Department of Physics and Measurement Technology

Master’s Thesis

Elastic Properties of Fe-Ni-Mg at High Pressure from First-Principles Study

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Elastische Eigenschaften von Fe-Ni-Mg bei hohem Druck aus Prinzipien der ersten Methoden

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The calculations are based on an \textit{ab-initio} method supported on the Density Functional Theory. The calculations were performed with a simulation package based on the Exact Muffin-Tin Orbitals theory, in conjunction with the Coherent Potential Approximation. The effects that small impurities can have on iron are remarkable.
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Chapter 1

Introduction

1.1 Background

The effects of alloying two or more metals to change the material properties has been known to mankind for many thousands of years, yet we still don’t know the full extent of this science. What has been a science of smelting metals together and measuring the materialistic properties is since the advent of quantum mechanics also a science of solving electronic structures. Analytically we can’t solve more than two-particle systems with quantum mechanics, with more particles it’s very hard or next to impossible to get exact solutions. Whenever we for any reason can’t acquire scientific results from experiments do we need to find another way. In the past few decades have we seen the power of computers skyrocket. In Parallel with the hardware development have the scientific applications developed in the same rate. It’s no easy matter to solve the quantum equations for a macroscopic sample of particles. Approximations have to be made to make this possible. Density Functional Theory provides us with the means to drastically simplify the calculations by replacing the many-body problem with many one-body problems, and still maintain a reasonable degree of accuracy.

It’s not yet possible to replicate the conditions at the inner core of our planet where the pressure is above 300GPa to get experimental data. That is why we instead turn to the science of computer modelling for answers.

1.2 Thesis outline

The diploma project was carried out at the Theoretical Physics group within the Department of Physics and Measurement Technology, at the University of Linköping under the supervision of Prof. Igor Abrikosov and Ph.D. Christian Asker. The thesis consists of six chapters that are typesetted using \LaTeX. The graphs have been made in Matlab. Here follows a brief description of the chapters.
Chapter 2: Density Functional Theory
A description of the Density Functional Theory with derivation of the Kohn-Sham equations and ways to approximate the exchange and correlation energy.

Chapter 3: Numerical methods
A description of how to solve the Kohn-Sham equations with a self consistent method and how the EMTO basis in constructed. Ways to approximate the potential in the medium is also explained.

Chapter 4: Elastic properties
The basic theory behind elastic constants and the ways to calculate them is explained.

Chapter 5: Results
Presentation of the results and discussion about what they tell us.

Chapter 6: Conclusion and outlook
Summation and final conclusions of the results and suggestions of possible future extensions of this work.
Chapter 2

Density Functional Theory

2.1 Schrödinger equation

Any electronic structure can be described with wavefunction theory from the field of quantum mechanics. A well-known problem from quantum mechanics is the “single particle in a one-dimensional box”. This problem with only one particle can easily be solved analytically. If we add more than two particles to this problem, then it becomes impossible to solve with pen and paper. We need to find another way. To solve these problems with either one particle or N particles, we use the Schrödinger equation, which in its time-independent version has the general form

$$\hat{H} \Psi = E \Psi .$$  \hspace{1cm} (2.1)

Where $\hat{H}$ is the Hamiltonian, $\Psi$ is a wavefunction and $E$ is the energy of our system. In a system with atoms we will not only have electron-electron interaction but also electron-nuclei and nuclei-nuclei interactions. This gives us a Hamiltonian of the form

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne} ,$$  \hspace{1cm} (2.2)

where:

- $\hat{T}_n$ = The kinetic energy of the nuclei.
- $\hat{T}_e$ = The kinetic energy of the electrons.
- $\hat{V}_{nn}$ = Coulomb-interaction between the nuclei.
- $\hat{V}_{ee}$ = Coulomb-interaction between the electrons.
- $\hat{V}_{ne}$ = Coulomb-interaction between the electrons and nuclei.

This Hamiltonian can be easily simplified. Since the mass of the nuclei is thousands of times larger than the mass of the electrons, we can consider it as frozen. This means that we can neglect the kinetic energy of the nuclei ($\hat{T}_n$). Furthermore, if the nuclei are frozen, then the Coulomb-interaction between the nuclei will be constant. This doesn’t mean that we can neglect it, but it can be added later on, so we don’t need to worry about it right now. The last term ($\hat{V}_{ne}$) can be considered
Density Functional Theory

as “external”, and also, if there are other fields present, then we can add them to the \((V_{ne})\). \(\hat{V}_{ext} = V_{ne}(\text{+external potentials})\). Our Hamiltonian Eq.(2.2) will now have the simpler form\[^1\]

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} = \frac{1}{2} \sum_i \nabla_i^2 + \sum_{i \neq l} \frac{1}{|r_i - r_l|} + \sum_{i,k} Z_i |r_i - R_k| .
\]

The equation is in atomic units\[^1\]. The general form of the wavefunction will be

\[
\Psi = \Psi(r_1, r_2, ..., r_N, R_1, R_2, ..., R_N) ,
\]

where the \(r\):s comprise of the electrons space and spin coordinates, and the \(R\):s are the coordinates of the nuclei. Even though we have managed to simplify our system, it’s still far too complicated to be solved numerically if we have more than a few atoms. For this reason, we apply Density Functional Theory (DFT)\[^19\]. Every electron has three degrees of freedom. Which for \(N\) electrons means that we have a total of \(3N\) degrees of freedom. DFT allows us to replace this electronic \(3N\) degrees of freedom with a charge density, \(n(r)\), which only has three degrees of freedom. The DFT has its foundation in two mathematical theorems formulated by Pierre Hohenberg and Walter Kohn, called the Hohenberg-Kohn theorems \[^16\].

The two theorems states that:

1. The external potential \(V_{ext}(\mathbf{r})\) in a system of interacting particles is determined by the ground-state electron density \(n_0(\mathbf{r})\).

2. For any external potential, there exists a universal energy functional \(F[n]\). The minimum value of the energy functional for a specific external potential \(V_{ext}(\mathbf{r})\) is the ground state energy where the density that minimize the functional is the ground state density \(n_0(\mathbf{r})\).

2.2 Kohn-Sham equations

The next step is to find the density and the corresponding energy. In 1965, Walter Kohn and Lu Jeu Sham provided us with the means to do so. Their idea was to introduce some auxiliary system to replace the hard-to-solve many-body system Eq.(2.2), with a non-interacting system with the same ground state density. From the Hohenberg-Kohn theorems do we know that this manoeuvre is right.

From Ref\[^2\] the Kohn-Sham energy functional can be written as

\[
E_{KS}[n] = T_s[n] + E_{ext}[n] + E_{xc}[n] + U[n] = T_s[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n] + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' ,
\]

\[^1\hbar = m_e = e = 1\]
2.2 Kohn-Sham equations

where:

\( T_s[n] \) = The kinetic energy of the non-interacting particles.

\( E_{xc}[n] \) = The exchange-correlation energy for a system of interacting particles with density \( n \).

\( U[n] \) = The Hartree energy (or Coulomb).

For an arbitrary density \( n(r) \), the general form of the exchange-correlation is unknown. However, if \( n(r) \) is varying sufficiently slowly, one can assume that

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

where \( \epsilon_{xc} \) is the exchange-correlation energy per electron in a uniform gas of density \( n \). With the help of homogeneous electron gas theory can we learn more about \( \epsilon_{xc} \). We will be content with considering it as known. From Eq.(2.5) and the condition

\[
\int \delta n(r) d\mathbf{r} = 0,
\]

do we get [2]

\[
\int \delta n(r) \left\{ \varphi(r) + \frac{\delta T_s[n]}{\delta n(r)} + \mu(n(r)) \right\} d\mathbf{r} = 0,
\]

where

\[
\varphi(r) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|} d\mathbf{r'}
\]

and

\[
\mu(n) = \frac{d(\epsilon_{xc}(n))}{dn} = V_{xc}(r).
\]

\( \mu \) can be recognised as the chemical potential (\( \mu = \frac{\Delta E}{\Delta N} \)). Our \( \mu \) is the exchange-correlation contribution to the chemical potential for a uniform gas of electrons with density \( n \). In a system with non-interacting particles, the effective potential will be given by

\[
V_{eff} = \varphi(r) + \mu(n(r)) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|} d\mathbf{r'} + V_{xc}(r).
\]

If we know \( \varphi \) and \( \mu \), the \( n(r) \) that satifies Eqs.(2.7) and (2.8) can be found by simply solving the one-particle Schrödinger equation

\[
\left\{ -\frac{1}{2} \nabla^2 + V_{eff}(r) \right\} \psi_i(r) = \epsilon_i \psi_i(r)
\]

and setting

\[
n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2,
\]
Density Functional Theory

where \( N \) is the number of electrons. Eqs.(2.11),(2.12) and (2.13) are referred to as the Kohn-Sham equations. With the help of Eq.(2.12), the Kohn-Sham total energy functional can be written as [1]

\[
E_{KS}[n] = \sum_i \epsilon_i - \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} \, dr \, dr' - \int V_{xc}(r)n(r) \, dr + E_{xc}[n].
\]  

(2.14)

Keep in mind that the one-particle orbitals (the \( \psi \)'s) are not those of real particles. They are non-interacting quasi-particles whose purpose is to yield a correct groundstate density. These equations are much easier to solve than the many-body ones. The problem we face is that we don’t know the form of the exchange-correlation functional. In the next section we will look at two ways to approximate the exchange-correlation energy.

2.3 Exchange and correlation energy

2.3.1 Local density approximation (LDA)

As mentioned in the previous section, the exchange-correlation energy can be approximated as

\[
E_{LDA}^{xc}[n] = \int n(r) \epsilon_{xc}[n(r)] \, dr.
\]  

(2.15)

This is called the Local Density Approximation (LDA). It depends solely on the electronic density at each point in space. \( \epsilon_{xc} \) is the exchange-correlation energy for a single particle in a homogeneous gas. It’s common to split \( \epsilon_{xc} \) into an exchange and a correlation part to be solved separately

\[
\epsilon_{xc}[n] = \epsilon_x[n(r)] + \epsilon_c[n(r)].
\]  

(2.16)

The LDA works well for many systems, especially for uniform electron gas, where the functional can be found in conjunction with the homogeneous electron gas model. For smaller systems it’s not as good, a single atom is quite different from a uniform electron gas. Since DFT requires the charge density to be homogeneous, it’s not always very accurate. Real charge densities will not be homogeneous and if our system shows too much varying in charge density, then we need to find a way to improve our approximation.

2.3.2 Generalized Gradient Approximation (GGA)

Knowing that varying charge density causes errors to our approximation; finding a way to include the gradient of the charge density could improve our approximation. This is called the Generalized Gradient Approximation

\[
E^{GGA}_{xc}[n] = \int f[n(r), \nabla n(r)]n(r) \, dr.
\]  

(2.17)
2.4 Limitations of DFT

There is no universal form of the functional \( f[n(r), \nabla n(r)] \), it is found by parametrization and fitting to the calculations. There are many ways to construct this functional. The size of the molecules in the real system are often a hint to what functional to use.

2.4 Limitations of DFT

DFT has been a very successful theory in many various calculations. It has been used to calculate the interactions between electrons in many fields of research. It has worked particularly well for predictions of structure and thermodynamic properties of molecules and solids. The DFT formalism is exact and yet efficient. Success or failure is often decided by how well we can approximate the exchange and correlation energies. For many applications there are approximations for the exchange and correlations that works very well, for some, there is not. Some of the known shortcomings of the DFT are the underestimating of band gaps for materials and the energies of dissociating molecular ions. The two problems have the same root, it’s caused by the delocalization error of approximate functionals, due to the dominating Coulomb term that pushes electrons apart. Another problem is the difficulty to describe the interaction between degenerate states with a electron density function.

DFT is a ground state theory, the Kohn-Sham ansatz is used to replace the many-body system with a non-interacting system that has the same ground-state density. From this, we can find all ground- and excited states but we will have trouble finding a good approximation for the exchange and correlation energy in the total energy functional Eq.(2.14).

The elastic constant calculation is not that of excited state properties, but to calculate them for very high pressures provides a big challenge for DFT.
Density Functional Theory
Chapter 3

Numerical Methods

3.1 Solving the Kohn-Sham equations numerically

The Kohn-Sham equations [(2.11) to (2.13)] can be solved iteratively with a self-consistent method until convergence is reached in the following way:

1. Make a guess for the charge density \( n(r) \).
2. Use this density in the equation for the effective potential (2.11).
   \[
   V_{\text{eff}} = V_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|} dr' + V_{\text{xc}}(r)
   \]
3. Use the obtained effective potential to solve the Kohn-Sham Schrödinger equation (2.12).
   \[
   \{-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r)\} \psi_i(r) = \epsilon_i \psi_i(r)
   \]
4. Use the obtained solutions to the Schrödinger equation to calculate the charge density (Eq.2.13).
   \[
   n(r) = \sum_{i=1}^{N} |\psi_i(r)|
   \]
5. If the new density from step 4 is close enough to the density in the previous iteration, then we say that the calculation has converged and we can calculate the total energy. If not, we feed this new charge density into the equation for the effective potential as a better guess.

This way of feeding the new density back into the loop

\[
 n_{j+1}^{in} = n_j^{out} , \quad (3.1)
\]

is very simple but it often causes problems, one of those problems is oscillations when we are close to convergence. A way to help avoid this is by using linear
mixing, where more previous densities are included.

Differential equations are not well-suited to be solved on a computer, thus, the first step is to transform our single particle Schrödinger equation (2.11) into an algebraic one. This is done by expanding the wavefunctions in a basis set

\[ |\psi_i\rangle = \sum_j c_j |\varphi_j\rangle \]  

(3.2)

Inserting this into our single particle Schrödinger equation gives us

\[ H \sum_j c_j |\varphi_j\rangle = \epsilon_j \sum_j c_j |\varphi_j\rangle \]  

(3.3)

If we then multiply this equation with the bra-vector \( \langle \varphi_k | \) from the left, we get

\[ \sum_j c_j \langle \varphi_k | H | \varphi_j \rangle = \sum_j \epsilon_j c_j \langle \varphi_k | \varphi_j \rangle O_{kj} \]  

(3.4)

where \( H_{kj} \) are the matrix element of the hamiltonian, \( O_{kj} \) is the overlap matrix and \( \epsilon_j \) is the eigenvalue for state \( j \). This equation will only have non-trivial solutions if

\[ \det \{ H_{kj} - \epsilon_i O_{kj} \} = 0 \]  

(3.5)

### 3.2 Exact Muffin-Tin Orbital Method

One of the complications when constructing a basis is that greater accuracy of results requires more computational effort. While there are many ways to construct a basis, in this project we will be using the Exact Muffin-Tin Orbitals (EMTO) method [3], which I will explain in the section. The EMTO method is ideal for our purposes because it is an efficient way to find an approximation that is sufficiently accurate.

The EMTO is an expansion of the Muffin-Tin (MT) approximation. The MT approximation of the Kohn-Sham potential is spherically symmetric around the atom. The MT spheres are divided into two different radial parts, a smaller one with radii \( a_R \), which is non-overlapping “hard spheres”, and an outer part which overlaps with other spheres. To solve the one-particle Schrödinger equation (2.12) for the MT approximation of the potential, the wavefunction is expanded in a basis set [3]

\[ \psi_i(r) = \sum_{RL} \tilde{\Psi}_{RL}^i(\epsilon_i, r_R) u_{RL,i}^a \]  

(3.6)

The \( \tilde{\Psi}_{RL}^i(\epsilon_i, r_R) \) are the exact muffin tin orbitals and \( L = (l, m) \), denoting the orbital and magnetic quantum numbers. We want to expand our wavefunction so
3.2 Exact Muffin-Tin Orbital Method

that we get two different basis sets for the two regions of the MT potential. This
is done by expanding \( \psi_i(\mathbf{r}) \) as a sum of wavefunctions for the two regions [4]

\[
\psi_i(\mathbf{r}) = \sum_{RL} \phi(\epsilon_i, \mathbf{r}_R) \Theta(\mathbf{r}_R) \psi_{RL,\epsilon}^a(\mathbf{r}_R) + \sum_{RL} \tilde{\psi}_{RL}(k_i, \mathbf{r}_R) [1 - \Theta(\mathbf{r}_R)] \psi_{RL,\epsilon}^a(\mathbf{r}_R) .
\]

(3.7)

Here \( k = \epsilon - v_0 \), where \( v_0 \) is the constant potential in the interstitial region.
The \( u_{RL,\epsilon}^a \) and \( v_{RL,\epsilon}^a \) are expansion coefficients, which are determined from the
condition that the wavefunction \( \psi_i(\mathbf{r}) \) and its first derivative must be continuous in
the MT sphere. \( \epsilon_i \) is the one-particle energy. \( \Theta(\mathbf{r}_R) \) is a type of function such that

\[
\Theta(\mathbf{r}_R) = \begin{cases} 
1 & \text{if } \mathbf{r}_R \text{ inside the Muffin-Tin sphere} \\
0 & \text{if } \mathbf{r}_R \text{ outside the Muffin-Tin sphere}
\end{cases}
\]

(3.8)

The basis function \( \phi(\epsilon_i, \mathbf{r}_R) \) has the form

\[
\phi(\epsilon_i, \mathbf{r}_R) = \phi_{RL}(\epsilon_i, \mathbf{r}_R) Y_L(\hat{\mathbf{r}}) ,
\]

(3.9)

where \( \phi_{RL}(\epsilon_i, \mathbf{r}_R) \) are so-called partial-waves, which are solutions to the radial
Schrödinger equation, and \( Y_L(\hat{\mathbf{r}}) \) are spherical harmonics. In the interstitial region,
where the potential is approximated by \( v_0 \), the wavefunction is given by the
solutions to the Helmholtz equation:

\[
\left\{ \frac{1}{2} \nabla^2 + k^2 \right\} \psi_{RL}(k^2, \mathbf{r}_R) = 0 .
\]

(3.10)

The \( \psi_{RL}(k^2, \mathbf{r}_R) \) are referred to as screened spherical waves. Like the name im-
plies, these spherical waves have boundary conditions. The boundary conditions
are defined together with the non-overlapping hard spheres. The screened spherical
waves behave like pure real harmonics on their own hard spheres, while the
projection of the spherical harmonics on the other hard spheres must be zero. The
screened spherical waves form a complete basis in the region between the hard
spheres.

There is one more region that needs attention. It’s the region between the hard
spheres and the MT spheres. This is done by introducing a free-electron solution
\( \varphi_{RL}(\epsilon, \mathbf{r}_R) Y_L(\hat{\mathbf{r}}) \). This wavefunction links up with the partial- and screened spher-
ical waves both continuously and differentiably when the equation for the whole
crystal is solved. With all regions defined, we can now produce a complete basis
for all space. The exact muffin tin orbitals will have the form [4]:

\[
\tilde{\psi}_{RL}(\epsilon_i, \mathbf{r}_R) = \left[ \phi_{RL}(\epsilon, \mathbf{r}_R) - \varphi_{RL}(\epsilon, \mathbf{r}_R) \right] Y_L(\hat{\mathbf{r}}) + \psi_{RL}(k^2, \mathbf{r}_R) .
\]

(3.11)

The radial parts of \( \phi_{RL}(\epsilon, \mathbf{r}_R) \) and \( \varphi_{RL}(\epsilon, \mathbf{r}_R) \) are cut off at the muffin-tin sphere
and at the hard sphere, respectively. The function \( \psi_{RL}(k^2, \mathbf{r}_R) \) is cut off at the
hard sphere boundary. However, high \( l \) components can penetrate into the hard
sphere to cause kinks. The requirement for these kinks to vanish leads us to the
Korringa, Kohn, and Rostocker equation (KKR). The solutions to these equations
will give us the one-electron energies and eigenfunctions.
3.3 Coherent Potential Approximation

In a completely random binary alloy with A and B type of atoms of concentrations $c$ and $(1-c)$, the chance of finding an A or B atom at any site is given by its concentration. If we were to look at a very small part of our alloy, it wouldn’t look perfectly random. There would be clusters of A and/or B atoms. To give us a good representation of a random alloy, we would need a very large number of atoms. This is not yet possible because of the computational effort it would require.

One way to improve our model is to introduce a so-called effective medium. In the effective medium approach, the original alloy is replaced by a medium that describes the average properties of the system. We can then place “real” atoms into this environment and do our calculations. A schematic figure of this is shown in Fig.(3.1).

Figure 3.1. A random alloy is replaced by an effective medium (left), into which we can place real atoms one at the time.

The next step is to find a way to construct such effective medium. The simplest way is to calculate the average potential of our system - this is called the Virtual Crystal Approximation (VCA).

$$V_{\text{VCA}} = c \cdot V_A + (1-c) \cdot V_B . \quad (3.12)$$

Here, $V_A$ and $V_B$ are the potentials of two different types of atoms in our binary alloy. This approximation works fairly well when the atoms have similar potential.

A better way to approximate the effective medium potential is by using Coherent Potential Approximation (CPA)[17], proposed in 1967 by Paul Soven. A problem with the previous approximation was the scattering of electrons. An electron moving in the effective medium needs on average to scatter in the same way as in the real system. If we add a real atom to effective medium, we don’t want this atom to cause more scattering. The equation to be solved is the following [1]

$$[c \cdot V_A + (1-c) \cdot V_B] - V_0 = (V_A - V_0) \cdot \mathcal{G}_0 \cdot (V_B - V_0) , \quad (3.13)$$

where $\mathcal{G}_0$ is the Green function that solves the inhomogeneous differential equation, which is the result of the electron’s scattering in the medium. $V_0$ is the potential for the effective medium.
Chapter 4

Elastic properties

Elastic properties of materials are of great importance. A construction engineer needs to know the strain of a material when under stress from the forces acting on the construction. But, the elastic properties won’t just tell us how hard or strong materials are, they also help us understand how waves propagate in the material. The following basic theory for calculating elastic constants from first principle methods is, by most part, taken from the book *Introduction to Solid State Physics* by Charles Kittel [5].

### 4.1 Basic theory

The strain and stress are the two fundamentals when calculating the elastic properties for materials. We find them in *Hooke’s law*, which states that the strain on a elastic solid is directly proportional to the stress. In euclidean geometry we have three orthogonal vectors, $\hat{x}, \hat{y}, \hat{z}$ of unit length. These three vectors are emebedded into our (so far) unstrained solid. If we subject our solid to a uniform deformation, we can define the deformation by introducing three new vectors $x', y', z'$ as:

$$
\begin{align*}
x' &= (1 + \epsilon_{xx})\hat{x} + \epsilon_{xy}\hat{y} + \epsilon_{xz}\hat{z} \\
y' &= \epsilon_{yx}\hat{x} + (1 + \epsilon_{yy})\hat{y} + \epsilon_{yz}\hat{z} \\
z' &= \epsilon_{zx}\hat{x} + \epsilon_{zy}\hat{y} + (1 + \epsilon_{zz})\hat{z}.
\end{align*}
$$

The dimensionless coefficients $\epsilon_{\alpha\beta}$ define the deformation. They are to be kept very small. If we look at an atom at position $\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z}$, it will after a uniform deformation be at the position $\mathbf{r}' = x\hat{x}' + y\hat{y}' + z\hat{z}'$. We can now define the displacement $\mathbf{R}$ as

$$
\mathbf{R} \equiv \mathbf{r}' - \mathbf{r} = x(x' - \hat{x}) + y(y' - \hat{y}) + z(z' - \hat{z}).
$$

---

1In a uniform deformation, all primitive cells of the crystal is deformed in the same way.
From Eq.(4.1), we can write \( R \) as
\[
R \equiv (x\epsilon_{xx} + y\epsilon_{yx} + z\epsilon_{zx})\mathbf{x} + (x\epsilon_{xy} + y\epsilon_{yy} + z\epsilon_{zy})\mathbf{y} + (z\epsilon_{xz} + y\epsilon_{yz} + x\epsilon_{zz})\mathbf{z}.
\] (4.3)
By introducing \( u, v, w \), we can write the expression as
\[
R(r) = u(r)\mathbf{x} + v(r)\mathbf{y} + w(r)\mathbf{z}.
\] (4.4)
By Taylor expansion of \( R \) with \( R(0) = 0 \), we get
\[
x\epsilon_{xx} \approx \frac{\partial u}{\partial x}; \quad y\epsilon_{yx} \approx \frac{\partial v}{\partial y}; \quad \text{etc.}
\] (4.5)

4.1.1 Strain Components
Instead of \( \epsilon_{\alpha\beta} \), it’s common to use \( e_{\alpha\beta} \) as coefficients. They are called strain components and are defined as
\[
e_{xx} \equiv \epsilon_{xx} = \frac{\partial u}{\partial x}; \quad e_{yy} \equiv \epsilon_{yy} = \frac{\partial v}{\partial y}; \quad e_{zz} \equiv \epsilon_{zz} = \frac{\partial w}{\partial z}.
\] (4.6)
It’s evident that the strain components are defined as the change in length of the spatial axes. The other strain components \( e_{\alpha\beta}(= e_{\beta\alpha}) \) are defined as the change in angle between the axes
\[
e_{xy} \equiv x' \cdot y' \approx \epsilon_{yx} + \epsilon_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x};
\]
\[
e_{yz} \equiv y' \cdot z' \approx \epsilon_{yz} + \epsilon_{zy} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y};
\]
\[
e_{zx} \equiv z' \cdot x' \approx \epsilon_{zx} + \epsilon_{xz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}.
\] (4.7)

4.1.2 Stress Components
There are nine stress components: \( X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z \). The capital letter denotes the direction of the force and the subscript denotes the planes normal to which the force is acting. These nine stress components can be reduced to six by the condition that the angular acceleration is zero. Hence, there can’t be any torque. Therefore, \( X_y = Y_x, Y_z = Z_y \) and \( X_z = Z_x \). These are all shearing forces. The dimension of stress components is force per unit area or energy per unit volume. From Hooke’s law which states that the strain is proportional to the stress, we can define the stress components as [1]
\[
\sigma_{\alpha} = \sum_{\beta=1}^{6} c_{\alpha\beta} \cdot u_{\beta},
\] (4.8)
where the \( c \)’s are the elastic constants and the \( u \)’s are the stress components. The new notation for the stress components are related to the old one as
\[
\begin{pmatrix}
u_1 \\ u_6 \\ u_5 \\ u_4 \\ u_5 \\ u_4 \\ u_3
\end{pmatrix} =
\begin{pmatrix}
\epsilon_{xx} & 2\epsilon_{xy} & 2\epsilon_{xz} \\
2\epsilon_{xy} & \epsilon_{yy} & 2\epsilon_{yz} \\
2\epsilon_{xz} & 2\epsilon_{yz} & \epsilon_{zz}
\end{pmatrix}
\] (4.9)
4.2 Hexagonal Close Packed lattice

4.1.3 Elastic Energy Density

The potential energy for a spring is \( E_p = \frac{1}{2} kx^2 \), where \( k \) is the spring constant and \( x \) is the length by which the spring has been extended or compressed. The elastic energy density has the same form, in our simplified notation Eq.(4.8), the elastic energy density can be written as [1]

\[
U = \frac{1}{2} \sum_{\alpha=1}^{6} \sum_{\beta=1}^{6} c_{\alpha\beta} \cdot u_{\alpha} u_{\beta} .
\] (4.10)

Just like the potential energy of a spring, the elastic energy density for crystals is of harmonic form. As mentioned earlier, this is just valid for small deformations. The energy is the difference in energy between the distorted and undistorted crystal. The relation between energy and the elastic constant can be written as [1]

\[
\Delta E \approx A \cdot V \cdot c \cdot \delta^2 ,
\] (4.11)

where \( A \) is a constant that depends on the type of deformation, \( V \) is the volume of the unit cell, \( c \) is the elastic constant and \( \delta \) is the strain component. In practice, to find the elastic constants, we calculate the energy for several small deformations \( \delta = (0.00, 0.01, ..., 0.05) \). After this is done, the elastic constant can be found by linear fitting with \( x = \delta^2 \), where the slope of the curve will correspond to \( A \cdot V \cdot c \).

4.2 Hexagonal Close Packed lattice

The hexagonal close packed lattice has five independent elastic constants: \( c_{11}, c_{12}, c_{13}, c_{33}, c_{44} \). We will calculate \( c_{44}, c_{66}, R \) and \( c_s \). \( R \) and \( c_s \) are defined as [1]

\[
R = -\frac{d\ln(c/a)_{0}(V)}{d\ln V} \quad \text{(4.12)}
\]

\[
c_s = \frac{9(c/a)^2_0}{2V} \frac{\partial^2 E(V, c/a)}{\partial(c/a)^2} .
\] (4.13)

When we have these, then the rest of the elastic constants can be found by the relations [1]

\[
c_{66} = \frac{1}{2} (c_{11} - c_{12}) \quad \text{(4.14)}
\]

\[
B = \frac{c^2}{c_s}
\]

\[
c^2 \equiv c_{33}(c_{11} + c_{12}) = 2c_{13}^2
\]

\[
c_s \equiv c_{11} + c_{12} + 2c_{33} - 4c_{13}
\]

\[
R = \frac{c_{33} - c_{11} - c_{12} + c_{13}}{c_s} .
\]
By rearranging these we obtain the relations:

\[
\begin{align*}
    c_{11} &= \frac{1}{2} c_s + c_{66} + \frac{2 c_s}{9} (1 + R)(R - 2) + B \\
    c_{12} &= \frac{1}{2} c_s - c_{66} + \frac{2 c_s}{9} (1 + R)(R - 2) + B \\
    c_{13} &= B + \frac{c_s}{9} (1 + R)(2R - 1) \\
    c_{33} &= B + \frac{2 c_s}{9} (1 + R)^2.
\end{align*}
\]  

So, with the use of \( c_{66}, c_s, R \) and \( B \) we can calculate all the elastic constants for the hexagonal closed packed lattice, all except \( c_{44} \), which we need to calculate separately. \( c_s \) and \( R \) are not very interesting in themselves, they are auxiliary elastic constants that helps us obtain \( c_{11}, c_{12}, c_{13} \) and \( c_{33} \). \( B \) is called the bulk modulus and is explained in section 4.3, along with \((c/a)\) from Eqs.(4.12 and 4.13).

4.2.1 Polycrystalline elastic constants

When measuring the elastic properites of a material we need to remember that most materials found in nature are polycrystalline. This means that the many single crystals in our material will be oriented in different directions relative to each other. We know that the elastic constants for single crystals are direction-dependent. Therefore we need to find a way of averaging the elastic properties. On a large scale, the material can be statistically seen as isotropic. An isotropic system is completely descried by its bulk modulus \( (B) \) and shear modulus \( (G) \). The shear modulus can be calculated by the use of the Voigt and Reuss definition of shear moduli \( (G_V \) and \( G_R) \). In the Voigt shear modulus, the strain is uniform, while in the Reuss shear modulus, the stress is uniform. The Voigt and Reuss shear moduli are defined as [3]

\[
\begin{align*}
    G_V &= \frac{12 c_{44} + 12 c_{66} + c_s}{30} \\
    G_R &= \frac{5}{2} \frac{c_{44} c_{66} c_s^2}{(c_{44} + c_{66}) c_s^2 + 3 B_V c_{44} c_{66}},
\end{align*}
\]  

where \( B_V \) is the Voigt bulk modulus, defined as

\[
B_V = \frac{2(c_{11} + c_{12}) + 4 c_{13} + c_{33}}{9}.
\]  

The anisotropy can be calculated by use of the Voigt-Reuss-Hill definition of anisotropy

\[
A = \frac{G_V - G_R}{G_V + G_R},
\]  

which is the difference between the Voigt- and Reuss shear moduli.
4.3 Calculating elastic constants

Another interesting property is the propagation of sound in a polycrystalline material. The sound velocity is isotropic but different for the transversal and longitudinal propagation. The sound velocities are given by

\[ \rho v_T^2 = B + \frac{4}{3}G \]
\[ \rho v_L^2 = G \]

where \( \rho \) is the density.

4.3 Calculating elastic constants

In this diploma project I used an EMTO software package written by L. Vitos et al to do my calculations. The program’s function is to solve the Kohn-Sham equations (2.11-2.13) iteratively by a self-consistent method, as explained in section 3.1. The EMTO software package uses the exact muffin tin orbitals basis set which is described in section 3.2.

I will go through the process of calculating elastic constants for the hexagonal closed packed lattice, step by step. The results can be seen in the results chapter.

4.3.1 c over a ratio

The first thing to do is to find the optimal \((c/a)\) for the HCP crystal, meaning the \(c\) over \(a\) ratio that yields the lowest energy and therefore the most stable state. From simple geometry we know that the ideal value for the \((c/a)\) is \(\frac{8}{3}\)\(^{1/2}\) \(\approx 1.633\), but the actual value departs somewhat from the ideal value. To find the optimal value I calculated the energy for seven different \((c/a)\), I chose 1.54 to 1.66 in steps of 0.02. The resulting energies as function of the \((c/a)\) is then fitted to a curve and the \((c/a)\) that results in the lowest energy is found. This has to be done for every volume of the Wigner-Seitz cell, which is the primitive cell.

4.3.2 Equation of State and Bulk Modulus

The equation of state (EOS) is the relation between the pressure on the crystal and the volume of the Wigner-Seitz cell. The calculations was done for eleven different volumes with the corresponding optimal \((c/a)\). The parameter when choosing the volume is the Wigner-Seitz radius \((R_{ws})\), which is the radius of a sphere that has the same volume as the Wigner-Seitz cell. The chosen radii where 2.10 to 2.60 au in steps of 0.05 au. The energies are then calculated as a function of volume. The EOS and bulk modulus are found by use of the relations

\[ P = -\frac{\partial E}{\partial V} \]
\[ B = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E}{\partial V^2} \]
The EOS was calculated by the use of a program written by I. A. Abrikosov. The program allowed a curve to be fitted to the data points. The type of fitting I used is called Birch-Murnaghan EOS\cite{BirchMurnaghan} given by the following expression

\[ P = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \cdot \left[ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \]

where \( V_0 \) is the equilibrium volume and \( B_0 = B(V_0) \).

### 4.3.3 Elastic constants

The elastic constants were calculated for the same volumes as the EOS with the use of volume conserving deformations. This means that the Wigner-Seitz cells in the distorted and undistorted crystal is of the same volume. To calculate the \( c_{44} \) elastic constant, I used a simple monoclinic\textsuperscript{2} lattice, with the following deformations

\[ u_2 = \delta^2 \left( \frac{1}{1 - \delta^2} \right), \quad u_5 = 2\delta. \]  

As mentioned in section 4.1.3, this was done for five small deformations and also including calculations for the undistorted simple monoclinic lattice (i.e. \( \delta = 0.00 \)). The energy for each distortion is calculated. After that, the elastic constants can be calculated from linear fitting, as explained in section 4.1.3.

The \( c_{66} \) elastic constant were calculated by the use of a base-centered orthorhombic lattice with the following deformations

\[ u_1 = \delta, \quad u_2 = -\delta, \quad u_3 = \delta^2 \left( \frac{1}{1 - \delta^2} \right). \]  

### 4.3.4 Density

The density which is pressure/volume dependent can be calculated by the use of the simple formula

\[ \rho = \frac{\sum_i m_i \cdot c_i}{V}, \]  

where \( m \) is the atomic mass, \( V \) is the volume of the Wigner-Seitz cell and \( c_i \) is the concentration for each element in the alloy.

### 4.3.5 Polycrystalline properties

When we have acquired all the elastic constants and the density, the polycrystalline properties can easily be found by the use of the relations in section (4.2.1). The sound velocity anisotropy can be plotted in maps to give a graphical representation.

\textsuperscript{2}With the right choice of basis, this forms an HCP structure.
Chapter 5

Results

We will focus our attention on the pressure of 300 GPa, which is roughly the pressure at the inner core of our planet. I have made tables with data taken from the plots at 300 GPa. The rightmost column is the difference in percentage from the value of pure iron. The results for Fe and Fe-Ni are taken from Ref[7] and the results for Fe-Mg are from Ref[6].
5.1 Equilibrium c/a ratio

The \((c/a)\) ratio doesn’t vary a lot with pressure. From 0 to 300 GPa, it changes less than 1%. Adding of nickel and/or magnesium changes the \((c/a)\), but not by much. What we can see is that the \((c/a)\) increases with increasing amounts of nickel. The \((c/a)\) for equivalent amounts of magnesium instead of nickel is higher. Also, the \((c/a)\) changes faster with increasing amounts of magnesium than with nickel. We see a further increase if we mix both nickel and magnesium into our iron. The theoretical \((c/a)\) value is \((\frac{2}{3})^{1/2} \approx 1.633\).

<table>
<thead>
<tr>
<th>((c/a)) at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
</tr>
<tr>
<td>Fe0.95Ni0.05: Ref[7]</td>
</tr>
<tr>
<td>Fe0.90Ni1.0: Ref[7]</td>
</tr>
<tr>
<td>Fe0.95Mg0.05: Ref[6]</td>
</tr>
<tr>
<td>Fe0.90Mg1.0: Ref[6]</td>
</tr>
<tr>
<td>Fe0.85Ni1.0Mg0.05</td>
</tr>
<tr>
<td>Fe0.80Ni1.5Mg0.05</td>
</tr>
</tbody>
</table>

Figure 5.1. Optimal \((c/a)\) ratio as a function of pressure.
5.2 Equation of State

The equation of state for iron doesn’t change much if we add magnesium and/or nickel. The effect becomes smaller with increasing pressure, which means that they are converging towards the equation of state for pure iron. It’s hard to distinguish the different alloy compositions in Fig.(5.2) for high pressures. Fig.(5.3) is a close-up of the equation of state at around 300 GPa. Magnesium has yet again more effect than nickel and the result for Fe90Mg10 are very similar to that of Fe85Ni10Mg05. Iron and nickel atoms are very similar in size and weight so we don’t expect the equation of state for Fe-Ni alloys to differ much from that of pure iron. Magnesium atoms take up a lot of space and thus causes an increase in volume for the Fe-Mg and Fe-Ni-Mg alloys. The effect decreases with pressure because of the great compressibility of magnesium atoms.

![Equation of state in HCP](image)

**Figure 5.2.** Volume as a function of pressure.
Figure 5.3. Volume as a function of pressure.

5.2.1 Density

The difference in volume between the alloys isn’t large when we are at 300 GPa and thus we don’t see a big difference in density. The Fe-Ni alloy is slightly heavier than pure iron and this is mainly because of nickel being heavier than iron. Fe-Mg is a bit lighter than pure iron because of magnesium being a lot lighter than iron. In the Preliminary Reference Earth Model (PREM), 300 GPa corresponds to the pressure just outside the inner core. This is the reason to why the densities don’t match very well. When entering the inner core, the density takes a big leap. For this reason have I also calculated the densities at 330GPa and compared them to the PREM’s densities at 330GPa, which according to PREM puts us in the inner core.

<table>
<thead>
<tr>
<th>Density ((kg/m^3)) at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
</tr>
<tr>
<td>PREM: Ref[15]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density ((kg/m^3)) at 330 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
</tr>
<tr>
<td>PREM: Ref[15]</td>
</tr>
</tbody>
</table>
5.3 Elastic constants

5.3.1 Bulk modulus

Adding nickel hardly has any effect on the bulk modulus at all. At the pressure of 300 GPa, the effects on the bulk modulus from 5% and 10% nickel is less than 1 Gpa. Magnesium, on the other hand, does have an ample effect on the bulk modulus. Adding 5% magnesium will roughly lower the bulk modulus at 300 GPa by 35 GPa. 10% magnesium will lower it by 72 GPa. The bulk modulus for Fe85Ni10Mg05 and Fe80Ni15Mg05 is very close to that of Fe95Mg05, which again tells us that nickel doesn’t have much effect on the bulk modulus and that nickel together with magnesium won’t change that.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bmod at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>1335</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>1336 ≈ 0%</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>1336 ≈ 0%</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>1300 − 2.6%</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>1263 − 5.4%</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>1298 − 2.8%</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>1298 − 2.8%</td>
</tr>
</tbody>
</table>

![Bulk modulus as a function of pressure.](image)

Figure 5.4. Bulk modulus as a function of pressure.
5.3.2 $c_{44}$

Except for the bulk modulus, $c_{44}$ and $c_{66}$ are the only elastic constants that have been calculated directly without the use of the auxiliary elastic constants $R$ and $c_s$. The $c_{44}$ elastic constant changes a lot with alloy composition and the effect increases with increasing pressure. Both nickel and magnesium have a softening effect with the latter being the more potent. The result for Fe85Ni10Mg05 is similar to that of Fe95Mg05, which tells us that the softening effect of nickel and magnesium in the Fe-Ni-Mg alloy isn’t simply the sum of the softening effects of the Fe-Ni and Fe-Mg alloys together.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$c_{44}$ (GPa)</th>
<th>Softening (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>488</td>
<td></td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>457</td>
<td>−6.3%</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>431</td>
<td>−11.7%</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>388</td>
<td>−20.2%</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>329</td>
<td>−32.4%</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>392</td>
<td>−19.6%</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>376</td>
<td>−23.0%</td>
</tr>
</tbody>
</table>

**Figure 5.5.** $c_{44}$ elastic constant as a function of pressure.
5.3 Elastic constants

5.3.3 $c_{66}$

The $c_{66}$ elastic constant changes a lot with alloy composition. Nickel has a small softening effect on the crystal structure while the softening effects on magnesium is significant. The softening effect of Fe-Ni and Fe-Ni-Mg roughly remains the same when we alter the pressure while the effects of Fe-Mg increase with increasing pressure. The softening effect of magnesium is decreased when we also introduce nickel in the alloy.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>$c_{66}$ at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>623</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>611 $-1.9%$</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>598 $-4.0%$</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>467 $-23.5%$</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>393 $-37.0%$</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>553 $-11.2%$</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>544 $-12.7%$</td>
</tr>
</tbody>
</table>

Figure 5.6. $c_{66}$ elastic constant as a function of pressure.
5.3.4 $c_{11}$

Nickel doesn’t have much effect on the $c_{11}$ elastic constant and it doesn’t change with increasing pressure. Magnesium has a softening effect and it increases with pressure and also with the amount of magnesium in the alloy. The softening effect of magnesium is reduced when we also introduce nickel in the alloy.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Reference</th>
<th>$c_{11}$ at 300 GPa</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>2207</td>
<td>-0.4%</td>
<td></td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>2199</td>
<td>-0.4%</td>
<td></td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>2184</td>
<td>-1.1%</td>
<td></td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>2011</td>
<td>-8.9%</td>
<td></td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>1881</td>
<td>-14.8%</td>
<td></td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>2088</td>
<td>-5.4%</td>
<td></td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>2076</td>
<td>-5.9%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.7. $c_{11}$ elastic constant as a function of pressure.
5.3 Elastic constants

5.3.5 $c_{12}$

For the $c_{12}$ elastic constant, adding nickel and/or magnesium will have a hardening effect. Once again, magnesium has far more effect than nickel. The elastic constants for the Fe-Ni and Fe-Ni-Mg alloys are similar, which tells us that the hardening effect of magnesium almost vanishes when we also add nickel to the alloy. We can also notice that the elastic constant for Fe-Mg increases faster with increasing pressure than those for the other alloy compositions.

<table>
<thead>
<tr>
<th>$c_{12}$ at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
</tr>
<tr>
<td>961</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
</tr>
<tr>
<td>977</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
</tr>
<tr>
<td>987</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
</tr>
<tr>
<td>1076</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
</tr>
<tr>
<td>1112</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
</tr>
<tr>
<td>982</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
</tr>
<tr>
<td>989</td>
</tr>
</tbody>
</table>

Figure 5.8. $c_{12}$ elastic constant as a function of pressure.
5.3.6 $c_{13}$

It’s hard making sense out of the $c_{13}$ data. What we can tell from looking at the plot is that the $c_{13}$ elastic constant doesn’t vary a lot with alloy composition and that when the pressure raises, some of the curves cross. It might be because of numerical difficulties or a result of the methods used.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$c_{13}$ at 300 GPa</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>815</td>
<td>-0.5%</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>810</td>
<td>-0.5%</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>817</td>
<td>+0.3%</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>799</td>
<td>-1.9%</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>805</td>
<td>-1.1%</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>810</td>
<td>-0.5%</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>817</td>
<td>+0.3%</td>
</tr>
</tbody>
</table>

Figure 5.9. $c_{13}$ elastic constant as a function of pressure.
5.3 Elastic constants

5.3.7 $c_{33}$

Adding nickel to iron hardly has any effect on the $c_{33}$ elastic constant, but nickel together with magnesium has more softening effect than just having magnesium. This effect doesn’t increase much when we alter the amount of nickel from 5% to 10% in the Fe-Ni-Mg alloy. The Fe-Mg alloy with 10% of magnesium has the most softening effect.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$c_{33}$ at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>2420</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>2430 +0.4%</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>2415 −0.2%</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>2330 −3.7%</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>2236 −7.6%</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>2300 −5.0%</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>2285 −5.6%</td>
</tr>
</tbody>
</table>

![Figure 5.10. $c_{33}$ elastic constant as a function of pressure.](image-url)
5.3.8 Voight and Reuss shear moduli

<table>
<thead>
<tr>
<th></th>
<th>$G_V$</th>
<th>$G_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>663</td>
<td>583</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>587</td>
<td>562</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>569</td>
<td>540</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>494</td>
<td>465</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>428</td>
<td>395</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>526</td>
<td>497</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>513</td>
<td>482</td>
</tr>
</tbody>
</table>

$G_V$ and $G_R$ at 300 GPa

The Voight and Reuss shear moduli appear very similar. The two plots look almost identical, $G_V$ and $G_R$ are approximately separated by 28 GPa. This tells us that the anisotropy for HCP iron alloys isn’t very pressure dependent. Both nickel and magnesium have a softening effect, with the latter being the more potent. The softening effect of magnesium is hampered if we also add nickel to the alloy.

![Figure 5.11. Voigt shear modulus as a function of pressure.](image)
5.3 Elastic constants

![Graph showing Reuss shear modulus as a function of pressure.](image)

**Figure 5.12.** Reuss shear modulus as a function of pressure.
5.3.9 Anisotropy

The HCP crystal is almost isotropic for iron alloys but the low level of anisotropy increases slightly with the adding of nickel and/or magnesium. The anisotropy for Fe-Mg increases a bit with pressure while the others roughly remains the same.

<table>
<thead>
<tr>
<th></th>
<th>Anisotropy at 300 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: Ref[7]</td>
<td>1.6%</td>
</tr>
<tr>
<td>Fe95Ni05: Ref[7]</td>
<td>2.2%</td>
</tr>
<tr>
<td>Fe90Ni10: Ref[7]</td>
<td>2.6%</td>
</tr>
<tr>
<td>Fe95Mg05: Ref[6]</td>
<td>3.0%</td>
</tr>
<tr>
<td>Fe90Mg10: Ref[6]</td>
<td>4.0%</td>
</tr>
<tr>
<td>Fe85Ni10Mg05</td>
<td>2.9%</td>
</tr>
<tr>
<td>Fe80Ni15Mg05</td>
<td>3.2%</td>
</tr>
</tbody>
</table>

Figure 5.13. Anisotropy as a function of pressure.
Chapter 6

Conclusion and outlook

6.1 Conclusion

The purpose of this diploma project was to investigate the elastic properties of the HCP Fe-Ni-Mg alloy at high pressure. The question I want to answer is: what distinguishes the Fe-Ni-Mg alloy from the Fe-Ni and Fe-Mg alloys? Magnesium has a softening effect on the HCP iron alloy for all elastic constants, except for $c_{12}$ (and possibly $c_{13}$), and I don’t know the reason for this. The results for $c_{13}$ are not very pleasing. Some of the curves cross each other. This is probably because of very weak dependence of $c_{13}$ on alloy composition. The two shear elastic constants $c_{44}$ and $c_{66}$ display the biggest relative changes in elastic constant with different iron alloys. They are also the two elastic constants where the softening effects of nickel and/or magnesium show the most pressure dependence. An isotropic system is completely described by its bulk- and shear modulus. I’ve shown that the HCP Fe-Ni-Mg alloys are almost isotropic, so the bulk- and shear modulus plots should tell us what we want to know. A recurring effect of the Fe-Ni-Mg alloy is that the effects of magnesium are stronger when not mixed with nickel. Fe95Mg05 is softer than Fe85Ni10Mg05 even tough they both have 5% magnesium. Add nickel to Fe and it has a softening effect. Add nickel to Fe-Mg and you could say it has a hardening effect. The bulk modulus doesn’t vary much with alloy composition. The effects of nickel are insignificant but magnesium has a slight softening effect, which isn’t hampered when we also add nickel to the alloy.

The conclusion is that small amounts of nickel and/or magnesium can have great effect on the elastic properties of iron. The most interesting result of my work is the weakening effect of nickel when mixed into Fe-Mg.

6.2 Outlook

In these calculations, the kinetic energy of the nuclei is set to zero. This is done by choosing the fixed temperature of 0°K. This is one of the shortcomings of this method. With better computers it would be possible to do more accurate calcu-
lations. This would mean we would not have to make this assumption regarding the kinetic energy of the nuclei.

If possible, the elastic properties of Fe-Ni-Mg need to be investigated for more crystal structures. It could also be interesting to investigate what effect a very small impurity of magnesium could have on iron. We know that 5% of magnesium can have a big effect on the elastic properties. What about 1% of magnesium? I would also like to know what happens if we add just a few percent of nickel to the Fe-Mg alloy, would the small amounts nickel have a substantial effect on the elastic properties?
Bibliography


