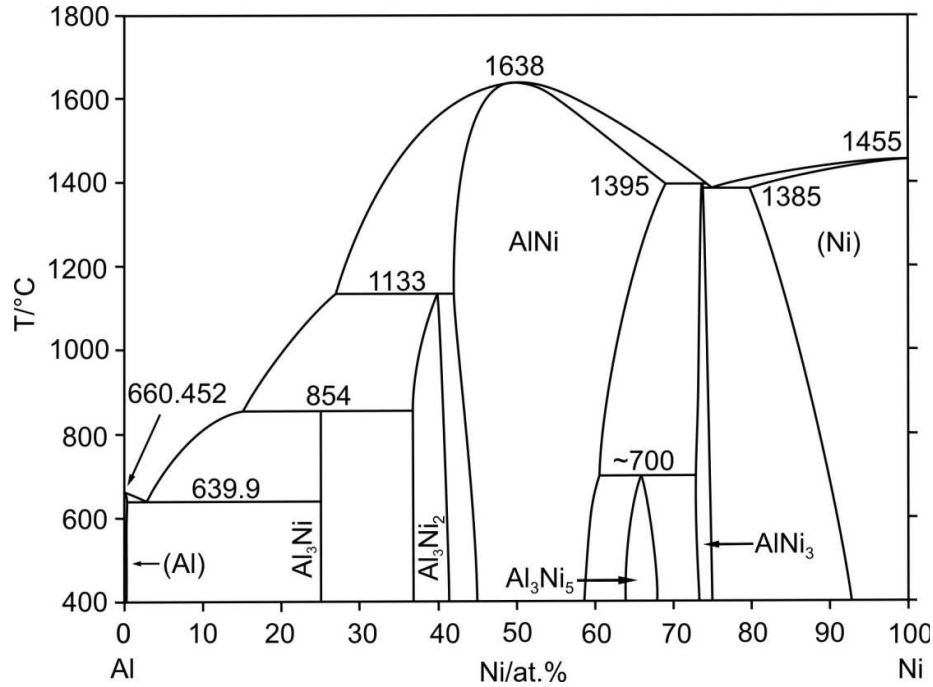


Fig. 3: Al-Ni phase diagram according to Singleton and Nash [23]

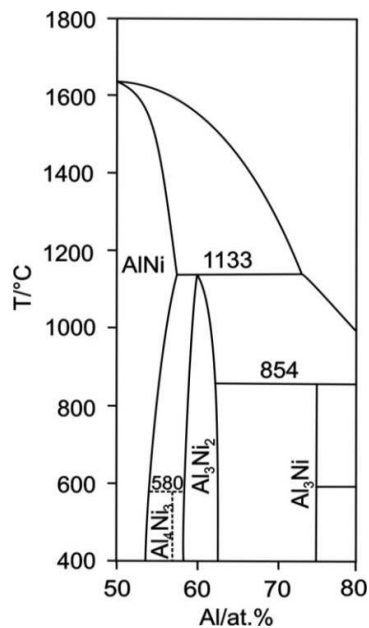


Fig. 4: partial Al-Ni phase diagram according to Ellner et al. [25]

In addition to the solid solutions (Al) and (Ni) they found 5 intermetallic phases: Al_3Ni , Al_3Ni_2 , AlNi , Al_3Ni_5 and AlNi_3 , where Al_3Ni_5 is considered to be stable only by Robertson and Wayman [24].

A further intermetallic compound, Al_4Ni_3 , was found by Ellner et al. [25], who suggested that a part of the phase diagram should be redrawn as shown in Fig. 4. The crystal structure data of the phases are summarised in Tab.

1.

Although there were different explanations for the formation of AlNi_3 , the authors decided on the peritectic reaction $\text{L} + \text{AlNi} \rightleftharpoons \text{AlNi}_3$ at 1395 °C according to the work of Alexander and Vaughan [26].

Tab. 1 Al-Ni Crystal structure data according to Singleton and Nash [23]

Phase	Composition/ at.% Ni	Pearson symbol	Space group	Prototype	Strukturbericht designation
(Al)	0 to 0.11	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	Cu	A1
Al ₃ Ni	25	<i>oP16</i>	<i>Pmma</i>	Fe ₃ C	D0 ₁₁
Al ₃ Ni ₂	36.8 to 40.5	<i>hP5</i>	<i>P$\bar{3}m1$</i>	Al ₃ Ni ₂	D5 ₁₃
Al ₄ Ni ₃	42.9	<i>cI112</i>	<i>Ia$\bar{3}d$</i>	Ni ₃ Ga ₄	/
AlNi	42 to 69.2	<i>cP2</i>	<i>Pm$\bar{3}m$</i>	CsCl	B2
Al ₃ Ni ₅	~64 to 68	/	<i>Cmmm</i>	Ga ₃ Pt ₅	/
AlNi ₃	73 to 76	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	AuCu ₃	L1 ₂
(Ni)	78.8 to 100	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	Cu	A1

After this first assessment a lot of new investigations in the Al-Ni system were done, especially about the eutectic and peritectic reactions around the formation of AlNi₃. During this newer work it emerged that a reaction schema based on Schramm [27] is the more reliable one. He suggested the peritectic reaction $L + (Ni) \rightleftharpoons AlNi_3$ at a much lower temperature of 1362 °C.

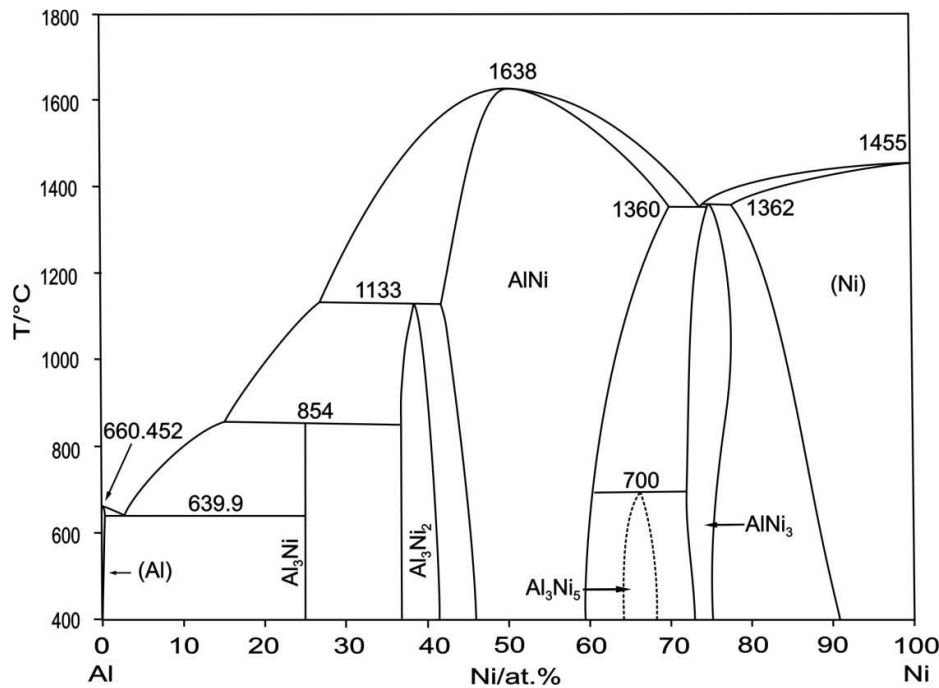


Fig. 5: Al-Ni phase diagram according to Okamoto [28]

Furthermore the boundaries of the two-phase field $\{(Ni)+AlNi_3\}$ shifted according to new experimental and thermodynamic modelling data of Jia [29] and the composition of Al₃Ni₂ at 1133 °C was changed to less than 40 at.% Ni after Okamoto and Massalski [30].

All this new perceptions including a new version of the phase diagram, shown in Fig. 5, were summarised by Okamoto [28].

Recently Bitterlich et al. [31] reassessed the solidus temperatures in the range of 45 to 57 at.% Ni. They found a much higher solidus temperature of 1681 °C for the stoichiometric NiAl. Moreover the solidus lines on both sides of the maximum show nearly the same slopes.

2.1.3 Ge-Ni phase diagram

Although there had been many investigations in this system, it still cannot be regarded as very reliable.

A first assessment was given by Nash and Nash [32], who showed a phase diagram (Fig. 6) mainly based on the works of Ruttewit and Masing [33], Ellner et al. [34] and Dayer and Feschotte [35].

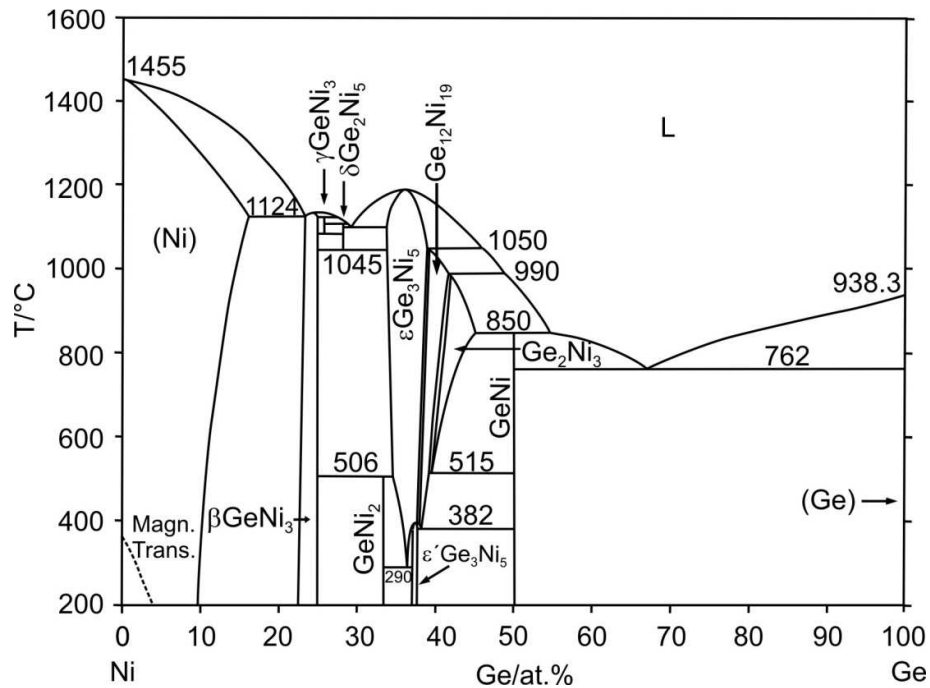


Fig. 6: Ge-Ni phase diagram according to Nash and Nash [32]

The system Ge-Ni is a real complex one with many invariant reactions, intermediate high- and low-temperature phases and also some superstructures. The five intermetallic phases βGeNi_3 , γGeNi_3 , $\delta\text{Ge}_2\text{Ni}_5$, $\epsilon\text{Ge}_3\text{Ni}_5$ and GeNi are well established and reported by all the named authors [33-35].

Given that Dayer and Feschotte did a lot of DSC measurements with high purity starting materials [35] their data, especially their determined temperatures, were taken as the most reliable ones in the assessment [32].

So the phases βGeNi_3 and $\varepsilon\text{Ge}_3\text{Ni}_5$ melt congruently at 1132 °C and 1185 °C, respectively. GeNi is a stoichiometric line compound and forms out of a peritectic reaction at 850 °C. The high temperature phase γGeNi_3 forms in a peritectic reaction at 1118 °C as well as the high temperature phase $\delta\text{Ge}_2\text{Ni}_5$ at 1102 °C. They both decompose in eutectoid reactions at 1082 °C and 1045 °C. The exact reactions in the whole system and their temperatures are summarised in Tab. 2.

Ruttewit and Masing found indications for another high temperature phase γ' [33], but the existence of this phase could not be confirmed by any other author. Dayer and Feschotte postulated a high- and a low-temperature form of the $\varepsilon\text{Ge}_3\text{Ni}_5$ phase with a transition temperature of about 980 °C [35].

Tab. 2 Reactions in the system Ni-Ge according to Nash and Nash [32]

Reaction	Composition/ at.% Ge			T /°C	Reaction type
$\text{L} \rightleftharpoons (\text{Ni}) + \beta\text{GeNi}_3$	23	~16	~23.3	1124	Eutectic
$\text{L} \rightleftharpoons \beta\text{GeNi}_3$		~24		1132	Congruent
$\text{L} + \beta\text{GeNi}_3 \rightleftharpoons \gamma\text{GeNi}_3$	27.3	~25	~25.6	1118	Peritectic
$\text{L} + \gamma\text{GeNi}_3 \rightleftharpoons \delta\text{Ge}_2\text{Ni}_5$	28.9	25.6	28	1082	Peritectic
$\gamma\text{GeNi}_3 \rightleftharpoons \beta\text{GeNi}_3 + \delta\text{Ge}_2\text{Ni}_5$	25.6	~25	28	1102	Eutectoid
$\delta\text{Ge}_2\text{Ni}_5 \rightleftharpoons \beta\text{GeNi}_3 + \varepsilon\text{Ge}_3\text{Ni}_5$	28	25	33.6	1045	Eutectoid
$\text{L} \rightleftharpoons \delta\text{Ge}_2\text{Ni}_5 + \varepsilon\text{Ge}_3\text{Ni}_5$	29	28	33.6	1099	Eutectic
$\beta\text{GeNi}_3 + \varepsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \text{GeNi}_2$	25	34.5	33.5	506	Peritectoid
$\varepsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \text{GeNi}_2 + \varepsilon'\text{Ge}_3\text{Ni}_5$	36.3	33.5	37	290	Eutectoid
$\text{L} \rightleftharpoons \varepsilon\text{Ge}_3\text{Ni}_5$		36.5		1185	Congruent
$\varepsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \varepsilon'\text{Ge}_3\text{Ni}_5$		37.4		~398	Congruent
$\text{L} + \varepsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \text{Ge}_{12}\text{Ni}_{19}$	~45.5	38.8	39	1050	Peritectic
$\text{L} + \text{Ge}_{12}\text{Ni}_{19} \rightleftharpoons \text{Ge}_2\text{Ni}_3$	47	~41.5	~41.7	990	Peritectic
$\text{L} + \text{Ge}_2\text{Ni}_3 \rightleftharpoons \text{GeNi}$	~45	54.5	50	850	Peritectic
$\text{Ge}_2\text{Ni}_3 \rightleftharpoons \text{Ge}_{12}\text{Ni}_{19} + \text{GeNi}$	~39.6	~39.2	50	515	Eutectoid
$\varepsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \varepsilon'\text{Ge}_3\text{Ni}_5 + \text{Ge}_{12}\text{Ni}_{19}$	~37.7	~37.5	~38	~394	Eutectoid
$\text{Ge}_{12}\text{Ni}_{19} \rightleftharpoons \varepsilon'\text{Ge}_3\text{Ni}_5 + \text{GeNi}$	~38.2	~37.6	50	382	Eutectoid
$\text{L} \rightleftharpoons \text{GeNi} + (\text{Ge})$	67	50	~100	762	Eutectic

The only investigations of the low temperature region were done by Ellner et al., who found the two intermetallic low-temperature phases GeNi_2 and $\epsilon'\text{Ge}_3\text{Ni}_5$ [34]. They also investigated the broad homogeneity range of the NiAs-type structure $\epsilon\text{Ge}_3\text{Ni}_5$ and found this area split into three sections: $\epsilon\text{Ge}_3\text{Ni}_5$, $\text{Ge}_{12}\text{Ni}_{19}$ and Ge_2Ni_3 . Although Ellner et al. were not sure about the formation and decomposition of $\text{Ge}_{12}\text{Ni}_{19}$ their suggestions were implemented in the assessment of Nash [32].

The crystal structures of the NiAs-type superstructures $\epsilon'\text{Ge}_3\text{Ni}_5$, $\text{Ge}_{12}\text{Ni}_{19}$ and Ge_2Ni_3 were first investigated by Ellner et al. [34]. A newer study on electron diffraction of this phases by Larsson and Withers [36] ratified Ellners results. The phases of the Ge-Ni system and their crystal structures are given in Tab. 3.

More recently Liu et al. [37] calculated the phase diagram of Ge-Ni by thermodynamic modelling. They presented a new version of the phase diagram (Fig. 7) with slightly changed phase boundaries. Especially the homogeneity range of βGeNi_3 was adapted according to the results of Ikeda et al. [38].

Tab. 3 Ge-Ni crystal structure data according to Nash and Nash [32]

Phase	Composition/ at.% Ge	Pearson symbol	Space group	Prototype	Strukturbericht designation
(Ni)	0 to 12	<i>cF4</i>	<i>Fm\bar{3}m</i>	Cu	A1
βGeNi_3	22.5 to 25	<i>cP4</i>	<i>Pm\bar{3}m</i>	AuCu_3	L1_2
γGeNi_3	25.6	/	/	/	/
$\delta\text{Ge}_2\text{Ni}_5$	28	<i>hP84</i>	<i>P6_3/mmc</i>	Pd_5Sb_2	/
GeNi_2	33.5	<i>oP12</i>	<i>Pnma</i>	Co_2Si	C23
$\epsilon'\text{Ge}_3\text{Ni}_5$	~37	<i>mC32</i>	<i>C2</i>	Ge_3Ni_5	/
$\epsilon\text{Ge}_3\text{Ni}_5$	35 to 44	<i>hP4</i>	<i>P6_3/mmc</i>	NiAs	B8_1
$\text{Ge}_{12}\text{Ni}_{19}$	38 to 41	<i>mC62</i>	<i>C2</i>	$\text{Ge}_{12}\text{Ni}_{19}$	/
Ge_2Ni_3	41 to 43	<i>hP4</i>	<i>P6_3/mmc</i>	NiAs	B8_1
GeNi	50	<i>oP8</i>	<i>Pnma</i>	B31	MnP
(Ge)	100	<i>cF8</i>	<i>Fd\bar{3}m</i>	C(diamond)	A4

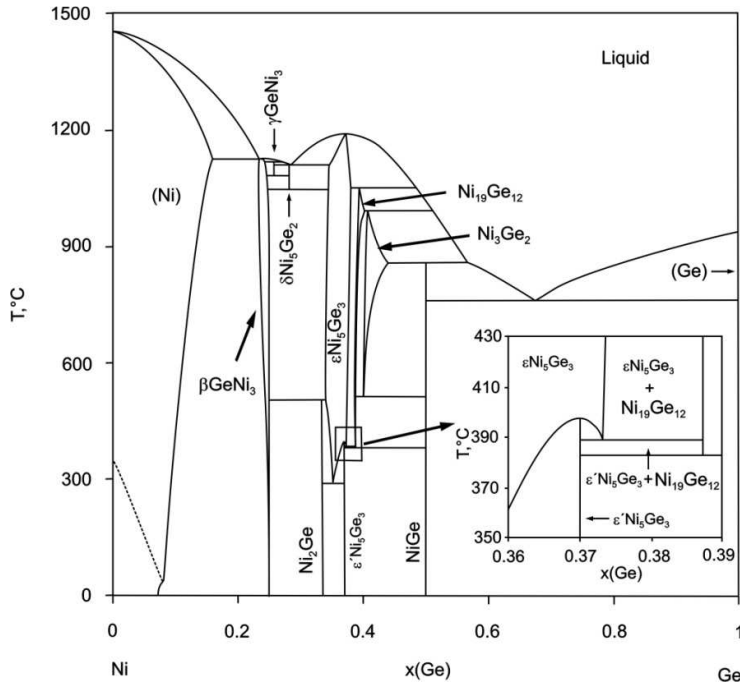


Fig. 7 Ge-Ni phase diagram according to Liu et al. [37]

2.2 The ternary system Al-Ge-Ni

Concerning the ternary phase diagram Al-Ge-Ni, there has been one investigation by Yanson et al. [39] in the past. They determined an isothermal section through the whole system at 770 K, shown in Fig. 8. It was drawn according to powder XRD structural data and microscopic analysis of 150 samples.

The authors found a new ternary phase Σ with the nominal composition Ni_4AlGe , a complete solid solution of AlNi_3 and GeNi_3 , and solubilities of germanium in Al_3Ni_2 of 3 at.% and in AlNi of 7 at.%.

The crystal structure of the ternary phase Σ was not established, but the authors claimed the line pattern and intensities to be analogous to those of “ Ni_4AlSi ”, which was not confirmed by Richter et al. [40] and Chandrasekaran et al. [41].

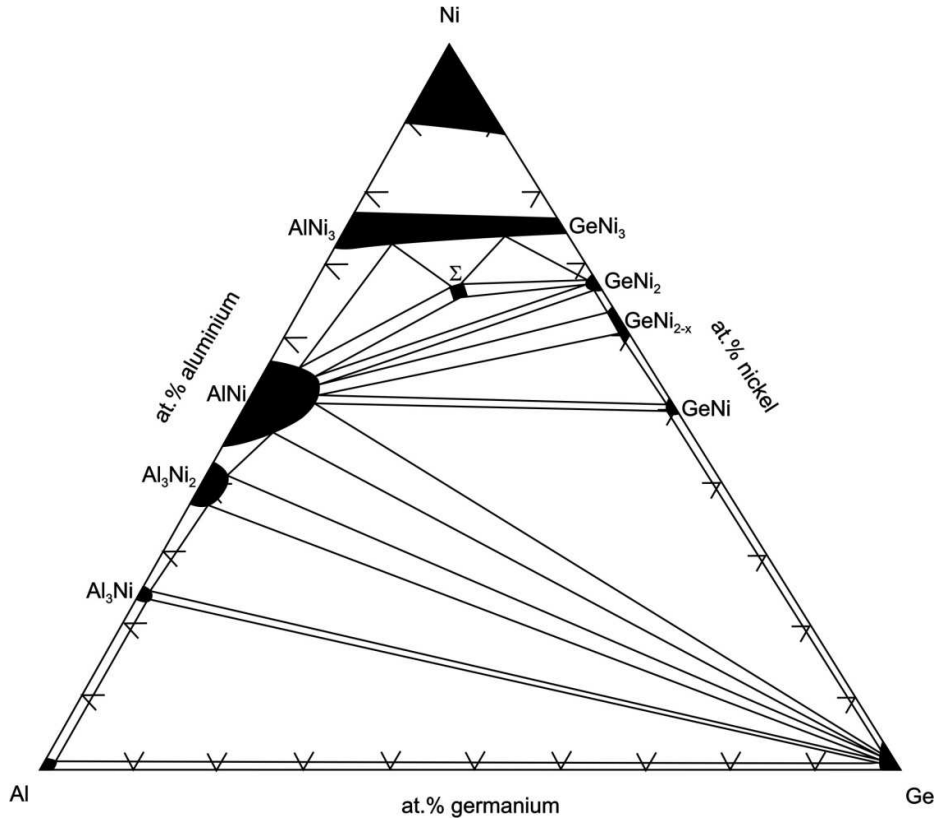


Fig. 8: Al-Ge-Ni 770 K isothermal section according to Yanson et al.[39]

A recent investigation of the Al-Ge-Ni phase diagram, especially the Ni-poor part, was done by Reichmann [42]. He presented an isothermal section at 400 °C of the Ni-poor part of the system (see Fig. 9), where he found three new ternary phases. τ_1 with a composition of $\text{Al}_x\text{Ge}_{2-x}\text{Ni}$ crystallises in the orthorhombic space group *Cmca*. The crystal structure of the new ternary phase τ_2 at $\text{Al}_{67.5}\text{Ge}_{18.0}\text{Ni}_{14.5}$ is not clarified yet, but a cubic crystal structure is predicted. The third phase τ_4 crystallises in a very small homogeneity range around $\text{Al}_{25.5}\text{Ge}_{40.0}\text{Ni}_{34.5}$ in the CaF_2 structure type.

Furthermore he determined a partial isothermal section at 700 °C (see Fig. 10), which differs a lot from the previous one. The complete solid solution of the phases AlNi_3 and GeNi_3 as well as a large ternary solution of the NiAl phase could be confirmed, but a ternary phase Σ with a composition of Ni_4AlGe was not found. Instead a new ternary phase τ_3 and a very much extended ternary solution of Ge_3Ni_5 were detected. τ_3 ($\text{Al}_y\text{Ge}_{9-y}\text{Ni}_{13\pm x}$) crystallises in the trigonal space group $P3_121$, that corresponds to the $\text{Ga}_3\text{Ge}_6\text{Ni}_{13}$ structure type. This structure type is related to the Ni_2In type by doubling the *a* and *b* axes and tripling the *c* axis as well as vacancies at the Wyckoff position 2*c*.

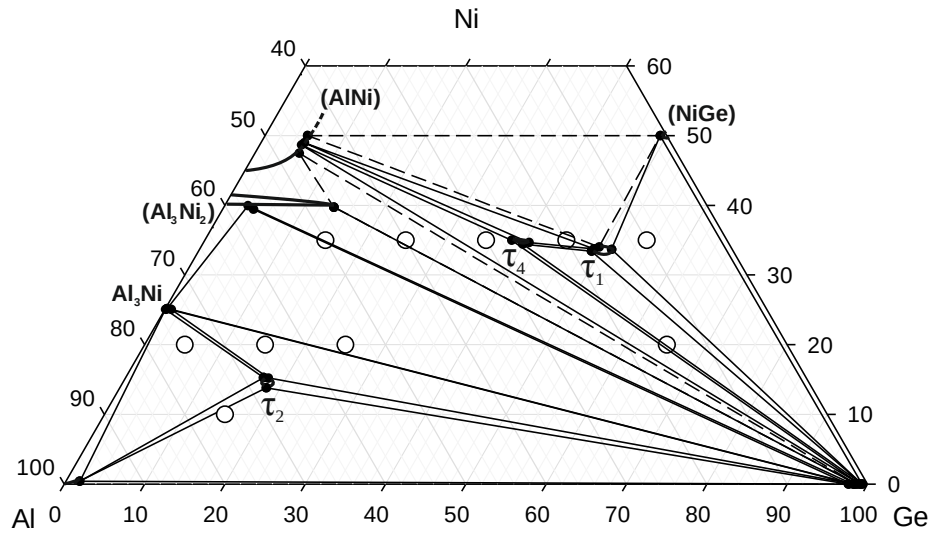


Fig. 9 Partial isothermal section at 400 °C according to Reichmann [42]

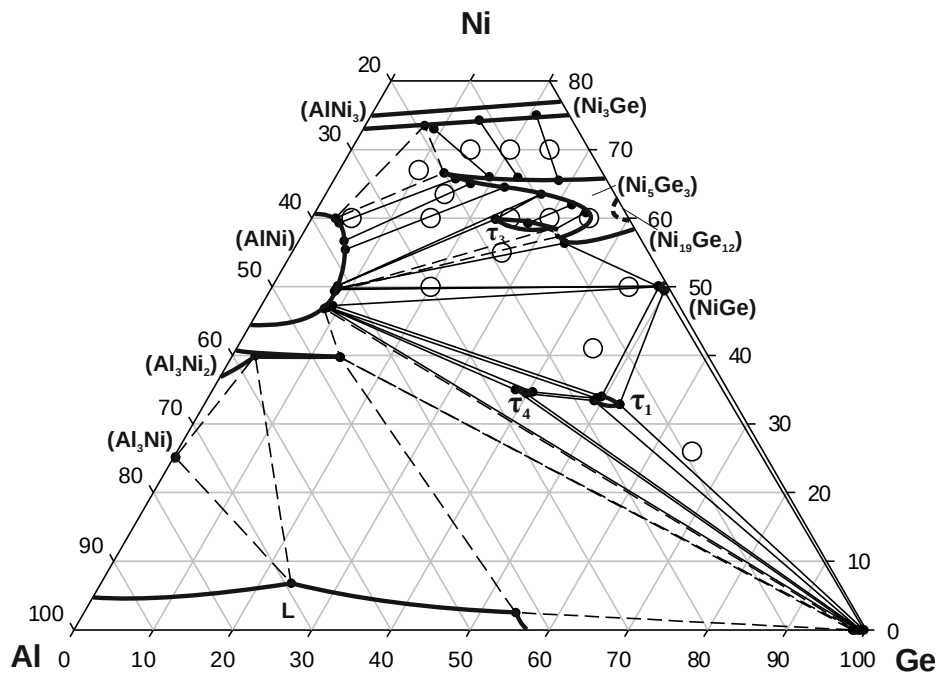


Fig. 10 Partial isothermal section at 700 °C according to Reichmann [42]

3. Applied methods

3.1 Theoretical methods

3.1.1 Density Functional Theory (DFT) [43]

The density functional theory is the basis for the determination of ground-state properties of electronic systems. It is particularly useful for the calculations of structural and electronic properties of molecules and solids.

The basis of modern DFT calculations is the Hohenberg-Kohn Theorem [44], which states that the electron density $\rho(\vec{r})$ determines the ground state of a system. In principle, all other properties of the ground state can be calculated from the density $\rho(\vec{r})$. However, the calculation of the density by solving the Schrödinger equation

$$\hat{H}\Psi(X_1, X_2, \dots, x_1, x_2, \dots) = E\Psi(X_1, X_2, \dots, x_1, x_2, \dots)$$

is a very complex task.

$\hat{H}$...Hamiltonian for all nuclei and electrons

Ψ ...total wave function

X_i, x_j ...coordinates of nuclei, electrons

In a first approximation, to ease the calculations, the oscillations of the nuclei are neglected (Born-Oppenheimer approximation), so that nucleus- and electron- Schrödinger equations can be separated. By also neglecting the electron-electron interactions (nearly-free electron model) the electronic Schrödinger equation can be further separated into one-electron Schrödinger equations.

To determine the density such one-electron Schrödinger equations, the so-called Kohn-Sham equations [45] are used

$$h_s\phi_i = \left(-\frac{1}{2}\vec{\nabla}^2 + v_{eff}(\vec{r}) \right) \phi_i = \varepsilon_i\phi_i.$$

Where h_s is the one-electron Hamiltonian and v_{eff} is the effective potential. ϕ_i are orbitals that correspond to the one-electron wave functions and have no physical meaning due to the non-interacting system. Then the density is calculated as the sum over the products of the orbitals of all occupied states

$$\rho(\vec{r}) = \sum_{i=1}^N \sum_s |\phi_i(\vec{r}, s)|^2$$

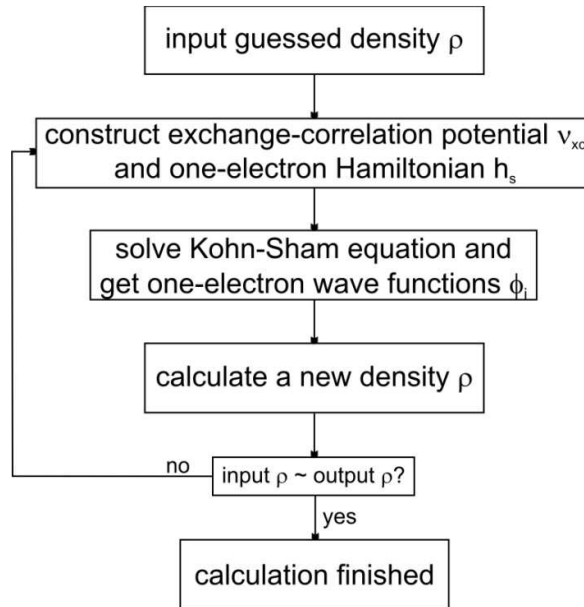
Also the effective potential depends on the density by

$$v_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + v_{xc}(\vec{r}) + v(\vec{r}).$$

The first term describes the interaction of electrons with each other, $v_{xc}(\vec{r})$ is the so-called exchange-correlation potential and $v(\vec{r})$ is the external potential that describes the attraction between nuclei and electrons.

In order to determine the electron density, a self-consistent technique is necessary.

An SCF circle illustrated in the following scheme is followed till self-consistency.



A problem is the exchange-correlation potential that is actually dependant on the density in all points of space and therefore cannot be calculated exactly. In many cases the following approximation (local density approximation, LDA) yields good results. Thereby, the exchange-correlation potential, $v_{xc}(\vec{r})$, is obtained in a particular point $\vec{r}$ from a homogeneous, interacting electron gas corresponding to the inhomogeneous electron density in this point. A more exact method is the generalized gradient approximation (GGA) that also includes the gradient of the electron density to describe $v_{xc}(\vec{r})$.

Then the total electronic energy is derived from the sum over all one-electron energies ε_i and terms for the electron-electron interactions $J(\rho)$, the exchange-correlation energy $E_{xc}(\rho)$ and the electron-nucleus interactions V_{en} :

$$E = \sum_{i=1}^N \varepsilon_i - J(\rho) + E_{xc}(\rho) - V_{en}$$

To get the total energy of the system W also the nuclei have to be reincluded, as they were excluded within the Born-Oppenheimer approximation.

$$W = E_{electronic} + E_{nucl.-nucl.}$$

3.2 Experimental Methods

3.2.1 Light optical microscopy (LOM) [46]

The fundamental aim of light optical microscopy is the magnified representation and the enhanced resolution of objects, respectively.

In very simple microscopes the magnification is achieved by combination of two lenses (objective and ocular). The objective creates a magnified image at an intermediate level, which can be observed further magnified through the ocular, like through a magnifying glass.

However, modern instruments work according to the ICS principle (Infinity Colorcorrected System) and have an additional tube integrated. In such systems the objective creates parallel beams, thus an image at the infinite. The tube forms the intermediate image, that is again observed via the ocular. A great advantage of this method is the opportunity to insert filters without additional lenses into the light path. The magnification V of a microscope is given by the following equation:

$$V_{total} = V_{objective} \cdot V_{ocular}$$

Besides the magnification, resolution is a further important criterion for the performance of a microscope. Ernst Abbe defines a resolution limit as the minimal distance d_0 up to that objects can be seen independently.

$$d_0 = \frac{\lambda}{2 \cdot N.A.}$$

Whereat λ is the wavelength of light and $N.A.$ is the so-called numerical aperture of the lense $N.A. = n \cdot \sin \alpha$, with n =refraction index and α = semi-aperture angle of the scattered light.

As the minimal distance d_0 is directly proportional to the wavelength λ of the used light, the best resolution is obtained with the smallest wavelength. In LOM this is conform to about 400 nm. The numerical aperture $N.A.$ is indirectly proportional to the minimal distance d_0 . So a better resolution can be achieved by increasing the values of the refraction index n and the angle α .

Furthermore, to get the best possible resolution, it is important to set up the illumination according to Köhler by adjusting the luminous-field diaphragm and the aperture diaphragm.

There are two basic types of light optical microscopes:

- Transmitted light microscope: the samples will be transmitted with light from below, so they have to be transparent. This method is mainly used to analyse biologics.
- Reflected-light microscope: is used to investigate opaque samples like metals. The samples will be illuminated from above and the reflected light is recaptured from the objective.

To further increase the contrast of the image there are different methods besides the usual bright field:

- Dark field: better contrast because of bright structures on dark background.
- Polarisation contrast: contrast due to optical properties and orientation of the sample.
- Differential interference contrast (DIC): contrast due to small differences in height.
- Phase contrast (only in transmitted light microscopy): contrast due to different refraction indices in different sample-components.

The analysis of the samples with this different methods results in several information. The observed microstructure might show the amount of phases, their grain size and distribution, as well as information about the crystallisation sequence and types of reactions.

3.2.2 Scanning electron microscopy (SEM) [47]

In scanning electron microscopy, instead of visible light, an electron beam is used to observe the sample surface. To avoid disturbing interactions of the electrons the whole instrument is kept under vacuum.

The electron beam can be generated by an incandescent cathode or by the use of field emission. These generated primary electrons are accelerated by d.c. voltage with up to 60 kV and then focused by electron lenses to a beam of a few nm thickness. The electron lenses are not conventional lenses, but are magnetic lenses with tuneable focal length. Then the electron beam scanners an area of the sample surface. A schematic illustration of a scanning electron microscope is shown in Fig. 11.

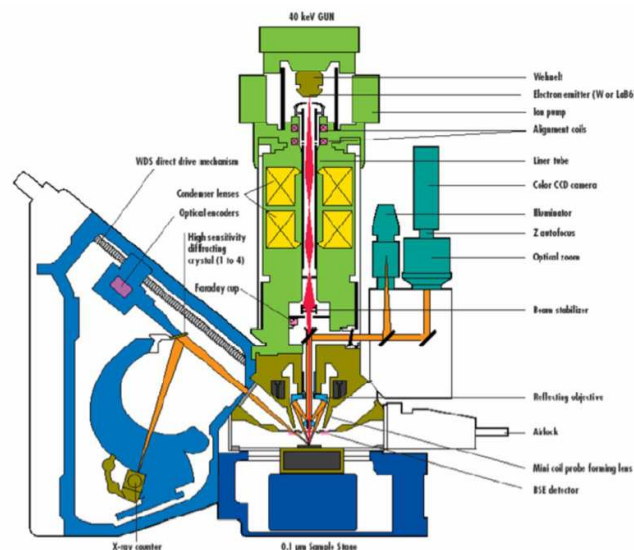


Fig. 11 Schematic illustration of a SEM [48]

As in LOM the obtainable resolution depends directly proportional on the wavelength and indirect proportional on the aperture. So the smaller the wavelength and the larger the aperture the merrier is the resolution.

Due to interactions of the electron beam with the sample the following effects occur:

- Secondary electrons
- Backscattered electrons
- Absorbed electrons
- Characteristic X-rays
- Auger-electrons

- Cathodoluminescence

Secondary electrons are low energy electrons that emerge from the sample surface. They appear only from a thin surface layer and therefore serve to display the sample topography.

Backscattered electrons are reflected impinging electrons. So they have nearly the same energy as the primary electron beam. Given that heavier atoms reflect the electrons more than the light ones, contrast arises by reason of the atomic number. Hence, this method is mainly used to display material differences of the sample.

To detect both, secondary electrons as well as backscattered electrons, scintillation detectors or solid state detectors are used usually.

By investigation of the characteristic X-rays it is also possible to determine the composition of the sample or of individual phases of the sample. The X-rays are detected by electron-dispersive X-ray spectroscopy (EDX) or wavelength dispersive X-ray spectroscopy (WDX).

EDX enables a simultaneous measurement of the whole X-ray spectrum. Whereas WDX measures the radiation of one element at a certain wavelength, which is indeed more accurate, but needs much more time.

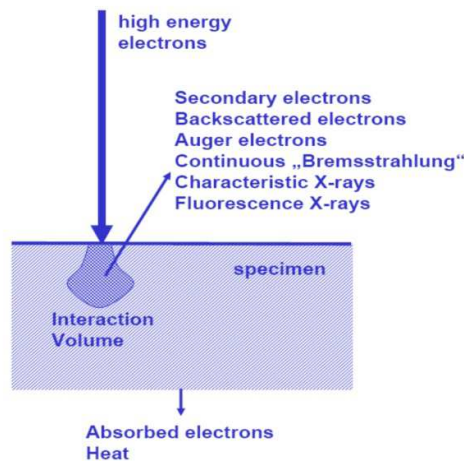


Fig. 12 Interaction of an electron beam with the sample [48]

During investigations of a sample with scanning electron microscopy, especially during analysis of characteristic X-rays, one must always consider the interactions of the electron beam with the sample. Even though the electron beam is only a few nm in size, the interaction volume with the sample is much larger as shown in Fig. 12. So the

characteristic X-rays emerge from a pear-shaped volume around the point, where the electron beam impinges at the sample surface. If you want to analyse the composition of a phase, you should measure in large areas of this phase to make sure, that you don't measure different phases below or beneath additionally.

3.2.3 Differential Thermal Analysis (DTA)

DTA is a dynamic method for thermal analysis. Whereupon dynamic means the observation of a sample, while it runs through a defined temperature program. As the name implies, by differential thermal analysis the temperature difference between reference and sample is observed and measured.

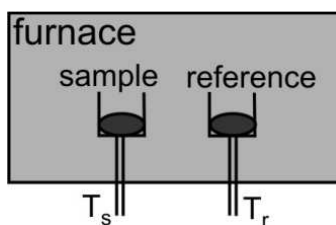


Fig. 13 Setup for DTA measurements

Reference and sample are put in crucibles, with which they should not react, on a symmetric sample-holder in a tubular furnace. During the experiment the temperature is measured with thermocouples at the bottom of the sample and the reference crucible at a time (see Fig. 13). The reference should show no thermal effects during the measurement, so that all obtained signals are due to heat exchange of the sample. As all thermal reactions, like all phase transformations, are connected with heat exchange, DTA can show that a reaction takes place at a certain temperature.

As already mentioned, DTA is a dynamic method. So heat is always transferred during the experiment by convection, radiation and conduction. Therefore the temperature distribution is never completely homogeneous. So the instrumental setup as well as a lot of other parameters affects the shape of the measured DTA curves, therefore accurate calibration is necessary.

3.2.4 Powder X-ray diffraction (XRD) [49]

Powder X-ray diffraction is a very important tool for phase identification. It can be further used in related fields like structural model refinement, crystal structure determination and so on.

Basically diffraction is a phenomenon that occurs if the spacing of the gridlines in a diffraction grating has the same order of magnitude as the wavelength of the striking wave. A typical distance for atoms in a crystal is about 0.2 nm, which is equivalent to the wavelength of X-rays. Therefore the periodic electronic density pattern of crystalline solids appear like 3-dimensional diffraction gratings to X-rays.

X-rays are diffracted by electrons, which causes diffracted waves that have the same frequency but different phase as the incoming wave. The diffracted waves interfere with each other and create a certain diffraction pattern. At this the locations of the reflexes result from the shape of the unit cell and the intensities result from the arrangement of atoms within the cell.

Bragg describes crystals as built of parallel layers that correspond to the crystallographic planes denoted by the Miller Indices (h, k, l). For each set of planes only light that strikes at particular angles show diffraction and positive interference (see Fig. 14).

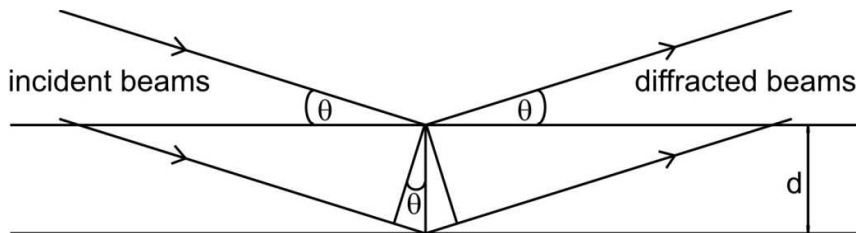


Fig. 14 X-ray diffraction

The spacing d of these planes is related to the angle θ according to the Bragg-equation:

$$2d \sin \theta = n\lambda$$

It is only possible to measure the angle θ at positive interference and the intensity of the diffracted X-rays, not the phase shift. By measurement of the angle θ one can calculate the spacing d . If the crystal system is known, one can also calculate the lattice parameters then.

If the crystal structure is not known, the intensity I of the diffracted X-rays is used to determine the exact position of the atoms within the unit cell. It results from the so-called structure factor F and additional correction factors:

$$I_{hkl} = F_{hkl}^2 \cdot H \cdot LP \cdot A$$

with H as multiplication factor, LP as Lorenz-polarisation factor and A as absorption factor.

The structure factor F characterises the scattering power of the unit cell and is calculated from the sum of all atomic positions multiplied with their atomic scattering factors f_n :

$$F_{hkl} = \sum_{n=1}^N f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

Here the atomic scattering factor f describes the scattering power of an atom for a certain diffraction angle at a certain wavelength. As the thermic motion of the electrons influences the scattering power, the atomic scattering factor is often corrected by a temperature factor:

$$f_n(T) = f_n e^{-B \frac{\sin^2 \theta}{\lambda^2}}$$

3.3 Evaluation

3.3.1 Rietveld refinement

To identify the phases, their XRD patterns will be compared with already known structures from literature. By comparison and refinement of these measured and calculated diffraction patterns, parameters, such as the exact atomic positions, of the measured phases are determined.

Before starting a refinement a suitable starting model including all relevant structural information has to be calculated. This is done with crystallographic data from different databases, like [50]. The expected intensities of each phase are then calculated using the atomic scattering factors and the structure factor as explained before. The overall calculated pattern is a function, containing the background and additional terms for each phase including several correction terms:

$$y_{ci} = y_{bi} + S \cdot F_{hkl}^2 \cdot H \cdot LP \cdot A \cdot \Phi(2\theta_i - 2\theta_{hkl}) \cdot P_{hkl} \cdot S_r \cdot E$$

y_{bi} ...background at i

S ...scaling factor (for each phase)

Φ ...profile function

P_{hkl} ...factor for preferred orientation

S_r ...function for surface roughness

E ...extinction factor

As the atomic scattering factor varies with the number of electrons, it is easier to distinguish between atoms with highly different atomic number. If there are similar structures, like a crystal structure and its superlattice there are only very small differences in the diffraction pattern, and it can be difficult to distinguish between them.

Rietveld refinement is a whole pattern structure refinement developed by Hugo Rietveld [51], which uses empirical parameters to calculate the curve. Nowadays the measured pattern is described mathematically by using the Fundamental Parameters Approach, where only phase specific parameters and parameters concerning the instrumental setup and no empirical parameters serve to calculate the profile of the pattern.

As shown in Fig. 15 the measured (blue) and calculated (red) diffraction patterns are compared. One can see a shift in the line positions and intensities, showing that the starting model does not describe all structural parameters in a correct way.

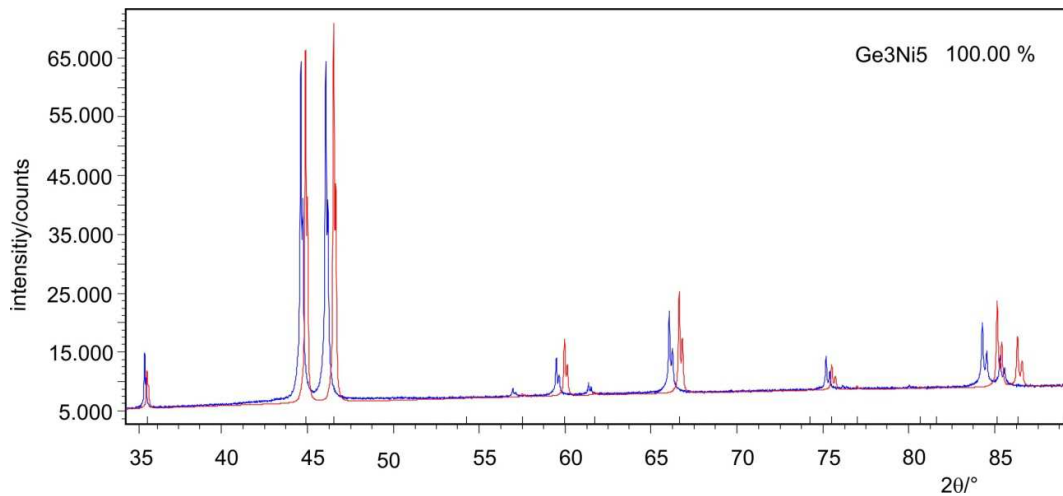


Fig. 15 Comparison of measured (blue) and calculated (red) diffraction pattern (starting model)

The refinement is using a least square process to find the optimal set of parameters.

During this least square process χ_1^2 should converge to a minimum value:

$$\chi^2_1 = \frac{\sum_i w_i (y_{oi} - y_{ci})^2}{\sum_i w_i y_{oi}}$$

w_i ...weight factor

y_{oi} ...observed intensity at point i

y_{ci} ...calculated intensity at point i

The quality of the refinement is described by different R-values. The smaller the R-value the better is the refinement. The most important R-value is the so-called weighted pattern R_{wp} :

$$R_{wp} = \sqrt{\frac{\sum_i w_i |y_{oi} - y_{ci}|^2}{\sum_i w_i y_{oi}^2}}$$

Moreover not all available parameters should be refined at a time and the sequence in which they are refined has to be selected carefully to obtain physically correct results.

4. Experimental

4.1 Performed calculations

To investigate the B8 structures in the system Al-Ge-Ni in detail, several calculations were carried out in addition to the experimental work.

As the binary B8-type structure Ge_3Ni_5 has a broad homogeneity range and a large solid solubility of Al in the ternary, it was interesting to look at the structural, energetical and electronic properties of this structure in more detail. So the hypothetical boundary structures with NiAs- and Ni_2In -type, both in the Al-Ni and the Ge-Ni system were used to draw comparisons. Furthermore it was investigated how the binary superstructure $\text{Ge}_{12}\text{Ni}_{19}$ fits into the picture.

Structural relaxations and calculations of the total-energies of Al, Ge, Ni in their stable structures, AlNi, GeNi as B8₁, AlNi₂, GeNi₂ as B8₂ and $\text{Ge}_{12}\text{Ni}_{19}$ as well as calculations of the densities of states of the latter five were done using the program VASP (Vienna Ab-initio Simulation Package) [52-55].

The Kohn-Sham equations within VASP were constructed using the projector augmented wave (PAW) method [56, 57]. This method uses plane waves to describe the valence and conduction electrons, whereas the region around the nucleus is described separately by additional wave functions. For the exchange-correlation terms the generalized gradient approximation according to Perdew et al. [58] was applied. The plain wave energy cut-off was set to 500 eV. The density was calculated at special points in the reciprocal space. These k-points were set according to Monkhorst-Pack [59] including the centred Γ point. The k meshes were set, in relation to the lattice parameters, to 19x19x13 for AlNi, 19x19x14 for GeNi, 19x19x15 for Al₂Ni and Ge₂Ni and 9x9x6 for a primitive cell assembly of $\text{Ge}_{12}\text{Ni}_{19}$.

A generalised gradient algorithm [60] was used for the structural relaxations to obtain optimised lattice parameters and atomic positions. The k-point integration for the calculation of the densities of states was done by using the linear tetrahedron method [61].

4.2 Sample preparation

As starting materials for all prepared alloys served aluminium slug (Alfa Aesar, 99.999%), germanium pieces (Alfa Aesar, 99.999%) or germanium pieces (Advent, 99.9999%) and nickel foil (Advent, 99.99%).

From these starting materials, samples with 1000 mg each were prepared. The calculated amounts of the elements were weighed with a semi-micro balance with an accuracy of at least 0.5 mg. The proper amounts of the elements were then mixed and melted in an arc-furnace (Johanna Otto GmbH, MAM1). The furnace consists of a water-cooled copper-plate, with the sample on it, and a tungsten-needle as electrodes. The arc occurs in between (see Fig. 16). For homogenisation the samples were turned around and melted three times in an inert argon atmosphere. To further protect the samples from oxidation a zirconium getter was used in the arc chamber.



Fig. 16 Arc-furnace chamber

The now produced sample-pills were sealed in evacuated quartz glass ampoules (Fig. 17). To provide samples containing aluminium from reactions with the quartz glass, these samples were put in alumina-crucibles before sealing.

The sealed samples underwent specific annealing treatments in muffle furnaces and were afterwards quenched in cold water to keep the adjusted equilibrium conditions.



Fig. 17 Samples sealed in quartz glass

For investigation of the phases with NiAs crystal structure in the binary system GeNi 20 samples were prepared. The exact sample compositions as well as the annealing procedures are summarised in Tab. 4. Samples that were annealed at 550 °C were slowly cooled from 1000 to 550 °C over a period of 5 days. To investigate the phase equilibria and reaction-schema in the Ni-rich part of the ternary system Al-Ge-Ni 47 samples were prepared and analysed (see Tab. 4 and Fig. 18). The samples with the notation TR were prepared by Thomas Reichmann and reannealed for this work.

The mass loss due to arc melting was used to calculate the actual composition. For most samples the difference is only small, except for the samples ZT5, ZT6, ZT10 and ZT14, which were not used for analysis because of extremely high mass losses of more than 5 at.% during arc melting.

Tab. 4 Sample compositions and annealing procedures

Sample	nominal composition /at%			actual composition /at%			Annealing Temperature /°C	Annealing Duration
	Al	Ge	Ni	Al	Ge	Ni		
B1	0,00	36,00	64,00	0,00	36,02	63,98	550	7 weeks
B2	0,00	38,80	61,20	0,00	38,79	61,21	550	7 weeks
B3	0,00	40,50	59,50	0,00	40,49	59,51	550	7 weeks
B4	0,00	33,00	67,00	0,00	33,01	66,99	800	30 days
B5	0,00	34,00	66,00	0,00	34,01	65,99	800	30 days
B6	0,00	35,00	65,00	0,00	35,01	64,99	800	30 days
B7	0,00	36,00	64,00	0,00	36,01	63,99	800	30 days
B8	0,00	37,00	63,00	0,00	36,99	63,01	800	30 days
B9	0,00	38,00	62,00	0,00	38,00	62,00	800	30 days
B10	0,00	39,00	61,00	0,00	39,00	61,00	800	30 days
B11	0,00	40,00	60,00	0,00	40,00	60,00	800	30 days
B12	0,00	41,00	59,00	0,00	40,99	59,01	800	30 days
B13	0,00	42,00	58,00	0,00	42,00	58,00	800	30 days
B14	0,00	43,00	57,00	0,00	43,00	57,00	800	30 days
B15	0,00	44,00	56,00	0,00	44,00	56,00	800	30 days
B16	0,00	45,00	55,00	0,00	45,00	55,00	800	30 days
B17	0,00	46,00	54,00	0,00	46,00	54,00	800	30 days
ZT1	0,00	35,00	65,00	0,00	35,04	64,96	700	30 days
ZT6	0,00	39,00	61,00	0,00	38,99	61,01	700	30 days
ZT10	0,00	41,00	59,00	0,00	41,00	59,00	700	30 days
TR15	35,00	5,00	60,00	34,99	5,02	59,99	550	7 weeks
TR16	30,00	10,00	60,00	29,94	10,03	60,02	550	7 weeks
TR17	25,00	15,00	60,00	24,96	15,02	60,02	550	7 weeks
TR18	15,00	25,00	60,00	15,03	25,01	59,96	550	7 weeks
TR19	10,00	30,00	60,00	10,04	30,03	59,92	550	7 weeks
TR20	5,00	35,00	60,00	4,91	35,07	60,02	550	7 weeks
TR21	20,00	10,00	70,00	19,98	10,05	69,98	550	7 weeks
TR22	15,00	15,00	70,00	15,01	15,01	69,98	550	7 weeks
TR23	10,00	20,00	70,00	10,08	20,00	69,92	550	7 weeks
TR24	5,00	25,00	70,00	5,00	25,02	69,98	550	7 weeks
TR25	24,00	6,00	70,00	23,95	6,04	70,01	550	7 weeks
TR26	23,00	10,00	67,00	23,01	10,03	66,96	550	7 weeks
TR27	21,50	15,00	63,50	21,57	15,00	63,43	550	7 weeks
TR28	20,00	20,00	60,00	19,99	20,02	60,00	550	7 weeks
TR29	18,50	26,50	55,00	18,51	26,52	54,97	550	7 weeks
A1	5,00	40,00	55,00	5,01	40,00	54,99	550	7 weeks
A2	10,00	35,00	55,00	9,98	35,00	55,02	550	7 weeks

Sample	nominal composition /at%			actual composition /at%			Annealing Temperature /°C	Annealing Duration
	Al	Ge	Ni	Al	Ge	Ni		
A3	15,00	30,00	55,00	15,01	30,00	54,99	550	7 weeks
A4	25,00	20,00	55,00	25,00	20,00	54,99	550	7 weeks
A5	16,25	16,25	67,50	16,30	16,24	67,47	550	7 weeks
A6	16,25	16,25	67,50	16,25	16,25	67,50	550	7 weeks
ZT2	4,00	31,00	65,00	4,05	30,97	64,98	700	30 days
ZT3	8,00	27,00	65,00	8,04	27,00	64,96	700	30 days
ZT4	12,00	23,00	65,00	12,06	22,97	64,97	700	30 days
ZT5	16,00	19,00	65,00	15,98	19,03	64,99	700	30 days
ZT7	2,00	37,00	61,00	2,05	36,98	60,97	700	30 days
ZT8	4,00	35,00	61,00	3,95	35,02	61,03	700	30 days
ZT9	6,00	33,00	61,00	5,94	33,04	61,02	700	30 days
ZT11	4,00	37,00	59,00	4,10	36,93	58,96	700	30 days
ZT12	8,00	33,00	59,00	7,97	33,00	59,03	700	30 days
ZT13	12,00	29,00	59,00	12,00	29,00	59,00	700	30 days
ZT14	16,00	25,00	59,00	16,02	24,97	59,02	700	30 days
C1	2,00	45,00	53,00	2,02	45,00	52,98	700	24 days
C2	5,00	40,00	55,00	5,02	39,99	54,98	700	24 days
C3	12,00	35,00	53,00	11,98	35,02	53,00	700	24 days
C4	20,50	5,00	74,50	20,45	5,01	74,54	700	30 days
C5	15,00	10,00	75,00	15,01	10,01	74,97	700	30 days
C6	10,00	15,00	75,00	9,99	15,02	74,99	700	30 days
C7	4,50	20,00	75,50	4,48	20,01	75,51	700	30 days
C8	11,25	3,75	85,00	11,27	3,77	84,96	700	30 days
C9	7,50	7,50	85,00	7,57	7,48	84,95	700	30 days
C10	3,75	11,25	85,00	3,77	11,24	84,98	700	30 days
D1	4,00	37,00	59,00	4,02	36,98	59,00	1000	24 days
D2	8,00	33,00	59,00	8,04	32,98	58,98	1000	24 days
D3	12,00	29,00	59,00	12,02	29,01	58,97	1000	24 days
D4	16,00	25,00	59,00	15,99	25,02	58,99	1000	24 days
D5	20,00	21,00	59,00	19,98	21,02	59,00	1000	24 days

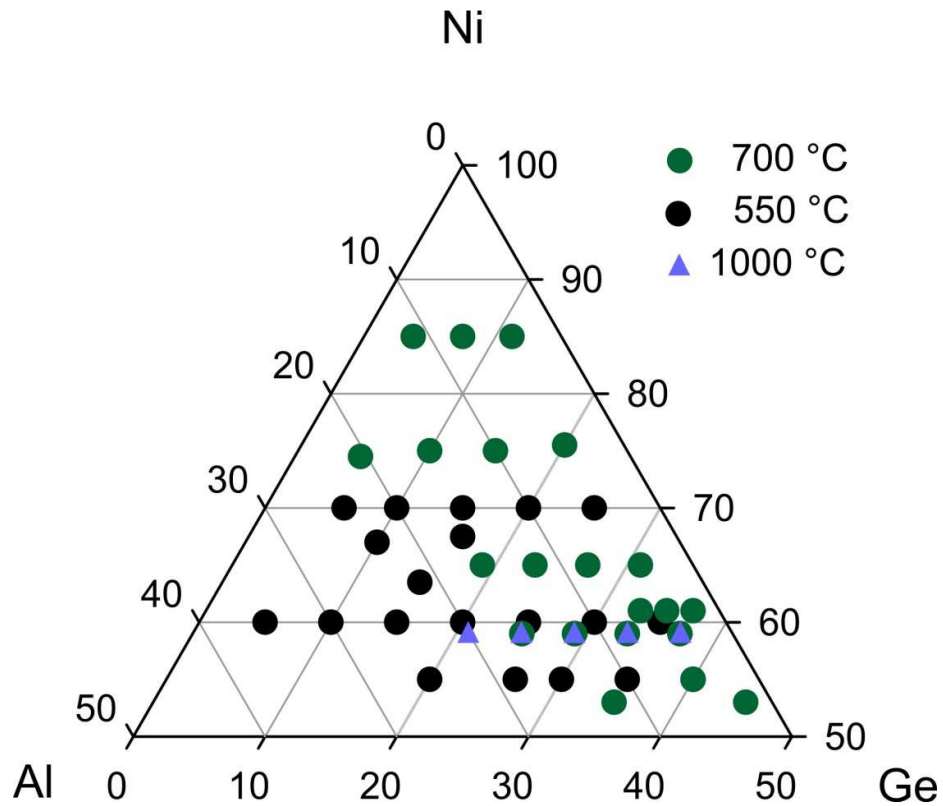


Fig. 18 Prepared ternary samples

4.3 Metallography



Fig. 19 embedded samples

The annealed samples were cut into pieces by a Buehler low speed saw with a diamond saw blade, for further investigations. One piece of each sample was embedded in phenolic hot mounting resin (Struers, PolyFast, thermosetting, carbon as filler material) at

180 °C with 15 kN for 5 minutes (Fig. 19).



Fig. 20 Grinder/polisher Metaserv 2000

The surfaces of the embedded samples were then ground with different SiC abrasive papers and finally polished with corundum powder (Buehler grinder/polisher Metaserv 2000; Fig. 20) to obtain a flat shiny surface for further investigations by means of LOM and SEM.

4.4 Investigations

4.4.1 LOM (Light Optical Microscopy)

Light optical microscopy (LOM) was used to take a first look on the sample appearance. A binocular reflected-light microscope (Zeiss Axiotech 100; Fig. 21) was used for this purpose. If there are no too fine phase structures, one can see the microstructure of the sample. Via dark field illumination one can also see if there are scratches and holes on the polished surface.

Another important modus is the polarised light microscopy where you can see if a certain phase of the sample is anisotropic and therefore does not have a cubic crystal structure.



Fig. 21 Zeiss Axiotech 100

4.2.2 SEM (Scanning Electron Microscopy)

The exact composition of the sample phases was measured with a scanning electron microscope (Zeiss Supra 55 VP ESEM; Fig. 22 [62]) in combination with energy dispersive X-ray spectroscopy (EDX). An acceleration voltage of 20 kV was applied.

A secondary electron detector as well as a backscattered electron detector was used to display the microstructure of the samples. The composition of each phase was measured at least three times at different points for statistically improved results.



Fig. 22 Zeiss Supra 55 VP {61}

4.2.3 DTA (Differential Thermal Analysis)

To identify phase transformations and their temperature differential thermal analysis (DTA), implemented on a Netzsch DSC 404 C Pegasus and a Setaram Setsys Evolution 2400 (Fig. 23), was used. For temperature measurement Pt/Pt10%Rh thermocouples were used. To get reliable data calibration, at the melting points of pure Al, Au and Ni, was performed before the actual sample measurements.



Fig. 23 NetzschDSC 404 C (left) and Setaram Setsys Evolution (right)

By using the Netzsch palladium served as reference material. Reference and sample were put in covered alumina crucibles on the sample holder. The measurement took place under constant argon flow of about 50 mL/min.

A specific temperature program for each measurement was applied: First quick heating (20K/min) from room temperature to about the annealing temperature of the measured sample. Then an isothermal section of 30 min was slid in before the actual measurement starts with a heating rate of 5 K/min. The maximum temperature was set slightly higher than the melting point of the sample. A measurement up to 1450 °C was possible with the used equipment.

For each sample two heating and cooling circles like shown in Fig. 24 schematically were performed.

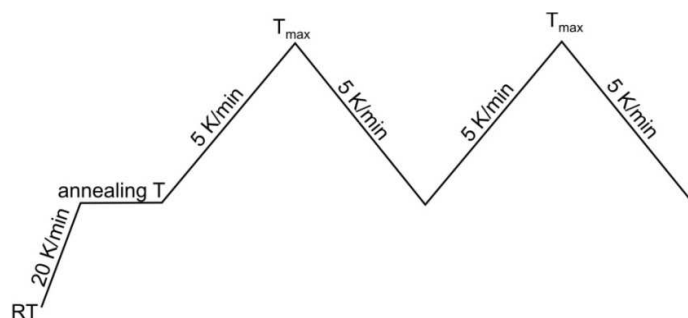


Fig. 24 Schematic temperature program for DTA measurements

4.4.4 XRD (X-Ray Diffraction)

To identify the phases, of which a sample consists of, powder X-ray diffraction was used.

A small piece of each sample was powdered in a tungsten carbide mortar until the particles reached a size of 0.18 mm or smaller. Some of the very hard samples were powdered using a ball mill (Retsch MM301) with a frequency of 30/s for 30 min. As this procedure induced stress in the crystal structure of the samples, they have to be stress annealed afterwards by sealing them again in evacuated quartz glass ampoules and reanneal them for 30 minutes at the designated temperature.

A thin layer of the received powders was fixed on a silicon wafer with Vaseline to analyse it with a Bruker D8 diffractometer (Discover Serie 2; Fig. 25) in Bragg-Brentano pseudo-focusing geometry using Cu-K α radiation and a silicon strip detector (LynxeyeTM). The measurement took place in a $\theta/2\theta$ arrangement, with a variable slit aperture of 12 mm for one hour. Analysis of the obtained powder patterns was done by Rietveld refinement with the software program Topas. As starting values for the refinement served phase data from literature [50].



Fig. 25 Bruker D8 diffractometer

5. Results and discussion

5.1 Calculations

5.1.1 Structural relaxations

First of all, starting from extrapolated experimental values, the structural parameters of NiAl and NiGe in the simple NiAs-type structure, of Ni₂Al and Ni₂Ge in the filled Ni₂In-type structure and of the superstructure Ge₁₂Ni₁₉ (*C2*, *mC62*) were calculated. The optimised values are given in Tab. 5. As the NiAs and Ni₂In structure type have only fixed atomic positions, only the ones for Ge₁₂Ni₁₉ were optimised. For the corresponding values see Tab. 6.

Tab. 5 Calculated optimised structural parameters

Structure	Lattice parameters
AlNi	$a = 3.6095 \text{ \AA}$, $c = 5.0473 \text{ \AA}$
GeNi	$a = 3.6504 \text{ \AA}$, $c = 4.9464 \text{ \AA}$
AlNi ₂	$a = 4.0368 \text{ \AA}$, $c = 4.9943 \text{ \AA}$
GeNi ₂	$a = 4.0342 \text{ \AA}$, $c = 5.1032 \text{ \AA}$
Ge ₁₂ Ni ₁₉	$a = 11.6748 \text{ \AA}$, $b = 6.7354 \text{ \AA}$, $c = 10.1063 \text{ \AA}$, $\beta = 90.156^\circ$
Ge ₁₂ Ni ₁₉ .exp.	$a = 11.6093 \text{ \AA}$, $b = 6.6989 \text{ \AA}$, $c = 10.0337 \text{ \AA}$, $\beta = 90.014^\circ$

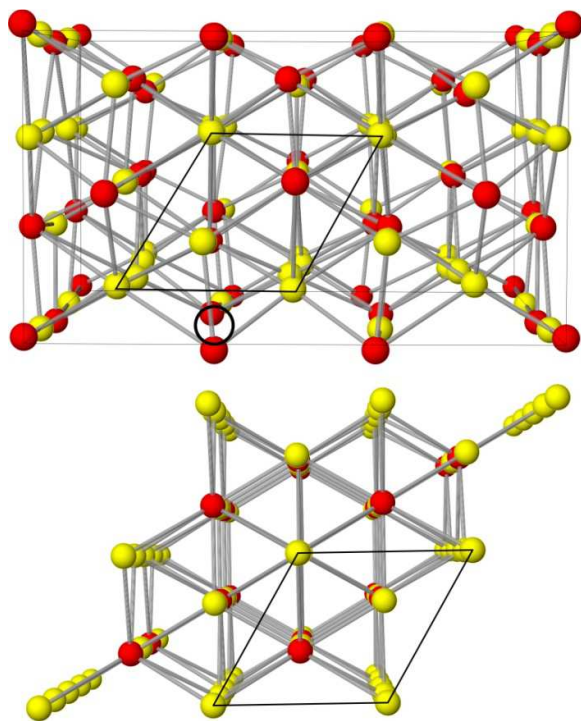
Germanium has a slightly smaller covalent atomic radius (122 pm) than Aluminium (125 pm) [63]. In the NiAs-type structures the lattice parameter a is larger in GeNi than in AlNi, whereas the parameter c is larger in AlNi. In the Ni₂In-type structures the opposite effect, but in a smaller dimension, is observable.

Ge₁₂Ni₁₉ evolves from the simple NiAs structure by doubling the b and c axes and tripling the a axis. The superstructure forms due to vacancy ordering in the position equivalent to Wyckoff position $2d$. Fig. 26 shows the crystal structure along the c axis in comparison with the Ni₂Ge structure. The simple hexagonal unit cell is drawn in. Also a vacancy in a chain of alternate Ni and Ge atoms is marked by a circle. Such vacancies are found in most of the Ni-Ge chains.

The calculated lattice parameters of Ge₁₂Ni₁₉ differ at most by 0.07 Å from measured experimental data, also the atomic positions are in good agreement.

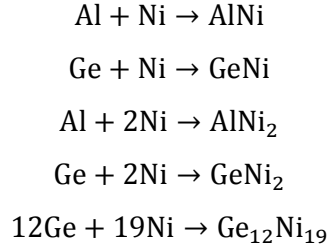
Tab. 6 Calculated atomic positions of $\text{Ge}_{12}\text{Ni}_{19}$

Site	Wyckoff position	x	y	z
Ge1	2a	0	0.0224	0
Ge2	2b	0	0.9769	0.5
Ni1	2b	0	0.3276	0.5
Ge3	4c	0.0162	0.3483	0.2523
Ge4	4c	0.3511	0.9820	0.0020
Ge5	4c	0.3244	0.0045	0.4966
Ge6	4c	0.3179	0.3483	0.2488
Ge7	4c	0.3317	0.3012	0.7514
Ni2	4c	0.0009	0.9980	0.2569
Ni3	4c	0.3342	-0.0001	0.2524
Ni4	4c	0.3304	0.3301	0.0003
Ni5	4c	0.1598	0.1749	0.1257
Ni6	4c	0.1720	0.1787	0.3770
Ni7	4c	0.1767	0.1538	0.6237
Ni8	4c	0.1610	0.1659	0.8741
Ni9	4c	0.5045	0.1568	0.1260
Ni10	4c	0.5116	0.1644	0.3774

Fig. 26 Crystal structures of $\text{Ge}_{12}\text{Ni}_{19}$ (above) and GeNi_2 (below); red spheres – Ge, yellow spheres – Ni

5.1.2 Energy of formation

To take a look at the stability of the calculated phases the energies of formation were calculated from the obtained optimised energy values according to the following reaction equations:



Therefore the structures of the elements aluminium, germanium and nickel have to be also calculated and optimised. Then the energy of formation $\Delta_f E$ was determined due to the following relations:

$$\begin{aligned}\Delta_f E &= [E(\text{AlNi}) - E(\text{Al}) - E(\text{Ni})]/2 \\ \Delta_f E &= [E(\text{GeNi}) - E(\text{Ge}) - E(\text{Ni})]/2 \\ \Delta_f E &= [E(\text{AlNi}_2) - E(\text{Al}) - 2E(\text{Ni})]/3 \\ \Delta_f E &= [E(\text{GeNi}_2) - E(\text{Ge}) - 2E(\text{Ni})]/3 \\ \Delta_f E &= [E(\text{Ge}_{12}\text{Ni}_{19}) - 12E(\text{Ge}) - 19E(\text{Ni})]/31\end{aligned}$$

The determined values for one mole of atoms are given in Tab. 7.

Tab. 7 Calculated energies of formation

B8-type phase	$\Delta_f E/(\text{kJ/mol})$	Stable phase	$\Delta_f E/(\text{kJ/mol})$
AlNi	-32.69	CsCl-type	-65.60
GeNi	-27.21	MnP-type	-30.34
AlNi ₂	-47.97	Fe ₂ Si (ht)-type*	-50.03
GeNi ₂	-28.12	Co ₂ Si-type	-30.89
Ge ₁₂ Ni ₁₉	-31.44		

* Not stable in the phase diagram

The energies of formation of all five calculated structures are negative. For Ge₁₂Ni₁₉ the calculated structure corresponds to a stable, experimentally confirmed phase. In accordance with the calculations GeNi₂ is more stable than GeNi. This is in good agreement with the experimental results, the boundary structures are indeed not pre-

sent in the system, but the homogeneity range of the B8-type structure reaches much more to the GeNi_2 side.

In the Al-Ni binary system, similar as in Ge-Ni, AlNi_2 is much more stable than AlNi . Both compounds are actually more stable than the corresponding ones with Ge.

As the four boundary structures did not exist in the experimentally approved phase diagrams, the energies of formation of existing structure types were calculated too (Tab. 7). It was found, that in the Ge-Ni system the structures with MnP ($Pnma$, $oP8$) and Co_2Si ($Pnma$, $oP12$) type are more stable than the B8 type structures. In the Al-Ni system the high temperature Fe_2Si ($P\bar{3}m1$, $hP6$) structure is more stable than the Ni_2In structure type, but the most stable structure by far is the CsCl ($Pm\bar{3}m$, $cP2$) type, which is the predominant structure type in the binary assessed phase diagram. $\text{Ge}_{12}\text{Ni}_{19}$ was found to be more stable than both GeNi and GeNi_2 in B8-type structure, consistent with its existence in the equilibrium phase diagram.

5.1.3 Density of states (DOS)

To analyse the electronic properties of the four boundary structures (AlNi , GeNi , AlNi_2 , GeNi_2) and the superstructure ($\text{Ge}_{12}\text{Ni}_{19}$) the densities of states were calculated. Also, the local partial densities of states, split up according to the atoms and the quantum number l , were determined to estimate bonding relations in the named structures.

Additionally, the partial charges, also split up according to the atoms and the quantum number l , were calculated and used for interpretation. They especially served for a more detailed analysis of interactions between certain atomic orbitals.

The densities of states of the calculated compounds have mainly d contributions for Ni. The contributions from Ge are predominantly from s states at lower energies (ca. -9 eV) and from p states at energies above the Ge s-band. From Al the s and p states contribute with peak maxima at about -5 eV for the s and -2.5 for the p states (Fig. 27).

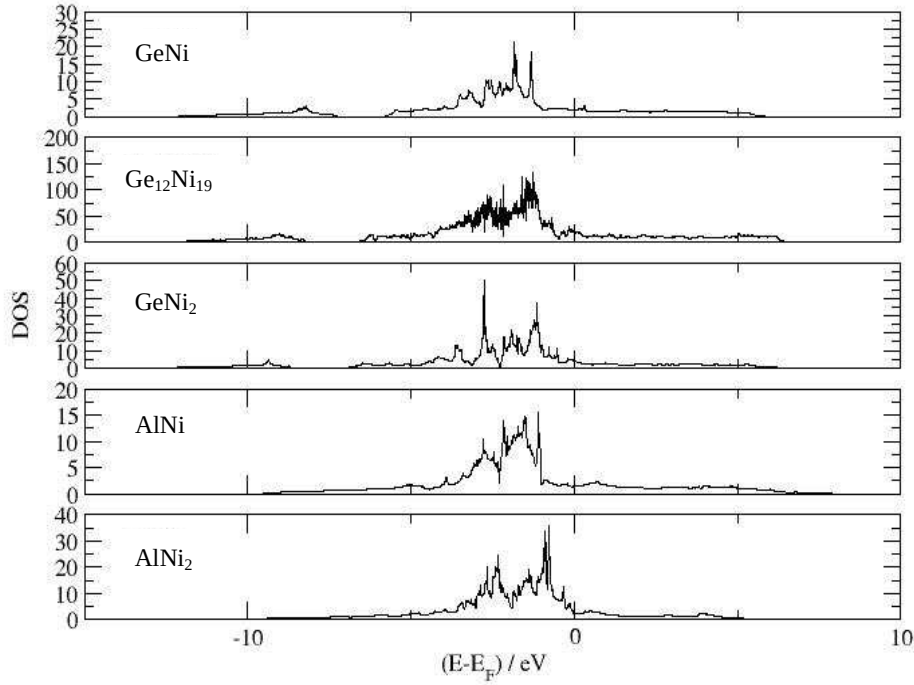


Fig. 27 Total densities of states from VASP calculations. Units are in number of states/eV/unit cell.

At energies from -12 to -7 eV the total density of state for GeNi shows mainly contributions from Ni-s, Ni-p and Ge-s states (Fig. 28). Above this energy particularly contributions from Ni-d and Ge-p states are observed (Fig. 29). At about 1.3 eV below the Fermi energy especially Ni-d states are present, which indicates also interactions between the nearest Ni atoms.

So the main bonding interactions for NiGe in the given approximate energy regions are:

- Ge-Ni s - s,p from -12 to -7 eV
- Ge-Ni p - d from -6 to -1.8 eV
- Ni-Ni d - d from -1.8 to 0 eV

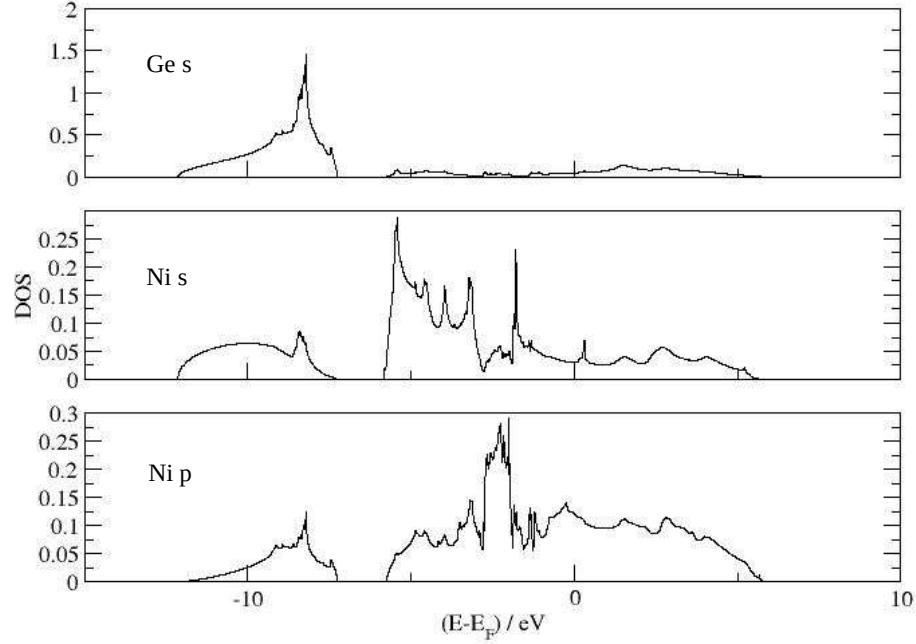


Fig. 28 Local partial densities of states for GeNi from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

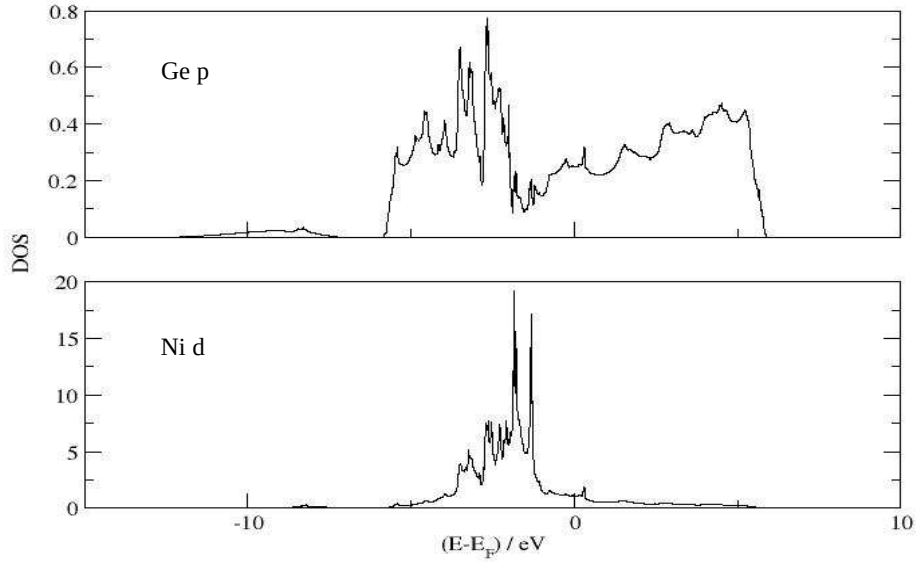


Fig. 29 Local partial densities of states for GeNi from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

For GeNi_2 the situation is analogous. The same interactions as for GeNi, but at slightly lower energies, were observed. Therefore the main bonding interactions are:

- Ge-Ni s - s,p from -12.6 to 8.6 eV
- Ge-Ni p - d from 7.1 to 2.3 eV
- Ni-Ni d - d from -2.3 to 0 eV

A comparison between GeNi and GeNi₂ shows, additionally to the lower energy of the bands in GeNi₂, a narrower Ge-s band with increasing Ni content (Fig. 30). Smaller distances between Ni and Ge in GeNi lead to slightly wider bands as compared to GeNi₂.

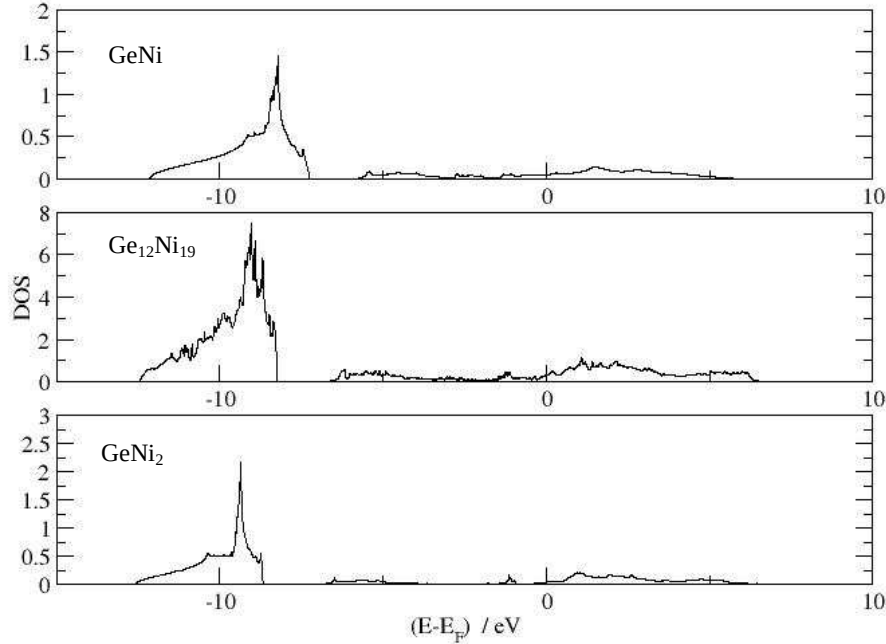


Fig. 30 Local partial densities of states for Ge-s states from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

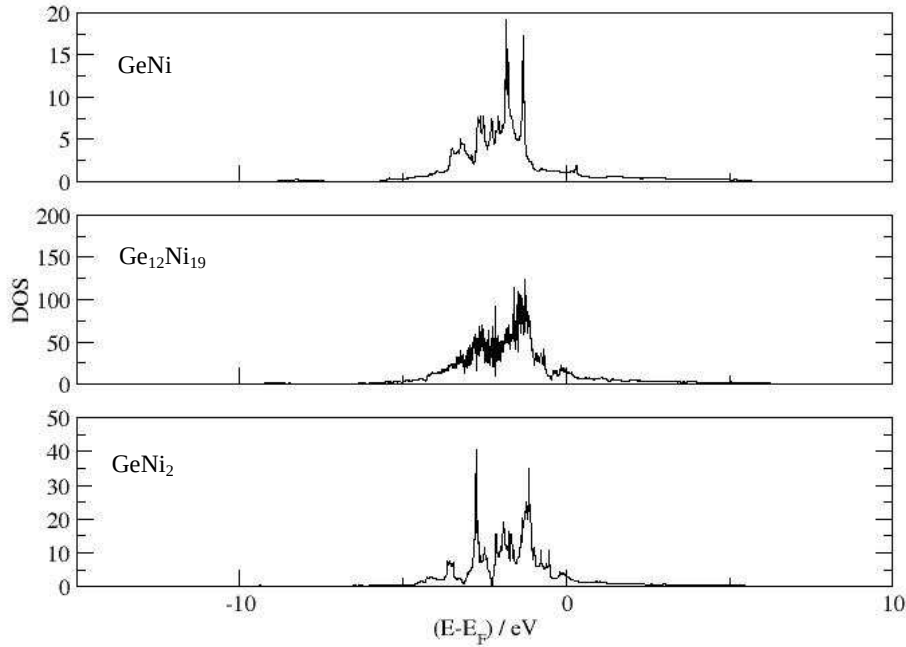


Fig. 31 Local partial densities of states for Ni-d states from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

The Ni-bands have a different shape as well, because more Ni states are filled for higher Ni contents. Therefore the region below the Fermi energy, where mainly Ni-d interactions occur becomes broader (Fig. 31). Furthermore the Ge-p band becomes a little broader with increasing Ni content and shifts to lower energies (Fig. 32). Ge-p states interact with Ni-d states, thus the smaller Ni Ni distances and the different coordination of Ge (Fig. 33) in GeNi_2 cause a bigger splitting of the Ge-p band.

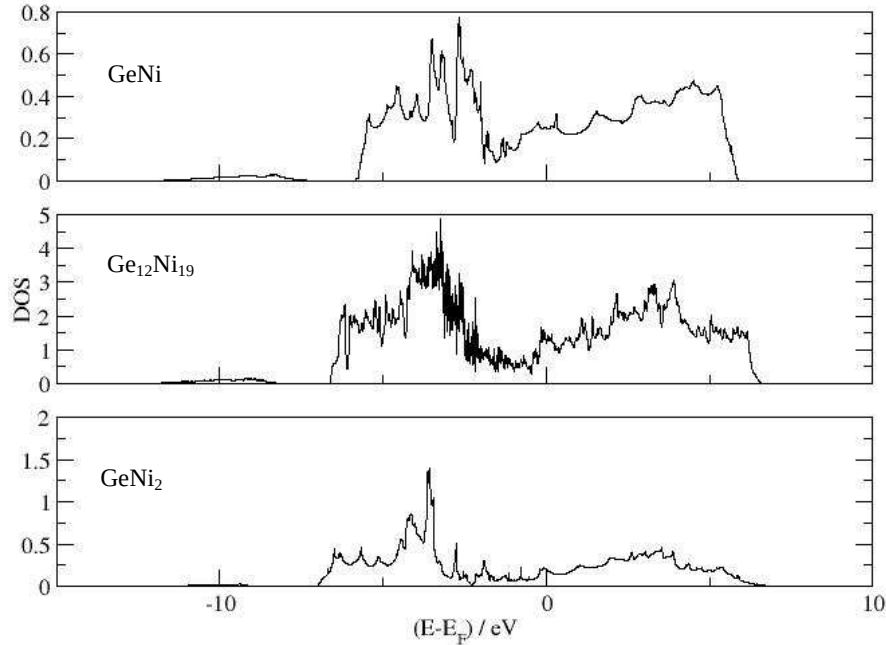


Fig. 32 Local partial densities of states for Ge-p states from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

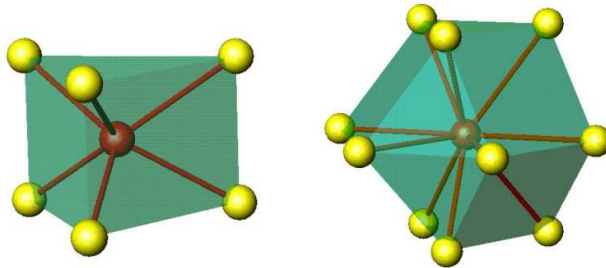


Fig. 33 Ge-coordination polyhedra of GeNi (left) and GeNi_2 (right); red spheres – Ge, yellow spheres - Ni

The superstructure $\text{Ge}_{12}\text{Ni}_{19}$ fits in between GeNi and GeNi_2 very well (Fig. 30, Fig. 31, Fig. 32). The already described bonding interactions occur at the following approximate energy values:

- Ge-Ni s - s,p from -12.5 to 8.3 eV

- Ge-Ni p - d from 6.6 to 1.8 eV
- Ni-Ni d - d from -1.8 to 0 eV

Also the widths of the Ge-s and Ge-p bands follow the noticed trends.

In the hypothetical AlNi structure there are also interactions between Ni-s, Ni-p and Al-s states at lower energies (Fig. 34). Above that there are contributions of Al-p, Ni-d and some Ni-p (Fig. 35). A big contribution of Ni-d to the total density of state at about -1 eV (marked in Fig. 35) seems to come from Ni-Ni interactions, because no overlap with Al states is found in this energy region. Immediately below the Fermi energy the DOS for Ni d is small.

The main observed bonding interactions and the according approximated energy values are:

- Al-Ni s - s,p -9.6 to -4.5 eV
- Al-Ni p - p,d -4.5 to 0 eV
- Ni-Ni d - d -1 eV

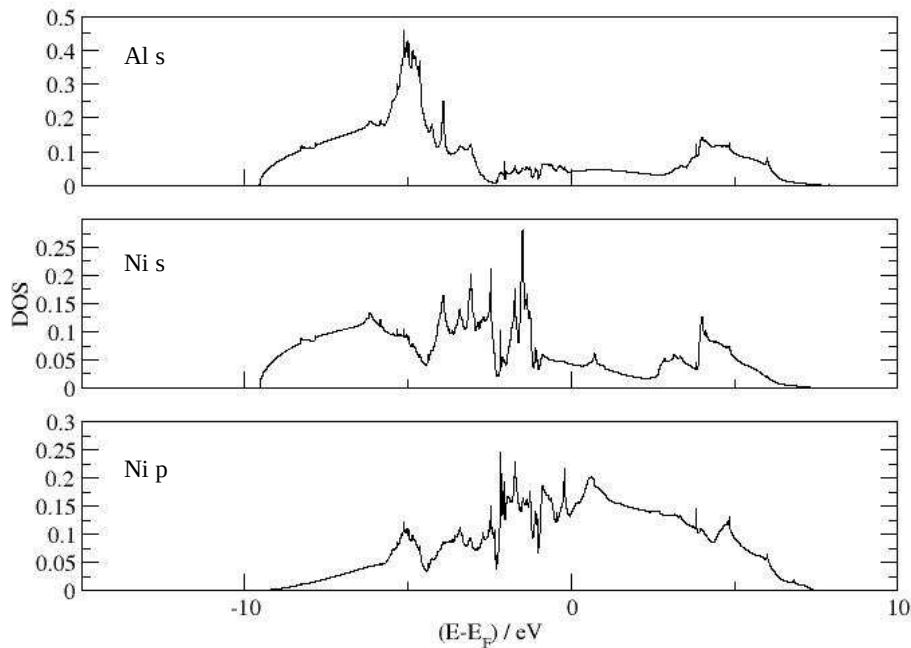


Fig. 34 Local partial densities of states for AlNi from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

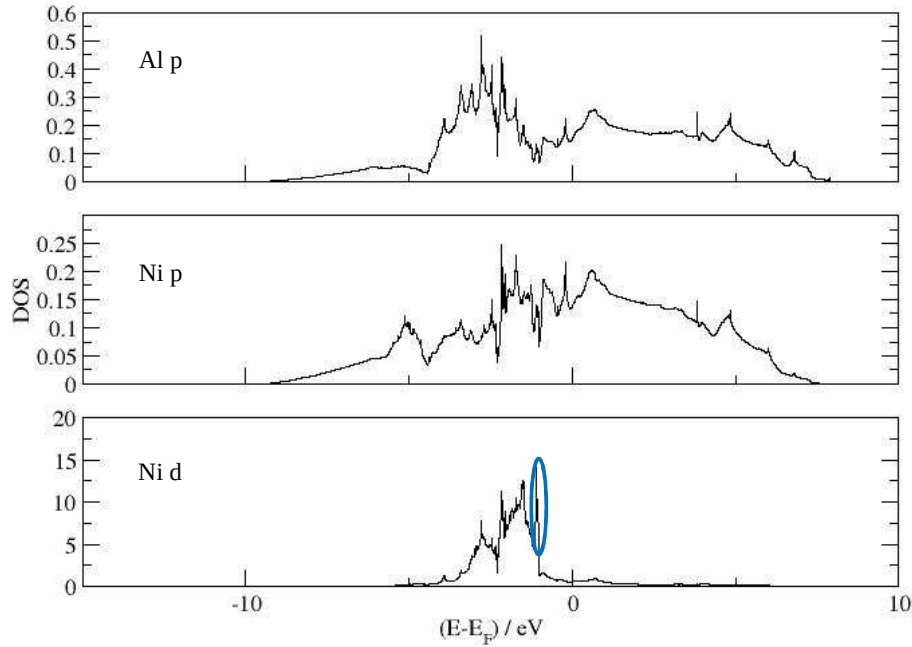


Fig. 35 Local partial densities of states for AlNi from VASP calculations. Units are in (number of states) $\times$ (number of equivalent atoms)/eV/unit cell.

In AlNi₂ the situation is very similar except for the lower energy values of s and p states. The most significant bonding interactions are:

- Al-Ni s - s,p -10 to -5.6 eV
- Al-Ni p - p,d -5.6 to 0 eV
- Ni-Ni d - d about -0.8 eV (main Ni-d peak)

In contrast to AlNi the Ni-d states in AlNi₂ are at higher energies and extend to a wider region, because the Ni concentration is higher and therefore a larger number of Ni-d states are occupied. Furthermore the s band becomes smaller with increasing Ni content, like for the Ge compounds.

A comparison of the Al and Ge containing compounds shows, that in the Ge containing ones the Fermi energy is higher with respect to the lowest valence state, due to an additional valence electron. As shown in Fig. 36 the peak of the Al-s band is at -5 eV in AlNi and for the Ge-s band at -8 eV in GeNi. Likewise the bottom edges of the s bands are at -10 eV for AlNi and at -12 eV for GeNi. Another big difference is the overlap of the s and p states in the Al containing compounds (compare Fig. 36). Band overlap depends on the relative orbital energies of the involved atoms and on the lattice parameters of the structure. The smaller lattice parameters of the Al containing structures

and hence smaller distances between the atoms together with Al-s valence states which are found at higher energies compared to the corresponding Ge states lead to stronger broadening of the Al s and p states and larger overlap of the Al states with the Ni states.

In general the Ni states are very similar in Al and Ge containing compounds, whereas more Al-s states than Ge-s are occupied near the Fermi level.

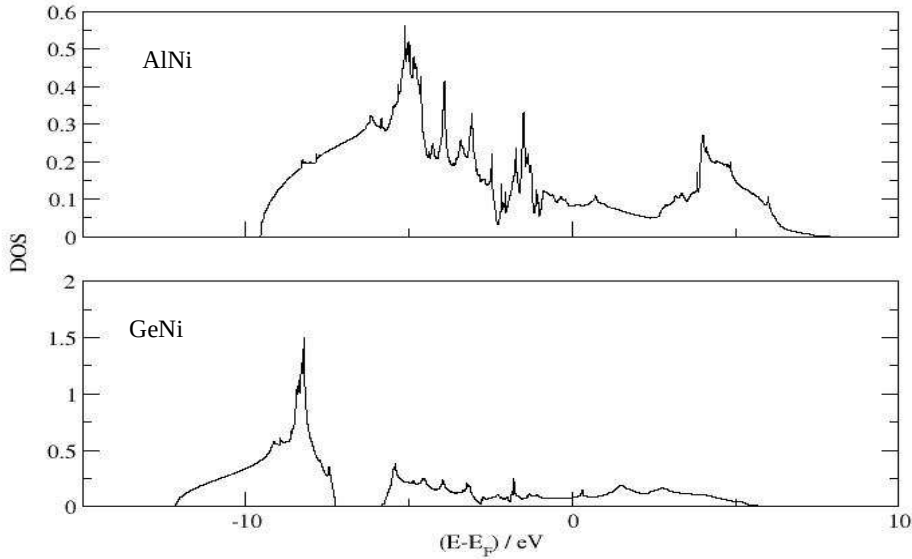


Fig. 36 Partial densities of states for s states from VASP calculations. Units are in (number of states)x(number of equivalent atoms)/eV/unit cell.

As already seen from the calculations of the energies of formation all five calculated structures are negative and could exist naturally. But only $\text{Ge}_{12}\text{Ni}_{19}$ is an experimentally approved structure, whereas for the other four compounds more stable ordered structures exist (see Tab. 7). However, the intermediate solid solution phase with B8 structure is formed in a large area of the ternary phase diagram Al-Ge-Ni.

5.2 The central part of the binary Ge-Ni phase diagram

During the investigations of the ternary phase diagram Al-Ge-Ni some inconsistencies concerning the B8-type structures and superstructures in the binary subsystem Ge-Ni were detected. So it was decided to perform an additional study in this region.

Therefore 14 samples in the range of 33 to 46 at.% Ge, one sample at each atomic per cent, were produced and annealed at 800 °C. The samples were investigated by means

of powder XRD and DTA measurements. The samples with the according XRD results are listed in Tab. 8.

Tab. 8 XRD results for the central part of the Ge-Ni phase diagram

Sample/ nom. comp. /at. %	Phase	XRD
		Lattice parameters
B2 Ge _{38.8} Ni _{61.2}	Ge ₁₂ Ni ₁₉	a=11.6093 Å, b=6.6989 Å, c=10.0338 Å, β=90.014°
B3 Ge _{40.5} Ni _{59.5}	Ge ₁₂ Ni ₁₉ Ge ₃ Ni ₅	a=11.5477 Å, b=6.6664 Å, c=9.9855 Å, β=90.068° a=3.8490 Å, c=4.9925 Å
B4 Ge ₃₃ Ni ₆₇	Ge ₃ Ni ₅ GeNi ₃ GeNi ₂	a=3.9394 Å, c=5.0797 Å a=3.5719 Å a=5.0855 Å, b=3.8368 Å, c=7.2727 Å
B5 Ge ₃₄ Ni ₆₆	Ge ₃ Ni ₅ GeNi ₃ GeNi ₂	a=3.9390 Å, c=5.0811 Å a=3.5718 Å a=5.0871 Å, b=3.8365 Å, c=7.2717 Å
B6 Ge ₃₅ Ni ₆₅	Ge ₃ Ni ₅ GeNi ₂	a=3.9404 Å, c=5.0681 Å a=5.0698 Å, b=3.8416 Å, c=7.2827 Å
B7 Ge ₃₆ Ni ₆₄	Ge ₃ Ni ₅	a=3.9370 Å, c=5.0500 Å
B8 Ge ₃₇ Ni ₆₃	Ge ₃ Ni ₅ ε'-Ge ₃ Ni ₅	a=3.9088 Å, c=5.0427 Å a=11.6881 Å, b=6.7897 Å, c=6.3703 Å, β=52.325°
B9 Ge ₃₈ Ni ₆₂	Ge ₃ Ni ₅ ε'-Ge ₃ Ni ₅	a=3.8857 Å, c=5.0260 Å a=11.6695 Å, b=6.7240 Å, c=6.3440 Å, β=52.389°
B10 Ge ₃₉ Ni ₆₁	Ge ₁₂ Ni ₁₉	a=11.6068 Å, b=6.7006 Å, c=10.0292 Å, β=90.065°
B11 Ge ₄₀ Ni ₆₀	Ge ₁₂ Ni ₁₉ Ge ₃ Ni ₅	a=11.5632 Å, b=6.6766 Å, c=9.9983 Å, β=90.093° a=3.8552 Å, c=4.9988 Å
B12 Ge ₄₁ Ni ₅₉	Ge ₁₂ Ni ₁₉ Ge ₃ Ni ₅	a=11.5363 Å, b=6.6608 Å, c=9.9713 Å, β=90.012° a=3.8457 Å, c=4.9863 Å
B13 Ge ₄₂ Ni ₅₈	Ge ₃ Ni ₅	a=3.8407 Å, c=4.9752 Å
B14 Ge ₄₃ Ni ₅₇	Ge ₃ Ni ₅	a=3.8352 Å, c=4.9665 Å
B15 Ge ₄₄ Ni ₅₆	Ge ₃ Ni ₅ GeNi	a=3.8359 Å, c=4.9670 Å a=5.3866 Å, b=3.4424 Å, c=5.8134 Å
B16 Ge ₄₅ Ni ₅₅	Ge ₃ Ni ₅ GeNi	a=3.8358 Å, c=4.9663 Å a=5.3844 Å, b=3.4417 Å, c=5.8124 Å
B17 Ge ₄₆ Ni ₅₄	Ge ₃ Ni ₅ GeNi	a=3.8359 Å, c=4.9657 Å a=5.3840 Å, b=3.4419 Å, c=5.8126 Å

First of all the XRD measurements revealed no sign of a Ge₂Ni₃ superstructure as proposed by Ellner et al. [34]. Hence, all patterns of the according samples were refined

with a Ni_2In -type structure with vacancies at the position $2d$, as also Ge_3Ni_5 was. The powder pattern of sample B13 at 42 at.% Ge, which contains solely Ge_3Ni_5 is shown in Fig. 37.

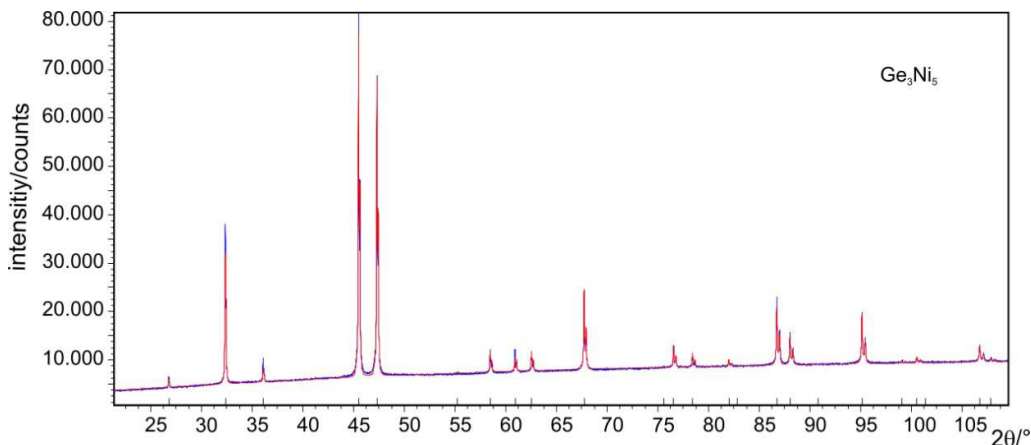


Fig. 37 Powder XRD pattern of sample B13; blue curve – measured; red curve - calculated

The superstructure $\text{Ge}_{12}\text{Ni}_{19}$ was found in the XRD patterns of five annealed samples in the area of 38.8-41 at.% Ge. The lattice parameters of this phase do not show a significant variation, so the homogeneity range is probably rather small.

In some samples the low temperature phases GeNi_2 or $\epsilon\text{-Ge}_3\text{Ni}_5$ were detected. They were most likely formed during quenching of the samples and do not occur at equilibrium conditions. Therefore these phases were not considered for the construction of the phase diagram.

For the determination of reaction temperatures, DTA experiments of all samples were performed. To test the reestablishment of phase equilibria on cooling, two heating/cooling circles of each sample were measured.

The two invariant reactions on the Ge-poor side of the investigated region, $\text{L} \rightleftharpoons \delta\text{Ge}_2\text{Ni}_5 + \epsilon\text{Ge}_3\text{Ni}_5$ at 1099 °C and $\delta\text{Ge}_2\text{Ni}_5 \rightleftharpoons \beta\text{GeNi}_3 + \epsilon\text{Ge}_3\text{Ni}_5$ at 1045 °C, were confirmed, but slightly higher temperatures were obtained. The eutectic reaction took place at 1115 °C and the eutectoid decomposition of $\delta\text{Ge}_2\text{Ni}_5$ at 1056 °C. The peritectic reaction at 850 °C proposed as $\text{L} + \text{Ge}_2\text{Ni}_3 \rightleftharpoons \text{GeNi}$ from Ellner et al. [34] could be confirmed as $\text{L} + \text{Ge}_3\text{Ni}_5 \rightleftharpoons \text{GeNi}$. The phase was renamed to Ge_3Ni_5 , as no sign for a superstructure formation of Ge_2Ni_3 was found. The proposed reaction temperature [32] was reproduced very well with 854 ± 2 °C.

The two invariant reactions $L + \epsilon\text{Ge}_3\text{Ni}_5 \rightleftharpoons \text{Ge}_{12}\text{Ni}_{19}$ at 1050 °C and $L + \text{Ge}_{12}\text{Ni}_{19} \rightleftharpoons \text{Ge}_2\text{Ni}_3$ at 990 °C could not be confirmed. There were no according invariant DTA peaks observable, although the samples B15-B17 (44-46 at.% Ge) show wide peaks at about 920 °C, whereat the peaks in the latter two samples occur only in the first heating curves. At the current state of investigations no definite assigning of these peaks to a phase transition is possible. However, the proposed invariant reactions seem not to be responsible for the observed DTA signals. Further investigations are required to clarify this problem.

The samples B10 and B11 show wide peaks starting at about 800 and 820 °C, respectively. Two additional samples (B2, B3), slightly beneath B10 and B11, were annealed at 550 °C and show also wide peaks in this temperature region, that occur only during the first heating. These peaks are possibly due to the formation/decomposition of $\text{Ge}_{12}\text{Ni}_{19}$, as the according XRD measurements show the diffraction pattern of the superstructure. Due to the observed situation, a congruent decomposition of $\text{Ge}_{12}\text{Ni}_{19}$ seems plausible.

Based on all obtained results a new version of the phase diagram for the region between 33 and 46 at.% Ge including the measured DTA data, was estimated (Fig. 38). Especially the Ni-rich part of this section is not clarified satisfying and further investigations are planned. The expected congruent decomposition behaviour of the superstructure $\text{Ge}_{12}\text{Ni}_{19}$ is drawn with dashed lines.

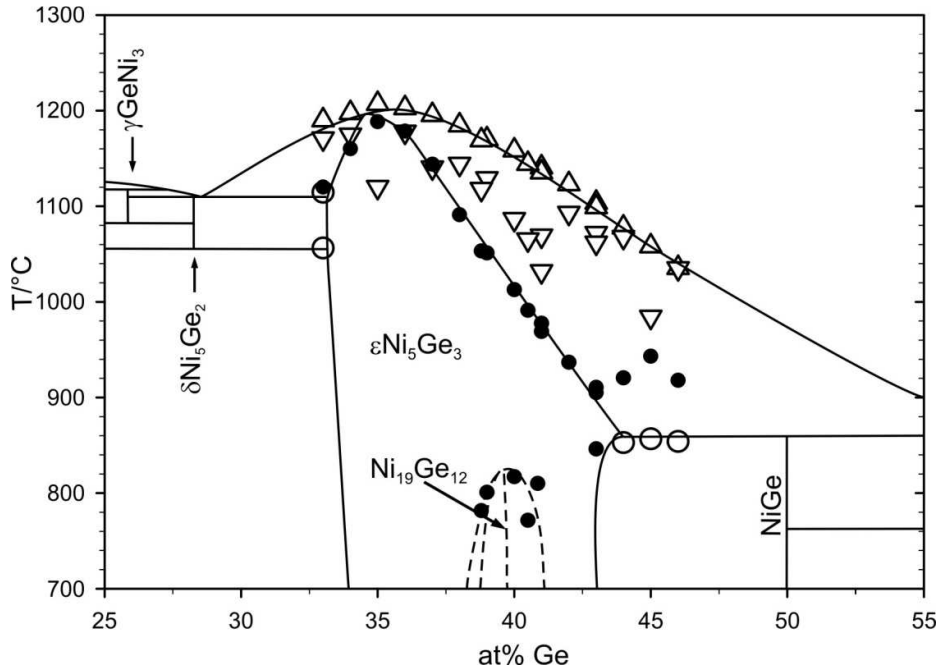


Fig. 38 Partial binary Ge-Ni phase diagram; $\triangle$ liquidus on heating; ∇ liquidus on cooling; $\circ$ invariant thermal effect; $\bullet$ other thermal effect

5.3 Ni-rich part of the Al-Ge-Ni phase diagram

5.3.1 Partial isothermal section at 550 °C

The annealed samples in the Ni-rich part of the Al-Ge-Ni system were analysed by powder XRD and SEM. The obtained results lead to the isothermal section shown in Fig. 39.

Tab. 9 shows the results concerning this section in detail. For each sample all phases found by powder XRD and their related refined lattice parameters as well as the measured phase compositions are given.

The investigations showed that the solid solubility of (AlNi) extends to 61.3 at% Ni, which is slightly more than in the binary at 550 °C. The content of Ge rises from about 2.8 at.% in the Ni-richer part to 6.0 at.% at 51 at.% Ni.

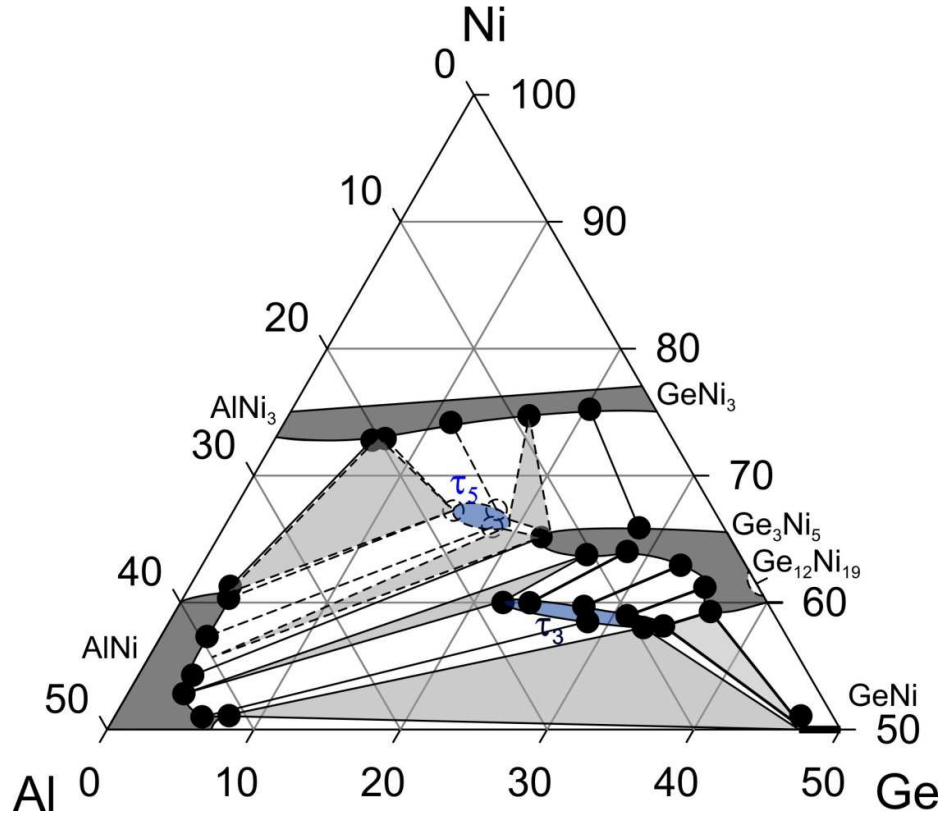


Fig. 39 Partial isothermal section at 550 °C. Black circles: phase compositions measured by EDX; dashed lines: assumed phase fields

Tab. 9 XRD and SEM results for the partial isothermal section at 550 °C

Sample/ nom. comp. /at.%	XRD		SEM		
	Phase	Lattice parameters/Å	Al/at.%	Ge/at.%	Ni/at.%
TR15	(AlNi)	a=2.8747	37.0	2.8	60.2
Al ₃₅ Ge ₅ Ni ₆₀	τ5	unknown structure	17.9	13.9	68.2
TR16	(AlNi)	a=2.8771	39.5	3.2	57.3
Al ₃₀ Ge ₁₀ Ni ₆₀	τ5	unknown structure	15.8	18.3	65.9
TR17	(AlNi)	a=2.8824	42.0	3.7	54.3
Al ₂₅ Ge ₁₅ Ni ₆₀	(Ge ₃ Ni ₅)	a=3.9676, c=4.9981	12.9	22.1	65.4
TR18	τ3	a=7.8780, c=15.0073	16.2	23.8	60.0
Al ₁₅ Ge ₂₅ Ni ₆₀	(Ge ₃ Ni ₅)	a=4.0828, c=4.9981	7.5	28.4	64.0
TR19	τ3	a=7.8674, c=15.0278	12.7	27.7	59.7
Al ₁₀ Ge ₃₀ Ni ₆₀	(Ge ₃ Ni ₅)	a=3.9091, c=5.0178	4.5	32.6	62.9
TR20	(Ge ₃ Ni ₅)	a=3.8860, c=5.0119	3.7	36.2	61.2
Al ₅ Ge ₃₅ Ni ₆₀	τ3	a=7.8496, c=15.0365	10.1	31.0	59.0
TR21	(Al,Ge)Ni ₃	a=3.5747	19.6	7.5	72.9
Al ₂₀ Ge ₁₀ Ni ₇₀	τ5	unknown structure	17.8	14.7	67.5

TR22	(Al,Ge)Ni ₃	a=3.5727	14.5	11.4	75.2
Al ₁₅ Ge ₁₅ Ni ₇₀	τ 5	unknown structure	14.8	17.9	67.3
TR23	(Al,Ge)Ni ₃	a=3.5712	8.9	16.4	74.7
Al ₁₀ Ge ₂₀ Ni ₇₀	τ 5	unknown structure	indistinguishable		
	(Ge ₃ Ni ₅)	a=3.9750, c=5.0107			
TR24	(Al,Ge)Ni ₃	a=3.5704	4.5	20.3	75.2
Al ₅ Ge ₂₅ Ni ₇₀	(Ge ₃ Ni ₅)	a=3.9763, c=5.0330	5.8	28.3	65.9
TR25	(Al,Ge)Ni ₃	a=3.5751	20.6	6.7	72.3
Al ₂₄ Ge ₆ Ni ₇₀	(AlNi)	a=2.8682	36.0	2.8	61.3
TR28	(AlNi)	a=2.8859	43.4	3.8	52.8
Al ₂₀ Ge ₂₀ Ni ₆₀	(Ge ₃ Ni ₅)	a=3.9519, c=5.0045	10.4	25.8	63.8
	τ 3	a=7.8861, c=14.9842	17.9	22.0	60.1
	(Ge ₃ Ni ₅)	a=3.8677, c=4.9963	4.2	36.5	59.3
A1	τ 3	a=7.8043, c=15.0145	8.0	33.9	58.1
Al ₅ Ge ₄₀ Ni ₅₅	GeNi	a=5.3852, b=3.4356, c=5.8140	2.2	47.0	50.9
	τ 3	a=7.8094, c=14.9978	9.4	32.5	58.1
A2	GeNi	a=5.3936, b=3.4304, c=5.8152	1.9	45.8	52.3
Al ₅ Ge ₄₀ Ni ₅₅	(AlNi)	a=2.8809	37.8	11.5	50.6
	τ 3	a=7.8117, c=14.9964	9.6	32.5	58.0
A3	GeNi	a=5.3952, b=3.4324, c=5.8133	1.6	47.0	51.5
Al ₁₅ Ge ₃₀ Ni ₅₅	(AlNi)	a=2.8892	40.7	8.1	51.2
A4	τ 3	a=7.8519, c=15.0133	13.0	28.5	58.5
Al ₂₅ Ge ₂₀ Ni ₅₅	(AlNi)	a=2.8892	43.0	6.0	51.0

However, these results have to be considered with caution, because AlNi has a very high melting point of more than 1600 °C. Therefore, at the here applied annealing temperature diffusion is quite slow. A rule of thumb predicts good diffusion for temperatures above two thirds of the absolute melting temperature. So at 550 °C it is not assured that all samples containing (AlNi) are in equilibrium.

GeNi shows a solubility of 2.2 at.% Al. As this phase is a line compound in the binary and the lattice parameter refinement shows hardly any difference from the original data there was no additional solubility of Ni assumed. Therefore the phase equilibria in the figure are drawn to 50 at.% Ni although the SEM data revealed a small deviation in the Ni content in the ternary.

Based on the SEM measurements it was assumed that the two L1₂ structures, AlNi₃ and β GeNi₃, form a complete solid solution. As the lattice parameters of these two

phases are almost identical, it is difficult to distinguish between them by means of powder XRD.

As for the binary Ge-Ni system, it was not possible to make any distinction between the binary NiAs-type structures Ge_3Ni_5 and Ge_2Ni_3 . Hence, they were both refined by using the Ni_2In structure data with vacancies on the $2d$ position. The binary superstructure $\text{Ge}_{12}\text{Ni}_{19}$ was not found in the ternary system, so a small two phase field was assumed in the isothermal section. The solubility of Al in the B8 structure, Ge_3Ni_5 , varies from about 18 at.% in the Ni-rich part to 4.2 at.% in the Ni-poor part of the phase. Additionally to the solubilities of the binary phases two ternary phases were obtained. The ternary phase τ_3 was first characterised by Reichmann [42], who suggested a crystallisation in the $\text{Ga}_3\text{Ge}_6\text{Ni}_{13}$ structure type, which could be confirmed. It shows a narrow phase field between $\text{Al}_{18}\text{Ge}_{22}\text{Ni}_{60}$ and $\text{Al}_8\text{Ge}_{34}\text{Ni}_{58}$ at 550 °C, that is confirmed by several tie-lines.

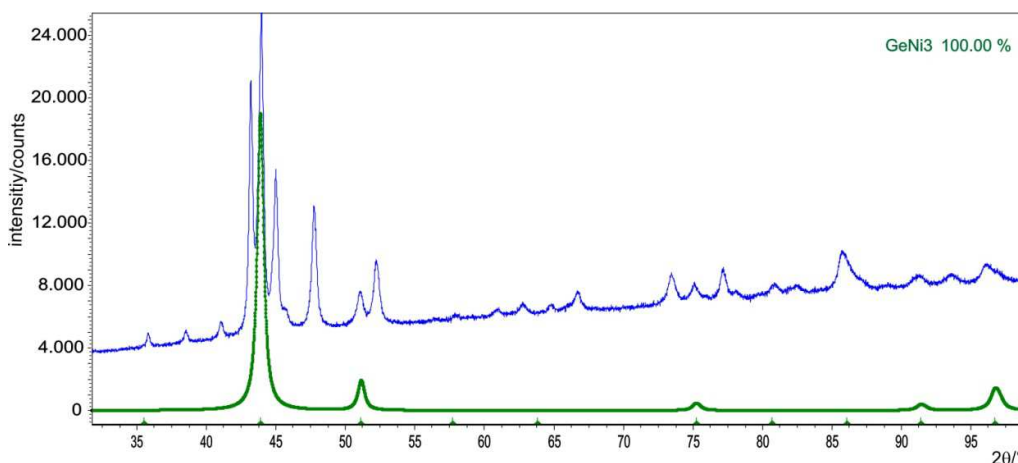


Fig. 40 Powder XRD pattern from sample A5: blue curve - measured

The second ternary phase in this section is new and was not reported up to now. In the following text it will be named τ_5 , as it is the fifth ternary phase in the system Al-Ge-Ni. It appears as small phase field around the composition $\text{Al}_{16}\text{Ge}_{17}\text{Ni}_{67}$. A new ternary phase is suggested because of additional peaks in the diffraction patterns of the samples TR15, TR16, TR21, TR22 and TR23. According to these observations a new sample with the supposed composition of τ_5 was prepared and analysed. The powder pattern shows (Fig. 40) apart from $(\text{Al,Ge})\text{Ni}_3$ several peaks, which could not be related to other structures around. Indexing the powder pattern to reveal the crystal structure

was not successful until now. The pattern resembles that of τ_3 , so the new ternary compound τ_5 might be another superstructure of the NiAs-type. Further investigations are required to determine the crystal structure.

The possibility of τ_5 to be a metastable phase should not be disregarded. The B8-phase has a very large solid solubility at higher temperatures, so it could have been formed in this area at the initiate arc melting step. During the following annealing process the temperature might have been too low to assure good diffusion, triggering a (martensitic) phase transformation to a metastable phase of the same composition. Further investigations would be required to distinguish between these two possibilities. However, DTA experiments for samples containing τ_5 show endothermic decomposition on heating, which points to a stable phase τ_5 .

The mentioned single phase fields are connected via different three phase fields: $\{(AlNi), \tau_3, (Ge_3Ni_5)\}$, $\{GeNi, \tau_3, (Ge_3Ni_5)\}$ and $\{(AlNi), GeNi, \tau_3\}$. The latter two are in disagreement with the phase equilibria Reichmann [42] found at 700 °C, who predicted a three phase field $\{(AlNi), GeNi, (Ge_3Ni_5)\}$.

In this work, both defined three phase fields are confirmed by one sample (A1 and A2). The resulting SEM images and diffraction patterns are shown in Fig. 41 and Fig. 42. The SEM images clearly show two different three phase equilibria. The according phase compositions are given in Tab. 9.

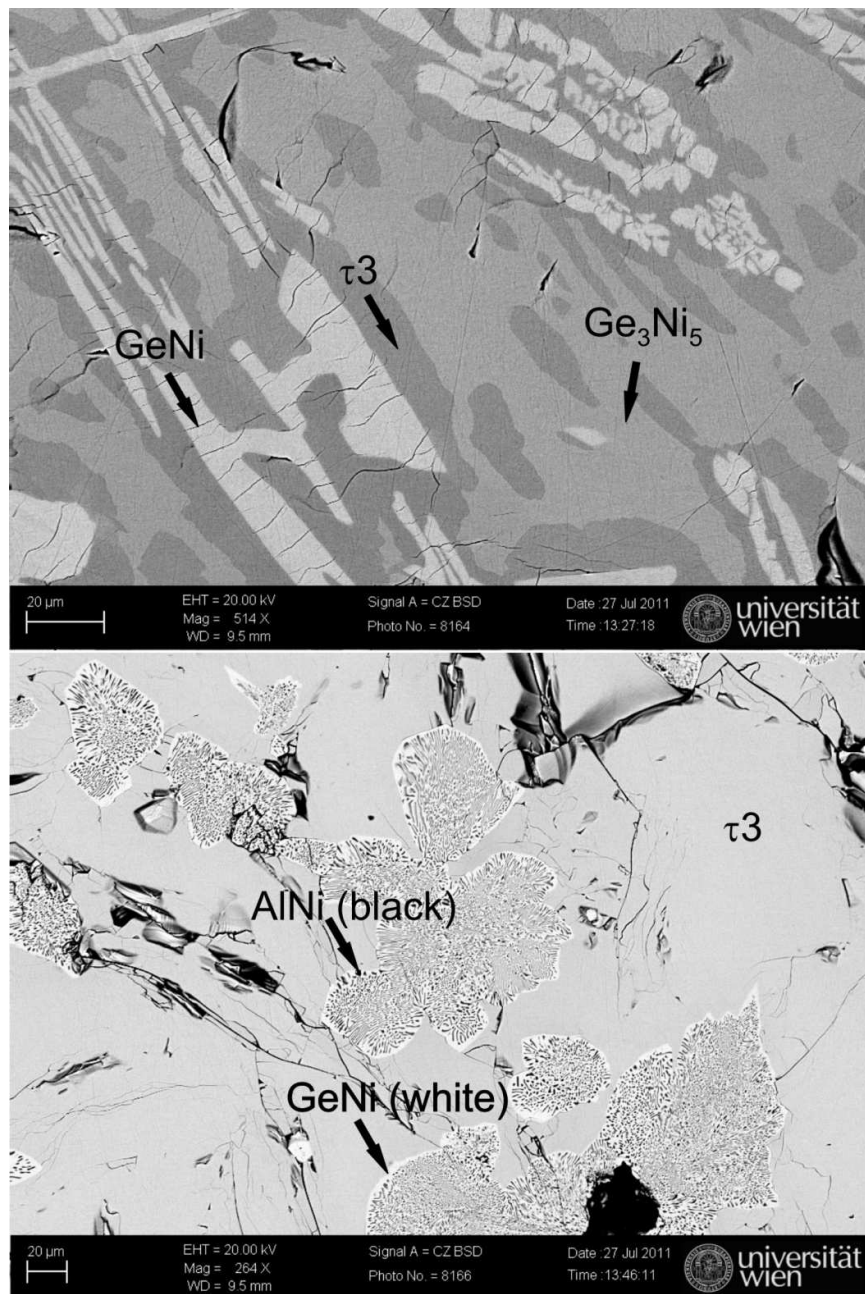


Fig. 41 SEM images of samples A1 (above) and A2 (below)

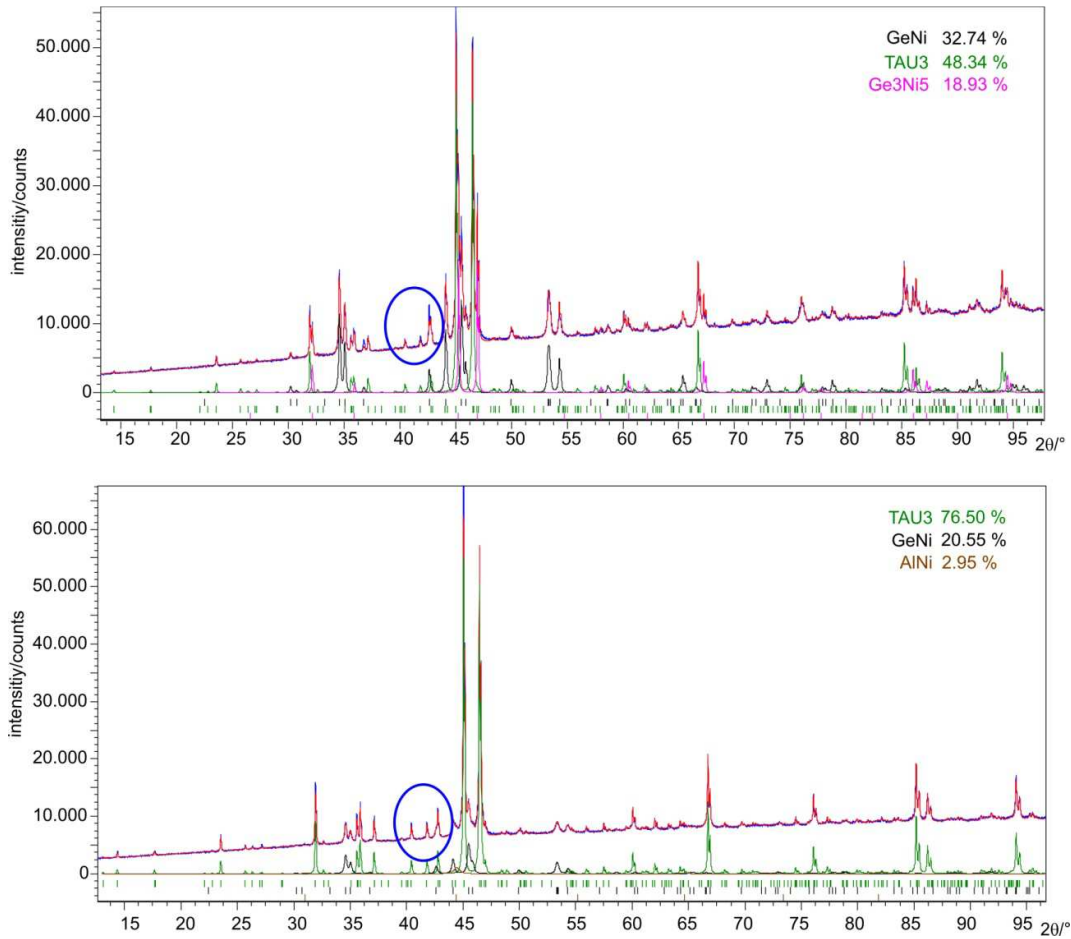


Fig. 42 Powder XRD pattern of sample A1 (above) and A2(below): blue curve – measured; red curve – calculated

To differentiate between the pattern of τ_3 and Ge₃Ni₅, especially if there is only a small amount of τ_3 , is often very difficult due to the similarities of the patterns. But in this case, especially the marked three peaks are a clear indication for τ_3 .

The phase fields {(AlNi), (Al,Ge)Ni₃, τ_5 }, {(AlNi), τ_5 , (Ge₃Ni₅)}, and {(Al,Ge)Ni₃, τ_5 , (Ge₃Ni₅)} are assumed according to the other data.

Dashed tie-lines drawn in the section are assumed as only one phase could be measured appropriately via SEM. An accurate measurement of the second phase was not possible because of too fine phase structures.

5.3.2 Partial isothermal section at 700 °C

The samples annealed at 700 °C, located especially at the area of the NiAs-structures and at the very Ni-rich corner of the system, were characterised by powder X-ray diffraction and scanning electron microscopy. Based on these new investigations and data from Reichmann [42] an isothermal section of the Al-Ge-Ni phase diagram at 700 °C was constructed as shown in Fig. 43.

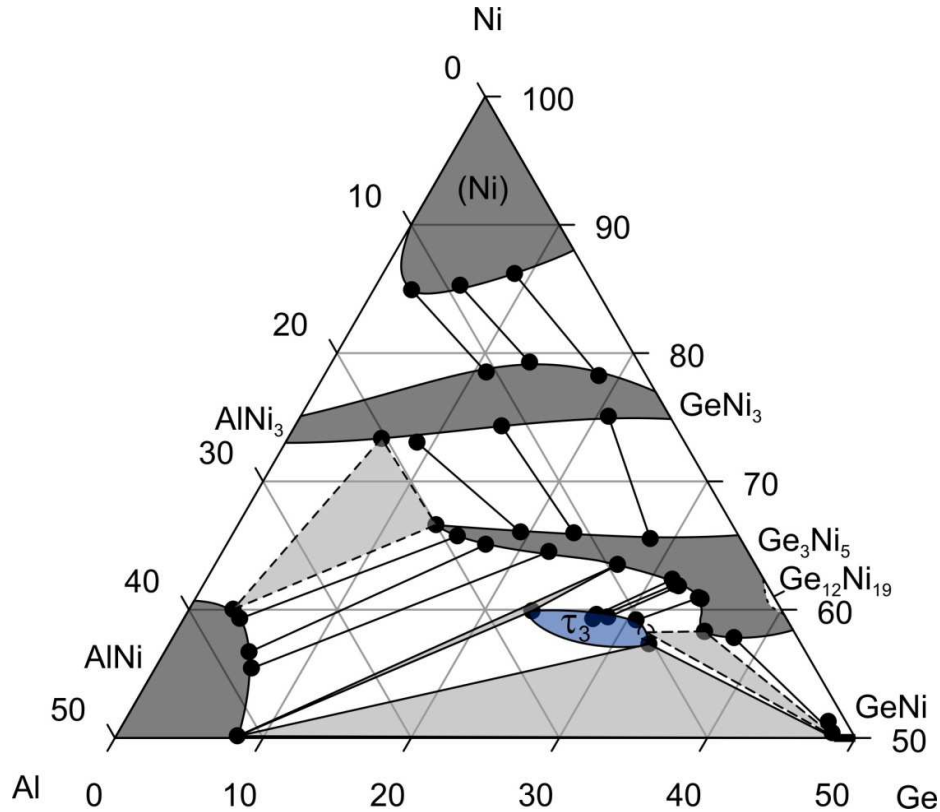


Fig. 43 Partial isothermal section at 700 °C. Black circles: phase compositions measured by EDX; dashed lines: assumed phase fields

Tab. 10 shows the results concerning this section in detail. For each sample all phases found by powder XRD and their related refined lattice parameters as well as the measured phase compositions are given.

The solid solubility of (AlNi) was drawn according to the new results from Reichmann [42]. GeNi shows only a very limited solid solubility of Al. The maximum value measured by SEM was 2.1 at.% Al. As in the isothermal section at 550 °C it was no further solubility of Ni assumed due to no significant changes in the lattice parameters during refinement.

Tab. 10 XRD and SEM results for the partial isothermal section at 700 °C

Sample/ nom. comp. /at.%	Phase	XRD Lattice parameters/Å	SEM		
			Al/at.%	Ge/at.%	Ni/at.%
C1	(Ge ₃ Ni ₅)	a=3.8935, c=4.9899	4.3	37.9	57.8
Al ₂ Ge ₄₅ Ni ₅₃	GeNi	a=5.4848, b=3.3565, c=5.8481	1.2	47.8	51.0
C2	(Ge ₃ Ni ₅)	a=3.8804, c=5.0034	too fine structures to measure accurate		
Al ₅ Ge ₄₀ Ni ₅₅	GeNi	a=5.3823, b=3.4411, c=5.8170			
	τ3	a=7.8398, c=15.0240			
C3	(Ge ₃ Ni ₅)	a=3.8701, c=4.9912	11.6	33.8	54.6
Al ₁₂ Ge ₃₅ Ni ₅₃	GeNi	a=5.3862, b=3.4397, c=5.8139	2.1	46.8	51.1
	(AlNi)	a=2.9475	42.6	7.1	50.3
C8	(Al,Ge)Ni ₃	sample too hard to	10,68	10,84	78,48
Al _{11.25} Ge _{3.75} Ni ₈₀	(Ni)	powder	12,51	2,60	84,89
C9	(Al,Ge)Ni ₃	sample too hard to	7,36	13,38	79,27
Al _{7.5} Ge _{7.5} Ni ₈₀	(Ni)	powder	9,05	5,70	85,25
C10	(Al,Ge)Ni ₃	sample too hard to	3,21	18,58	78,22
Al _{3.75} Ge _{11.25} Ni ₈₀	(Ni)	powder	4,92	8,92	86,16
ZT9	(Ge ₃ Ni ₅)	a=3.9007, c=5.0150	6.0	32.2	61.8
Al ₆ Ge ₃₃ Ni ₆₁	τ3	a=7.8516, c=15.0198	12.0	28.6	59.4
ZT11	(Ge ₃ Ni ₅)	a=3.8759, c=5.0013	too fine structures to measure accurate		
Al ₄ Ge ₃₇ Ni ₅₉	τ3	a=7.7968, c=14.9729			
ZT12	(Ge ₃ Ni ₅)	a=3.8882, c=5.0101	5.1	34.0	60.9
Al ₈ Ge ₃₃ Ni ₅₉	τ3	a=7.8463, c=15.0286	10.2	30.6	59.2
ZT13	(Ge ₃ Ni ₅)	a=3.9288, c=5.0076	6.2	31.5	62.4
Al ₁₂ Ge ₂₉ Ni ₅₉	τ3	a=7.8612, c=15.0229	12.7	27.7	59.6

The formation of a complete solid solution of the L₁₂ phases AlNi₃ and GeNi₃ was confirmed. To analyse the melting behaviour and lattice parameter variations of the solid solution, four samples were produced directly in the phase field. Due to the hardness of the samples the only way to gain powders for XRD measurements was ball milling. The thereby induced stress was successfully reduced by stress annealing of the powders. The obtained patterns shown in Fig. 44 were analysed using Rietveld refinement. Although the structures are equal and the lattice parameter *a* differs only by 0.001 Å, it was possible to estimate the phase composition of a sample. The diffraction patterns show an enlargement of the intensities of the (001), (011) reflexes and also of the tiny reflex (021) to the Al richer side (upwards in Fig. 44). So the occupation of the

Al/Ge mixed position could be refined and the obtained values agree very well with the sample compositions.

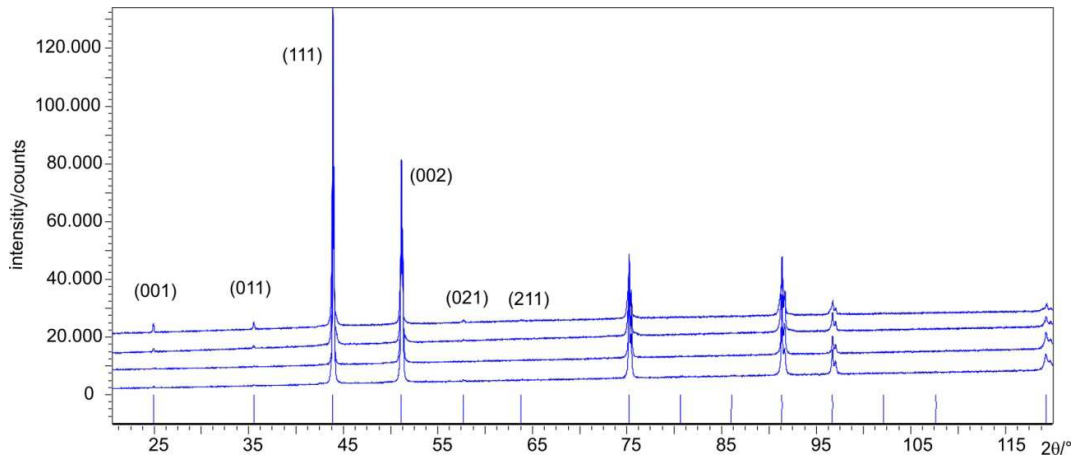


Fig. 44 X-ray diffraction patterns of the samples C4-C7 (C4 at the top)

Analysis of these four samples in the predicted solid solution with SEM showed a separation in Al-richer and Ge-richer parts. Each sample is composed of AlNi_3 and GeNi_3 with a composition of about 5 at.% away from the nominal sample composition. This effect is considered to be due to segregation. AlNi_3 has a much higher melting point than GeNi_3 , so an enrichment of Al in the primary crystals of the ternary solid solution appears to be likely

In the very Ni-rich part of the system three samples were placed to investigate the phase boundaries of (Ni) and the boundary of the $(\text{Al,Ge})\text{Ni}_3$ solid solution at the Ni-rich side. Due to the extreme hardness and ductility of these samples, it was not possible to produce powders for XRD investigation. So only SEM measurements were applied. The resulting tie-lines are shown in the isothermal section. (Ni) solves up to 15 at.% Al and Ge. The phase boundary shows an asymmetric progression with the maximum at the Al-rich side. The solid solution $(\text{Al,Ge})\text{Ni}_3$ shows the biggest extension into the Ni-rich part of the system at around 12 at.% Ge.

Due to the high melting point of Ni (1455 °C) and the in comparison low annealing temperature (700 °C) diffusion might be too slow to reach equilibrium conditions and the here shown relations are valid only for higher temperatures.

To analyse the B8 structures in more detail and to verify the presumed two phase field $\{\text{Ge}_3\text{Ni}_5, \text{Ge}_{12}\text{Ni}_{19}\}$ several samples were prepared in this area according to the isothermal section of Reichmann.

As for 550 °C, there was no signal found for a Ge_2Ni_3 phase, so all patterns in this region were refined using Ni_2In structure data with vacancies at the $2d$ position, as also were used for refinement of Ge_3Ni_5 . The resulting Ge_3Ni_5 phase field has a solid solubility of about 17 at.% Al at the Ni-rich side and 5.2 at.% Al at the Ni-poor side, which is confirmed by one sample that also contains traces of τ_3 . The related tie-line was not drawn because an accurate measurement of the phase composition of τ_3 was not possible due to a very fine microstructure.

The samples ZT7 and ZT8 ($\text{Al}_2\text{Ge}_{37}\text{Ni}_{61}$; $\text{Al}_4\text{Ge}_{35}\text{Ni}_{61}$) revealed the phase $\text{Ge}_{12}\text{Ni}_{19}$ in the diffraction pattern. But examination of these samples via SEM showed only homogeneous surfaces. Therefore it was assumed that only the simple B8 structure existed at the temperature of annealing, and the superstructure crystallised during quenching of the samples. Hence, only a small two-phase field was estimated in the isothermal section.

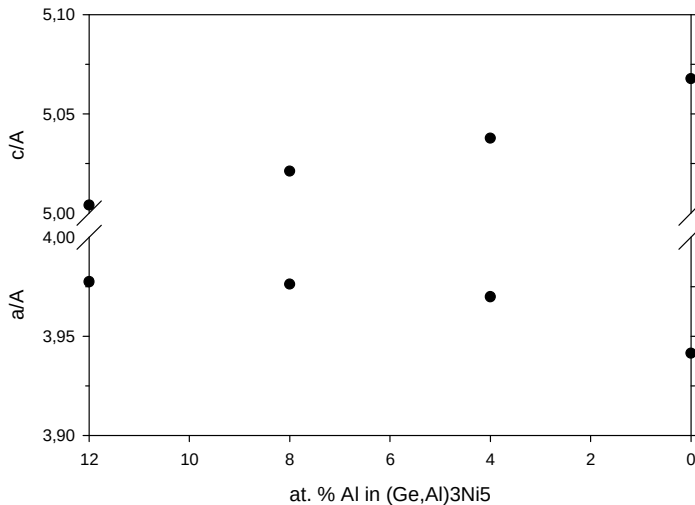


Fig. 45 Lattice parameter variation of Ge_3Ni_5 at 65at.% Ni with increasing Al content

Along the large solid solubility in the Ni-rich part, the lattice parameter variation (Fig. 45) of (Ge_3Ni_5) was investigated. It appears that the lattice parameter a increases with increasing Al content, whereas the lattice parameter c decreases with increasing Al content. Furthermore the refined cell volume shows no significant change with in-

creasing Al content. This is in good agreement with the nearly identical atomic radii of Al (125 pm) and Ge (122 pm) [63].

In addition to the solid solutions of the binary phases, also the ternary phase τ_3 was detected at 700 °C. The phase ranges from 23 to 33 at.% Ge and from 60 to 63 at.% Ni. The τ_5 phase field was not found at 700 °C.

The three phase fields $\{(AlNi), (Al,Ge)Ni_3, (Ge_3Ni_5)\}$ and $\{(AlNi), (Ge_3Ni_5), \tau_3\}$ were drawn in accordance with Reichmann [42]. As in the isothermal section at 550 °C, the other three phase fields involving τ_3 were not confirmed. Instead the three phase fields $\{(AlNi), GeNi, \tau_3\}$ and $\{GeNi, \tau_3; (Ge_3Ni_5)\}$ were found to exist. The field $\{(AlNi), GeNi, \tau_3\}$ was confirmed by XRD and SEM measurements. The SEM image shows the same black and white structure (Fig. 46) as sample A2 from the isothermal section at 550 °C.

The three phase field $\{GeNi, \tau_3; (Ge_3Ni_5)\}$ was approved by XRD measurements. The related SEM image shows extreme fine structures, so that it was impossible to measure them appropriate. Therefore the phase field was drawn with dashed lines in the figure.

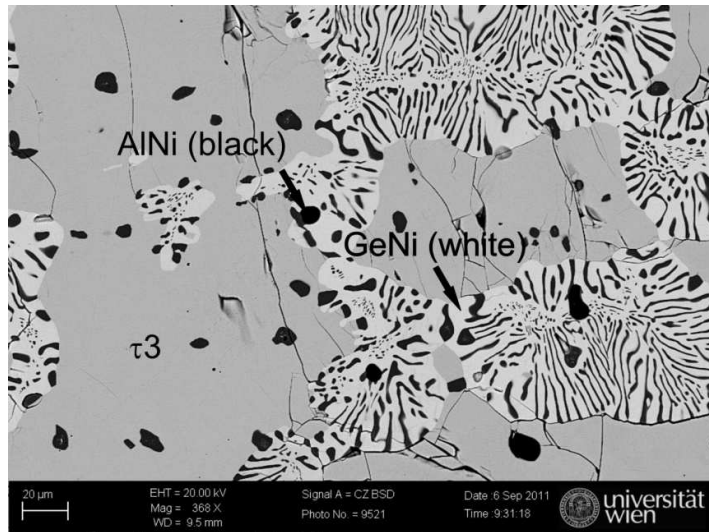


Fig. 46 SEM image of sample C1

5.3.3 Vertical sections

Another important display format of ternary phase diagrams are the so-called isopleths. They are vertical sections through the 3-dimensional phase diagram at definite compositions of one element or at a constant ratio of two elements. They contain information of thermal reactions which are usually determined by dynamic methods like DTA.

Additionally to XRD and SEM measurements, several samples were investigated by means of differential thermal analysis (DTA) to detect phase reactions and their according temperatures at the defined compositions.

Based on all available experimental results and rules for the construction of phase diagrams vertical sections at 55, 60, 70, 75 and 85 at.% Ni were drawn. Furthermore, the Ni-rich part of a vertical section at a constant Al:Ni ratio of 1:3 was determined. The obtained phase equilibria and experimental DTA data are illustrated in the figures 48-53.

For each measured sample two heating- and cooling curves were determined. It was seen, that decomposed ternary compounds during the first heating circle were not formed during cooling, so the according DTA effects did not occur in the second heating and cooling curve. Exemplarily Fig. 47 shows the measured DTA curves of sample A5, which originally contained τ_5 after annealing at 550 °C. It is clearly evident that the peak at about 700 °C, where τ_5 decomposes, appears only in the first heating curve. Therefore a cooling rate of 5 K/min seems too fast to allow the formation of the ternary phases.

The other effects were successfully reproduced in the second DTA circle. So average values were taken for the graphical representation.

Due to supercooling effects the peaks of the cooling curves were not further analysed, except for the liquidi on cooling, which are also presented in the vertical sections.

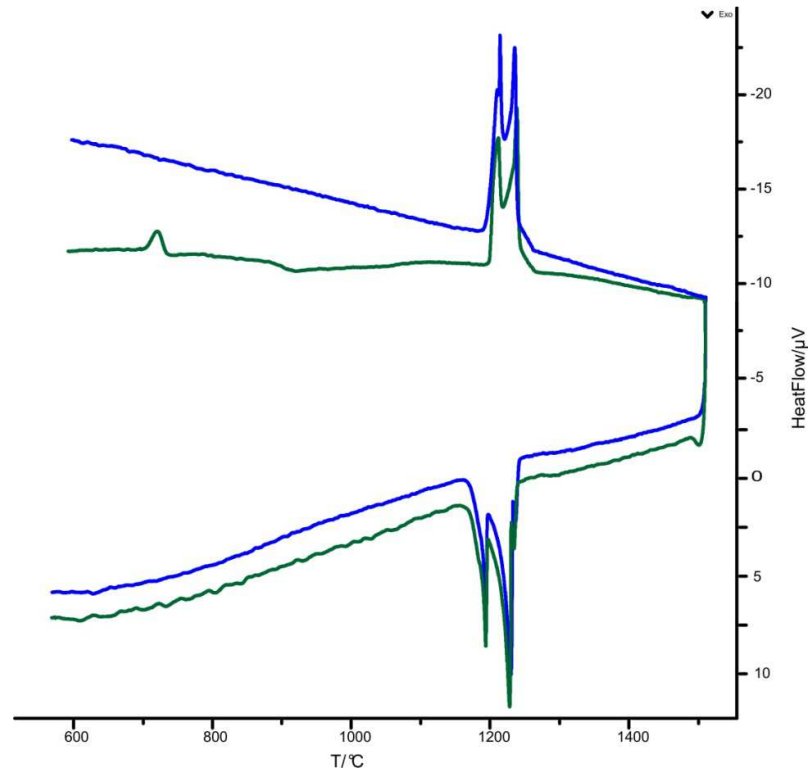


Fig. 47 DTA curves of sample A5; green – 1. circle; blue – 2. circle

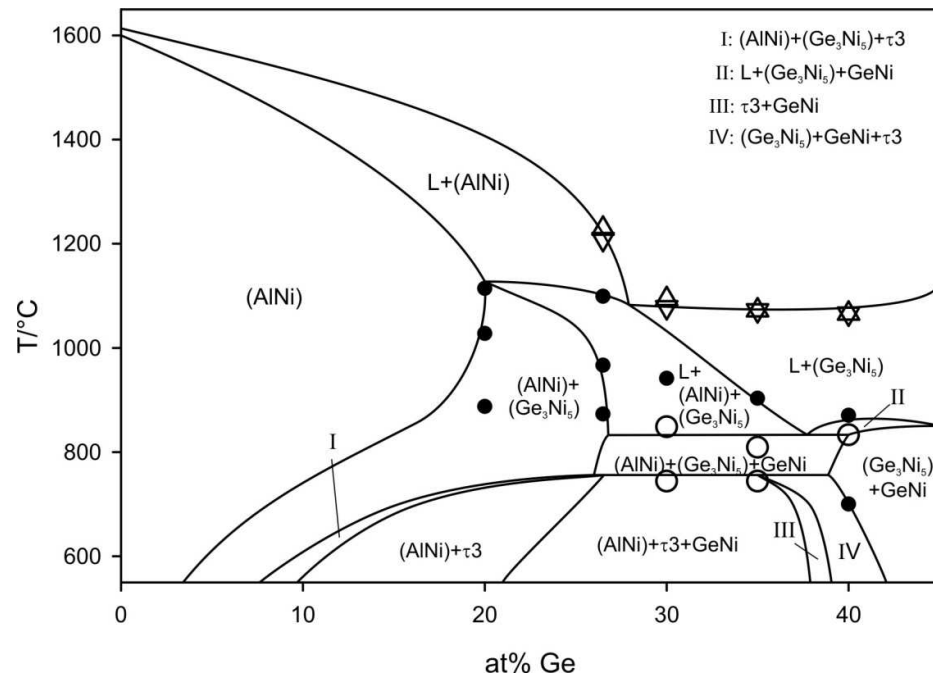


Fig. 48 Vertical section at 55 at.% Ni; $\triangle$ liquidus on heating; ∇ liquidus on cooling; O invariant thermal effect; $\bullet$ other thermal effect

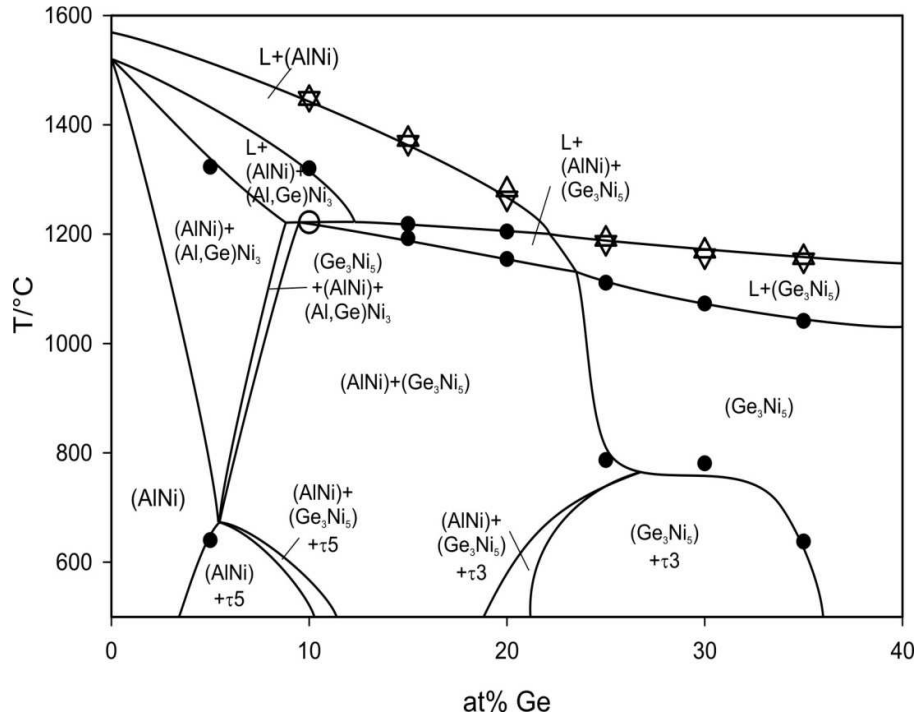


Fig. 49 Vertical section at 60 at.% Ni; $\triangle$ liquidus on heating; ∇ liquidus on cooling; O invariant thermal effect; $\bullet$ other thermal effect

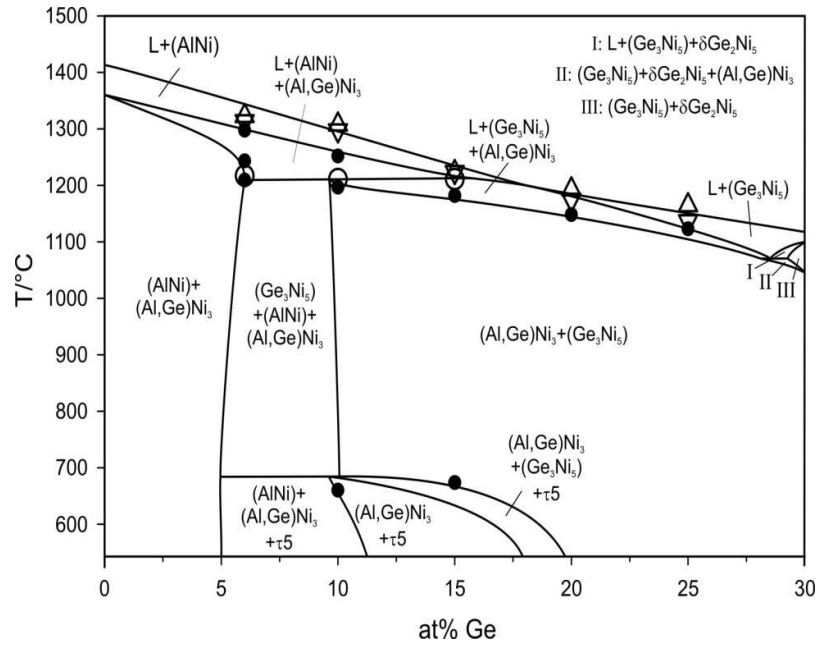


Fig. 50 Vertical section at 70 at.% Ni; $\triangle$ liquidus on heating; ∇ liquidus on cooling; O invariant thermal effect; $\bullet$ other thermal effect

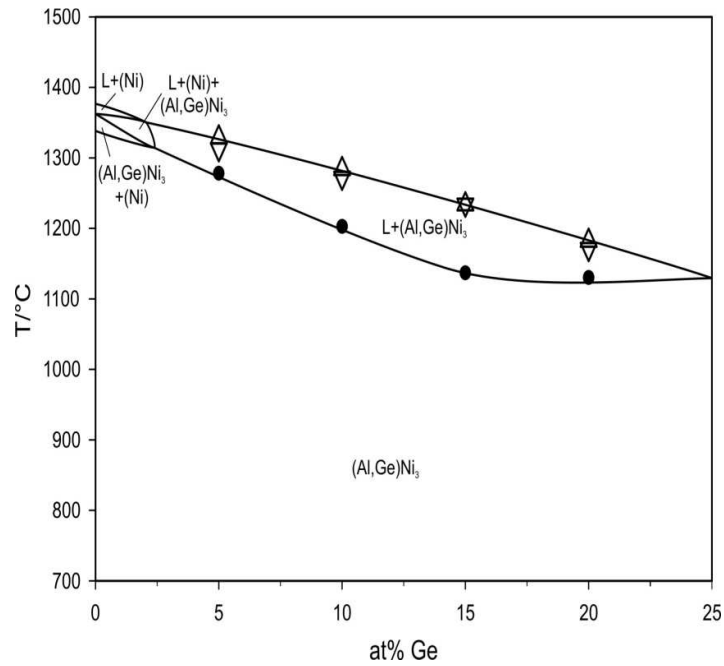


Fig. 51 Vertical section at 75 at.% Ni; $\triangle$ liquidus on heating; ∇ liquidus on cooling; $\circ$ invariant thermal effect; $\bullet$ other thermal effect

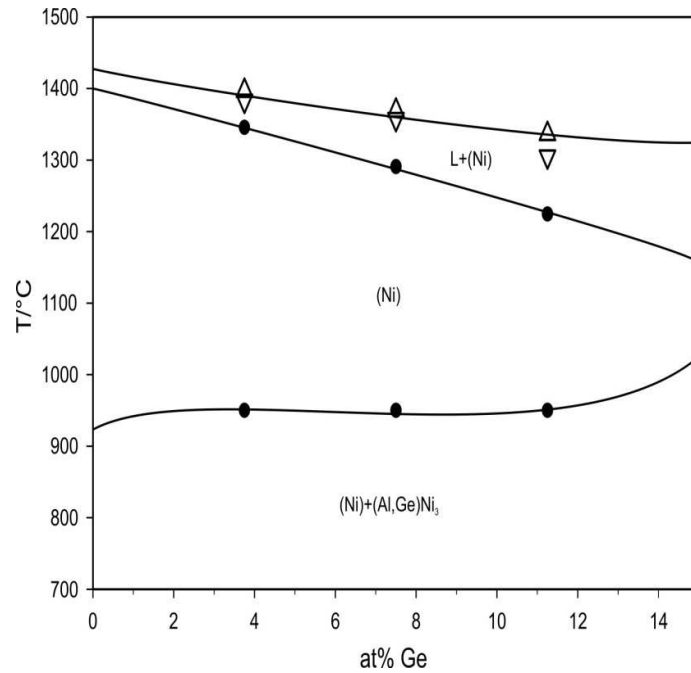


Fig. 52 Vertical section at 85 at.% Ni; $\triangle$ liquidus on heating; ∇ liquidus on cooling; $\circ$ invariant thermal effect; $\bullet$ other thermal effect

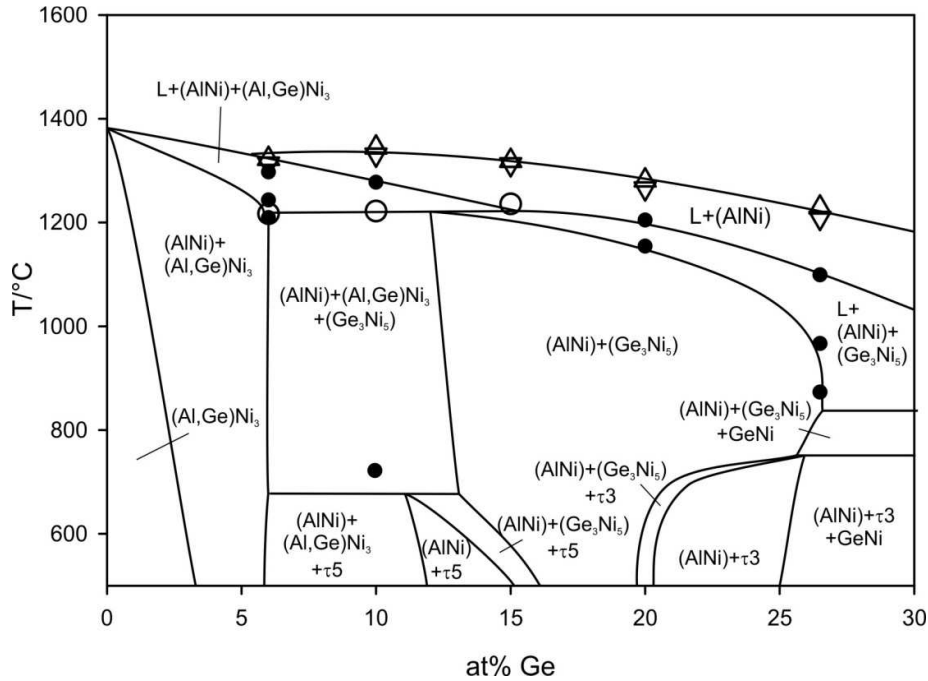


Fig. 53 Partial vertical section at constant Al:Ni ratio of 1:3; $\triangle$ liquidus on heating; ∇ liquidus on cooling; O invariant thermal effect; $\bullet$ other thermal effect

It should be stated, that the evaluation and interpretation of DTA effects as shown in figs. 48-53 was not always straight forward. This may be due to the sluggish reactions (especially for solid state equilibria) and possibly also due to the limits of equilibration at low temperatures. The phase equilibria drawn in the figures are the best compromise to interpret the observed effects in all sections.

Furthermore the melting behaviour of (Ge_3Ni_5) was studied at 65 and 61 at.% Ni up to 12 and 6 at.% Al, respectively (Fig. 54).

The measured samples composed only of the solid solution (Ge_3Ni_5) , were annealed at 700 °C. The vertical sections show no further phase transformation at higher temperatures, apart from the melting. The temperature for the beginning of the melting as well as the temperature where everything becomes liquid increases with increasing Ni content, whereas the beginning of the melting increases much more. Moreover addition of Al slightly increases the melting point of (Ge_3Ni_5) .

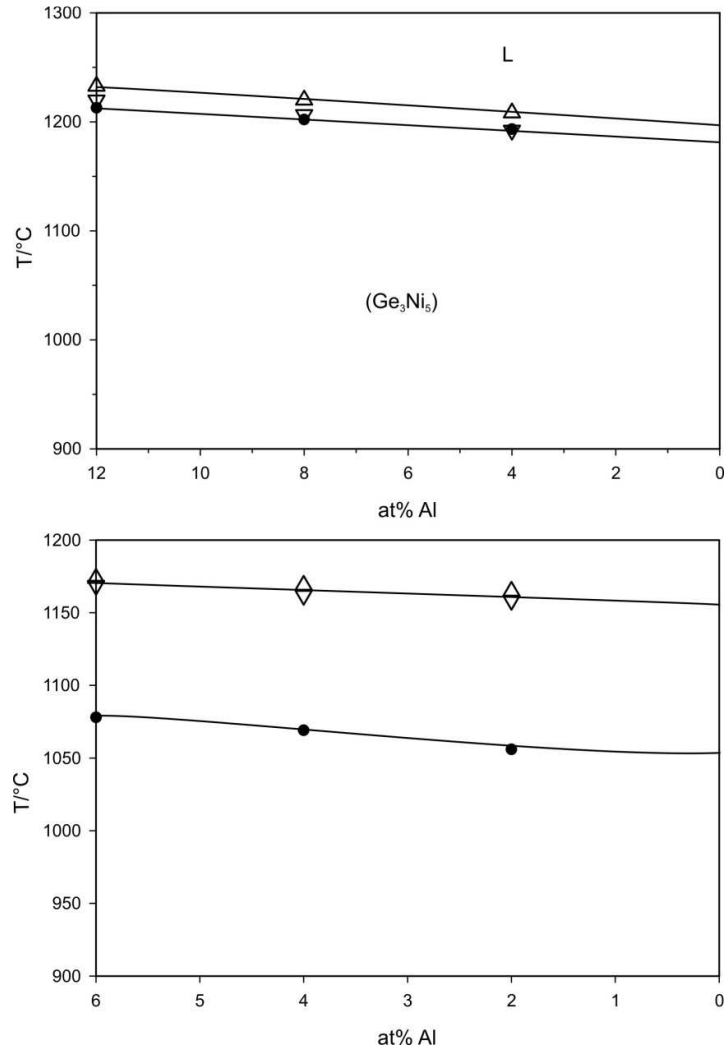


Fig. 54 vertical sections at 65 at.% Ni (above) and 61 at.% Ni (below); $\triangle$ liquidus on heating; ∇ liquidus on cooling; $\bullet$ other thermal effect

5.3.4 Ternary phase reactions

Based on the obtained experimental results, especially the DTA data, six ternary four phase equilibria are proposed. The according reactions are the peritectic decompositions of τ_3 and τ_5 (P3, P4), one ternary peritectic reaction (P1), one ternary transition reaction (U1) and two not clearly definable reactions (EU1) and (PU2). All ternary reactions including estimated phase compositions are listed in Tab. 11.

Tab. 11 Ternary phase reactions

Phase reaction	T/°C	Phase	Composition/at.%		
			Al	Ge	Ni
P1: L + (AlNi) + (Al, Ge)Ni ₃ ⇌ (Ge ₃ Ni ₅)	1215±5	L	14	16	70
		(AlNi)	34	10	56
		(Al, Ge)Ni ₃	21	5	74
		(Ge ₃ Ni ₅)	20	12	68
PU2: L + (Al, Ge)Ni ₃ + (γGeNi ₃) ⇌ (δGe ₂ Ni ₅) or L + (γGeNi ₃) ⇌ (Al, Ge)Ni ₃ + (δGe ₂ Ni ₅)	1082- 1118	L	2	26	72
		(Al, Ge)Ni ₃	3	22	75
		(γGeNi ₃)	0	27	73
		(δGe ₂ Ni ₅)	1	26	73
EU1: L ⇌ (Al, Ge)Ni ₃ + (Ge ₃ Ni ₅) + (δGe ₂ Ni ₅) or L + (Al, Ge)Ni ₃ ⇌ (Ge ₃ Ni ₅) + (δGe ₂ Ni ₅)	1045- 1118	L	2	26	72
		(Al, Ge)Ni ₃	3	22	75
		(Ge ₃ Ni ₅)	30	5	65
		(δGe ₂ Ni ₅)	1	26	73
U1: L + (Ge ₃ Ni ₅) ⇌ (AlNi) + GeNi	833±15	L	2	55	43
		(Ge ₃ Ni ₅)	8	35	57
		(AlNi)	43	7	50
		GeNi	1	49	50
P3: (AlNi) + GeNi + (Ge ₃ Ni ₅) ⇌ τ3	~760	(AlNi)	43	7	50
		GeNi	1	49	50
		(Ge ₃ Ni ₅)	10	33	57
		τ3	12	32	56
P4: (AlNi) + (Al, Ge)Ni ₃ + (Ge ₃ Ni ₅) ⇌ τ5	~680	(AlNi)	7	33	60
		(Al, Ge)Ni ₃	6	20	74
		(Ge ₃ Ni ₅)	15	19	66
		τ5	12	20	68

The DTA data for the peritectic decompositions of the ternary phases were difficult to analyse. As mentioned above, the signals were not only obtained singly in the first heating curves, but also the peaks were often very small and wide. Hence, a definite reaction temperature could not be determined and only an approximate value is given. For the decomposition of τ5 a temperature at about 680 °C is predicted. It has to be considered, that in the isothermal section at 700 °C the ternary phase τ5 was not found, so the reaction has to take place below 700 °C.

The ternary transition reaction U1 was already reported by Reichmann [42] as U7. He predicted a reaction temperature of 844±3 °C, which is slightly higher than the here found value of 833±15 °C, but lies within the error limit.

The ternary peritectic reaction P1 appears in several samples with 60 and 70 at.% Ni, although the reaction temperature differs slightly. So an average value of 1215 ± 5 is stated.

Neither the reaction PU2 nor EU1 were confirmed by experimental results. However, the according reactions have to take place to build a complete reaction scheme. PU2 does not occur in any vertical section. The involved binary reactions allow either a ternary peritectic reaction $L + (Al, Ge)Ni_3 + (\gamma GeNi_3) \rightleftharpoons (\delta Ge_2Ni_5)$ or a ternary transition reaction $L + (\gamma GeNi_3) \rightleftharpoons (Al, Ge)Ni_3 + (\delta Ge_2Ni_5)$ in a temperature range from 1082-1118 °C. Also EU1 is near the binary subsystem Ge-Ni and therefore was not detected in any sample. Either a ternary eutectic reaction $L \rightleftharpoons (Al, Ge)Ni_3 + (Ge_3Ni_5) + (\delta Ge_2Ni_5)$ or a ternary transition reaction $L + (Al, Ge)Ni_3 \rightleftharpoons (Ge_3Ni_5) + (\delta Ge_2Ni_5)$ fits in here. As the reaction was not found in any sample, the reaction temperature was estimated according to the involved binary reactions between 1045 and 1118 °C. Thereby it has to be considered, that the temperature of the reaction EU1 must be below the temperature of the reaction PU2. Additional samples in this narrow region would be necessary to solve these questions.

A reaction scheme of this ternary phase reactions in the Ni-rich part of the Al-Ge-Ni phase diagram is given in Fig. 55 in terms of a Scheil Diagram. The phase field $\{L+(AlNi)+GeNi\}$, coming from the ternary transition reaction U1, is drawn with an open end. This phase field links to the Ni-poor part of the system, which was investigated by Reichmann [42].

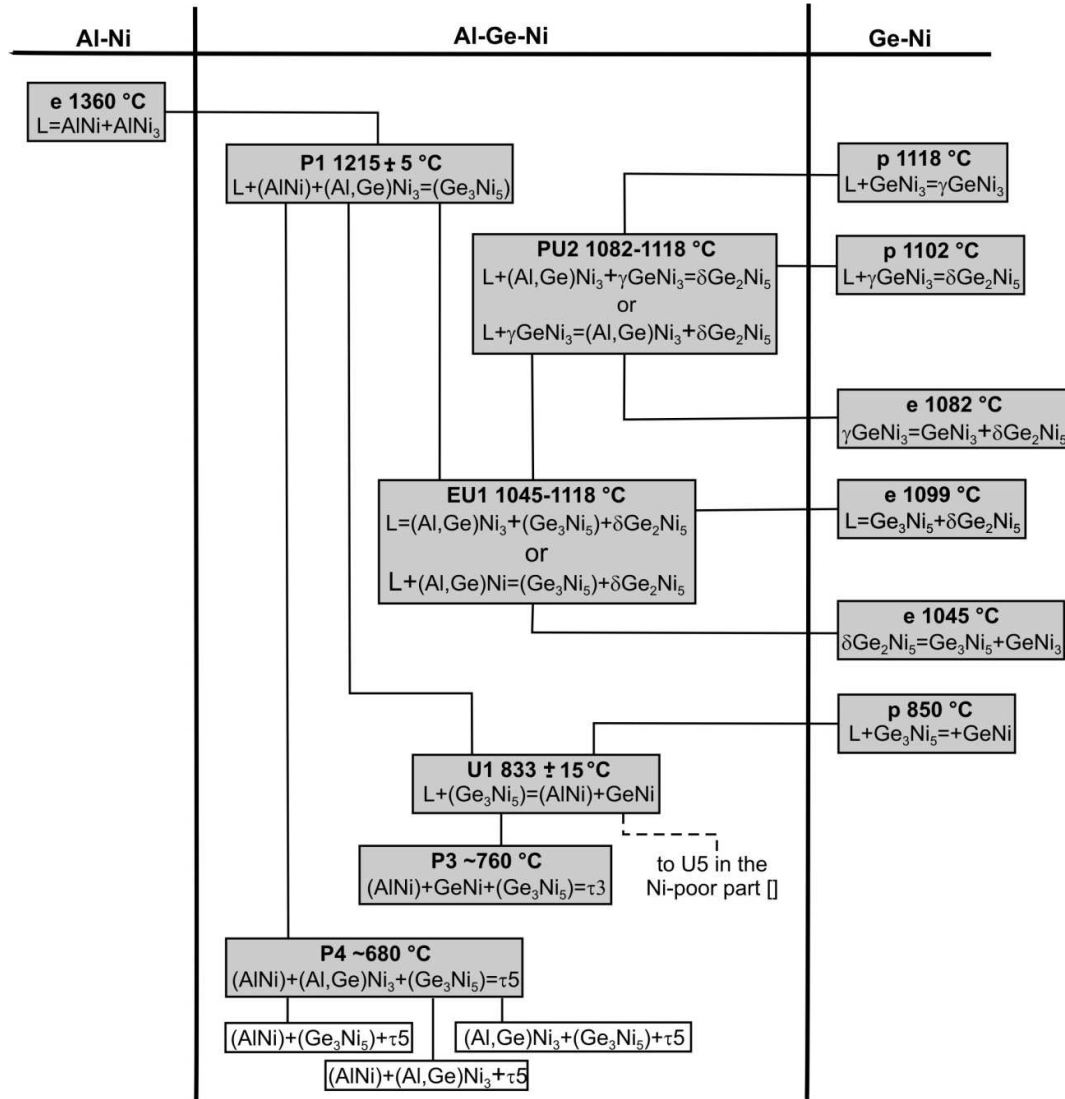


Fig. 55 Partial Scheil Diagram for Al-Ge-Ni

5.3.4 Liquidus surface

A further important way to display a ternary phase diagram, especially the melting behaviour, is a liquidus surface projection. All observed liquidus points from DTA measurements and literature data of the binary subsystems served to obtain a liquidus surface of the Ni-rich part of the Al-Ge-Ni system, shown in Fig. 56.

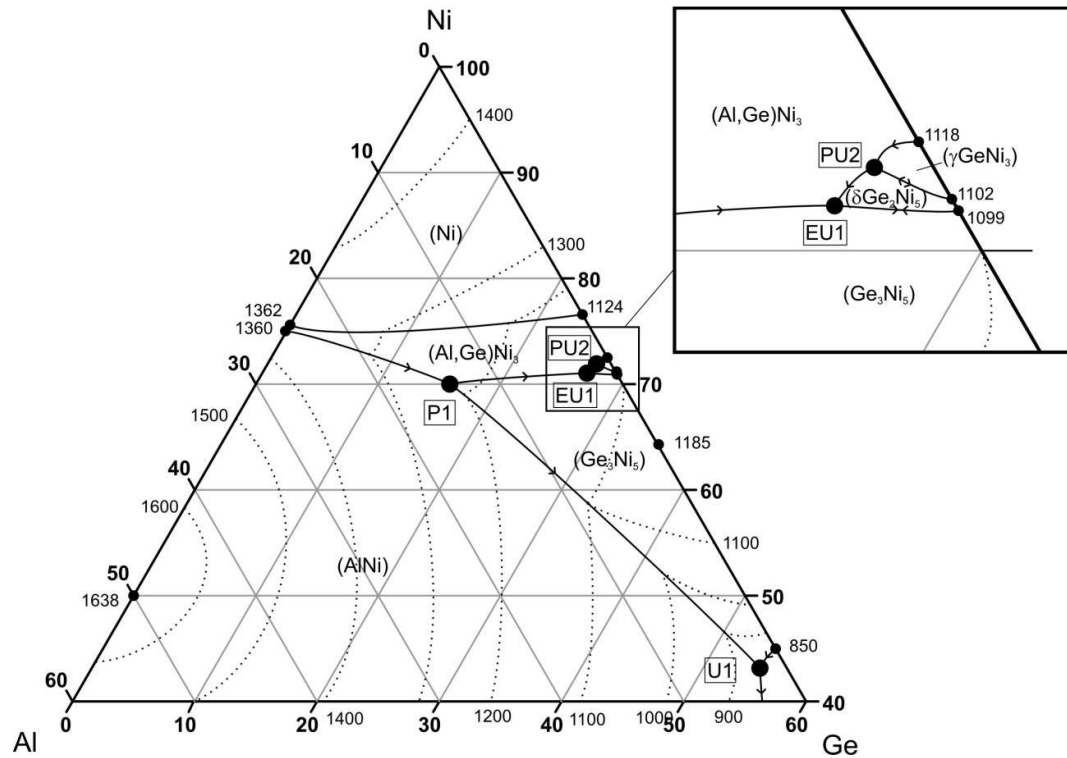


Fig. 56 Partial liquidus surface projection for Al-Ge-Ni

Big circles in the projection indicate the composition of the liquid in the ternary phase reactions, whereas small circles mark the position in the binary invariant reactions. Solid lines correspond to the liquidus valleys, whereas arrows point to lower temperatures. The isotherms between 900 and 1600 °C were drawn as dotted lines.

The liquidus surface reveals a very large primary crystallisation field of (AlNi), that reaches to 2 at.% Al at U1. So in many samples primary crystallisation of (AlNi), as dark spots in the SEM images, was observed (see Fig. 57).

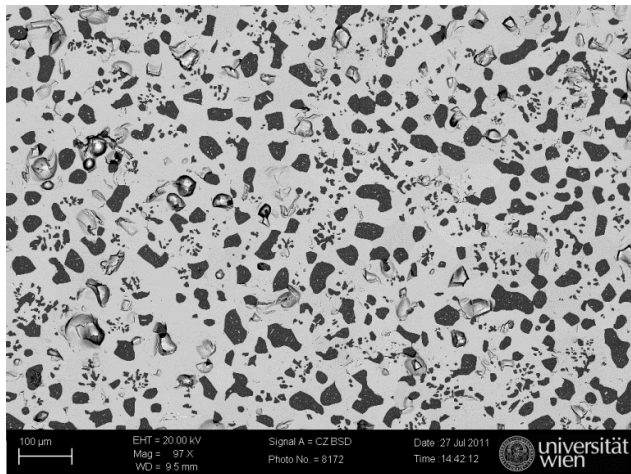


Fig. 57 SEM image of sample TR29

In the Ni-rich part a large primary crystallisation field of (Ni) dominates the projection. The solid solution (Al,Ge)Ni₃ shows a continuous primary crystallisation field that begins very narrow at the Al-rich side and grows wider with increasing Ge content.

The primary crystallisation field of (Ge₃Ni₅) reaches to about 14 at.% Ge at the Ni-rich side and grows smaller with decreasing Ni content.

Furthermore there are the two very small primary crystallisation fields of γ GeNi₃ and δ Ge₂Ni₅, which were not confirmed experimentally. An enlarged picture of the estimated situation is shown in Fig. 56.

6. Summary

The investigation of phase equilibria and structures in binary and ternary alloy systems is the fundamental basis for design and application of complex materials in science and technology.

Within this work the ternary system Al-Ge-Ni, as well as parts of the binary subsystem Ge-Ni were studied. This system is of great interest, because of the widely spread NiAs structure type (Strukturberichtsdesignations B8), which is under investigation for applications in contacts for compound semiconductor devices, insertion electrodes for lithium-ion batteries and joining technologies. Furthermore the Ni-rich Nickel aluminides are used as so-called superalloys in high temperature applications.

The phase diagrams were investigated using powder X-ray diffraction (XRD), light optical microscopy (LOM), scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDX) and differential thermal analyses (DTA). Additionally the structural, energetically and electronic properties of the B8 structures in the systems Al-Ni and Ge-Ni were studied by ab-initio density functional theory calculations.

The ab-initio calculations reveal negative energies of formation for the boundary compounds with NiAs and Ni₂In structure in the two systems, although other more stable compounds exist in the real binary systems. Moreover, bonding interactions in these structures were discussed.

Two partial isothermal sections at 550 °C and 700 °C as well as five vertical sections at 55, 60, 70, 75 and 85 at.% Ni and a partial vertical section at a constant Al:Ni ratio of 1:3 were investigated experimentally. A new ternary phase τ_5 around the composition Al₁₆Ge₁₇Ni₆₇ was found in the isothermal section at 550 °C. The extension, the lattice parameter variation and the melting behaviour of the B8 phase was analysed in detail. Furthermore a liquidus surface projection and a reaction scheme of the Ni-rich part of the system were determined. Altogether, six ternary invariant phase reactions, including three peritectic, one transition and two not clearly referable reactions were discovered.

7. Zusammenfassung

Die Untersuchung von Phasengleichgewichten und Strukturen in binären und ternären Legierungssystemen ist die grundlegende Basis für Design und Anwendung von komplexen Materialien in Wissenschaft und Technik.

In dieser Arbeit wurden das ternäre System Al-Ge-Ni und Teile des binären Subsystems Ge-Ni analysiert. Dieses System ist aufgrund des weit verbreiteten NiAs Strukturtyps (Strukturbericht Designation B8), der in Kontakten in Halbleiterbauteilen, als Elektroden für Lithiumionen Batterien und in Verbindungstechnologien Anwendung finden könnte, interessant. Außerdem werden Ni-reiche Nickelaluminide als sogenannte Superlegierungen für Hochtemperatur Anwendungen gebraucht.

Die Phasendiagramme wurden mittels Pulverröntgendiffraktometrie (XRD), Lichtmikroskopie (LOM), Rasterelektronenmikroskopie (SEM) in Verbindung mit energiedispersiver Röntgenspektroskopie (EDX) sowie Differenzthermoanalyse (DTA) untersucht. Zusätzlich wurden strukturelle, energetische und elektronische Eigenschaften der B8 Strukturen in den Systemen Al-Ni und Ge-Ni mittels ab-initio Rechnungen nach Dichtefunktionaltheorie bestimmt.

Die ab-initio Berechnungen ergaben negative Bildungsenergien für die Randverbindungen mit NiAs- und Ni_2In -Struktur, obgleich andere stabilere Verbindungen in den realen binären Systemen existieren. Weiters wurden auch die Bindungswechselwirkungen in diesen Strukturen untersucht.

Zwei partielle isotherme Schnitte bei 550 und 700 °C, sowie fünf vertikale Schnitte bei 55, 60, 70, 75 und 85 at.% Ni und ein partieller vertikaler Schnitt bei konstantem Al:Ni Verhältnis von 1:3 wurden experimentell bestimmt. Im Bereich der Zusammensetzung $\text{Al}_{16}\text{Ge}_{17}\text{Ni}_{67}$ konnte eine neue ternäre Phase τ_5 im isothermen Schnitt bei 550 °C gefunden werden. Die Ausdehnung, die Variation der Gitterparameter und das Schmelzverhalten der B8 Phase wurden detailliert untersucht.

Weiters wurden eine Liquidusprojektion und ein Reaktionsschema vom Ni-reichen Teil des Systems erstellt. Insgesamt wurden sechs ternäre invariante Reaktionen (3 Peritektika, 1 Übergangsreaktion und zwei nicht genau definierbare Reaktionen) festgestellt.

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List of Publications

1. I. Jandl, K.W. Richter, H. Ipser, Incongruent, time-dependent chemical vapour transport in multi-component systems: A case study in Cr-Ge-Si, Solid State Sci., 13 (2011) 1108-1114.
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