Towards a complete description of aluminium from atomistic modeling

A parameter-free study of hardening precipitates in
Al alloys

Per Harald Ninive
Gjøvik University College

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Acknowledgments

The work on this thesis can be compared to ascending the Galdhøpiggen mountain. The journey is long and tedious, constantly walking uphill, first steeply, then more gently. Lots of small hindrances make you stumble a lot, and once you think you are reaching the summit, another one shows up behind it. The goal is out of sight until you are almost there. But when the highest point is finally reached, you can stop, take a breather, look around, and receive the reward for your hard work. However, while Galdhøpiggen can relatively easily be climbed on your own, the accomplishment of this PhD would have been virtually impossible without help and support from others.

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List of papers

Paper I

P. H. Ninive, A. Strandlie, S. Gulbrandsen-Dahl, W. Lefebvre, C. D. Marioara, S. J. Andersen, J. Friis, R. Holmestad, and O. M. Løvvik
Detailed atomistic insight into the β'' phase in Al-Mg-Si alloys
 Acta Mater. **69**, 126 (2014)

In this paper I made the atomistic precipitate models and performed the DFT simulations.

Paper II

P. H. Ninive, O. M. Løvvik, and A. Strandlie
Density functional study of the β'' phase in Al-Mg-Si alloys
 Metall. Mater. Trans. A **45A**, 2916 (2014)

I performed the DFT simulations, made the following analysis, and wrote the paper.

Paper III

P. H. Ninive, K. E. Moen, A. Strandlie, and O. M. Løvvik
Self-consistent multi-scale model of precipitates in aluminium alloys
 Submitted to Modelling and Simul. Mater. Sci. Eng.

I performed the DFT calculations of the elastic parameters and wrote parts of the paper related to these.

Paper IV

P. H. Ninive, O. M. Løvvik, and A. Strandlie
Density functional study of solute impurity elements in aluminium alloys
 Submitted to Modelling and Simul. Mater. Sci. Eng.

I created the atomistic models, performed the DFT calculations, and wrote the paper.

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Part I

Thesis

Abstract

The increased focus on energy saving, environment and sustainability in modern industry has led to a large interest in strong, light and recyclable materials. Among the most widely applied of these is aluminium.

In order to optimize the mechanical properties, many aluminium alloys undergo heat treatment and aging, during which their hardness is significantly increased. This is due to the formation of nano-scale particles called precipitates. Even though precipitates have been studied for several decades, mostly via electron microscopy, there are still several aspects of them that are not fully understood.

The key to a proper understanding of precipitates lies in a better insight into their physical properties and their interactions with the host metal at atomic scale. In this regard, theoretical studies based on quantum mechanical calculations and atomistic modeling are crucial in order to complement experimental studies, and to make predictions of physical properties of interest. The improved knowledge gained from this can make it possible to design optimized alloys in the future.

Making good theoretical predictions of material properties requires realistic atomistic models, accurate approximations of the electronic structure, and consequently, large amounts of computational power. The constant development of more powerful computers thus entails the ability to run precise calculations on increasingly more comprehensive atomistic models.

This work presents a theoretical study of the β'' phase, which is the major contributor to the precipitation hardening in Al-Mg-Si alloys. Applying density functional theory (DFT) on atomistic models including both the precipitate and the surrounding aluminium matrix provided new insight into the interaction between the precipitates and the aluminium matrix, and an appropriate way in which the chemical composition of the β'' phase could be calculated.

The model allowed for simulation of elastic strain in both the aluminium matrix and in the precipitates due to the lattice mismatch between the aluminium- and the β'' crystal structures. The main results of this research were as follows:

The simulated strain field in the aluminium lattice showed a nearly exponential fall-off as a function of distance from the precipitate interface, and was found to have decreased to below 1% at a distance of 1 nm from the precipitate interface for all of the considered precipitate sizes.

The precipitate structure was found to be contracted near the interfaces, particularly at the corners, while the interior structure was more equilibrium-like.

The thermodynamically favored composition of the β'' unit cells was found to be $\text{Mg}_5\text{Al}_2\text{Si}_4$. This was not in accordance with the most recent observational analysis, which had indicated that $\text{Mg}_4\text{Al}_3\text{Si}_4$ is the correct

composition. The discrepancy was tentatively explained as a result of kinetic barriers during nucleation and growth of the precipitates. Nevertheless, this is a clear confirmation that Al is present in the β'' structure.

Further, it was shown that atomistic models of β'' precipitates can be combined with continuum mechanical models by using calculated elastic constants from the former as input in the latter. The strain field in the aluminium matrix could then be calculated in the continuum mechanical model. It was found to be in very good agreement with that simulated in the atomistic model. Thus, it was demonstrated that a multi-scale study of precipitates based on input from first principles calculations is feasible.

DFT and atomistic modeling were also used to study impurity elements, in the form of substitutional solute atoms, and how they affect aluminium alloys. A correlation was found between the strain field range from the various types of solute atoms and their respective solubilities. Due to its high solubility in Al, the concentration of solute Zn can be very large compared to other typical trace elements, without affecting mechanical properties. On the other hand, solute atoms of most of the other $3d$ metals were found to have a potentially large impact on mechanical properties due to long ranged strain fields.

Chapter 1

Overview: Aluminium alloys and precipitation

Aluminium is one of the most abundant elements in the Earth's crust, and the most abundant metal. However, it has only been in common production since late 19th century, when effective technologies for extracting metallic aluminium from ore were developed [1]. Today aluminium has become the second most produced metal on world basis, exceeded only by iron [2]. Its many beneficial properties, like low weight, high strength and good formability and weldability have made aluminium a very attractive and widely applied material.

Due to the fact that effective and economical methods for producing metallic aluminium were developed relatively late in history, aluminium products have not been in common use for very long compared to other metals, like iron, copper, zinc, lead, silver and gold. However, the last 100 years have seen an almost exponential growth in produced aluminium worldwide, and the demand for aluminium products is still growing.

This is of course much due to the crucial role aluminium came to play in the automotive, aircraft and aerospace industry during the 20th century. It has also found great use in the construction industry due to its durability and anti-corrosive properties. Not only has aluminium gained huge importance in industry, but also in households and in general everyday life.

The growing environmental concerns and the demand for energy efficiency ensures that aluminium will become an even more important material in the future.

1.1 Alloys and applications

Manufactured aluminium products are in almost all cases alloyed, since this greatly improves the mechanical properties of the material. These properties are strongly dependent on which alloying elements are being used. There

Alloy group	Main alloying elements	Applications
1xxx	–	electrical, chemical
2xxx	Cu	aircraft, aerospace
3xxx	Mn	general purpose
4xxx	Si	architectural
5xxx	Mg	architectural, marine constructions
6xxx	Mg, Si	aircraft, boats, automotive parts, etc.
7xxx	Zn, Mg, Cu	aircraft, aerospace, bicycle frames
8xxx	other elements	

Table 1.1: List of the major series of wrought alloys, and some of their applications. The 1xxx-group represents pure aluminium, that is, alloys containing minimum 99% Al, the rest being trace elements.

exists a large number of different aluminium alloys, spanning a wide range of application areas. The most common alloying elements are copper, zinc, magnesium, silicon and manganese. Generally, aluminium alloys are divided into two main categories - wrought and cast alloys. The former constitute the major part of manufactured aluminium. These are given names following a four-number digit scheme, where the first digit indicates the major alloying element(s). The second digit indicates if the alloy is original (0) or modified (1-9). The last two digits serve to identify the different alloys in the group. The major groups of wrought aluminium alloys are listed in Table 1.1.

A more detailed overview of wrought alloys and their compositions can be found in ref. [3]. Cast alloys are designated by a similar digit system.

In addition, there is also a temper designation system, that is, a system that indicates which types of treatments (annealing, aging, straining, etc.) the different alloys have been exposed to. The two main categories are cold-worked alloys, designated by an H, and heat-treated alloys, designated by a T. A digit is usually added after the H or T for further specifications. More details on these can be found in ref. [3]. Of particular relevance for this work are alloys designated T6, which indicates that they have been solution heat-treated followed by an artificial aging.

The search for further applications of aluminium is an ongoing and active field of study. The high strength-to-weight ratio makes the use of aluminium alloys desirable for energy saving purposes. Engineers and materials researchers are also working hard on finding additional new application areas.

One example is aluminium-lithium (Al-Li) alloys. Lithium is the lightest elemental metal, thus making the interest in developing commercially applicable Al-Li alloys large. Due to their low densities they are particularly attractive for the aerospace and the aircraft industry. The weight reduction in Al-Li alloys leads to greatly reduced fuel costs and increased performance. Some examples of current uses are in jetliner airframes, launch vehicles and

in space shuttle fuel tanks.

Aluminium also has great potential for further use in transport vehicles. Its great weight reduction as compared to iron or copper leads to great reductions in fuel consumption and greenhouse gas emissions. It is thus desirable to extend its use even more in the automotive industry. The challenge is then to optimize or design alloys such that they satisfy required performance criteria (mechanical strength, stiffness, etc.) for various vehicle components.

Another focus area for future use of aluminium is in buildings. The light weight and high strength makes aluminium a well-suited material for building constructions. E.g. usage of aluminium sheets as cladding is advantageous since it does not require a heavy substructure. Also, the high flexibility and formability have made aluminium very attractive for architectural purposes, offering an almost infinite range of potential designs.

Aluminium is also considered for extended use in the offshore industry [4]. This is particularly due to its corrosion resistance and its light weight, making it desirable as a replacement to steel in marine environment.

These are only a few examples of future prospects of aluminium usage. There are also several new usage areas being considered, like e.g. in solar panel frames and power cables.

In order to fully exploit the many advantages of a more extensive usage of aluminium in the future, research on aluminium alloys and their material properties is currently more important than ever.

1.1.1 Recycling

Recycling of aluminium has become a major aspect of the aluminium industry during the latter decades due to growing environmental and economic concerns.

Compared with primary aluminium production, the production of recycled aluminium only needs about 5% of the energy. Currently, more than a third of the aluminium produced globally originates from old, traded and new scrap [5].

Aluminium scrap can, if treated and sorted appropriately, be recycled for use in almost all aluminium applications. Also, since the crystal structure of Al is unaffected by melting, it can in principle be recycled infinitely.

Unavoidably, recycled aluminium alloys will contain increased amounts of impurities. As a consequence of the increased focus on recycling, the behavior of impurities in Al has become a highly relevant field of research. Particularly, it is important to gain knowledge on how and to which degree the mechanical properties of recycled aluminium are affected by the increased amount of impurities. How large concentrations of different types of impurities can be allowed in the recycled material without weakening its desired mechanical properties, and thus, the performance of the products? Undoubtedly, much insight can be provided by combining experiments and

Figure 1.1: Evolution of production of primary and recycled Al since 1950. Figure taken from "Global Aluminium Recycling: A Cornerstone of Sustainable Development" [5].

higher-scale modeling with atomic scale theoretical modeling and calculations, especially on smaller impurities. E.g., aluminium containing substitutional solute atoms of any element can easily be modeled. This is discussed closer in Chapter 3.

1.2 Precipitation hardening in Al-Mg-Si alloys

The most versatile group of aluminium alloys are the 6xxx series alloys, in which magnesium and silicon are the major alloying elements, henceforth referred to as Al-Mg-Si alloys. The Mg- and Si contents are typically in the range 0.5 - 1 wt%. These alloys constitute the majority of the extruded aluminium products in Western Europe, and are used in a large variety of applications. Some examples are aircraft structures, boats, automotive parts, electronic components, architectural structures and high strength structural applications [1].

Al-Mg-Si alloys have been a subject of great interest and extensive study due to the tremendous increase in strength and hardness obtained during precipitation hardening.

The alloys are normally extruded at temperatures of 400-500 °C, followed by cooling to room temperature. During the extrusion the alloying elements become dissolved in the Al matrix. A rapid cooling after extrusion provides optimal conditions for precipitation since the alloy then will contain a supersaturated solid solution (SSSS) of Mg and Si, and also have a high vacancy concentration. The solutes will then start clustering as the alloy is naturally aged at room temperature.

After storage at room temperature for typically a few hours, Al-Mg-Si alloys undergo a final heat treatment, also called artificial aging. This leads to a large increase in the hardness of the alloy. Optimal strength is reached

Phase	Shape	Crystal structure	Composition	Ref.
GP-zones	needle	monoclinic	AlMg ₄ Si ₆	[10, 11]
	plate	cubic	Mg:Si=1	[12]
β''	needle	monoclinic	Mg ₅ Si ₆	[7]
			Mg ₅ Al ₂ Si ₄	[13]
			Mg ₄ Al ₃ Si ₄	[14]
β'	rod	hexagonal	Mg ₉ Si ₅	[15]
U1 (Type A)	needle	hexagonal	Al:Mg:Si = 4:1:5	[16]
		trigonal	MgAl ₂ Si ₂	[17, 18]
U2 (Type B)	needle	orthorombic	Mg ₄ Al ₄ Si ₄	[17, 19]
B' (Type C)	lath	hexagonal	Mg:Si < 1	[6, 16]
			Mg ₉ Al ₃ Si ₇	[20]
β	plate	cubic	Mg ₂ Si	[21]

Table 1.2: Overview of reported precipitate phases in Al-Mg-Si alloys.

for a heat treatment duration of 4 to 8 hours, in the temperature range 150-200°C.

The precipitate evolution sequence in Al-Mg-Si alloys during natural and artificial aging is agreed to be [6, 7]

$$\text{SSSS} \rightarrow \text{GP-zones} \rightarrow \beta'' \rightarrow \beta', \text{U1, U2, B'} \rightarrow \beta.$$

Reported shapes, crystal structures and chemical compositions of the various phases are summarized in Table 1.2.

The evolution of the precipitate phases in Al-Mg-Si alloys is a complex process that is governed by thermokinetics. What happens in the early precipitation stages strongly influences the evolution of later stage precipitates. Their size and the density are influenced by aging time and temperature in addition to the concentration of quenched-in vacancies in the alloy before the artificial aging [8]. A high concentration of vacancies will lead to a rapid precipitation, since the diffusion speed is proportional to the vacancy concentration.

The hardness has been tested for different heat treatment durations. Maximum strength was found for alloys containing a high concentration of the β'' phase [9]. It is thus agreed that β'' is the most effective hardening precipitate in Al-Mg-Si alloys.

The microstructure of the precipitates is influenced by the Mg-to-Si ratio in the alloy. The precipitates in Si-rich alloys have been found to have a finer microstructure than in Mg-rich alloys [22]. A high hardness is then

produced despite a low volume fraction of each precipitate. This is because the fine structure allows for a higher density of precipitates. Mg-rich alloys on the other hand, have been found to produce a generally coarser precipitate structure. Nevertheless, β'' is responsible for hardening in both cases.

Overaging will lead to coarsening of the alloy and formation of larger precipitate structures, like β' and β , and a greatly reduced number density of hardening precipitates [16, 22].

1.3 Properties of the β'' phase

The β'' precipitates typically have lengths of about 50 nm and cross sections of about $4 \times 4 \text{ nm}^2$. The crystal structure of β'' has earlier been determined by use of transmission electron microscopy (TEM) and electron diffraction [7]. It will be presented in more detail in Chapter 3.

The precipitates are coherent with the aluminium matrix in the longitudinal direction, while coherency strains arise in the cross sectional plane due to periodic mismatch between the crystal structures of β'' and aluminium. These strain fields pin dislocations, thus hindering them to spread throughout the matrix.

It has proven to be a more difficult task to determine the chemical composition of β'' . For a long time it was believed to be Mg_5Si_6 , since this was indicated by both TEM and energy dispersive X-ray spectroscopy (EDS) measurements. This was also supported by the indication of the presence of a Si backbone structure that was believed to be preserved throughout the earliest precipitate phases [11, 23]. However, the possibility of the presence of aluminium in the structure could not be entirely excluded. A more recent study of the β'' structure combining atom probe tomography (APT) and DFT [13] showed that aluminium is indeed likely to be present in β'' . The formation enthalpies of several various theoretical β'' compositions were calculated, and a minimum was found for the $\text{Mg}_5\text{Al}_2\text{Si}_4$ composition. This was in good agreement with the APT studies which had indicated that the structure contained about 20% aluminium.

These results were in conflict with the earlier assumptions of the silicon backbone structure, which cannot exist if two of the Si-atoms in the β'' unit cell are replaced by Al. Earlier DFT studies of β'' had not considered the possibility of Al present at any of the Si sites. It had been believed that the larger metallic radius of Al as compared to Si would make it unlikely for Al atoms to be situated at any of the Si atomic sites [13]. A third composition, $\text{Mg}_4\text{Al}_3\text{Si}_4$, was reported from high angle annular dark field scanning TEM (HAADF-STEM) investigations presented in Paper I [14].

The composition of β'' is one of the main subjects of the present work. A more exact knowledge of the precipitate composition can contribute to the optimization of the amount of alloying elements in Al-Mg-Si alloys, and

thus to the performance of the alloys. A closer description of the theoretical framework and the atomistic models of the β'' -Al system used in this work follows in chapters 2 and 3.

1.4 Microscopy studies of precipitates

The major part of the knowledge that has been obtained about β'' (and most other precipitate types) comes from observational studies. In this section, a brief presentation of some of the most important observational techniques that are or have been used in studies of precipitates is given.

The first studies of precipitates in aged Al-Mg-Si alloys were performed via X-ray diffraction methods. These techniques employ elastic scattering of incident X-ray beams from the electrons in the crystal structure. Due to the periodicity of the crystal, a regular pattern is reflected and a 3-dimensional image of the electron density can be produced. This is then used to determine the mean positions of the atoms, as well as chemical bonds. Geisler et al. [25] and Guinier et al. [26] applied a X-ray diffraction technique that made it possible to study some of the smaller precipitate types in Al-Mg-Si alloys. The study of so-called Laue pattern zones of alloys aged at 200°C indicated that small needle-shaped particles having dimensions of approximately $2 \times 2 \times 10 \text{ nm}^3$, were formed in the alloys. These particles were subsequently named Guinier-Preston (GP) zones. It was also found that further aging led to formation of thicker rods (β') and plate-shaped particles (β), the latter known to have the composition Mg_2Si . It was then assumed that the other reported phases also had this composition.

However, for more comprehensive investigations of precipitates (like studies of crystal structures and chemical compositions), X-ray diffraction is of limited use. Due to the interruption of the periodicity, the diffraction peaks (and thus, the images) easily get blurred.

At the present, observational studies of precipitates are most commonly performed by use of various transmission electron microscopy techniques. Generally, in TEM electron beams are first accelerated using high voltages (in order to gain the desired energy and wavelength) and then transmitted through a very thin (typically $\sim 10 \text{ nm}$) specimen. An image is produced from the interactions of transmitted electrons with the specimen onto a detector plate. The image resolutions are determined by the de Broglie wavelengths of the accelerated electrons. A couple of examples of TEM techniques are electron diffraction and electron energy loss spectroscopy (EELS).

Atomic resolution can be obtained with HRTEM (high resolution TEM), in which the image arises from the interference of the electron wave with itself in the image plane. The highest point resolution achieved with HRTEM is presently about $0.5 \text{ \AA}$ [27]. This is sufficient for resolving individual atoms and defects in a crystal. Thus, HRTEM allows for a direct real space imag-

Figure 1.2: Transmission electron micrograph image of needle shaped precipitates in aluminium. Image taken from ref. [24].

ing of the atomic structure. Columns of individual atoms are imaged via phase-contrast, that is, additional contrast gained due to diffraction in the transmitted electron beam.

Due to incoherence effects and lens aberrations, the images formed are not directly interpretable. A technique called exit wave reconstruction is often used to interpret the images [28, 29, 30]. This is typically performed by quantifying the effects causing defocusing and utilize this information (via e.g. Fourier analysis) to reconstruct the wave function at the exit surface of the specimen (see e.g. [7]).

Although HRTEM images are very useful for determining crystal structures, they can not be used to distinguish directly between different elements. A method that is often used for elemental analysis in HRTEM is energy-dispersive X-ray spectroscopy (EDS). The impact of an electron beam from a TEM on the sample produces X-rays that are characteristic of the elements present in the sample. These are then identified by peaks in the resulting spectrum. The concentration of the various elements are quantified from the intensities of the characteristic X-ray peaks [31]. However, the accuracy of EDS is not optimal when studying inhomogeneous samples, as is the case with precipitates. It can then be affected by elements having overlapping peaks. Also, due to the small size of the precipitate cross sections, errors can easily occur due to stray or scattered electrons.

A more accurate technique for investigation of chemical compositions of nanoscale particles is atom probe tomography (APT) [32]. Here, the sample is formed as a needle with a very sharp tip (radius ≤ 100 nm). A high electrostatic field is generated at the tip, and high voltage laser pulses are then used to evaporate ionized atoms from the sample surface. These are

Figure 1.3: Exit-wave image of a β'' precipitate cross section. Image taken from ref. [22].

then projected onto a position sensitive detector. By measuring the time between the laser pulse and the detection of the ion, the mass-to-charge ratio can be determined. Also, the position of the ion impact on the detector allows to reconstruct the original position of the atoms on the sample tip. Several investigations of early precipitate phases in Al-Mg-Si alloys have been performed by use of APT [33, 34, 35]. However, errors have been found to occur in precipitate compound investigations due to evaporation effects. It turns out that Mg- and Si ions arrive at the detector at very short time intervals, resulting in a loss of counts of Mg and Si. The missing number of Mg and Si atoms is also influenced by defocusing, that is, Mg- and Si atoms originating from the precipitate have instead been found in a shell surrounding the precipitate core. Thus, the amount of Al in the compounds has been found to be overestimated, and also to be varying from precipitate to precipitate. A method that corrects these errors was presented in ref. [13]. Nevertheless, there are still difficulties in the determination of the exact amount of Al in the precipitates, although a lower limit can be estimated. In all of the β'' precipitates investigated in [13] the reported Al content was close to 20%.

The present state-of-the-art in observational studies of nanostructures is the technique called high angle annular dark-field (HAADF) [36, 37, 38]. This is a method of mapping samples in a scanning tunneling electron microscope (STEM). In annular dark-field imaging scattered electrons are collected with an annular dark-field detector. This detector collects electrons from an annulus around the beam, thus sampling more scattered electrons than can pass through an objective aperture.

This technique can be used to create Z -contrast images, i.e. images that are sensitive to variations in the atomic number. This way, the mean

Figure 1.4: HAADF-STEM image of a β'' precipitate cross section in Al.

atomic number of the columns can be determined, and the compositions of precipitates can directly be determined. Investigation of β'' precipitates by HAADF-STEM and a closer description of the technique used to determine the chemical compound are presented in Paper I.

Chapter 2

Theoretical background

Now that the subjects of this work have been presented, it is time to move onwards and take a closer look at *how* to perform theoretical studies of aluminium and precipitates.

In this chapter the theoretical framework of this work is presented, along with numerical implementations, and some of strengths and weaknesses of the methods are discussed.

The sections dealing with exchange-correlation functionals, pseudopotentials and plane-waves closely follow the accounts given in refs. [39] and [40].

2.1 Density Functional Theory

At the atomistic level, the physical properties of a material are determined by the solution of the Schrödinger equation for the system. However, when considering many-body systems, it soon becomes very complicated to find an exact solution, since all electrons and nuclei in the system are interacting with each other.

Density functional theory (DFT) has proven to be a very successful way around this problem. Instead of solving the Schrödinger equation for a system of N interacting particles, the problem is reformulated into that of a system of N non-interacting particles moving in an external potential.

The fundamental tenet of DFT is that the properties of a many-body system are determined by the ground-state electron density, $n_0(\mathbf{r})$. The proof for the existence of a functional that determines the ground-state properties of a many-body system are given by the Hohenberg-Kohn theorems [41]:

1. The external potential, and hence the total energy, is a unique functional of the electron density $n(\mathbf{r})$.
2. The electron density that minimizes the total energy functional is the exact ground-state density corresponding to the solution of the

Schrödinger equation.

However, these theorems give no description of how to actually construct such a functional. The practical usefulness of DFT is thanks to an approach first presented by Walter Kohn and Lu Jeu Sham. They stated that the ground-state density of the many-body system is equal to that of some system consisting of non-interacting particles in an effective potential, incorporating all the unknown interactions between the electrons into an exchange-correlation functional [42]. The many-body system can thus be described by a set of single-electron wave functions.

The Kohn-Sham equation for an electron at position $\mathbf{r}$ can be written on the form

$$\left[-\frac{\hbar}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.1)$$

The terms in brackets constitute the Kohn-Sham Hamiltonian, and ϵ_i are the energy eigenvalues. The total ground state energy of the system is a functional of the electron density, $n(\mathbf{r})$. For a system of N independent electrons, the density is given by

$$n(\mathbf{r}) = 2 \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \quad (2.2)$$

where the factor 2 is due to electron spin.

The first potential term, V_{ext} , is the external potential that describes the interaction between the considered electron and the atomic nuclei (and other external fields). V_H is the Hartree-potential, describing the Coulomb repulsion between the considered electron and the total electron density. Since this electron is also part of the total density, V_H contains a Coulomb interaction term between the electron and itself. This self-interaction is unphysical, and needs to be corrected. The final term, V_{xc} , defines the exchange and correlation interactions in the single-electron equations, which consequently also lead to the correction of the Coulomb self-interaction.

2.1.1 Exchange-correlation functionals

The exchange-correlation potential term in eq. (2.1) can be expressed as the functional derivative of the exchange-correlation energy:

$$V_{\text{xc}}[n(\mathbf{r})] = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (2.3)$$

The energy E_{xc} can further be expressed on the form

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})], \quad (2.4)$$

where $\epsilon_{xc}[n(\mathbf{r})]$ is the energy per electron at point $\mathbf{r}$, which depends only upon the density n close to the point $\mathbf{r}$. Thus, E_{xc} is approximated as a (nearly) local functional of the density.

Since both exchange and correlation tend to keep electrons apart, their contribution to the total energy can be described in terms of an exchange-correlation hole surrounding each electron, that is, an area where there is a reduced probability of finding an other electron. Thus, the potential exchange-correlation energy is given by the interaction of each electron with its hole:

$$\epsilon_{xc}^{\text{pot}}[n(\mathbf{r})] = \frac{e^2}{2n} \int d\mathbf{r} \frac{n_{xc}(\mathbf{r})}{|\mathbf{r}|},$$

where e^2 is a coupling constant describing the electron-hole interaction strength, and where $n_{xc}(\mathbf{r})$ is the density of the exchange-correlation hole.

The full exchange-correlation energy for a single electron can be expressed as

$$\epsilon_{xc}[n(\mathbf{r})] = \int d\mathbf{r}' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.5)$$

where $\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')$ is the hole density averaged over the coupling constant.

Local density approximation

The exact exchange-correlation functional that would give the exact same answer as the Schrödinger equation for the ground state of a given many-body system is generally unknown. The major challenge of DFT is thus to find the best possible approximation to the true exchange and correlation interactions between the electrons [43]. The approach chosen by Kohn and Sham was to assume that the exchange-correlation energy density at each spatial point is the same as in a homogeneous electron gas with that density. For solids this is a reasonable approximation since the valence electron density is slowly varying with $\mathbf{r}$, and can thus locally be considered as close to homogeneous. This is called the local density approximation (LDA). The energy density is in this case given by

$$E_{xc}^{\text{LDA}}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{\text{EG}}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})],$$

where $\epsilon_{xc}^{\text{EG}}[n(\mathbf{r})]$ represents the energy density in a homogeneous electron gas at position $\mathbf{r}$, and where $n^\uparrow$ and $n^\downarrow$ are the densities of electrons with spin up and spin down respectively. For unpolarized systems, $n^\uparrow(\mathbf{r}) = n^\downarrow(\mathbf{r}) = n(\mathbf{r})/2$.

LDA is the simplest class of exchange-correlation functionals since it only depends upon the local electron density. The exchange energy for a homogeneous gas is known, and has a simple analytic form. The exact correlation energy is not possible to determine analytically, but it has been calculated to great accuracy using quantum Monte Carlo methods [44]. A homogeneous electron gas is therefore more or less exactly described by the LDA. It provides a reasonably accurate description of solids, in which exchange and correlation effects are rather short ranged. On the other hand, LDA should not intuitively be expected to work very well for atoms and molecules, where the density continuously goes to zero outside of the atom or molecule. But surprisingly, it has also been found to work reasonably well even for these systems. The reason is that LDA is including certain terms that remain exact even where the density is highly non-uniform [45, 46].

A weakness of LDA is that the Coulomb self-interaction term is only approximately canceled, since the exchange interaction is local and short ranged. This gives only a negligible effect in solids, but it becomes large in confined systems. Also, the exchange-correlation energies have been found to be consistently too low [47].

As the strengths and weaknesses of LDA became known, the basis was laid for the development of more accurate and sophisticated approximations of the exchange-correlation functional, including additional exact constraints. The approximations have been classified in a hierarchy called the Jacob's ladder, a term introduced by J. P. Perdew [48]. Each rung upwards on the ladder represents the inclusion of a new "ingredient" that improves the accuracy of the density functional approximation. The LDA thus represents the lowest rung.

Generalized gradient approximation

Though LDA has proved to be a reasonably reliable approximation for solids and to work fairly well for surfaces, molecules and atoms, its accuracy is insufficient for many physical and chemical applications. This led to the development of the generalized gradient approximation (GGA), which represents the second rung on the Jacob's ladder. In addition to the local electron density, GGA functionals also include the density gradient at each point. The exchange-correlation energy functional is then expressed on the form

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} \, n(\mathbf{r}) \epsilon_x^{EG}(n) F_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|), \quad (2.6)$$

where $\epsilon_x^{EG}(n)$ is the exchange energy of the unpolarized electron gas and F_{xc} is a dimensionless enhancement factor.

There are many ways information from the gradient of the electron density can be included, i.e. there are many different ways in which to formulate

the enhancement factor F_{xc} . Consequently, there exist a large number of different GGA functionals. The two GGAs most used in physics are PW91 (Perdew-Wang) [49] and PBE (Perdew-Burke-Ernzerhof) [50]. These are non-empirical functionals, that is, they are based on known constraints of the true exchange-correlation functional, and all parameters are fundamental physical constants. Since they do not depend upon empirical data, calculations using these functionals are then from first principles.

In the following we make a closer investigation of the properties of the PW91 and PBE functionals, what their differences are, and in which ways they are an improvement over the LDA. This will motivate the choice of density functional used in this work.

The exchange-part of the enhancement factor is usually parametrized in terms of a dimensionless reduced gradient of the m 'th order, s_m . The first terms of the expansion of F_x are given by [51, 52]

$$F_x = 1 + \frac{10}{81}s_1^2 + \frac{146}{2025}s_2^2 + \dots \quad (2.7)$$

In PW91 and PBE only the first order term, s_1 , is used. It can be expressed as

$$s_1 \equiv s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla r_s|}{2(2\pi/3)^{1/3}r_s}, \quad (2.8)$$

where r_s is the average distance between electrons (which is equivalent to the radius of the exchange-correlation hole).

The parametrizations used in PW91 and PBE are somewhat refined from that of (2.7) in order to give a more correct behaviour in the small- and large-gradient limit. However, the LDA is recovered in the homogeneous electron gas limit, $s \rightarrow 0$, which gives $F_x = 1$. Generally, $F_x \geq 1$, which ensures that the exchange energy is lower in GGA than in LDA. This lowering is larger for atoms (for which the density gradient is large) than for solids. This results in a more correct binding energy than LDA gives, which is one of the major improvements of GGA over LDA.

The correlation part is difficult to determine analytically. Its contribution to E_{XC} is typically much smaller than from exchange. The correlation energy within GGA is generally expressed on the form

$$E_C^{\text{GGA}}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n(\mathbf{r}) [\epsilon_c^{\text{EG}}(r_s, \zeta) + H(r_s, \zeta, t)], \quad (2.9)$$

where ϵ_c^{EG} is the correlation energy in the uniform electron gas. The function $H(r_s, \zeta, t)$ represents the gradient part, which depends upon the range of the correlation hole r_s , the spin polarization ζ , and another reduced density gradient, t . As is the case with F_x , H has different parametrizations for different types of GGAs. Its analytical expression is given along with the parametrization of F_x in ref. [53].

One of the main motivations behind the construction of the PW91 functional was to cancel unphysical long range exchange- and correlation effects occurring in the second order expansion of the density gradient. This was achieved by letting the exchange-correlation holes have finite ranges. Its improvement over LDA and earlier GGA models in tests of atomization and ionization energies, electron affinities, electronegativities and lattice constants for various systems are summarized in ref. [53].

The desire for a simpler analytical parametrization of exchange and correlation, without altering the most relevant correct features of PW91, was a motivation behind the construction of the PBE functional. Here, the gradient expansion for the exchange energy is given by

$$F_x^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}, \quad (2.10)$$

where $\kappa = 0.804$, and $\mu = 0.21951$. The value of the first parameter was chosen to satisfy the so-called Lieb-Oxford bound [54], which put a lower bound on the exchange energy. The value of μ was chosen to recover the linear response form of the LDA, providing a more correct description of the uniform electron gas and of small variations around the uniform density. The gradient expansion of PW91 does not include this feature. On the other hand, the correct second order gradient term of the exchange enhancement factor is not recovered in the slowly varying limit, as it is in PW91. However, this feature is energetically less important than the linear response.

Otherwise, PBE retains all the correct features of PW91 for relevant s -values, that is, $0 \leq s \leq 3$ (valence electrons in metals have $s \leq 2$ [51]), as shown in Fig. 2.1. Thus, the two functionals yield virtually identical results on typical test systems like lattice constants, bulk moduli and atomization energies.

Although it has been demonstrated that GGA functionals provide better predictions than LDA for several physical properties of atoms, molecules and solids, there are still some cases in which LDA has been found to be more accurate than GGA. An important example is surface energies [55], which in turn leads to a better prediction of formation enthalpies of single vacancies within LDA than within GGA [56, 57].

However, due to its more correct cohesive energies and lattice constants in metallic systems, quantities that are of great importance in this work, GGA has been used in most of the calculations. In some cases LDA was used as well in order to compare with GGA, and to test the robustness of the results.

Meta-GGAs, Hybrid functionals and beyond

There are systems in which a higher level of accuracy is required than LDA or GGA can provide, e.g. in single atoms or molecules. Also, semiconductors

Figure 2.1: Enhancement factors of GGA-PBE plotted as a function of the reduced density gradient s in the range $0 \leq s \leq 3$ in an unpolarized system ($\zeta = 0$) and in a fully spin-polarized system ($\zeta = 1$) [50]. The circles denote the corresponding values for PW91 [53]. The corresponding enhancement factors of LDA are horizontal lines.

and insulators are not well described by the simplest approximations due to their inaccurate estimates of band gaps [58].

For such systems, higher level density functional approximations are usually employed. These are approximations that include additional exact constraints on the exchange-correlation functional. Since they have not been used in this work, they are only briefly presented here.

The third rung on the Jacob's ladder are the meta-GGAs [59, 60, 61]. In addition to the electron density $n(\mathbf{r})$ and the density gradient $\nabla n(\mathbf{r})$, these functionals also include the Laplacian of the electron density, $\nabla^2 n(\mathbf{r})$, which in practice is equivalent to the orbital kinetic energy density.

An important improvement that is obtained with meta-GGAs is a more correct treatment of covalent bonds, due to the ability to recognize regions in which the electron density is dominated by one orbital shape. These regions can thus be treated differently from those of slowly varying densities. Meta-GGAs can also cancel out the correlation energy of one-electron atoms (which have no correlation) and provide more exact exchange energies.

The fourth rung on the ladder are the hybrid functionals [62], also known as hyper-GGAs. Here, an exact exchange energy functional from Hartree-Fock theory is included. This functional is expressed in terms of Kohn-Sham orbitals rather than the electron density. The HF exchange energy is then linearly combined with one or more approximated exchange-correlation functionals like LDA or GGA. The most popular hybrid functional is the B3LYP (Becke, three-parameter, Lee-Yang-Parr) functional [63].

The most sophisticated density functional approximations to date, representing the fifth rung, are so-called random phase approximations (RPA), or RPA-like functionals [64, 65, 66]. Unlike the other types of density functionals presented here, RPAs also include unoccupied Kohn-Sham orbitals. A remarkable feature of RPA calculations is that, although they typically yield large total errors, these errors cancel out almost perfectly in energy difference calculations. The RPA has been found to work even better for solids than for molecules [65].

Meta-GGAs, hybrid functionals and RPA functionals will probably be the density functional approximations of choice in future DFT calculations due to their potential for very high accuracy in predictions of properties of molecules and solids. However, there is still much room for improvements. At the present, usage of such functionals on large systems is computationally very expensive compared to LDA and GGA. An important task for the future is thus to make their codes more effective. As for now, we have considered GGA to provide the best compromise of accuracy and computational efficiency for the purposes of this work.

2.1.2 Plane waves and pseudopotentials

The atomic structure of a metal repeats itself periodically in space, with the period given by the lattice constant. Thus, we can in principle represent an entire crystal by a periodic unit cell. According to Bloch's theorem, the solutions of the Schrödinger (and thus, the Kohn-Sham) equation(s) for a periodic system can be expressed as a sum of plane waves on the form

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}(\mathbf{r}), \quad (2.11)$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a function with the same periodicity as the considered unit cell, and is expressed as an expansion of plane waves:

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}], \quad (2.12)$$

where $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ is a vector in reciprocal space, defined so that $\mathbf{G} \cdot \mathbf{a}_i = 2\pi m_i$ for any real space lattice vector $\mathbf{a}_i$. Inserted into (2.11), this gives

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]. \quad (2.13)$$

Considering this expression, we see that the solution for each $\mathbf{k}$ need to be evaluated over an infinite number of possible values of $\mathbf{G}$. So in order to make practical calculations feasible, a so-called energy cut-off is introduced. Each solution has a kinetic energy

$$E = \frac{\hbar^2}{2m}|\mathbf{k} + \mathbf{G}|^2.$$

In most cases, solutions with very high energies are irrelevant. By choosing an upper limit for E , given by

$$E_{\text{cut}} = \frac{\hbar^2}{2m}G_{\text{cut}}^2, \quad (2.14)$$

the sum in eq.(2.13) becomes finite. Finding a proper value of E_{cut} is one of the most important preparations of any DFT calculation. It must be sufficiently large to include the relevant energies, but too high values will lead to unnecessary additional numerical effort.

The wave vector $\mathbf{k}$ specifies each solution of the Schrödinger equation. All solutions of the SE are periodic in $\mathbf{k}$ -space, which means that all unique solutions are given by $\mathbf{k}$ in one primitive unit cell of the reciprocal lattice. Many important physical properties, like e.g. electron density and total energy can be represented by periodic functions since they are the same in each unit cell. Thus, they can be expressed in terms of $\mathbf{k}$ via Fourier

transforms. A given ground state property P is then calculated in DFT by integrating over $\mathbf{k}$ throughout the Brillouin zone of the unit cell:

$$P = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} \sum_{\mathbf{k}} p_n(\mathbf{k}) f(E_n(\mathbf{k})) d\mathbf{k}, \quad (2.15)$$

where $V_{\text{BZ}} = \frac{(2\pi)^3}{V_{\text{cell}}}$ is the volume of the Brillouin zone, n enumerates states of the wave vector $\mathbf{k}$ with eigenvalue $\epsilon_n(\mathbf{k})$, and where $f(\epsilon_n(\mathbf{k}))$ is a filling factor denoting the occupation of the state n .

Integrals on this form are a very central part of DFT calculations in solids. In all numerical DFT calculations, the integrals are approximated with a finite number of $\mathbf{k}$ -points. Different methods for efficient numerical evaluations of such integrals have therefore been a subject of careful investigation. The central problem is to choose which and how many $\mathbf{k}$ -points to integrate over in the Brillouin zone.

The computational cost generally increases linearly with the number of $\mathbf{k}$ -points. However, for high-symmetry systems like e.g., fcc crystals, the numerical effort is greatly reduced since the integrals need only be evaluated in the so-called irreducible Brillouin zone (IBZ). This includes the lowest possible number of $\mathbf{k}$ -points needed to obtain the most accurate approximation of the full integral.

The Monkhorst-Pack method [67] provides a uniform set of $\mathbf{k}$ -points throughout the Brillouin zone, defined by a simple analytical formula. In 3 dimensions, the $\mathbf{k}$ -points are given by

$$\mathbf{k}_{x,y,z} = u_x \mathbf{b}_1 + u_y \mathbf{b}_2 + u_z \mathbf{b}_3 = \sum_{i=1}^3 u_i \mathbf{b}_i, \quad (2.16)$$

where $\mathbf{b}_i$ are the reciprocal lattice vectors, N_i is the number of integration points along each lattice vector, and where

$$u_i = \frac{2n_i + N_i - 1}{2N_i}, \quad n_i = 1, 2, \dots, N_i.$$

Eq. (2.16) thus defines a uniform $\mathbf{k}$ -point grid that is a scaled version of the reciprocal lattice.

Monkhorst-Pack grids can be automatically generated for a given density of $\mathbf{k}$ -points along each reciprocal lattice vector. Usually, the grids are centered at the Γ -point, which ensures that the highest symmetry points of the Brillouin zone is included. However, in some cases, like e.g. in cubic lattices, it can be more effective to omit the Γ -point, and choose an even number of $\mathbf{k}$ -points, N_i .

Integration over Fermi-surfaces - smearing

The integrals involved in DFT calculations are evaluated for continuous functions over the Brillouin zone. In this work more or less all systems considered

are metals, in which the Brillouin zone contains some regions that are occupied and some that are unoccupied by electrons. These regions are separated by the Fermi surface. Assuming zero temperature, the integrand will be discontinuous at the Fermi surface, where it goes from zero to a non-zero value. The filling factor in eq. (2.15) is then given by a step function. Very high $\mathbf{k}$ -point densities would then be needed in order to get well converged calculations. There are two different approaches used in DFT to solve this problem. One is called the tetrahedron method. The principle of this approach is to divide the Brillouin zone into a set of tetrahedra defined by a discrete set of $\mathbf{k}$ -points, and define a function that is integrated at every point in the tetrahedron using interpolation. There are different ways to interpolate this function, leading to different tetrahedron methods [68].

The other approach is to use smearing methods, which is the method used in the DFT calculations in this work. The principle here is to "smear out" the discontinuity, thus making the integrand continuous across the Fermi level. Again, different functions can be used for the smearing, defining different smearing methods. This is equivalent to introducing a finite temperature or entropy to our system.

Smearing methods will generally improve the $\mathbf{k}$ -point convergence, but the challenge is to make them converge to correct values, or at least to minimize the errors (entropy terms) that occur due to this approximation. One of the most sophisticated schemes is that of Methfessel and Paxton [69]. Generally, integrals over the Brillouin zone of a metal can be written on the form

$$I = \int_{-\infty}^{\infty} [1 - \theta(E(\mathbf{k}) - E_F)] \int_{\text{BZ}} f(\mathbf{k}) \delta(\epsilon - E(\mathbf{k})) d\epsilon, \quad (2.17)$$

where $\theta(E(\mathbf{k}) - E_F)$ is the step function.

The Methfessel-Paxton scheme approximates the δ -function by a smearing function that is given by an expansion of Hermite polynomials:

$$\delta(x) \approx \sum_{n=1}^N A_n H_{2n}(x) e^{-x^2},$$

where the coefficients A_n are given by

$$A_n = \frac{(-1)^n}{n! 4^n \sqrt{\pi}},$$

and H_{2n} are Hermite polynomials of even order (since the δ -function is even). The N th order approximation, $S_N(x)$, is then found by integrating the (approximated) δ -function:

$$S_N(x) = S_0(x) + \sum_{n=1}^N A_n H_{2n-1}(x) e^{-x^2}, \quad (2.18)$$

where $S_0(x) = \frac{1}{2}(1 - \text{erf}(x))$. The 0'th order corresponds to Fermi-Dirac smearing. The ground state density now minimizes the free energy, given by the ground state energy and an entropy term:

$$F = E - \sigma \sum_{n=1}^N \frac{1}{2} A_n H_{2n} \left(\frac{E_n - E_F}{\sigma} \right) e^{-\left(\frac{E_n - E_F}{\sigma} \right)^2},$$

where $\sigma = k_B T$ is the smearing width. The advantage of the Methfessel-Paxton method is that the entropy term can be calculated accurately, thus allowing for accurate energy corrections. Therefore, this method provides good results for energy calculations in metals. Mostly, the 1st order Methfessel-Paxton method has been used in the calculations in this work.

Pseudopotentials

In order to further reduce the computational effort of DFT calculations, it is useful to employ so-called pseudopotentials. The fundamental idea of a pseudopotential is to replace the electron density of the core electrons (which, opposed to the valence electrons, do not play an important role in defining chemical bonds and other physical characteristics of materials) and the strong Coulomb potential of the nucleus with a smoothed electron density that matches important physical and mathematical properties of the true ion core.

Pseudopotentials can be constructed by considering a single atom of one element, and the resulting pseudopotential can then (at least ideally) reliably be used in calculations involving this atom in any chemical environment. The pseudopotentials are then said to be transferable. Many current DFT codes provide a library of pseudopotentials for most of the elements in the periodic table.

As in the case of density functional approximations, there are many different approaches. Two of the most widely used methods in electronic structure calculations are ultrasoft pseudopotentials (USPP) [70], and the projector augmented wave (PAW) method [71]. The latter was chosen for the DFT calculations in this work.

The PAW method improves the computational efficiency of DFT calculations by transforming rapidly oscillating valence wave functions near the ion cores into smooth wave functions.

The predecessor of the PAW method is the orthogonalized plane wave (OPW) method, first introduced in 1940 [72]. OPWs were the basis for the first quantitative calculations of bands in materials other than sp-bonded metals. It was shown that the basis function for valence states can be divided into a localized part and a smoothed part, the latter describing the valence functions near the ion core. In a crystal, this can be represented by plane waves. It was further shown that the full eigenfunction for a valence state

can be recovered from the smoothed function via a linear transformation. This is the basic idea adopted in the PAW method.

The smoothed valence function $\tilde{\psi}$ is related to the full all-electron wave function ψ by a linear transformation, $\psi = T\tilde{\psi}$. The linear transformation T is assumed to be unity except in a sphere centered on each ion core:

$$T = \mathbf{1} + \sum_{\mathbf{R}} T_{\mathbf{R}}.$$

If the smoothed valence functions are expanded in spherical harmonics within each sphere,

$$|\tilde{\psi}\rangle = \sum_m c_m |\tilde{\psi}_m\rangle,$$

the full wave function can be written as

$$|\psi\rangle = T|\tilde{\psi}\rangle = \sum_m c_m |\psi_m\rangle.$$

The coefficients c_m are given by a projection $\tilde{p}$ in each sphere,

$$c_m = \langle \tilde{p}_m | \tilde{\psi}_m \rangle,$$

which must satisfy the condition

$$\langle \tilde{p}_m | \tilde{\psi}_{m'} \rangle = \delta_{mm'}.$$

The linear transformation can thus be expressed as

$$T = \mathbf{1} + \sum_{\mathbf{R},m} c_{\mathbf{R},m} \left\{ |\psi_{\mathbf{R},m}\rangle - |\tilde{\psi}_{\mathbf{R},m}\rangle \right\} \langle \tilde{p}_{\mathbf{R},m} |. \quad (2.19)$$

Then we see that the full wave function is retained in the linear transformation, along with the smoothed valence functions.

The PAW method has been found to describe bulk properties very accurately, and to be the pseudopotential approach that gives the best description of core states [73].

Ultrasoft pseudopotentials require low energy cut-offs compared to other pseudopotentials (thereby making it a "soft" pseudopotential). In this approach, the Fourier range needed in order to keep the required accuracy for a given set of valence properties is minimized. This allows for a proper numerical convergence at reasonably low computational costs. However, a disadvantage is that a number of empirical parameters need to be specified in the construction of the pseudopotentials. USPPs thus have a lower transferability than pseudopotentials constructed using PAW.

Since PAW in principle is equivalent with all-electron methods, it should thus be physically more accurate.

2.2 Numerical implementation of DFT

In this section I give a brief overview of the principles behind the numerical implementation of DFT calculations.

One of the most popular codes for implementation of DFT calculations is the Vienna *ab initio* simulation package (VASP) [74, 75, 76], which was the code of choice for DFT calculations in this work. It is widely used both in first principles electronic structure calculations and in quantum molecular dynamics.

The code employs plane-wave basis sets along with pseudopotentials (PAW or USPPs), and features all of the available density functional approximations (LDA, GGAs, meta-GGAs, hybrids and RPs).

2.2.1 Determining the structural ground state: relaxation

When performing DFT calculations on a given system, e.g., a supercell representing a crystal lattice, the Kohn-Sham equations are used to find its electronic ground state (that is, the electronic density that corresponds to the ground state). The ground state is found by minimizing the internal forces, pressures and total energy of the system. This is called an electronic relaxation.

The basic principle of an electronic relaxation is to adjust the ionic positions in the supercell, calculate total energies, forces, etc. and then make a new adjustment. The calculations are repeated until a predefined convergence criterion is reached. In relaxations of solids, VASP uses forces and the stress tensor as search directions to find the equilibrium positions of the atoms.

The approach for energy optimization is similar to that of numerically finding a minimum of a mathematical function. One of the most efficient methods for finding local minima of one-dimensional functions is Newton's method. If we want to use Newton's method to minimize the total energy of a many-body system it must be expanded to 3 dimensions. We let the derivative of the total energy $E(\mathbf{x})$ be given by

$$g_i(\mathbf{x}) = \frac{\partial E}{\partial x_i}.$$

To minimize $E(\mathbf{x})$ for a system of N atoms, we need to find a set of positions for which $g_i(\mathbf{x}) = 0$ simultaneously for $i = 1, \dots, 3N$. The series of iterates defined by Newton's method is then given by

$$\mathbf{x}_{i+1} = \mathbf{x}_i - H^{-1}(\mathbf{x}_i)\mathbf{g}(\mathbf{x}_i),$$

where H is the Hessian matrix, which has dimensions $3N \times 3N$, and elements given by $H_{ij} = \frac{\partial g_i}{\partial x_j}$. These elements are thus the second derivatives of the energy.

This is in principle similar to using Newton's method in the one-dimensional case. However, the method becomes computationally very demanding for large systems. E.g., for a system of 10 atoms, 55 distinct elements of the Hessian matrix would need to be calculated. It would also be very difficult to find all minima due to the high dimensionality. In other words, Newton's method or any other simple iterative optimization method normally used for one-dimensional functions becomes practically useless for most problems evaluated within DFT. Other methods are thus needed.

The two most widely used classes of algorithms for numerical optimization within DFT are conjugate-gradient methods and quasi-Newton methods. The VASP calculations performed in the current work used the latter. A brief presentation of the principles behind the quasi-Newton algorithm is thus given in the following. For further reading on conjugate gradient methods, see e.g. ref. [77].

Quasi-Newton algorithm

As is apparent from the naming, quasi-Newton (QN) methods are based on Newton's method. The main advantage of QN methods is that the inverse Hessian matrix does not need to be calculated. Instead, an approximation of the Hessian matrix, based on the change in gradient between iterations, is used. Each iteration generally only involves calculations of a function f and its gradient ∇f . The basic form of the QN algorithm goes as follows:

1. Let $\mathbf{x}_0$ be an initial guess at the minimum. Let J be an initial approximation to the inverse Hessian matrix. J_0 is then initialized as some appropriate positive definite matrix.
2. $\nabla f(\mathbf{x}_k)$ is computed and a search direction $\mathbf{h}_k = -J_k \nabla f(\mathbf{x}_k)$ is defined.
3. A line search from $\mathbf{x}_k$ in the direction $\mathbf{h}_k$ is performed, and the next step $\mathbf{x}_{k+1} = \mathbf{x}_k + t^* \mathbf{h}_k$ is defined, where t^* is a parameter that minimizes $f(\mathbf{x}_k + t \mathbf{h}_k)$.
4. J_{k+1} is computed by making an appropriate modification of J_k , and by defining $J_{k+1} = J_k + U_k$, where U_k is some updating matrix. $k = k + 1$ is set and the procedure is repeated from step 2.

So the main question is how to update from J_k to J_{k+1} . It is desirable to maintain the essential features of H_k^{-1} in J_k without having to actually compute or invert the Hessian matrix. Two main conditions need to be satisfied: The first is that J_k must be symmetrical, since the Hessian matrix also is symmetric. If the updating matrix U_k is symmetrical, then also J_{k+1} will be symmetrical. The second condition is called the QN-condition. It is fulfilled if the approximate Hessian matrix satisfies

$$\mathbf{x}_{i+1} - \mathbf{x}_i = \mathbf{J}_{k+1}(\nabla f(\mathbf{x}_{i+1}) - \nabla f(\mathbf{x}_i)) \quad (2.20)$$

for $0 \leq i \leq k$.

The specific QN algorithm used in our VASP calculations is called RMM-DIIS (residual minimization - direct inversion of iterative subspace) [76, 78]. Here, information from previous iterations is used to build up the inverse Hessian matrix.

Volume relaxation and Pulay stress

Generally, we do not only want to relax the ionic positions, but also the volume and shape of the supercell. This is useful for predictions of e.g. lattice constants of bulk solids.

In volume relaxations, systematic errors can arise in the stress tensor due to an effect called Pulay stress. This effect arises because the plane wave basis set is not complete with respect to volume changes, which may lead to underestimated equilibrium cell parameters.

The ground state energy calculated from a relaxation on a cell with a specified constant volume will give a set of plane waves with energies all lying below the default energy cut-off. However, if the shape and the volume of the cell is changed, the length of the reciprocal lattice vectors in the different directions will also change. The consequence is that the plane wave basis set specified by the energy cut-off will be incorrect, since the geometry of the cell is changed. This will in turn lead to a changed ground state energy for the relaxed cell. Since a constant plane wave basis set is used in all volume relaxations in VASP, these energy changes are consistent with the calculated stress tensor. Thus, the errors due to Pulay stress are seen in the diagonal elements of the stress tensor.

Such errors can be avoided by increasing the energy cut-off by about 30% from the default value. This will more or less ensure that our plane wave basis includes sufficiently high energies to give a correct stress tensor. The prize to pay is a higher computational cost.

An alternative method that minimizes Pulay stress is to conserve the cell volume during the relaxation, thus allowing only the ionic positions to relax. This is equivalent to model the material surrounding the cell as infinitely stiff.

Obviously, a cell with infinitely stiff cell edges is in and of itself not physically realistic. However, this method can nevertheless be used to calculate the equilibrium volume and energy of a given system. By running relaxations for various cell volumes and plot the energy as a function of cell volume, the equilibrium volume and energy can be obtained by fitting the curve to an equation of state. This method will often provide more correct results than volume relaxations, since the Pulay stress will be almost isotropic, so that only a constant value will be added to the diagonal elements of the stress tensor. Then it will be easier to calculate the correct structure.

2.2.2 Elastic constants

In contrast to the QN method used in relaxations, calculations of elastic constants in VASP involves the true Hessian matrix.

The Hessian matrix contains the second derivatives of the total energies with respect to the atomic positions, and is found by displacing the atoms by small distances from their equilibrium positions. From this the derivative of the reaction forces with respect to the displacements are calculated. Only symmetry non-equivalent displacements are considered, in order to reduce the computational effort. Since the Hessian matrix and its inverse are involved, calculations of elastic constants are clearly more demanding than relaxations.

The elastic tensor of a system with arbitrary symmetry is calculated from the stress-strain relationship, following a least-squares method proposed by Le Page and Saxe [79]. In the following, a brief summary of their approach is given.

The general stress-strain relation, Hooke's law, states that the stress σ caused by an applied strain ϵ is given by

$$\sigma_i = \sum_{j=1}^6 C_{ij} \epsilon_j, \quad (2.21)$$

where C_{ij} are the elastic coefficients of the relaxed material. Generally, this is a system of 6 equations (one for each σ_i) with 6 variables (each ϵ_i) involving 21 unknown independent elastic coefficients C_{ij} . If the material is under a known initial strain $\mathbf{E}$, the resulting stress is $\Sigma(\mathbf{E})$. This stress can be calculated with VASP. The total strain can then be written as $\mathbf{E} + \mathbf{e}$ if a small strain change $\mathbf{e}$ is applied. The total stress is then given by

$$\Sigma(\mathbf{E} + \mathbf{e}) = \Sigma(\mathbf{E}) + \mathbf{s} = \Sigma(\mathbf{E}) + \mathbf{C}(\mathbf{E})\mathbf{e}, \quad (2.22)$$

where $\mathbf{s}$ are the small stress changes caused by the small strain changes $\mathbf{e}$. We see that eq. (2.21) is recovered for zero initial strain ($\mathbf{E}=0$).

This is now a linear problem with 27 variables: the 6 components of the initial stress and the 21 independent elastic coefficients. The goal is to extract these variables from a number of selected values $\Sigma(\mathbf{E} + \mathbf{e})$, which is possible to obtain by employing a symmetry-general least squares method. For a chosen strain magnitude e , seven *ab initio* calculations are performed, one for each total strain, $\mathbf{E}$, $\mathbf{E} + \mathbf{e}_1$, $\mathbf{E} + \mathbf{e}_2$ and so forth. From eq. (2.22) we see that the elastic coefficients thus can be calculated from the stress changes $\mathbf{s}$. For each stress change, six elastic coefficients can be extracted. The number of calculations are reduced in cases where different $\mathbf{e}_i$ are symmetry-related. Different schemes for choices of strains for different symmetries are given in ref. [79].

2.2.3 Numerical convergence

As previously mentioned, there are two parameters that must be given particular attention in order to provide accurate and reliable results from DFT calculations, namely the number of $\mathbf{k}$ -points and the plane-wave energy cut-off.

VASP can automatically generate Monkhorst-Pack $\mathbf{k}$ -point grids that optionally can be centered on the Γ -point for a given density of $\mathbf{k}$ -points. The required $\mathbf{k}$ -point density needed to obtain well converged calculations is dependent on the number of non-equivalent $\mathbf{k}$ -points, and which physical quantity we want to calculate. Obviously, the higher the symmetry of the supercell, the fewer $\mathbf{k}$ -points are needed.

The energy cut-off generally depends upon the pseudopotential, which varies from element to element. In VASP, files describing PAW potentials are available for almost all elements in the periodic table. These include a default energy cut-off for the given element, which is safe to use in most cases as they lead to energies converged to within a few meV. However, as discussed earlier, the default energy cut-off is generally too low for performing sufficiently accurate volume relaxations. In these cases the cut-off should be increased by about 30%.

Another aspect that is of great importance in this work, is how well results are converged with respect to supercell sizes. E.g., if we want to calculate the impurity energy of a single atom solute element embedded in aluminium, a too small supercell will lead to incorrect energies. A rule of thumb is that the supercell must be large enough so that the impurity atom will not interact (i.e. not "feel" any elastic strains, forces) with its own periodic images. This will be further discussed in chapter 3.

2.3 Thermodynamics

The results presented in this work are based on calculations of ground state Kohn-Sham energies, which means that the systems are described at zero temperature ($T = 0$). However, in the real world we experience non-zero, finite temperatures.

In the following, a brief overview is given over which additional energy contributions an inclusion of finite temperature will lead to, along with some methods of how to take these effects into account in electronic structure calculations.

A closer discussion on the significance of an inclusion of temperature in the calculations performed in this work is given in chapter 4.

2.3.1 Energies

In very many cases, the central output of DFT calculations is the total energy of the considered system. The Gibbs free energy G of the system is in general given by

$$G = E + pV - TS, \quad (2.23)$$

where E is the total internal energy of the system, p is the pressure, V is the volume, T is the temperature, and S is the entropy. For zero temperature and pressure, we see that $G = E$. For solids, the total energy calculated by VASP is equivalent to the cohesive energy of the supercell, that is, the energy gained by arranging the atoms in a crystalline state as compared to being isolated atoms. The main contributions to the total energy are from electron-core- (pseudopotentials), ion-ion- and electron-electron (Hartree) interactions, in addition to the exchange-correlation interactions. If smearing is used, there will also be a small entropy term. In other words, we see that the electrostatic and exchange-correlation contributions to the total energy are constituted by the terms in the Kohn-Sham Hamiltonian from eq. (2.1). The full Kohn-Sham energy functional can be written as

$$E_{\text{KS}} = T[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{H}}[n] + E_{\text{ion}} + E_{\text{xc}}[n], \quad (2.24)$$

where the respective terms represent the kinetic energy, the electron-ion interactions, the Hartree energy, the interactions between nuclei, and the exchange-correlation energy.

This energy can be used to describe the stability of a system. The lower the energy, the higher is the stability. A phase diagram of the energy as a function of chemical composition can thus be used to predict the thermodynamically favored composition of a given system.

2.3.2 Temperature and entropy

For a finite temperature, all of the terms in eq. (2.23) are included in the total energy of the considered system. The system will then be in an excited energy state. When we model systems with finite temperature we then need to choose which types of excitations the "extra" energy contributions will lead to. This can be either atomic vibrations (i.e. excited phonons), electron excitations or some sort of configurational excitation.

In 1965, N. D. Mermin [80] made a finite temperature extension of DFT, including electronic excitations. This was a method for calculating thermodynamic ground states at some non-zero temperature. The single electron excitations were not resolved, but were rather averaged and put into the electronic free energy of the system.

The simplest effect of raising the temperature to a non-zero value is that the atoms in the material start to vibrate around their equilibrium positions.

Even at $T = 0$ there are vibrations in the lattice due to the ground state (zero-point) energy. The simplest way to model lattice vibrations is to treat the atoms as quantum mechanical harmonic oscillators. The vibrational energies are then described by the vibrational mode frequencies, i.e. phonons. This approach is called the harmonic approximation. There have also been developed more advanced methods for calculating high-precision phonon energies, using so-called quasiharmonic approximations, where temperature- and volume dependency of phonons are taken into account. This inclusion is necessary in order to give a correct description of e.g. thermal expansion of materials.

Another factor that is not taken into account in zero-temperature calculations is the configurational entropy. In reality all metals contain a certain amount of point defects, like vacancies, interstitials and substitutional impurities. The presence of point defects will contribute to the free energy of the system. This contribution is governed by the temperature dependent equilibrium concentration of point defects, given by

$$c_i = c_0 \exp(-F_i/k_B T),$$

where c_0 is the concentration of available sites where point defects can be formed, and F_i is the formation energy of the point defect. The ground state contribution to the formation energy can be calculated by taking the difference in formation energy between a lattice containing a point defect and a pure lattice. If a finite temperature is included, additional contributions to the point defect formation energy are added. These come from electronic and phonon excitations. The vacancy concentration in aluminium was calculated over a range of temperatures up to the melting point in ref. [81], using an approach including both electronic and quasi- and anharmonic contributions to the formation energy. The results were in very good agreement with experimentally measured concentrations.

Chapter 3

Atomistic modeling

Atomistic models provide the central input of *ab initio* calculations. It is therefore of utter importance that they represent the systems we want to study as correctly as possible.

One of the major challenges in supercell-based atomistic modeling is that a very large number of atoms is often needed to provide a realistic representation of a system due to periodic boundary conditions. A full 3-dimensional atomistic model of impurities like e.g. grains or precipitates would require several thousands of atoms when including the surrounding host lattice. Calculations on such systems would therefore be computationally very demanding, not to say beyond the very limit of what is possible to run on even the most powerful computers available. Even though increasingly more powerful computers are continuously being developed, some simplifications are usually needed to be made.

In many cases it is not necessary to make full 3-D models of the systems we study in order to provide reliable results. In the case of β'' precipitates, the only significant periodic mismatch with the aluminium structure, and thus all significant strain contributions, occur in the cross sectional plane of the precipitate needles. Thus, the β'' precipitates were modeled employing supercells that included only the precipitate cross section embedded in an Al matrix, and with only a single lattice period in the longitudinal direction. The model then treats the precipitates as infinitely long needles separated by a distance equal to the periodicity of the supercell.

In the following a closer presentation and discussion of this model is given, that is, the principles behind its construction, and its advantages and limitations. A step-wise approach is used, starting with the simple atomistic model of pure aluminium containing a single point defect. Then I will go onward to the bulk model of β'' , before I present the full precipitate model, in which the precipitate is embedded in the aluminium matrix. In the final section I give a brief discussion of other reported theoretical models of β'' .

Figure 3.1: The fcc aluminium unit cell.

3.1 Impurities in aluminium

The aluminium crystal lattice provides a very simple and highly symmetrical model basis, having a face-centered cubic (fcc) conventional unit cell consisting of 4 atoms. Physical properties like energies and elastic moduli can thus be calculated to great accuracy with a low computational cost. The bulk properties of aluminium are well defined from experiments, which makes aluminium a useful testing ground for *ab initio* calculations on metals.

The lattice constant has experimentally been measured to be 4.05 Å at room temperature [82, 83]. Calculating the zero-temperature lattice constant with DFT gives 4.04 Å within GGA and 3.99 Å within LDA.

3.1.1 Point defects

The simplest example of an impurity is a point defect, i.e. a vacancy or a single atom of another element situated at a lattice site in the host metal. Vacancies are simply empty sites in the crystal lattice, and are present in certain concentrations in all real metals. Single impurity atoms situated at host metal lattice sites are called substitutional phases, or solutes. These point defects are thus easy to model, and do not require large supercells.

As was mentioned in section 2.3, the required supercell size is determined by the range of interactions between the periodic images of the point defect. The presence of point defects will lead to strains in the surrounding matrix due to atomic misfits and electronic interactions, and thus provide a strain energy contribution to the total energy. If the periodic supercell is not sufficiently large, the strain fields will overlap with those from the neighboring supercells, and thus lead to an incorrect strain energy.

The supercells employed in the study of single atom impurities in Paper IV were based on cubic aluminium supercells. The total number of atoms in the cell is then given by $4n^3$, where n is the number of conventional

Figure 3.2: Examples of point defects in a host metal lattice: vacancy (left), substitutional impurity phase (middle), interstitial phase (right).

Al unit cells in each Cartesian direction. Supercells containing 500 atoms (corresponding to $n = 5$) was found to be sufficient in order to contain the entire strain field (i.e. the deviation of the lattice constant of Al was less than 0.1% at the cell boundaries) for all of the considered impurity elements.

Another example of point defects are so-called interstitials, that is, impurity atoms situated in the space in between the lattice sites of the host metal. Interstitials are only likely to arise when the impurity atom radius is much smaller than that of the host. Therefore, interstitials are in most cases non-metals. However, in some metals, so-called self-interstitials can occur, that is, interstitial defects that contain atoms of the same type as the host metal. In such cases two atoms are typically displaced symmetrically from their shared lattice site along one of the principal lattice directions, so that their center of mass is located at the lattice site [84].

The point defects considered in this work are in almost all cases metallic impurities, which are unlikely to occur as interstitial phases since most of them have atomic radii similar to that of aluminium. Interstitials were therefore not further investigated in this work.

The different types of point defects are illustrated in Fig. 3.2.

3.2 The monoclinic β'' cell

The simplest way to model a β'' precipitate is to consider its bulk structure. The crystal structure of β'' is clearly more complex than that of Al. The conventional periodic unit cell is monoclinic and contains 22 atoms, see Fig. 3.3a. The crystal structure of β'' was resolved experimentally in ref. [7], and the lattice vectors were found to be

$$\mathbf{a}_{\beta''} = 15.16 \text{ \AA}, \quad \mathbf{b}_{\beta''} = 4.05 \text{ \AA}, \quad \mathbf{c}_{\beta''} = 6.74 \text{ \AA}, \quad \beta = 105.3^\circ,$$

where β is the monoclinic angle. All the symmetrically non-equivalent atomic sites of the β'' structure are contained in the so-called asymmetrical unit cell, i.e. one half of the conventional unit cell, see Fig. 3.3b. The sites indicated

Composition	a (Å)	b (Å)	c (Å)	β (°)
Mg ₅ Si ₆	15.13	4.07	6.91	110.1
Mg ₅ Al ₂ Si ₄	15.32	4.07	6.77	105.8
Mg ₄ Al ₃ Si ₄	15.11	4.13	6.60	106.4
Experimental [7]	15.16	4.05	6.74	105.3

Table 3.1: Lattice vectors and monoclinic angle of the fully relaxed unit cell for each of the three earlier reported β'' compositions, along with the experimentally measured parameters.

in the figure are based on the original Mg₅Si₆ structure presented in ref. [7]. In the Mg₅Al₂Si₄ compound, the Si₃-sites are occupied by aluminium, while in the Mg₄Al₃Si₄ compound, aluminium occupies both the Si₃-sites and the Mg₁ site. The DFT-calculated equilibrium unit cell parameters for each of the three compositions are shown in Table 3.1. It is evident that they are affected by the composition of the unit cell. Most particular is the difference of nearly 5% in the length of the c -vector between Mg₅Si₆ and Mg₄Al₃Si₄. Also, the monoclinic angle of the Mg₅Si₆-cell deviates clearly more from the experimental value than it does for the other two compositions. Likely, small changes in the chemical composition will lead to a slight altering of the interatomic distances due to electronic interactions, thus resulting in slightly different cell parameters.

The relaxed unit cell represents the equilibrium structure of β'' . However, one should keep in mind that in reality, the β'' structure does not exist as a bulk material, but only as precipitate needles in Al-Mg-Si alloys. The actual crystal structure will be largely affected by elastic strains due to the mismatch along the interfaces between the precipitate and the aluminium matrix. Reported cross section sizes of β'' precipitates vary from about 3 nm² up to about 14 nm² [22, 85]. Even in the largest precipitate needles, it is not likely that any extended bulk-like regions in the interior is obtained. In other words, the equilibrium bulk model is generally an inaccurate representation of the true β'' crystal structure. Nevertheless, the bulk model is useful in the way that it can be used to predict the stress-free structure of β'' , which is expected to be recovered in the innermost regions of precipitates with large cross sections. Bulk model calculations can also be useful for predicting relative differences in the properties of the different chemical compositions of β'' . Besides, the bulk model is the only computationally feasible approach for calculation of elastic constants.

The distortion of the β'' structure due to the periodic mismatch with Al is further discussed in the next chapter.

Figure 3.3: Fig. a: The monoclinic unit cell of β'' , with composition $\text{Mg}_5\text{Al}_2\text{Si}_4$. The experimental cell parameters are shown. Fig. b: The β'' monoclinic cell seen along the **b**-axis. The dashed line indicates the boundary of the asymmetrical unit cell, that is, one half of the conventional unit cell. The different atomic sites in the asymmetrical unit cell are marked, with the naming based on the sites in the Mg_5Si_6 cell. In the $\text{Mg}_5\text{Al}_2\text{Si}_4$ composition, which is shown here, aluminium atoms are situated at the Si_3 -sites. The solid and the white-filled atoms are located at different heights, separated by 2.025 Å.

3.3 The precipitate model

Employing purely atomistic models that include an entire realistic sized, isolated precipitate surrounded by a sufficiently large region of aluminium in *ab initio* calculations is still well out of reach. Instead, as discussed in the chapter introduction, we employ a model that only includes the precipitate cross section embedded in a surrounding Al matrix. This way, all the interfaces and precipitate corners are included. The model will then provide correct strain- and interface energies, and the relaxed supercell will display the coherency strain field in both the aluminium matrix and in the precipitate.

3.3.1 Modeling scheme

The basis of the precipitate model is an aluminium supercell consisting of $N_x \times N_y \times 1$ Al unit cells, where N_x and N_y are the number of Al cells in the Cartesian x - and y -direction, respectively. In most cases we let $N_x = N_y$. The β'' precipitate is substituted into the aluminium lattice according to the orientational relationship between the fcc aluminium lattice and the monoclinic β'' unit cell, given by [86]

$$[100]_{\beta''} \parallel [230]_{\text{Al}}, \quad [010]_{\beta''} \parallel [001]_{\text{Al}}, \quad [001]_{\beta''} \parallel [\bar{3}10]_{\text{Al}}. \quad (3.1)$$

Along $[010]_{\beta''}$ the precipitates are to a good approximation fully coherent with the Al matrix, so that we deemed it sufficient to include only one period in that direction in the supercell. Thus, the precipitate model is semi-infinite, with the precipitates being infinite along the $b_{\beta''}$ -direction. The precipitate sizes were quantified by the number of β'' formula units, N_{FU} (see Fig. 3.4), contained in the precipitate cross section. Thus, the precipitates were constructed with a structure similar to that seen in Figs. 1.3 and 1.4. Four different sizes were modeled: $N_{\text{FU}} = 1$, $N_{\text{FU}} = 4$, $N_{\text{FU}} = 9$ and $N_{\text{FU}} = 16$. Each precipitate was modeled as "quadratic", that is, the number of formula units was chosen to be equal along $a_{\beta''}$ and $c_{\beta''}$. Although the precipitates are coherent with the aluminium matrix, there is a periodic mismatch along the two interfaces in the cross sectional plane. As shown in Table 3.1, the experimentally measured lattice parameters of β'' , which were used as a starting point in the precipitate model, are 15.16 Å and 6.74 Å along $a_{\beta''}$ and $c_{\beta''}$ respectively. The corresponding distances in the aluminium lattice are

$$|[230]_{\text{Al}}| = \sqrt{2^2 + 3^2} a_{\text{Al}} = 14.60 \text{ Å}, \quad \frac{1}{2} |[\bar{3}10]_{\text{Al}}| = \frac{1}{2} \sqrt{3^2 + 1^2} a_{\text{Al}} = 6.40 \text{ Å},$$

where $a_{\text{Al}} = 4.05$ Å. Thus, the periodic mismatch along $[100]_{\beta''}/[230]_{\text{Al}}$ is 3.9%, while that along $[001]_{\beta''}/[\bar{3}10]_{\text{Al}}$ is 5.3%.

Figure 3.4: Illustration of the placement of a single formula unit of β'' of composition $\text{Mg}_5\text{Al}_2\text{Si}_4$ into an aluminium lattice. The difference in size between the β'' formula unit and the replaced aluminium is shown.

For the smallest precipitate size ($N_{\text{FU}} = 1$), the periodic mismatch does not come into play. Unlike the larger precipitates, the modeled single formula unit precipitate is symmetrical about the Cartesian axes (that is, $[100]_{\text{Al}}$ and $[010]_{\text{Al}}$). The $\text{Si}_1\text{-Si}_1\text{-}$ and $\text{Si}_3\text{-Si}_3\text{-}$ site distances correspond to one and two aluminium lattice periods respectively (see Fig. 3.4). In the experimental β'' structure, the distance between the two $\text{Si}_1\text{-}$ site atoms in a formula unit is $5.24 \text{ \AA}$, while the distance between two $\text{Si}_3\text{-}$ site atoms is $8.77 \text{ \AA}$. The largest supercells that were constructed consisted of $12 \times 12 \times 1$ aluminium unit cells, corresponding to a supercell volume of $48.6 \times 48.6 \times 4.05 \text{ \AA}^3$, and a total number of 576 atoms. The distance between two nearest-neighbor precipitates is then about $44 \text{ \AA}$ in the $[100]_{\text{Al}}$ -direction and $40 \text{ \AA}$ in the $[010]_{\text{Al}}$ -direction.

The precipitates containing 4, 9 and 16 formula units were also constructed with the experimental β'' -structure as basis, and inserted into the aluminium matrix, keeping the geometrical center of the precipitate at the same position as the geometrical center of the "hole" in the matrix. Thus, the atomic misalignment between β'' and aluminium will be lowest at the center of the interfaces, and increase as we go towards the precipitate corners. The volume of the precipitate is slightly larger than the volume of removed aluminium atoms, as shown in Fig. 3.4. This means that at a certain cross section size, the precipitate will be too large to fit into the hole of removed aluminium atoms. This happens when the difference in length between a corresponding number of periods in the two structures exceeds the nearest-neighbor distance between two atoms in the aluminium matrix. In the xy -plane this distance corresponds to $2.025 \text{ \AA}$. The number of replaced Al atoms must then be larger than the number of atoms in the precipitate in order to avoid overlap of atomic positions at the interfaces. This is equivalent to introducing additional defects in the form of vacancies in the supercell.

Figure 3.5: Precipitate + matrix supercell, with $N_{\text{FU}} = 9$ (left) and $N_{\text{FU}} = 16$ (right).

However, for relatively small precipitates, a 1-to-1 correspondence between the number of Al atoms that is removed and the number of atoms in the inserted β'' -precipitate can be maintained. This was the case for all of the precipitates modeled in this work.

3.4 Strain fields

Investigation of the elastic strain fields arising around precipitates and solute impurities was a central part of this work.

Quantification of the strain fields was done by analyzing the atomic coordinates in the relaxed supercell. The strain, σ_q , along a given lattice direction q is here given by the local distortion of the lattice constant of the host lattice, in this case aluminium:

$$\sigma_q = \frac{a_q^* - a_{\text{Al}}^{\text{eq}}}{a_{\text{Al}}^{\text{eq}}}, \quad (3.2)$$

where a_q^* is the local distorted lattice parameter along the direction q . Along the $\langle 001 \rangle$ directions the equilibrium lattice constant $a_{\text{Al}}^{\text{eq}} = 4.04 \text{ \AA}$ in pure aluminium when relaxed within GGA. The strain along these directions was thus defined as the local deviation from this value. In the case where a single impurity atom is situated at a lattice site, the strain field will be symmetrical around the impurity. Therefore, the strain has identical behavior along all the base directions $\langle 001 \rangle$ in Al. One can also define strain similarly along any other direction in the lattice.

In supercells containing a single formula unit precipitate, the strain field is symmetrical around the precipitate. It is then most appropriate to calcu-

Figure 3.6: The precipitate model of a β'' - $\text{Mg}_5\text{Al}_2\text{Si}_4$ showing a section of the precipitate along the needle direction. Six periods are included in the $[001]_{\text{Al}}$ direction.

late the strain field in Al along either $[100]$ or $[010]$. This was also done for the other precipitate sizes.

In order to obtain a direct comparison of the strain in the matrix to that in the precipitate, it is useful to calculate it along the lattice directions that are coherent to the β'' unit cell vectors, that is, $[230]_{\text{Al}}$ and $[-310]_{\text{Al}}$.

The strain inside the precipitates was defined as the deviation of the $[100]_{\beta''}$ - and $[001]_{\beta''}$ cell vectors in the relaxed precipitate-matrix supercell from their corresponding lengths in the relaxed bulk model (shown in Table 3.1).

An alternative way to describe the lattice distortion is by calculating the anisotropy strain. This was defined as the ratio of the local lattice constant between the $[100]_{\text{Al}}$ ($a_{[100]}$) and the $[010]_{\text{Al}}$ ($a_{[010]}$) direction at a given site in the aluminium matrix:

$$\zeta = \frac{a_{[100]}}{a_{[010]}}. \quad (3.3)$$

Where $\zeta = 1$, the lattice is undistorted. An example of an anisotropy field around a β'' precipitate is shown in Fig. 3.8.

3.5 Energy calculations

A central physical quantity throughout this study is the formation enthalpy, that is, the energy cost or gain of a given atomic configuration relative to the formation energy of the constituents in their standard states. This quantity describes the stability of a given system, which in turn can be seen as a measure of the likelihood of actually finding this system in nature.

In the study of single-atom solute elements, this quantity was called the

Figure 3.7: The anisotropy is here defined as the local lattice parameter along $[100]$, $a_{[100]}$, divided by that along $[010]$, $a_{[010]}$.

Figure 3.8: Contour plot of the anisotropy field in the aluminium matrix around a β'' - $\text{Mg}_5\text{Al}_2\text{Si}_4$ precipitate consisting of 9 formula units. The color bar indicates the value of ζ .

impurity energy, and was defined as

$$E_{\text{imp}} = E_{\text{tot}}(\text{Al}_{N-1}X) - (N-1)E_{\text{coh}}(\text{Al}) - E_{\text{coh}}(X), \quad (3.4)$$

where X is the impurity element, N is the total number of atoms in the supercell, E_{tot} is the total energy of the supercell, $E_{\text{coh}}(\text{Al})$ is the cohesive energy (per atom) of aluminium, and $E_{\text{coh}}(X)$ is the cohesive energy (per atom) of the impurity element.

The stability of various compositions of β'' precipitates was determined by the energy gained by forming that composition from a solid solution, in which the solute atoms are spread infinitely far apart from each other. This was quantified by the so-called precipitate energy, which was defined in a similar way as the impurity energy. However, the reference energies of the "impurities" (Mg and Si) are here given by their energies per atom in solid solution instead of that in their standard crystal state. The precipitate energy per formula unit is then given by

$$E_{\text{prec}} = (E_{\text{tot}} - N_{\text{tot}}E_{\text{Al}} - N_{\text{Mg}}E_{\text{Mg}}^{\text{SS}} - N_{\text{Si}}E_{\text{Si}}^{\text{SS}})/N_{\text{FU}}. \quad (3.5)$$

E_{tot} is the total energy of the supercell, N_{tot} is the total number of atoms in the supercell, E_{Al} is the cohesive energy per aluminium atom, and $E_{\text{Mg}}^{\text{SS}}$ and $E_{\text{Si}}^{\text{SS}}$ are the solute energies per Mg- or Si atom in Al. These energies correspond to the energy cost for replacing an aluminium atom with a solute Mg- or Si atom.

Generally, for a cell containing a total number of N atoms including one solute atom of element X , the solute energy is given by:

$$E_X^{\text{SS}} = E_{\text{Al}_{N-1}X} - E_{\text{Al}_N}, \quad (3.6)$$

The solute energies of Mg and Si used in the precipitate energy calculations were calculated using a 256 atom cell with one Al atom replaced by Mg or Si.

3.6 Other models

Previously reported first principles studies of the interactions between β'' precipitates and the aluminium matrix have mostly been focused on the interfaces between the precipitate and the matrix.

In ref. [87] interfacial energies for each of the three Al- β'' interfaces were studied by using periodic supercells that were constructed by combining β'' unit cells and corresponding aluminium cells formed as monoclinic cells. Several different supercells were constructed, with varying interfacial alignments, solute intermixing configurations and terminations. Although this model might provide a correct description of the interface energies, it is an

incomplete model that is unable to give a full description of the precipitate-matrix interactions. E.g., it does not include the precipitate corners, which give important contributions to the strain energy. Also, the periodic mismatch along the two interfaces in the cross sectional plane will result in a continuously increasing strain along the considered interface. A whole strain cycle must then be included within the model in order to be compatible with the neighboring supercells.

Recently, another *ab initio* based interface modeling approach was presented [88]. Here, the entire interface was modeled by using a sequence of distorted precipitate-host lattice supercells. The distortions were designed in order to describe the local interface regions. The model takes into account the accumulation of strain along the cross sectional interfaces, and places the point of minimal misfit at the center of the interface. Outside the interface regions, the strain was approximated as zero. This provides a more complete and also more computationally effective model than that described in [87]. The perhaps clearest advantage of these interface models is that they are more computationally feasible than the full precipitate cross section models presented in this work. An *ab initio* based framework is kept, and they can easily be included in a larger scale hybrid atomistic scheme [89].

There are nevertheless some problems that are still retained in the interface modeling scheme. E.g., the precipitate corners are still not satisfactorily described since the interfaces having different orientations do not interact in those models. The precipitate model used in the present work includes corner effects without the need to involve interpolations. Also, the precipitate model provides a more complete picture of distortions and strains inside the precipitates.

3.7 Convergence

When performing DFT calculations using VASP it is important to ensure that the results are well converged with respect to the chosen $\mathbf{k}$ -point density and the energy cut-off. This is essential with regard to the accuracy of the calculated results.

3.7.1 Lattice constants

Most metals have relatively simple unit cells with high symmetries, consisting of a small number of atoms. Quantities like lattice constants and atomization energies are thus easily converged in such systems. Aluminium is the host metal for all of the compounded systems that are studied in this work, and several physical parameters of Al are of interest. For pure Al, the lattice constant and atomization energy are well converged at low $\mathbf{k}$ -point densities, see Fig. 3.9.

Figure 3.9: Convergence of the lattice constant of bulk aluminium as a function of the number of $\mathbf{k}$ -points per axis. Notice that a logarithmic scale is used.

However, as soon as we move on to consider larger systems of lower symmetry, considerably more computational effort is needed. Fig. 3.10 shows the convergence of the a lattice parameter of the monoclinic β'' unit cell as a function of $\mathbf{k}$ -point density.

The β'' unit cell is both larger (22 atoms) and more complex than the unit cell of aluminium. Since the cell is larger, a given $\mathbf{k}$ -point density corresponds to a much lower total number of $\mathbf{k}$ -points than it does in the Al unit cell. Thus, the convergence of the lattice parameters of bulk β'' will be clearly slower than for aluminium, making it more difficult to obtain accurate predictions on physical properties.

3.7.2 Energies

In studies employing the full precipitate models, we are particularly interested in the formation enthalpies of the precipitates, given by eq. (3.5).

Another way to define the formation enthalpy in a compounded system is to compare the energy of an atom in solution to that in its standard state, given by eq. (3.4). This definition was used in the study of substitutional trace elements in aluminium presented in paper IV.

In both cases we are considering energy differences. The convergence of the relative energy of solute silicon in aluminium with respect to the energy cut-off is shown in Fig. 3.11. In this calculation the energy difference is taken between a pure aluminium cell containing 256 atoms and an identical aluminium cell containing one substitutional Si atom. It shows that the energy is well converged at $E_{\text{cut}} = 320$ eV, which is approximately 30% above the default energy cut-off at 250 eV.

Figure 3.10: Convergence of the $a_{\beta''}$ lattice vector of the monoclinic β'' cell of composition $\text{Mg}_4\text{Al}_3\text{Si}_4$ as a function of $\mathbf{k}$ -point density. Notice that a logarithmic scale is used.

Figure 3.11: Convergence of the solute energy of Si in aluminium as a function of the energy cut-off.

Figure 3.12: Convergence of the precipitate energy, E_{prec} , in a supercell containing single formula unit precipitate, as a function of energy cut-off, E_{cut} .

The convergence of the precipitate energy, E_{prec} , as a function of the energy cut-off is plotted in Fig. 3.12 for an aluminium matrix containing a single formula unit precipitate. The plot shows that this convergence is clearly slower than for a single impurity atom.

3.7.3 Cell size

Having obtained well converged structural parameters and energies, we can be confident that our calculated quantities are correct for the supercell under consideration. Since we wish to study physical systems, it is also crucial that our supercell provides a reliable representation of that system. As mentioned earlier, periodicity puts restrictions on how large atomistic models we are able to employ in DFT calculations. In the case of the precipitate model, the precipitates should be sufficiently isolated, so that they do not interact with their own periodic images. That is, the aluminium host lattice surrounding the precipitates must be sufficiently large. If the supercell is too small, a significant strain will still be present at the cell edges, resulting in inaccurate precipitate energies. An investigation of the local lattice constant in the aluminium at the supercell edges (corresponding to the midpoint between two nearest-neighbor precipitates) in the relaxed supercell will indicate how large supercells are needed in order to obtain zero strain at the cell edges. If the aluminium lattice is still distorted, the cell size is not converged. The strain is not constant along the cell edges since the distance to the precipitate interface is varying with the position on the cell edge. The most appropriate is thus to measure the distortion at the point on the cell edge that is closest to the interface, where it will have its maximum value.

Fig. 3.13 shows the maximum distortion of the aluminium lattice constant at the cell edge plotted as a function of the distance to the nearest neighbor precipitate for the composition $\text{Mg}_5\text{Al}_2\text{Si}_4$. For the smallest precipitates

Figure 3.13: Plots of maximum strain at the supercell edge as a function of precipitate nearest-neighbor distance, for β'' precipitates having a single formula unit (Fig. a) and 4 formula units (Fig. b)

that were studied in this work, having cross sections consisting of only a single formula unit ($N_{\text{FU}} = 1$), the maximum lattice distortion at the midpoint between two nearest-neighbor precipitates is less than 1 pm when the precipitate spacing is larger than about 35 Å. This is obtained using supercells with dimensions of about $44 \times 44 \text{ Å}^2$ (11×11 Al unit cells) or more. For precipitates with cross sections of 4 formula units (or more), larger supercell dimensions are obviously needed in order to obtain the same precipitate spacings as with $N_{\text{FU}} = 1$. The largest supercells we were able to run in our calculations had dimensions of about $48 \times 48 \text{ Å}^2$ (12×12 Al unit cells) in the cross sectional plane, which corresponds to an average nearest neighbor distance of about 33 Å. From the plots in Fig. 3.13 we see that the maximum strain at the supercell edges drops below 0.1% at about the same nearest-neighbor distance as for supercells with $N_{\text{FU}} = 1$.

For precipitate cross sections containing 9 or 16 formula units, the strain at the supercell edges is non-negligible even for the largest supercells, see Fig. 3.14. This was expected since the corresponding nearest-neighbor distance is only 25 Å and 18 Å for $N_{\text{FU}} = 9$ and $N_{\text{FU}} = 16$, respectively. In addition, the fall-off rates of the strains was found to be slightly slower in these cases. This is probably due to the larger strain at the precipitate-matrix interface as the precipitate cross sections become larger. Assuming that the strain would be fairly well converged for a precipitate spacing of about 35 Å, this would require supercells with dimensions of approximately 14×14 Al unit cells (784 atoms) for $N_{\text{FU}} = 9$, and 16×16 Al unit cells (1024 atoms) for $N_{\text{FU}} = 16$.

Another way to investigate cell-size convergence is to consider the calculated precipitate energies, E_{prec} . As the strain contribution approaches zero at the cell edges, we should expect a convergence of the precipitate energy since new layers of Al atoms then should only add the corresponding aluminium energy to the total energy of the supercell.

However, as is shown in the convergence plots in Fig. 3.15, no clear

Figure 3.14: Plots of maximum strain at the supercell edge as a function of precipitate spacing, for β'' precipitates having 9 and 16 formula units.

Figure 3.15: Precipitate energy E_{prec} as a function of mean precipitate spacing for precipitates having cross sections of 1 and 4 formula units (Fig. a), and cross sections of 9 and 16 formula units (Fig. b).

correlation between E_{prec} and supercell size was found for any of the individual compositions (Mg_5Si_6 and $\text{Mg}_5\text{Al}_2\text{Si}_4$ were chosen here since most of the convergence test calculations performed in the precipitate studies were made using these two compositions. In the case of $\text{Mg}_4\text{Al}_3\text{Si}_4$ energy calculations were mostly performed using only the largest supercells). Nevertheless, the variations in the energies are very similar regardless of the precipitate composition. So even though the absolute precipitate energies are not well converged with respect to supercell size in all cases, the relative energies between the various theoretical compositions of the precipitates are more or less unaffected.

3.7.4 Elastic constants

The calculation of the elastic tensor of aluminium and of the β'' structure was an important part of the work presented in Paper III. For a cubic material (like aluminium) the elastic tensor has only three independent entries (i.e.

elastic constants), and is given by

$$\mathbf{C}^{\text{cub}} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}. \quad (3.7)$$

For a monoclinic structure (like β'') there are thirteen independent entries in the elastic tensor, which then is given by

$$\mathbf{C}^{\text{mc}} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{22} & C_{23} & 0 & 0 & C_{26} \\ C_{13} & C_{23} & C_{33} & 0 & 0 & C_{36} \\ 0 & 0 & 0 & C_{44} & C_{45} & 0 \\ 0 & 0 & 0 & C_{45} & C_{55} & 0 \\ C_{16} & C_{26} & C_{36} & 0 & 0 & C_{66} \end{bmatrix}. \quad (3.8)$$

As discussed in section 2.2, such calculations involve the full Hessian matrix. It turned out that these calculations were remarkably slow to converge, as very high $\mathbf{k}$ -point densities were needed. This is seen in Fig. 3.16a, which shows a logarithmic plot of the convergence of the elastic constant C_{11} of aluminium as a function of the number of $\mathbf{k}$ -points per axis. Fig. 3.16b shows the number of CPU hours needed for the calculations as a function of the number of $\mathbf{k}$ -points per axis.

Even though a very large number of $\mathbf{k}$ -points was needed to achieve well-converged elastic constants, the computational cost was nevertheless feasible due to the small size and high symmetry of the Al unit cell.

On the other hand, the relatively high complexity of the monoclinic β'' unit cell (as compared to Al) makes a convergence of the elastic constants not only slow, but also computationally very demanding.

The convergence of the elastic parameter C_{11} as a function of the $\mathbf{k}$ -point density is shown in Fig. 3.17a for the compositions $\text{Mg}_4\text{Al}_3\text{Si}_4$ and $\text{Mg}_5\text{Al}_2\text{Si}_4$. A similar tendency was seen also for the other elastic constants. Fig. 3.17b shows the computational time needed for the calculations.

Figure 3.16: Fig. a: The convergence of the calculated elastic constant C_{11} in fcc Al plotted as a function of the number of $\mathbf{k}$ -points along each axis. Notice the logarithmic scale. Fig. b: The number of CPU hours used for the calculations plotted in Fig. a, along with a least squares exponential fit (shown as a red dashed line), given by $y = 0.34e^{0.151x}$, with a R-factor of 0.98.

Figure 3.17: Fig. a: Logarithmic plot of the convergence of the calculated elastic constant C_{11} of bulk β'' with compositions $\text{Mg}_4\text{Al}_3\text{Si}_4$ (blue) and $\text{Mg}_5\text{Al}_2\text{Si}_4$ (red) as a function of the $\mathbf{k}$ -point density. The large computational cost of these calculations is illustrated in Fig. b, which shows the number of CPU hours as a function of the $\mathbf{k}$ -point density (for $\text{Mg}_4\text{Al}_3\text{Si}_4$), along with a least-squares exponential fit (shown as a red dashed line), given by $y = 1.2e^{0.348x}$, with an R-factor of 0.99.

Chapter 4

Results and discussion

In this chapter a brief review of the main results of this work is given, along with some additional figures and commentaries that were not included in the papers. I refer to the papers for a more thorough presentation.

4.1 Trace elements in Al

In paper IV, the strain field around various metallic single atom substitutional trace elements in aluminium were investigated. The atomistic models contained, as described in the previous chapter, a single impurity atom in a 500 atom cubic aluminium supercell.

As is seen in Fig. 4.1, the strain field exhibits an oscillatory pattern. A damped harmonic function could thus be used to fit the strain values, and from this the range of the strain fields was quantified. This was further used to define a "maximum" concentration of solutes, c_{ext} , at which the strain fields overlap.

The solutes that were considered was mainly *3d* metals and other typical alloying elements in Al, like Mg, Si and Li. The *3d* metals were mostly found to generate long ranged strain fields. Some examples are shown in Fig. 4.2.

One exception from this rule was Zn, for which a very weak strain field was calculated, and correspondingly, a large value of c_{ext} , at about 28000 ppm. Those of the other *3d* elements were found to be mostly below 1000 ppm. This indicated that these elements have a potentially large impact on mechanical properties of aluminium alloys when in solute form, while the opposite is the case for Zn.

Possible correlations between c_{ext} and atomic radii, electronegativities and solubilities were also investigated. It was found that the range of the strain fields is determined by electronic effects rather than in atomic misfits for most of the *3d* metals. Furthermore, a weak correlation between c_{ext} and solubility was found. Thus, elements forming long ranged strain fields in Al are more likely to be found in particles (e.g. precipitates or grains) than

Figure 4.1: The figure on the left hand side shows a contour plot of the elastic strain in the $[100]$ direction in an aluminium matrix containing a Mg-atom (shown as a white dot) in the center. The position of the Al atoms are indicated by black dots. The figure on the right hand side shows a 1-dimensional plot of the strain along the dashed line shown in Fig. a (the dashed line is a guide to the eye only).

Figure 4.2: Contour plots of strain fields (in pct.) in the Al matrix around a solute a) Li-atom, b) Si-atom, c) Fe-atom, and d) Cu-atom. The black dots designate the positions of the Al-atoms and the white dot designates the position of the solute atom. Notice the different color scales.

elements having high solubility, and are thus more likely to play an important role in the formation of precipitates and other hardening particles.

4.2 *Ab initio* study of β'' precipitates in Al

By performing DFT calculations on the atomistic precipitate models presented in the previous chapter, the following physical properties were studied: the elastic strain fields arising in the aluminium matrix, the distortion of the β'' structure, potential chemical compositions of β'' , and electronic structure. The latter included density of states (both in the precipitate and in the aluminium matrix), charge density and electron localization.

4.2.1 Strain fields

Fig. 4.3a shows the calculated strain in the aluminium matrix in the [100]-direction in a fully relaxed supercell. While the strain displayed an oscillating behavior as a function of distance in supercells containing single solute atoms, the strain field in this case displays an exponential fall-off, as illustrated in the plot shown in Fig. 4.3b. Thus, the strain can be approximated as an exponential function of the distance from the precipitate-matrix interface. The same is also seen for strain in the [010]-direction, as shown in Fig. 4.3c and d. Here, the maximum strain is somewhat lower than along [100] due to a lower mismatch in this direction. A similar behavior is also seen for larger precipitates when the strain is measured from the corners, that is, along the row or column of aluminium atoms starting from the interface by the Si_1 - or Si_3 sites. Contour plots of the strain around these precipitates are shown in Fig. 4.4.

As is seen in Figs. 4.4b and c, precipitates containing 9 and (particularly) 16 formula units are too large compared to the size of the surrounding aluminium matrix used in these calculations in order to contain the entire strain field within the supercell. The strain field near the boundaries of the supercell will thus be overlapping with those from the neighboring precipitates. Nevertheless, Fig. 4.4a provides a good qualitative image of the strain field near the interfaces. As expected, the strain values were found to be largest close to the precipitate corners, near the Si_3 and Si_1 site atoms.

Contour plots of the percent-wise strain along $[-310]_{\text{Al}}/[001]_{\beta''}$ are shown in Fig. 4.5 for each of the three reported compositions. Inside the precipitates, the bulk relaxed cell vector lengths were used as reference. The plots indicate that the distortion is lowest in the $\text{Mg}_4\text{Al}_3\text{Si}_4$ -precipitate and clearly highest in the Mg_5Si_6 -precipitate. This was expected since the $\mathbf{c}_{\beta''}$ vector of bulk Mg_5Si_6 (6.91 Å) is longer than for the other two compositions. The $\mathbf{c}_{\beta''}$ vector of $\text{Mg}_4\text{Al}_3\text{Si}_4$, on the other hand, has the lowest mismatch with the Al matrix. It is remarkable that, while the precipitates are compressed in most of the interior, there are also local areas of tension. This is

Figure 4.3: Fig. a and c show contour plots of the calculated elastic strain around a single formula unit β'' precipitate of composition $\text{Mg}_5\text{Al}_2\text{Si}_4$, measured along $[100]$ (Fig. a) and $[010]$ (Fig. b). The color scale indicates the local percent-wise deviation of the local lattice constant from the equilibrium aluminium lattice constant. Figs. b and d shows 1-dimensional plots of the strain as a function of the distance from the precipitate-matrix interface, measured along the lines indicated in the contour plots.

Figure 4.4: Contour plots of calculated elastic strain in the Al matrix around β'' precipitates of composition $\text{Mg}_5\text{Al}_2\text{Si}_4$ measured in the $[100]$ direction (horizontally on the figures). The color scale indicates the local percent-wise deviation of the local lattice constant from the equilibrium aluminium lattice constant.

seen along the entire $[100]_{\beta''}$ -direction near the interface, increasing near the precipitate corners.

The elastic strains generated in the aluminium matrix are also lower for $\text{Mg}_4\text{Al}_3\text{Si}_4$ than for the other two compositions. This can again be explained by the low mismatch between the $\mathbf{c}_{\beta''}$ -vector of $\text{Mg}_4\text{Al}_3\text{Si}_4$ and the $[-310]$ vector length in the aluminium lattice. Even though Mg_5Si_6 has the largest mismatch with Al (the $\mathbf{c}_{\beta''}$ vector is about 6.4% longer than the $[-310]_{\text{Al}}$ vector in the bulk relaxed structure), $\text{Mg}_5\text{Al}_2\text{Si}_4$ is found to generate a larger strain in Al near the interfaces. As seen in the contour plots in Fig. 4.5, this is because the $\text{Mg}_5\text{Si}_6 - \beta''$ precipitate is more compressed than $\text{Mg}_5\text{Al}_2\text{Si}_4$. This indicates that the latter composition provides a "harder" precipitate, which forces the Al lattice to be more adapted to the β'' structure near the interfaces.

Similar effects were seen for strains plotted along $[100]_{\beta''}/[230]_{\text{Al}}$ (see Paper II).

As mentioned above, the elastic strain in the aluminium matrix has an approximately exponential fall-off as a function of distance away from the matrix-precipitate interface. This was used to predict the range of the strain fields and thus to approximate an effective size of the precipitates (see Paper I). It was found that the strain field was reduced to below 1% at a distance of 1 nm away from the precipitate interface. Thus, the active radius of β'' precipitates is up to 1 nm larger than the measured radius of the precipitates.

4.2.2 Energetics: Composition of β''

The precipitate energy of the previously proposed compositions (Mg_5Si_6 , $\text{Mg}_5\text{Al}_2\text{Si}_4$ and $\text{Mg}_4\text{Al}_3\text{Si}_4$) were calculated, along with that of a large number of other theoretical compositions, $\text{Mg}_x\text{Al}_y\text{Si}_z$. The only restrictions that were put on the theoretical configurations was that only Mg or Al were allowed at Mg-sites, and only Si or Al were allowed at Si-sites. Thus, the allowed numbers of Si atoms per formula unit was either 0, 2, 4 or 6. In the compositions that contained 4 Si atoms, the Si_3 sites were occupied by Al, while in those containing 2 Si atoms, both the Si_2 and the Si_3 sites were occupied by Al. By plotting the precipitate energies as a function of the Mg-to-Si ratio in the precipitates, a phase diagram could be provided, from which the thermodynamically most stable composition could be read. The energies were calculated for precipitates containing 9 formula units.

It is clearly shown that $\text{Mg}_5\text{Al}_2\text{Si}_4$ is the composition with the lowest precipitate energy, and is thus the theoretically most favored composition. An evaluation of the precipitate energy as a function of the number of Si atoms, keeping the number of Mg atoms constant, shows a repeating tendency (see Fig. 4.6): Each curve has its minimum at 4 Si atoms per formula unit, provided that these are situated at the Si_1 - and Si_2 sites. Also, the curves show that an energy penalty must be paid for each Mg atom that is

Figure 4.5: Contour plots of the calculated elastic strain in the Al matrix and inside β'' precipitates measured in the $[-310]_{\text{Al}}/[001]_{\beta''}$ direction for each of the three proposed compositions. The color scale indicates the local percent-wise strain in the $[-310]$ direction in Al and in the $[001]$ direction in β'' .

Figure 4.6: Calculated precipitate energies for various theoretical compositions of β'' plotted as a function of the number of Si-atoms per formula unit. Each curve is plotted for a constant number of Mg atoms.

substituted by Al.

Fig. 4.7 shows that $\text{Mg}_5\text{Al}_2\text{Si}_4$ is favored for all of the four considered precipitate sizes.

4.2.3 Valence charge density

Fig. 4.8 shows contour plots of the calculated valence charge density for two different compositions of β'' (Mg_5Si_6 and $\text{Mg}_5\text{Al}_2\text{Si}_4$) embedded in aluminium. In Fig. 4.8a and b the system is viewed along the z -axis of the Cartesian coordinate system, in the $z=0$ -plane, while Fig. 4.8c and d are viewed along the x -axis, at $x=0$. Along both viewing directions, a charge pile-up between the Si-atoms is seen, forming a network of covalent bonds throughout the Mg_5Si_6 -structure. This feature was also reported in ref. [23]. For the $\text{Mg}_5\text{Al}_2\text{Si}_4$ -structure on the other hand, it is seen that the Al atoms that are substituted at the Si_3 -sites break up the covalent network. This is somewhat surprising, since a covalent Si network has been believed to be present as a pillar-like "skeleton" structure conserved throughout the early stages of the precipitation sequence [11]. However, this would require that the Si_3 site is occupied by Si, which is apparently not the case. This indicates that the covalent network plays a less important role than previously assumed. Also, since it is widely agreed that the Al content of the precipitate phases decreases in the later stages of the precipitation sequence (see Table 1.2), it is unlikely that Si is situated at the Si_3 (or corresponding) sites in earlier phases than β'' .

In light of these results, the structures of the earliest precipitate phases should be subjects of further investigations.

Figure 4.7: The calculated precipitate energies of the three reported compositions Mg_5Si_6 , $Mg_5Al_2Si_4$ and $Mg_4Al_3Si_4$ as a function of the number of formula units N_{FU} in the precipitate. It shows that $Mg_5Al_2Si_4$ is consistently the most stable composition regardless of the precipitate size, even though the relative energy differences between the compositions vary slightly. The tendency appears to be clearer for larger precipitates. Also included are the corresponding values calculated within LDA, shown as empty circles. This shows that the choice of density functional between LDA and GGA did not have any significant impact on the precipitate energies.

Figure 4.8: Calculated valence charge density (in units of $eV/\text{\AA}^3$) in β'' -precipitates embedded in aluminium.

4.3 Continuum mechanical coupling

Due to the size limitations of feasible *ab initio* based atomistic models, continuum mechanical models are often employed in analytical studies of larger scale systems. Particularly, the finite element method (FEM) has proven to be useful in studies of several precipitate systems [92, 93]. The smallest systems that can be well described by FEM are currently at similar size as the largest systems that can be employed in *ab initio* methods, like e.g. the atomistic precipitate model presented in the current work. In ref. [93] it was demonstrated that the coherency strain around the β' phase could be simulated in a finite element model, using elastic constants calculated from first principles as input. A similar study for β'' is presented in Paper III, in which the elastic strains and atomic displacements in the aluminium matrix were compared to those simulated in the atomistic model. The two models were found to be in good agreement when considering strains in the aluminium matrix at the supercell boundaries. However, in the precipitate interior and near the interfaces the finite element method is no longer capable of providing a correct description. Thus, atomistic modeling and *ab initio* calculations must be employed in order to provide a correct description of the precipitate interior and the interface regions, while continuum mechanical models can be used to describe the larger surroundings, which more or less are described by linear elastic theory.

This important result shows that continuum mechanical models can provide reliable results at nanometer scale provided boundary conditions from *ab initio* calculations, and paves the way for precipitate studies using larger scale models. A model of a complete full length precipitate should be a feasible next step within the finite element approach. Another prospect is to model regions containing several precipitates.

4.4 Discussion

This study has shown that large and complex atomistic models can be employed in DFT calculations. This allows for a more complete inclusion of effects like interface- and strain energies of β'' precipitates, and thus accurate and reliable energy calculations can be provided.

There are nevertheless several simplifications in both the theoretical framework (e.g. temperature and entropy are neglected, GGA is not among the most exact density functionals, etc.) and in the atomistic models. In the following, some of the implications of these simplifications are discussed. How could we have obtained even more accurate results? On this basis a further discussion is given on the outlooks for further theoretical studies of precipitates and the way forward for the use of atomistic modeling. Will we at any point in the future be able to provide a complete description of an

aluminium alloy based solely on theoretical models?

4.4.1 DFT and temperature

All of the DFT calculations made in this work consider systems at zero temperature. This also means that pressure and entropy are neglected, so that all of the energy considerations are based on the ground state energy of a given system.

Would an inclusion of temperature and entropy have significantly affected the results? There are many cases in which the inclusion of pressure, temperature and entropy is crucial in order to obtain reliable results, e.g., in predictions of thermal properties of materials (volume expansion, specific heat capacity, etc.), or in geology, where materials exposed to high pressures play a central role.

There are mainly three types of entropy contributions that are considered in finite temperature calculations - configurational, electronic and vibrational.

The inclusion of lattice vibrations, i.e. phonons, is the most well established way to include temperature and entropy effects in DFT calculations of solids. As mentioned in section 2.3, the energy contributions from lattice vibrations can be calculated by using the harmonic approximation, that is, by treating the atoms in the solid as quantum-mechanical harmonic oscillators.

More precise methods based on the harmonic approximation have more recently been developed. The quasi-harmonic approximation [94, 95] also takes into account the temperature dependency of phonons (so-called explicit anharmonicity). This provides an additional free energy contribution, which has proven to be significant in calculations of thermal expansions and heat capacities [81].

Vibrational entropy has been shown to play an important role in the prediction of the energetic stability of precipitates. E.g., in ref. [96] the relative energetic ordering of the θ and θ' phases in Al-Cu alloys was investigated via DFT. When temperature was neglected, the equilibrium θ phase was found to be less stable than the metastable θ' phase, which was clearly in conflict with experiments. However, when vibrational entropy was accounted for, the calculations showed that θ was favored over θ' for temperatures above 200°C. This demonstrates that temperature and entropy should be taken into account when comparing energetics of particles having different structures. Precipitate formation and evolution usually takes place at elevated temperatures, and this should thus be accounted for in order to obtain a correct description of these processes in theoretical studies.

Much of the focus of this work, however, is to compare energies of systems having almost identical structures and symmetries. In these cases entropy is probably less significant than in comparisons between different structures. Nevertheless, the varying Al content in the different β'' compositions has

been shown to give small variations in the unit cell parameters. Also, the presence of the surrounding Al matrix leads to a locally more distorted structure of β'' close to the interfaces. The possible consequences of this is more closely discussed in Paper I.

Precipitate evolution and Si-pillars

The presence of Al at the Si₃-sites makes it clear that there is no covalent Si backbone structure present in the β'' precipitates. The Si-pillars have been considered as the first ordered structure in the precipitation of Al-Mg-Si alloys [11]. Thus, the processes behind clustering and formation in the earliest phases must be reconsidered. These are governed by kinetic processes, both in the form of diffusion and by collective shifts within the precipitates (e.g. the pre- β'' to β'' transformation). One possible explanation is that the Si-pillars do not exist at any point in the precipitation sequence. Another is that they exist at the earliest stages, but are then dissolved at a later stage, before the formation of the β'' phase.

A DFT-study of early precipitate phases in Al-Mg-Si alloys was performed in ref. [97], in which a range of possible theoretical structures, i.e. various cluster structures (the very earliest phases) as well as initial- or pre- β'' structures, were investigated. However, the presence of Si-pillars was taken as a precondition, and was included in all of the employed supercells.

The study of diffusion and precipitate kinetics has been outside the scope of this work, but these factors should be included in future studies in order to provide a better insight into the earliest stages of the precipitation sequence. Hopefully, this will in combination with realistic atomistic models make us able to explain the issue of the Si-pillars.

4.4.2 Other error sources

As mentioned earlier, the atomistic precipitate models employed in this study should have been larger in order to provide a fully converged structure within a supercell for the largest precipitates. About the same fall-off rate of the strain as a function of distance from the precipitate-matrix interface was found for each precipitate size. According to this, it would mean that the precipitates with $N_{\text{FU}} = 16$ should have a nearest-neighbor distance of minimum 35-40 Å in order to obtain a relaxed structure. Since the precipitate itself has a corner-to-corner width of close to 40 Å (see Fig. 3.5), this would require a supercell of dimensions of about 80×80 Å² in the cross sectional plane, equivalent to about 20×20 primitive Al unit cells. This corresponds to a total number of 1600 atoms in the supercell, which is not far beyond what is currently feasible for *ab initio* calculations. However, it is unclear whether an appropriately large supercell for the largest precipitates would have affected our main results significantly. As seen in Fig. 3.15 the E_{prec}

is apparently not dependent on the precipitate spacing. However, a fully converged structure is required for appropriate calculations of e.g. strain- or interface energies.

Although the precipitate model presented in this work includes strain contributions from all corners and interfaces in the cross-sectional plane, it does not include the endpoints of the precipitate needles. We have also neglected any possible strains in the growth (longitudinal) direction of the precipitates. The relaxed cell parameters of the bulk β'' model showed that the $\mathbf{b}_{\beta''}$ vector deviates somewhat from the Al lattice constant (see Table 3.1). In the present precipitate model we let the precipitate and the Al matrix have common lattice planes (thus assuming full coherency), so that no strains due to mismatch occurred in the longitudinal direction. However, in reality the β'' phase is only semi-coherent with the Al matrix, so that in a full 3-D model including a finite length precipitate, non-zero strain contributions along the precipitate needles and from the end points can be expected. Due to the low mismatch, however, these contributions are expected to be small compared to those accounted for in the present work.

A more efficient algorithm for computation of elastic constants [98] could have provided more reliable values for the β'' cell. This would have allowed for running calculations with higher $\mathbf{k}$ -point densities, and thus better converged values of the elastic tensor could have been obtained.

Even though LDA and GGA are known to perform well for metals, it would be of interest to investigate whether a higher level functional like e.g. a hybrid or an RPA could improve the results further. However, as was mentioned in Chapter 2, the increase in computational cost would probably be comprehensive.

4.4.3 DFT vs experiments

As the available computational power is improved, an increasing number of material parameters can be predicted from theoretical models. Some of the information that can be obtained from DFT is not feasible to obtain experimentally. A notable example is the visualization of the strain field around precipitates.

Will we at any point be able to provide a complete theoretical description of an aluminium alloy without input from experiments? The real strength of the atomistic modeling approach is that we in principle can "experiment" by creating and simulating models of a virtually unlimited number of theoretical structures and compositions. This provides a unique ability to optimize existing alloys, or even design entirely new alloys with given desired properties.

At the present we are able to describe point defects and (small) precipitates more or less solely by use of first principles methods, and expand the description to larger particles by combining atomistic and macroscopic mod-

els. Even though DFT provides accurate zero-temperature predictions, a major challenge at the present is to obtain better insight of kinetic processes in the alloys, in which temperature and entropy effects play important roles. Particularly, the nucleation and clustering of the early precipitate phases and the transition mechanisms between them is still not completely understood. Also, the influence of point defects and other impurity particles on precipitate formation and mechanical properties in general needs more investigation. Some possible prospects for further studies on this are presented in the Outlooks-section.

4.5 Conclusions

This work has proved that we are now able to perform parameter-free theoretical studies of precipitates in aluminium alloys by employing more complete and realistic atomistic models than what has previously been obtained. By including both the precipitate and the surrounding Al matrix, our model made us able to obtain a proper description of the interactions between precipitate and matrix, allowing for reliable predictions of the precipitate energetics.

The main results of this work are as follows:

- Total energy calculations of the precipitate model supercells provided an appropriate prediction of the thermodynamically favored composition of β'' precipitates. Calculations of the precipitate formation enthalpies showed that the thermodynamically favored composition of β'' precipitates is $\text{Mg}_5\text{Al}_2\text{Si}_4$.
- The observed chemical composition of β'' precipitates according to state-of-the-art microscopy investigations is $\text{Mg}_4\text{Al}_3\text{Si}_4$. This is inconsistent with first principles calculations, which clearly show that this composition is less stable than $\text{Mg}_5\text{Al}_2\text{Si}_4$. It is likely that kinetic or entropy effects, which were not accounted for in the calculations presented here, play an active role under precipitate formation, and prevent the thermodynamically favored composition from being formed.
- The calculated elastic strain fields arising in the cross-sectional plane of the precipitates was found to have an approximately exponential fall-off as a function of distance from the precipitate-matrix interface. For small precipitates the strain fields were found to have a range of approximately 1 nm.
- *Ab initio* calculations can be used as boundary conditions in continuum mechanical models of β'' precipitates embedded in aluminium.

The simulated elastic strain and atomic displacements in a finite element model of β'' embedded in aluminium, using *ab initio* calculated elastic constants as input, were in excellent agreement with those simulated in the atomistic precipitate model. Thus, the largest atomistic precipitate models can be combined with continuum mechanical models, demonstrating that a multi-scale study of β'' is feasible.

- An *ab initio* based investigation of different types of common solute elements in aluminium alloys showed that solute 3d metals generally displayed long-ranged strain fields, indicating that they have a potentially large impact on mechanical properties of aluminium alloys. Zn atoms on the other hand, were found to have a very small strain effect on aluminium. The aluminium matrix can contain up to 28000 ppm of solute Zn without being mechanically affected.

4.6 Outlooks

This study has shown that realistic precipitate models can be employed in first principles calculations, and that these calculations further can be used as a starting point in multi-scale studies. Thus, it also paves the way for first principles investigations of other compounded systems that require large atomistic models.

The future will bring increasingly more powerful computers, which will make it possible to run calculations on increasingly larger, and thus, more realistic models. A natural way forward for future research is to exploit these possibilities to make further multi-scale studies. The goal is to improve the insight into a given material at several length scales, from macroscopic down to atomistic levels, and bridge the gaps between these.

As previously mentioned, a better insight is needed into precipitate formation and growth kinetics. A prospect for such an investigation is to use atomistic supercells in modeling of precipitate growth. A possible approach is to model a nucleation site in the form of a β'' precipitate consisting of a single formula unit in the middle of a cubic Al supercell, and an additional Mg- or Si-atom that is placed in the aluminium matrix at a certain distance from the precipitate. By placing a vacancy next to the solute atom, the solute will be allowed to "drift" towards the nucleation site. Then, by using a method called the nudged elastic band (NEB) method [99], a minimum energy path from the atom to the nucleation site can be determined. This way it is possible to predict where on the nucleation site the atom most likely will attach itself, and thus we will be able to predict the precipitate growth. Hopefully, such studies will bring further concrete knowledge about atomic interactions in supersaturated solutions, which further can be used to predict optimal alloy compositions for given desired mechanical properties.

In the long term atomistic modeling and simulations will play an increasingly more important role in materials science. Being less expensive and time consuming, it is expected that virtual testing and evolving of materials to some degree will replace testing of materials in laboratories in the future. Already, modern car industry requests that all materials used in production shall be model-able, with a complete set of material parameters.

An ultimate goal is to use materials modeling and theoretical calculations to predict new hypothetical materials with improved properties that can be of great use in both industry and otherwise in the community.

Bibliography

- [1] R. Cobden, *Aluminium: Physical Properties, Characteristics and Alloys*, TALAT Lecture 1501 (1994)
- [2] L. E. Hetherington, *World Mineral Production: 2001-2005*, British Geological Survey (2007)
- [3] *"International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys"*, Registration Record Series, The Aluminium Association, Inc. (2009)
- [4] *"Aluminium is 'metal of future' for offshore use"*, news article from www.hydro.com (2013)
- [5] World Aluminium - the website of the International Aluminium Institute, www.world-aluminium.org
- [6] G. A. Edwards, K. Stiller, G. L. Dunlop, and M. J. Couper, *Acta Mater.* **46**, 3893 (1998)
- [7] S. J. Andersen, H. W. Zandbergen, J. Jansen, C. Træholt, and O. Reiso, *Acta Mater.* **46**, 3283 (1998)
- [8] A. Falahati, M. R. Ahmadi, P. Warczok, P. Lang, E. Povoden-Karadeniz, and E. Kozeschnik, *"Materials Science and Technology 2011"*, pp. 292-299, Columbus, Ohio, October 16-20 (2011)
- [9] M. Takeda, F. Ohkubo, T. Shirai and K. Fukui, *J. Mater. Sci.*, **33**, 2385 (1998)
- [10] C. D. Marioara, S. J. Andersen, J. Jansen, and H. W. Zandbergen, *Acta Mater.* **49**, 321 (2001)
- [11] J. H. Chen, E. Costan, M. A. van Huis, Q. Xu, and H. W. Zandbergen, *Science* **312**, 416-419 (2006)
- [12] K. Matsuda, H. Gamada, K. Fujii, Y. Uetani, T. Sato, A. Kamio, and S. Ikeno, *Metall. Mater. Trans. A* **29**, 1161 (1998)

- [13] H. S. Hasting, A. G. Frøseth, S. J. Andersen, R. Vissers, J. C. Walm-
sley, C. D. Marioara, F. Danoix, W. Lefebvre, and R. Holmestad, *J.*
Appl. Phys. **106**, 123527 (2009)
- [14] P. H. Ninive, A. Strandlie, S. Gulbrandsen-Dahl, W. Lefebvre, C. D.
Marioara, S. J. Andersen, J. Friis, R. Holmestad, and O. M. Løvvik,
Acta Mater. **69**, 126-134 (2014)
- [15] R. Vissers, M. A. van Huis, J. Jansen, H. W. Zandbergen, C. D. Mar-
ioara, and S. J. Andersen, *Acta Mater.* **55**, 3815 (2007)
- [16] K. Matsuda, Y. Sakaguchi, Y. Miyata, Y. Uetani, T. Sato, A. Kamio
and S. Ikeno, *J. Mater. Sci.* **35**, 179-89 (2000)
- [17] A. G. Frøseth, R. Høier, P. M. Derlet, S. J. Andersen, and C. D.
Marioara, *Phys. Rev. B* **67**, 224106 (2003)
- [18] S. J. Andersen, C. D. Marioara, R. Vissers, A. Frøseth, and H. W.
Zandbergen, *Mater. Sci. Eng. A* **444**, 157 (2007)
- [19] S. J. Andersen, C. D. Marioara, R. Vissers, A. Frøseth, and H. W.
Zandbergen, *Mater. Sci. Eng. A* **390**, 127 (2005)
- [20] C. Ravi and C. Wolverton, *Acta Mater.* **52**, 4213 (2004)
- [21] M. H. Jacobs, *Philos. Mag.* **26**, 1 (1972)
- [22] C. D. Marioara, S. J. Andersen, H. W. Zandbergen and R. Holmestad,
Metall. Mater. Trans. A **36A**, 691-702 (2005)
- [23] P. M. Derlet, S. J. Andersen, C. D. Marioara, and A. Frøseth, *J. Phys.:
Condens. Matter* **14**, 4011-4024 (2002)
- [24] S. P. Ringer, K. Hono, and T. Sakurai, *Metall. Mater. Trans. A* **26**,
2207 (1995)
- [25] A. H. Geisler and J. K. Hill, *Acta Cryst.* **1**, 238 (1948)
- [26] A. Guinier and H. Lambot, *Compt. Rend.* **227**, 74 (1948)
- [27] B. Kisielowski et al., *Microscopy and Microanalysis*, **14**, 469 (2008)
- [28] W. J. Coene, G. Janssen, and M. Op De Beeck, *Phys. Rev. Lett.* **69**,
3743 (1992)
- [29] M. Op De Beeck and D. Van Dyck, *Ultramicroscopy* **64**, 153 (1996)
- [30] H. W. Zandbergen, D. Tang, J. Jansen, and R. J. Cava, *Ultrami-
croscopy* **64**, 231 (1996)

- [31] J. Goldstein, *Scanning Electron Microscopy and X-Ray Microanalysis*, Springer (2003)
- [32] E. Müller, J. A. Panitz, S. McLane, and S. Brooks, *Review of Scientific Instruments*, **39** (1), 83-86 (1968)
- [33] M. Murayama and K. Hono, *Acta Mater.* **47**, 1537-1548 (1999)
- [34] K. Matsuda, T. Naoi, K. Fujii, Y. Uetani, T. Sato, A. Kamio, and S. Ikeno, *Mater. Sci. Eng. A* **262**, 232 (1999)
- [35] F. De Geuser, W. Lefebvre, and D. Blavette, *Philos. Mag. Lett.* **86**, 227 (2006)
- [36] M. Haider et al., *Nature* **392**, 768 (1998)
- [37] P. E. Batson, N. Dellby, and O. L. Krivanek, *Nature*, **418**, 620 (2002)
- [38] H. Müller, S. Uhlemann, P. Hartel, and M. Haider, *Microsc. Microanal.* **12**, 442 (2006)
- [39] D. S. Sholl and J. A. Steckel, *Density Functional Theory - A Practical Introduction*, Wiley (2009)
- [40] R. M. Martin, *Electronic Structure - Basic Theory and Practical Methods*, Cambridge (2004)
- [41] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864-871 (1964)
- [42] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965);
W. Kohn, *Rev. Mod. Phys.* **71**, 1253 (1999)
- [43] A. E. Mattsson, *Science* **298**, 759 (2002)
- [44] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980)
- [45] D. C. Langreth and J. P. Perdew, *Solid State Commun.* **17**, 1425 (1975); *Phys. Rev. B* **15**, 2884 (1977)
- [46] O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976)
- [47] R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989)
- [48] J. P. Perdew and K. Schmidt in *Density Functional Theory and Its Applications to Materials*, V. E. Van Doren, K. Van Alsenoy, and P. Geerlings (Eds.), American Institute of Physics, Melville, New York (2001)
- [49] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992)

- [50] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
- [51] J. P. Perdew and K. Burke, *Int. J. Quant. Chem.* **57**, 309 (1996)
- [52] P. S. Svendsen and U. von Barth, *Phys. Rev. B* **54**, 17402 (1996)
- [53] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992)
- [54] E. H. Lieb and S. Oxford, *Int. J. Quant. Chem.* **19**, 427 (1981)
- [55] D. Alfè and M. J. Gillan, *J. Phys. Condens. Matter* **18**, L435 (2006)
- [56] K. Carling, G. Wahnström, T. R. Mattsson, A. E. Mattsson, N. Sandberg, and G. Grimvall, *Phys. Rev. Lett.* **85**, 3862 (2000)
- [57] D. Simonovic and M. H. F. Sluiter, *Phys. Rev. B* **79**, 054304 (2009)
- [58] M. Giantommasi, M. Stankovski, R. Shaltaf, M. Gruning, F. Bruneval, P. Rinke, and G. M. Rignanese, *Basic Solid State Physics* **248**, 275 (2011)
- [59] A. D. Becke, *J. Chem. Phys.*, **109**, 2092 (1998)
- [60] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, *Phys. Rev. Lett.*, **82**, 2544 (1999)
- [61] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.*, **91**, 146401 (2003)
- [62] A. D. Becke, *J. Chem. Phys.* **98** (2), 1372 (1993)
- [63] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988)
- [64] D. C. Langreth and J. P. Perdew, *Solid State Commun.* **31**, 567 (1979); *Phys. Rev. B* **21**, 5469 (1980)
- [65] F. Furche, *Phys. Rev. B* **64**, 195120 (2001)
- [66] J. Harl, L. Schimka, and G. Kresse, *Phys. Rev. B* **81**, 115126 (2010)
- [67] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976)
- [68] P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994)
- [69] M. Methfessel and A. T. Paxton, *Phys. Rev. B* **40**, 3616 (1989)
- [70] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990)

- [71] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994)
- [72] W. C. Herring, *Phys. Rev.* **57**, 1169 (1940)
- [73] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999)
- [74] G. Kresse and J. Hafner, *Phys. Rev. B* **7**, 558 (1993)
- [75] G. Kresse and J. Furthmüller, *J. Comput. Mater. Sci.* **6**, 15 (1996)
- [76] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996)
- [77] M. P. Teter, M. C. Payne, and D. C. Allan, *Phys. Rev. B* **40**, 12255 (1989)
- [78] P. Pulay, *Chem. Phys. Lett.* **73**, 393 (1980)
- [79] Y. Le Page and P. Saxe, *Phys. Rev. B* **65**, 104104 (2002)
- [80] N. D. Mermin, *Phys. Rev.* **137**, A1441 (1965)
- [81] B. Grabowski, L. Ismer, T. Hickel, and J. Neugebauer, *Phys. Rev. B* **79**, 134106 (2009)
- [82] W. P. Davey, *Phys. Rev.* **25**, 753 (1925)
- [83] W. Witt, *Z. Naturforsch. A* **22A**, 92 (1967)
- [84] P. Ehrhart, *Properties and interactions of atomic defects in metals and alloys*, New Series III, vol. 25, ch. 2, p.88, Springer, Berlin (1991)
- [85] C. D. Marioara, S. J. Andersen, J. Jansen, and H. W. Zandbergen, *Acta Mater.* **51**, 789-796 (2003)
- [86] G. A. Edwards, G. L. Dunlop, and M. J. Couper, *Conf. Proc. ICAA4* vol.1 (*Georgia Institute of Technology, Atlanta, GA, 11-16 September 1994*), p. 620
- [87] Y. Wang, Z. K. Liu, L. Q. Chen, and C. Wolverton, *Acta Mater.* **55**, 5934 (2007)
- [88] F. J. H. Ehlers and R. Holmestad, *Comput. Mater. Sci.* **72**, 146 (2013)
- [89] F. J. H. Ehlers, S. Dumoulin, K. Marthinsen, and R. Holmestad, *Model. Simul. Mater. Sci. Eng.* **21**, 085018 (2013)
- [90] H. Jones, *Aluminium*, **54**, 278 (1978)
- [91] P. H. Ninive, K. E. Moen, A. Strandlie, and O. M. Løvvik, submitted to *Journal of Alloys and Compounds* (2014)

- [92] N. Miyano, A. Takahashi, J. Miyazaki, and K. Ameyama, *Mater. Trans.* **49**, 471 (2008)
- [93] S. Gulbrandsen-Dahl, K. E. Moen, F. Ehlers, C. D. Marioara, K. O. Pedersen, and K. Marthinsen, *Mater. Sci. Forum* **638-642**, 229-234 (2010)
- [94] A. A. Quong and A. Y. Liu, *Phys. Rev. B* **56**, 7767 (1997)
- [95] B. Grabowski, T. Hickel, and J. Neugebauer, *Phys. Rev. B* **76**, 024309 (2007)
- [96] C. Wolverton and V. Ozolins, *Phys. Rev. Lett.* **86**, 5518 (2001)
- [97] M. A. van Huis, J. H. Chen, M. H. F. Sluiter, and H. W. Zandbergen, *Acta Mater.* **55**, 2183 (2007)
- [98] R. Yu, J. Zhu, and H. Q. Ye, *Comput. Phys. Commun.* **181**, 671 (2010)
- [99] H. Jónsson, G. Mills, and K. W. Jacobsen, *Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions*, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, Ed. B. J. Berne, G. Ciccotti, and D. F. Coker, World Scientific (1998)