First-principles investigations of ordering in binary alloys

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Doctoral thesis
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Stockholm, October, 2013
Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan framlägges
till offentlig granskning för avläggande av doktorexamen fredagen den 18 oktober 2013
kl 10:00 i sal B1, Kungliga Tekniska Högskolan, Brinellvägen 23, Stockholm.

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Tryck: Universitetsservice US AB
Abstract

The aim of the thesis is to study ordering in binary alloys on the basis of first-principles or \textit{ab-initio} techniques employing density functional theory (DFT). The ordering phenomena of materials are of crucial importance for technological applications. The results of the thesis are intended to demonstrate the applicability of the first-principles calculations to provide fundamental insight to the true, namely electronic structure, nature of ordering in binary alloys.

The main part of the thesis focuses on atomic short- and long-range order phenomena in binary alloys as a function of both temperature and chemical composition in FeCo and NiCr alloys. In particular, the influence of magnetism on atomic ordering in FeCo alloys is investigated using the disordered local moment. A large number of concentration dependent effective cluster interactions, derived without the use of any adjustable parameters, are obtained by the SGPM as it is implemented in the EMTO within the CPA. The SGPM interactions can subsequently be used in thermodynamic Monte-Carlo simulations or mean field approximations to determine the ordering phenomena in binary alloys.

First-principles calculations of intrinsic stacking-fault energies (SFE) and anti-phase boundary energies (APBE) in Al\textsubscript{3}Sc and the effects of temperature on SFE and APBE are investigated by using the axial Ising model and supercell approach. Temperature effects have been taken into consideration by including the one-electron thermal excitations in the electronic structure calculations, and vibrational free energy in the harmonic approximation as well as by using temperature dependent lattice constants. The latter has been determined within the Debye-Grüneisen model, which reproduces well the experimental data.

Within the framework of the quasiharmonic approximation, the thermodynamics and elastic properties of B2- FeCo alloy are studied using first-principles calculations. The calculated thermal and elastic properties are found to be in good agreement with the available measured values when the generalized gradient approximations is used for the exchange correlation potential. The calculated finite temperature elastic constants show that the FeCo alloy is mechanically stable in the ordered phase. Meanwhile, a large elastic anisotropy exhibits a moderate dependence on temperature.
List of included publications:

1. Magnetic state effect upon the order-disorder phase transition in FeCo alloys: A first-principles study.

2. Temperature dependence of stacking-fault and anti-phase boundary energies in Al$_3$Sc from \textit{ab initio} calculations.

3. An augmented space based cluster coherent potential approximation for binary random and short-range ordered alloys.


5. First-principles study of atomic ordering in fcc Ni-Cr alloys.
   Moshiour Rahaman, B. Johansson and A.V. Ruban, \textit{submitted}.

   Moshiour Rahaman, B. Johansson and A.V. Ruban, \textit{in manuscript}.

Comment on my contributions

- \textbf{paper 1:} 80\% of calculations, data presentation, literature review and the manuscript was prepared jointly.

- \textbf{paper 2:} 90\% of calculations, data presentation, literature review and the manuscript was prepared jointly.
paper 3: 90% of calculations, data presentation, literature review and the manuscript was prepared jointly.

paper 4: 90% of calculations, data presentation, literature review and the manuscript was prepared jointly.

paper 5: 90% of calculations, data presentation, literature review and the manuscript was prepared jointly.

paper 6: all calculations, data presentation, literature review and the manuscript was prepared jointly.

Publications not included in the thesis:

7. Study of disorder-order transitions in Fe$_x$Al$_{1-x}$ binary alloys using the augmented space recursion based orbital peeling technique.

8. Magnetic transitions in Ni$_{1-x}$Mo$_x$ and Ni$_{1-x}$W$_x$ disordered alloys.
   Prashant Singh, Moshiour Rahaman and Abhijit Mookerjee, IJMPB, 323, 2478 (2011)

   Moshiour Rahaman and Abhijit Mookerjee, IJMPB, 25, 735 (2011)


11. Time-independent excited-state density functional theory.

12. Study of phase stability in a class of binary alloys using augmented space recursion based orbital peeling technique.
Contents

1 Introduction .............................................. 1
   1.1 Density Functional Theory ............................ 3
       1.1.1 Definition of the problem ......................... 3
       1.1.2 The Hohenbergh-Kohn Theorem ...................... 4
       1.1.3 Kohn-Sham theory by Legendre transforms .......... 4
   1.2 Basic assumptions of electronic band theory .......... 7
   1.3 Green Function formalism ............................. 7
   1.4 Exact Muffin-Tin Orbital method .................... 10
   1.5 Comments ............................................ 13

2 Electronic structure calculation in random binary alloys 14
   2.1 Introduction ........................................ 14
   2.2 Theoretical approach ................................. 16
       2.2.1 Basic definitions ................................. 16
       2.2.2 Cluster expansion ................................ 18
   2.3 Coherent Potential Approximation .................... 19
       2.3.1 Scattering path operators ......................... 21
   2.4 Generalized perturbation method ..................... 22

3 Order-Disorder Phase Transition of FeCo alloys 25
   3.1 Introduction ........................................ 25
   3.2 Methodology ......................................... 27
       3.2.1 Effective cluster interactions for finite magnetization 27
       3.2.2 Details of the first principles calculations ......... 28
   3.3 Results and discussion ................................ 30
       3.3.1 Electronic structure and magnetic properties of Fe-Co alloy 30
       3.3.2 Effective cluster interactions and ordering energies in the FM state 33
       3.3.3 Order-disorder phase transition in the reduced ferromagnetic state 37
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2.1</td>
<td>Temperature-dependent properties</td>
<td>84</td>
</tr>
<tr>
<td>6.2.1.1</td>
<td>Vibrational contribution from DFPT</td>
<td>85</td>
</tr>
<tr>
<td>6.2.1.2</td>
<td>Vibrational contribution from the Debye-Grüneisen model</td>
<td>85</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Elastic Constants</td>
<td>86</td>
</tr>
<tr>
<td>6.2.3</td>
<td>Details of the first-principles and phonon calculations</td>
<td>88</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and discussion</td>
<td>88</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Thermal lattice expansion of B2-FeCo</td>
<td>88</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Elastic properties of FeCo</td>
<td>90</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Conclusion</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>Conclusion and future directions</td>
<td>95</td>
</tr>
<tr>
<td>7.1</td>
<td>General Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>7.2</td>
<td>Future directions</td>
<td>96</td>
</tr>
</tbody>
</table>

References | 98 |
Chapter 1

Introduction

All materials that surround us are built out of atoms. Atoms are themselves built out of a positively charged nuclei surrounded by negativity charged electrons. In solids, the atoms are closely packed and arranged in either a regular lattice or a random network. The atoms are so closely packed that the outer electronic shells of neighbouring atoms start to overlap. The atomic picture of electronic structure breaks down and a new picture emerges, in which the outer electrons are no longer attached to a single nucleus. In metals for instance, these electrons can jump from one atom to another, and can more or less move freely through the solid. The electronic structure of a solid can, however, still be deduced from the constituent atoms. The energy levels of the atomic orbitals spread out into the energy bands for solids. At T=0K, the highest energy filled by electrons is called the Fermi level, which marks the separation between occupied and unoccupied states. Many properties of solids are determined by the behaviour of the electrons in the bands that have energies close to the Fermi level. This is schematically shown in Fig. 1.1.

Assuming a knowledge of the types of atoms comprising any given material, a computational approach enables us to answer two basic questions:

- What is the atomic structure of the material?
- What are its electronic properties?

A number of methods to derive answers to these questions have been developed. These methods for computing the structure and properties of materials can conditionally be divided into two classes

- The empirical or semi-empirical methods, which directly depend on empirical or experimental derived quantities.
Figure 1.1: Solid - Schematic diagram of electronic structure of solid

- The first-principles or ab initio methods, which do not use any empirically or experimentally derived quantities.

First-principles electronic structure calculations begin with the basic Schrödinger equation, which governs all quantum phenomenon at a non-relativistic level. Clearly, the calculation for a material is truly a many-body problem. The Hamiltonian of the system contains kinetic energy of the nuclei and electrons as well as all kind of interactions between electron-electron, electron-nuclei, nuclei-nuclei. Let us begin by considering system consisting of $N_c$ ion-cores bonded in a solid by $N_e$ valence electrons. The many body non-relativistic Hamiltonian $[1]$ is:

$$H = \sum_{I=1}^{N_c} \frac{\nabla^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\nabla^2}{2m_e} + V_{ee}(\{r\}) + V_{el}(\{r_i\}, \{R_I\}) + V_{ll}(\{RI\}) \quad (1.1)$$

where $V_{ee}$, $V_{ll}$ and $V_{el}$ are the Coulomb interactions between the electrons, the ions themselves and between the electrons and ions. The many-particle wave function of the system $\Psi$ depends on both electron and nucleus coordinates

$$\Psi = \Psi(r_1, r_2, \ldots, r_{N_e}; R_1, R_2, \ldots, R_{N_c}) \quad (1.2)$$

According to Born-Oppenheimer approximation$[2]$, the nuclei, which are much heavier than electrons, move relatively slowly and may be treated as stationary, while electrons move relative to them. Hence, the nuclei can be thought as being fixed, which makes it possible to solve the Schrödinger equation for the wave function of electrons alone. However, the electron energy depends on the nucleus positions

$$\Psi(\{R_I\}, \{r_i\}) \approx \chi(\{R_I\})\psi(\{r_i\}|\{R_I\}) \quad (1.3)$$
1.1 Density Functional Theory

Thus, the Schrödinger equation for the electrons leads
\[
\left[-\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + V_{el}(\{r_i\}|\{R_I\}) + V_{ee}(\{r_i\}) \right] \psi(\{r_i\}|\{R_I\}) = E_e(\{R_I\}) \psi(\{r_i\}|\{R_I\}) \quad (1.4)
\]

The total energy of the system is a sum of electron and nucleus energies. The problem in trying to solve this equation is the number of variables involved. This is \( \sim O(10^{20})! \)
We have to therefore bypass the difficulty by trying to describe physical properties not in terms of the many-body wave-function with enormous degrees of freedom but describe them with respect to a function of a few variables only.

1.1 Density Functional Theory

Most electronic structure calculations for solids are based on density functional theory (DFT) \[3, 4\], which results from the work of Hohenberg, Kohn and Sham. In DFT, the electronic orbitals are solutions to a Shrödinger equation which depends on the electron density rather than on the individual electron orbitals.

1.1.1 Definition of the problem

Density-functional theory in its earliest formulation by Hohenburg, Kohn and Sham \[3, 4\] aims at a description of ground state properties of many-electron systems in terms of the electron density. Consider a Hamiltonian of a stationary many-body system
\[
\hat{H}_v = \hat{T} + \hat{V} + \hat{W} = \sum_{i=1}^{N} -\frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N} v(\{r_i\}) + \sum_{i>j}^{N} w(|\{r_i - r_j|) \quad (1.5)
\]

where \( \hat{T} \) is the kinetic energy of the electrons, \( \hat{V} \) the external potential, and \( \hat{W} \) the two-particle interaction. We denote the Hamilton operator \( \hat{H}_v \) with a subindex \( v \) to indicate that we will consider the Hamiltonian as a functional of the external potential \( v(r) \). We are interested in electronic systems, i.e. molecules and solids. For all these systems the kinetic energy operator \( \hat{T} \) and two-particle interaction \( \hat{W} \) are identical. They only differ in the form of the external potential \( v(r) \) and the number of electrons \( N \). The properties of all these systems can therefore be regarded as a functional of the external potential \( v(r) \). So, the corresponding wave function \( |\Psi[v]\rangle \) and the total energy \( E[v] \), which are of course related by the Schrödinger equation
\[
(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \quad (1.6)
\]
1.1 Density Functional Theory

where the external potential specifically can be written as

\[ \hat{V} = \int d^3rv(r)\hat{n}(r) \]  

(1.7)

The electron density corresponding to a normalized \(N\)-electron wave function is defined as

\[ n(r) = N \int |\Psi(r, r_2, ..., r_N)|^2 dr_2 ... dr_N \]  

(1.8)

1.1.2 The Hohenbergh-Kohn Theorem

At the heart of DFT is the Hohenbergh-Kohn theorem\[3\], which states that for a given ground states density \(n(r)\) it is possible, in principle, to calculate the corresponding ground state wave functions \(\Psi(r_1, r_2, ..., r_N)\). In mathematical terms, \(\Psi\) is a functional of \(n(r)\). For future reference, we provide a commented summary\[5, 6\] of the Hohenbergh-Kohn theorem.

The density \(n(r)\) corresponding to a non-degenerate ground state specifies the external potential \(v(r)\) up to a constant and the ground state wavefunction \(|\Psi[n]\rangle\) up to a phase factor.

1. Any ground state expectation value corresponding to an observable \(\hat{O}\) is a functional of the density

\[ O[n] = \langle \Psi[n]|\hat{O}|\Psi[n]\rangle \]  

(1.9)

2. The ground state energy of a system with a nondegenerate ground state and an external potential \(v\) can be obtained from

\[ E[v] = \inf_{n \in A} \left\{ \int n(r)v(r)\,dr + F[n] \right\} ; \]  

(1.10)

where \(F[n] = \langle \Psi[n]|\hat{T} + \hat{W}|\Psi[n]\rangle\) and \(A\) is a set of density. The infimum is a minimum. This restricted minimization procedure is usually referred to as the Levy-Lieb\[5, 6\] constrained search.

3. \(F[n]\) is differentiable over \(A\).

1.1.3 Kohn-Sham theory by Legendre transforms

The method described here is based on the work of De Dominics and Martin\[7\] and Fukuda\[8\]. We have seen from equation (1.6) that the ground state energy \(E[v]\) and wave function \(|\Psi[v]\rangle\) are functionals of external potential. We have

\[ (\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \]  

(1.11)
1.1 Density Functional Theory

Now multiplying by $\langle \Psi \rangle$ on both sides of the above equation, we get

$$E[v] = \langle \Psi[v] | H_v | \Psi[v] \rangle \langle v $$

(1.12)

Our goal is to make a relation demonstrating that the density and the potential are conjugate variables. We will use this relation when we take the functional derivative of the energy functional $E[v]$ with respect to the potential $v(r)$

$$\frac{\delta E}{\delta v(r)} = \langle \frac{\delta \Psi}{\delta v(r)} | \hat{H} | \Psi \rangle + \langle \Psi | \frac{\delta \hat{H}_v}{\delta v(r)} | \Psi \rangle$$

(1.12)

where we used the Schrödinger equation $\hat{H}_v | \Psi \rangle = E[v] | \Psi \rangle$ and the normalization condition $\langle \Psi | \Psi \rangle = 1$. Note that the equation above is nothing but a functional generalization of the well-known Hellmann-Feynman\cite{10} theorem. Now we can go to the density as our basic variable by defining a Legendre transform

$$F[n] = E[v] - \int d^3 r n(r) v(r) = \langle \Psi[v] | \hat{T} + \hat{W} | \Psi[v] \rangle$$

(1.13)

where $v(r)$ must now be regarded as a functional of $n(r)$. Again, take derivative of the above equation (1.13) with respect to $n(r)$, we have

$$\frac{\delta F}{\delta n(r)} = -v(r)$$

(1.14)

This is our basic relation. In order to derive the Kohn-Sham equations we define the following energy functional for a system of noninteracting particles with external potential $v_s$ and with ground state wave function $| \Phi[v_s] \rangle$,

$$E_s[v_s] = \langle \Phi[v_s] | \hat{T} + \hat{V}_s | \Phi[v_s] \rangle$$

(1.15)

with Legendre transform

$$F_s[n] = E[v_s] - \int d^3 r n(r) v_s(r) = \langle \Phi[v_s] | \hat{T} | \Phi[v_s] \rangle$$

(1.16)

and derivatives

$$\frac{\delta E_s}{\delta v_s(r)} = n(r)$$

(1.17)

$$\frac{\delta F_s}{\delta n(r)} = -v_s(r)$$

(1.18)
1.1 Density Functional Theory

We see that $F_s[n]$ in equation (1.16) is the kinetic energy of a noninteracting systems with potential $v_s$ and density $n$. For this reason the functional $F_s$ is usually denoted by $T_s$. Finally, we define the exchange-correlation functional $E_{xc}[n]$ by the equation

$$F[n] = F_s[n] + \frac{1}{2} \int d^3r d^3r' n(r)n(r') w(|r-r'|) + E_{xc}[n]$$  \hspace{1cm} (1.19)

This equation assumes that the functionals $F[n]$ and $F_s[n]$ are defined on the same domain of densities. We thus assume that for a given ground state density of an interacting system there is a noninteracting system with the same density. If we differentiate equation (1.19) with respect to the density $n$, we obtain

$$v_s(r) = v(r) + \int d^3r' n(r') w(|r-r'|) + v_{xc}(r)$$  \hspace{1cm} (1.20)

where

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$

defines the exchange-correlation potential. Now the state $|\Phi[v_s]\rangle$ is a ground state for a system of noninteracting particles, and can therefore be written as an antisymmetrized product of single-particle orbitals $\varphi_i(r)$. Finally, we have found the ground state problem with the following set of equations

$$E[v] = \sum_{i=1}^{N} -\frac{1}{2} \int d^3r \varphi_i^*(r) \nabla^2 \varphi_i(r) + \int d^3r n(r) v(r) + \frac{1}{2} \int d^3r d^3r' n(r)n(r')w(|r-r'|)+E_{xc}[n]$$

(1.21)

$$\left(-\frac{1}{2} \nabla^2 + v(r) + \int d^3r' n(r')w(|r-r'|) + v_{xc}(r)\right) \varphi_i(r) = \epsilon_i(r)$$  \hspace{1cm} (1.22)

$$n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2$$  \hspace{1cm} (1.23)

The above equations (1.21,1.22,1.23) constitute the ground state Kohn-Sham equations[4]. These equations turn out to be of great practical use. If we can find a good approximation for the exchange-correlation energy, we can calculate the exchange-correlation potential $v_{xc}$ and solve the orbital equations self-consistently. The density we find in this way can then be used to calculate the ground state energy of the system. Various approximations for the exchange-correlation exist in literature. In our calculations we shall specify the particular approximation used.
1.2 Basic assumptions of electronic band theory

A large number of electrons contained in a macroscopic crystal prohibits a direct solution of the Schrödinger equation for such a system. Reduction to the single particle-like Kohn-Sham equation\cite{Kohn1965} is a starting point. Fortunately, the solid may have lattice periodic symmetry in the bulk, and this can be exploited to reduce the size of the problem significantly, using Bloch’s theorem\cite{Bloch1928}, which enables us to replace the problem of solving the Kohn-Sham equation for electrons in an infinite periodic solid by that of solving the equation in a unit cell. The Kohn-Sham equation for an electron in a crystal can be solved in two limiting cases:

- the nearly free electron approximation, in which the potential is considered to be weak everywhere and
- the tight-binding approximation, in which it is assumed that the states are tightly bound to the nuclei.

In *ab-initio* methods, potential is usually determined self-consistently with the electron density according to the density functional scheme. In a general electronic structure calculation we must give the basis functions a good deal of attention since we know that by cleverly choosing the basis states we can reduce their number, which has a huge impact on the computer time needed as the latter is dominated by matrix diagonalisations. To solve the Kohn-Sham equation (1.4) with a periodic potential we can distinguish two main approaches based on the expansion of basis wave function.

- Energy independent basis set such as plane waves in the pseudo-potential method, plane waves orthogonalized to core states in the orthogonalized plane wave method, linear combination of the atomic orbitals in the tight-binding method.

- Energy dependent partial wave like the cellular method, the augmented plane wave method, the Korringa-Kohn-Rostoker (KKR) \cite{Korringa1957} method and its linearized version the linear muffin-tin orbitals method (LMTO) \cite{Lundqvist1980, Andersen1980, Skriver1980, Kresse1993} and exact muffin-tin orbital (EMTO) \cite{Kresse1994, Kresse1996} method.

As a part of our calculations we shall use the EMTO methods.

1.3 Green Function formalism

In systems like random alloys, surfaces and interfaces, defects in solids, spin-glasses, amorphous materials the conventional Bloch theorem is no longer valid due to lack
1.3 Green Function formalism

of periodicity of the lattice. In this situation Green’s function is an alternative approach for the electronic structure calculation. The Green’s function is nothing but a propagator [20]. For a given Hamiltonian $H$, the time-dependent Schrödinger equation determines the time evolution of the wave function $\psi(t)$ as

$$i\frac{\partial}{\partial t}\psi(t) = H\psi(t)$$

(1.24)

with a formal solution

$$\psi(t) = \exp^{-iHt}\psi(0)$$

(1.25)

here $\psi(0)$ is the initial wave function. We can define two propagators, $G^R(t)$ (retarded) and $G^A(t)$ (advanced), as

$$\left(i\frac{\partial}{\partial t} - H\right)G^{R(A)}(t) = \delta(t)$$

(1.26)

which correspond to the above Schrödinger equation with boundary conditions

$$G^R(t) = 0 \quad t < 0$$
$$G^A(t) = 0 \quad t > 0$$

The formal solution of these equation is:

$$G^R(t) = -\Theta(t)i e^{-iHt}$$
$$G^A(t) = \Theta(-t)i e^{-iHt}$$

for all $t$, where $\Theta(t)$ is zero for $t < 0$ and unity for $t > 0$. Clearly the Green’s function coincides with the time evolution operator (up to a factor). To propagate the wave function forward in time one use $G^R(t)$ and $G^R A(t)$ for the backward in time. Now for a given perturbing potential $V(\vec{r})$ to the Hamiltonian $H_0$, the Green’s function $G_1$ corresponding to the perturb Hamiltonian $H = H_0 + V$ can be written in terms of the Green’s function $G_0$ corresponding to $H_0$ via the Dyson integral as:

$$G_1(t) = G_0(t) + \int_0^t G_0(t - t') V G_1(t') dt'$$

(1.27)

and the wave function $\psi_0(t)$ of system without interaction evolves into the wave function $\psi_1(t)$ by the Lippmann-schwinger equation as

$$\psi_1(t) = \psi_0(t) + \int_0^t G_0(t - t') V \psi_1(t') dt'$$

(1.28)
1.3 Green Function formalism

Taking the Fourier transformation of the $G(t)$ we can write the energy dependent Green’s function as:

$$G(z) = (z - H)^{-1}$$  \hspace{1cm} (1.29)

where $z = E + i\delta$ is a complex number with very small imaginary part $\delta$. Clearly the energy dependent Green’s function is the resolvent of the time-dependent Hamiltonian and it’s singularities determines the eigenvalue spectrum; in particular, it has poles at the eigenenergies of the bound states, and a branch cut along the energies of the continuous spectrum as it is shown in Fig. 1.2. For $\text{Im}(z) > 0$, $G(z)$ is an analytical function of $z$ and has certain analytic properties, which are collectively called the Harglotz properties

1. $\text{Im}G(z) < 0$ when $z > 0$
2. Singularities of $G(z)$ lie on the real axis.
3. $G(z) \to \frac{1}{z}$ when $\text{Re}(z) \to \infty$

Using the complete basis set of eigen function $|\psi_i\rangle$ corresponding to the eigenvalues $\epsilon_i$ of the Hamiltonian, the spectral representation of the Green’s function can be written as:

$$G(z) = \sum_i |\psi_i\rangle \frac{1}{z - \epsilon_i} \langle \psi_i|$$  \hspace{1cm} (1.30)

and in real space it is represented as

$$G(\vec{r}, \vec{r'}, z) = \sum_i \psi_i(\vec{r})\psi_i^*(\vec{r'}) \frac{1}{z - \epsilon_i} = \frac{1}{z - H}$$  \hspace{1cm} (1.31)

in the limit of the $\text{Im}(z) = \delta \to 0$ for an outgoing wave vector at $\vec{r}$ with a source term at $\vec{r'}$.

It is known that for $z = E \pm i\delta$ and $\delta \to 0$

$$\frac{1}{z - \epsilon_i} \to P \left( \frac{1}{E - \epsilon_i} \right) \mp i\pi\delta(E - \epsilon_i)$$

Where $P$ denotes the principal part. So, as follows from the spectral representation of the Green’s function in the real space the imaginary part is directly related to the spectral and space resolved density of state.

$$n(r; E) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} G(\vec{r}, \vec{r}; E + i\delta)$$  \hspace{1cm} (1.32)

and the spectral density of state is then given by

$$n(E) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} \int G(\vec{r}, \vec{r}; E + i\delta) d^3r = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Tr} G(E + i\delta)$$  \hspace{1cm} (1.33)
Also the charge density is found as an integral of \( n(\vec{r}; E) \) over the energies up to Fermi level \( E_f \)

\[
\rho(\vec{r}) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} \int_{-\infty}^{E_f} G(\vec{r}, \vec{r}, E + i\delta) dE = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} \int_{-\infty}^{E_f} \text{Tr}(\hat{r}G(\vec{r}, \vec{r}, E + i\delta)) dE
\]

with \( \hat{r} \) is the position operator. In general, the expectation value of any physical quantity represented by an operator \( \hat{O} \) can be obtain by the relation

\[
\langle \hat{O} \rangle = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im} \int_{-\infty}^{E_f} \text{Tr}(\hat{O}G(\vec{r}, \vec{r}, E + i\delta)) dE
\]

From the above relations we can say that the Green’s function contains all the informations about the system. Therefore, if it is possible to calculate the Green’s function of the system then we can able to obtain all the physical properties of the system.

### 1.4 Exact Muffin-Tin Orbital method

The EMTO [17, 18, 19] method, by combining the precision of the cellular methods such as KKR and numerical efficiency of the basis sets methods such as LCAO, offers a very efficient scheme for solving the Kohn-Sham equations. The main idea of the EMTO approach, in contrast to the LMTO methods, is to use optimized overlapping MT-spheres instead of non-overlapping ones, which greatly improves the representation of the full potential in terms of the MT-potential shown in Fig. 1.3. The effective potential \( v(r) \), as it appears in the Kohn-Sham equation, is defined within the EMTO methods as
1.4 Exact Muffin-Tin Orbital method

\[ v(r) \approx v_{MT}(r) \equiv v_0 + \sum (v_r(r_R) - v_0), \quad (1.36) \]

where \( v_R(r_R) \) is the spherical potential defined inside the MT spheres centered at \( R \) and having radii \( s_R \); \( v_0 \) is the constant potential defined in the interstitial region and called MT zero; \( r_R = |r_R| \).

**Figure 1.3: Muffin-Tin - Muffin-tin potential**

The solutions of the Kohn-Sham equations are expressed in terms of exact muffin-tin orbitals, \( \Psi_{aRL} \),

\[ \Psi_j(r) = \sum_{RL} \Psi_{aRL}(\epsilon_j, r_R) v_{RL,j}^a, \quad (1.37) \]

where coefficients \( v_{RL,j}^a \) are determined by demanding that the solutions are smooth functions in the entire space. This is a full set expansion, but in practice, the summation is truncated at \( l = l_{max} \), where \( l_{max} = 2, 3 \) (for spd and spdf basis, respectively).

The exact MT-orbitals are energy dependent and consist of two parts: screened spherical waves defined in the interstitial region and penetrating into the potential spheres to a certain depth; and partial waves defined inside the potential spheres.

The screened spherical waves, \( \Psi_{aRL}(\kappa^2, r_R) \), are constructed from the solutions of the Schrödinger equation for the constant potential \( v_0 \), i.e.,

\[ (\nabla^2 + \kappa^2) \Psi_{aRL}(\kappa^2, r_R) = 0, \quad \kappa^2 = \epsilon - v_0, \quad (1.38) \]

subjected to boundary conditions on a set of non-overlapping spheres with radii \( a_R \) and centered at \( R \). The spherical waves satisfy the following conditions:

\[ \Psi_{aRL}(\kappa^2, r_R) \big|_{r_R=a_R} = Y_L(\hat{r}_R), \quad (1.39) \]
1.4 Exact Muffin-Tin Orbital method

for own spheres $a_R$, and on other spheres their projection on spherical harmonics must vanish,

$$
\int \Psi_{RL}^a(\kappa^2, r'_R) |_{r'_R=a_R} Y_L(\hat{r}'_R) d\hat{r}'_R = 0, \quad R' \neq R. \quad (1.40)
$$

Explicitly, the screened spherical waves are written as

$$
\Psi_{RL}^a(\kappa^2, r_R) = f_{RL}^a(\kappa^2, r_R) Y_L(\hat{r}_R) \delta_{RR'} \delta_{LL'} + \sum_{L'} g_{RL'}^a(\kappa^2, r'_R) Y_{L'}(\hat{r}_R') S_{RL'RL}^a(\kappa^2), \quad (1.41)
$$

where $f_{RL}^a(\kappa^2, r_R)$ and $g_{RL}^a(\kappa^2, r_R)$ are the head and tail functions, respectively, $S_{RL'RL}^a(\kappa^2)$ the screened structure constants related to the usual KKR structure constants. The head and tail functions are expressed in terms of the Bessel and Neumann functions.

Inside the potential spheres, the basis set is represented by partial waves $\phi_{RL}^a(\epsilon, r_R)$

$$
\phi_{RL}^a(\epsilon, r_R) = N_{RL}^a(\epsilon) \phi_{RL}^a(\epsilon, r_R) Y_L(\hat{r}_R), \quad r_R < s_R, \quad (1.42)
$$

where the normalization factor $N_{RL}^a(\epsilon)$ is used for smooth matching of the partial waves and spherical waves. The functions $\phi_{RL}^a(\epsilon, r_R)$ are the solutions of the radial Schrödinger

$$
\frac{\delta(r_R \phi_{RL}^a(\epsilon, r_R))}{\delta r_R} = \left( \frac{l(l+1)}{r_R^2} + v_R(r_R) - \epsilon \right) r_R \phi_{RL}^a(\epsilon, r_R). \quad (1.43)
$$

The boundary conditions for the screened spherical waves are defined on $a_R$-spheres, $a_R < s_R$, while the partial waves are defined only inside $s_R$-spheres, which means that the two types of functions are defined in the overlapping domain. To glue the functions together smoothly, auxiliary free electron solutions $\phi_{RL}^a(\epsilon, r_R)$ defined in the region between the two spheres are introduced,

$$
\phi_{RL}^a(\epsilon^2, r_R) = f_{RL}^a(\kappa^2, r_R) + g_{RL}^a(\kappa^2, r_R) D_{RL}^a(\epsilon), \quad (1.44)
$$

where $D_{RL}^a(\epsilon) = D\{\phi_{RL}^a(\epsilon^2, r_R)\}$ is the logarithmic derivative calculated at $a_R$. The logarithmic derivative is defined as

$$
D\{f(r_R^0)\} = \frac{f(r_R^0)}{f'(r_R^0)} \frac{\delta f(r_R^0)}{\delta r_R} |_{r_R=r_R^0}. \quad (1.45)
$$

Finally, we get the basis functions $\bar{\psi}_{RL}$.

$$
\bar{\psi}_{RL}^a = \psi^a_{RL} + N_{RL}^a(\epsilon) \phi_{RL}(\epsilon, r_R) Y_L(\hat{r}_R) - \phi_{RL}^a(\epsilon, r_R) Y_L(\hat{r}_R). \quad (1.46)
$$
The trial function can then be written as
\[ \Psi(r_R) = \sum_L N_{RL}(\epsilon) \phi_{RL}(\epsilon, r_R) Y_L(\hat{r}_R) v_{RL}^a. \] (1.47)

In order for the solution \( \Psi_j(r_R) \) to be valid inside the potential spheres for \( l < l_{\text{max}} \), a so-called 'kink cancelation equation', equivalent to the KKR secular equation, must hold,
\[ \sum_{RL} a_R^j \left( S_{RL}^{a_j L} - \delta_{RR'} \delta_{LL'} D_{RL}^{a_j}(\epsilon_j) \right) v_{RL,j}^a = 0 \] (1.48)
which, by introducing the kink matrix, \( K_{RL}^{a_j L}(\epsilon_j) \equiv a_R^j S_{RL}^{a_j L} - \delta_{RR'} \delta_{LL'} D_{RL}^{a_j}(\epsilon_j) \), can be written as,
\[ \sum_{RL'} K_{RL'}^{a_j L}(\epsilon_j) g_{RL'}^{a_j L}(\epsilon_j) = \delta_{RR'} \delta_{LL'}, \] (1.49)
where the path operator \( g_{RL'}^{a_j L}(\epsilon_j) \) is introduced. Each pole of the path operator corresponds to a single state. However, to get the total Green’s function, the path operator must be properly normalized with the overlap of the basis functions. It can be shown that the overlap is given by
\[ \int \Psi_{RL}^a(\epsilon, r) \Psi_{RL}^a(\epsilon, r) dr = a_R^s S_{RL}^{a_s L} - a_R^s D_{RL}^{a_s}(\epsilon) = \hat{K}_{RL}^{a_s L}(\epsilon) \] (1.50)
and the Green’s function is then calculated as
\[ G(z) \equiv \sum_{RL'} g_{RL'}^{a_j L}(\epsilon_j) K_{RL'}^{a_j L}(\epsilon_j) - \sum_{RL} \left( \frac{D_{RL}^{a_j}(\epsilon_j)}{D_{RL}^{a_j}(\epsilon_j)} - \sum_{RL}^1 \frac{1}{z - \epsilon_{RL}^D} \right), \] (1.51)
where the first term in the second sum is needed to remove the unphysical poles of \( K_{RL'}^{a_j L}(\epsilon_j) \), while the second term in this sum restores the poles of \( \frac{1}{D_{RL}^{a_j}(\epsilon_j)} \).

1.5 Comments

In this chapter we have described the basic theoretical tools for the study of electrons in a solid: density functional theory, which reduces the many-body Schrödinger equation with a plethora of variables to a single-electron Kohn-Sham the EMTO method, which allows us to obtain the solutions of the Kohn-Sham equations in a minimal basis set and the method of Green functions. These techniques form the basis of the applications we shall describe in this thesis.

In the next chapter we shall go on to describe those techniques which will allow us to address the problem of disorder.
Chapter 2

Electronic structure calculation in random binary alloys

2.1 Introduction

The concept of disorder is primitive and intuitive; it deals with statistical terms such as 'random', 'stochastic', 'unpredictable', which can only be defined within a specific context of what is already known or can be taken for granted. In the crystalline state, long-range order for positions of atoms and orientations of atomic rows are apparent; in random alloys, the positional order for atomic sites remains, but the occupation of atomic sites by different species of atoms is somewhat random. The effect of disorder is always to break some symmetry. In the physics of disordered systems we can no longer rely upon some of the most powerful mathematical tool in the theory of the solid state. Theorems and principles that we cheerfully prove and accept for crystalline materials may not be taken for granted in the study of disordered systems.

There are several different ways in which disorder may be present in material.

- Substitutional disorder: The binary alloy is formed by replacing atoms of element A in a perfect crystal by that of another element B randomly with almost no disturbance in the crystal lattice.

- Topologically disorder: The topology of the lattice itself may be perturbed and the crystalline lattice replaced by a random network.

- Magnetic disorder: In a magnetic material, the $R$-th site (or unit cell) of a regular crystal can carry a net magnetic moment. If this moment varies randomly in
2.1 Introduction

magnitude or direction or both, from site to site (or cell to cell) we have magnetic disorder.

- Other kinds of disorder: disorder can also enter through randomness in local polarization or random distribution in local strains. Good examples are multiferroic glasses.

This has been schematically shown in Fig. 2.1. The reason for the increased interest in disordered materials are many and varied. The interest in disordered systems is growing up due to the technological importance of such systems in our modern world. Steels alloys, amorphous semiconductors, liquid metals and glasses, to mention only a handful, are at the core of further technological progress, and the properties of such systems like electrical, magnetic, optical, structural, elastic are important to verify the systems. The design of alloys to meet specific engineering requirement demands at the microscopic level the first-principles electronic structure calculations of these systems. In contrast to the ordered solids, the calculations of most physical properties of disordered alloys required configurational averaging over all realizations of the random

![Different types of disorder](image)

**Figure 2.1:** Different types of disorder: - (from top left clockwise) Ordered lattice, substitutional disorder, topological disorder and magnetic disorder.
variable characterizing the disorder. In this chapter we shall first overview of the general formalism used in the description of the configuration thermodynamics of alloys.

2.2 Theoretical approach

2.2.1 Basic definitions

Thermodynamic properties of random alloys, in general, depend on local atomic arrangements in crystalline solids. The state of order of the crystal is defined by order parameters, which define correlations between the occupancy of sites. In this section, we examine how correlations are defined, and how averaging techniques lead to the concepts of short-range order in random alloys.

Let there be $s$ kinds of atoms in an alloy. The alloy is described by a crystal lattice, defined by site positions $R_i$, and occupation numbers specifying the sort of an atom residing at a given site. An alloy configuration, $\xi$, is fully described by the occupation numbers,

$$c_s^i(\xi) = \begin{cases} 1, & \text{if site } i \text{ is occupied by an atom of type } s, \\ 0, & \text{otherwise} \end{cases}$$

By definition, the occupation numbers satisfy the identity

$$\sum_s c_s^i(\xi) = 1 \quad (2.1)$$

stating that each site is occupied by exactly one atom.

Each configuration in an equilibrium state of the alloy is characterized by a statistical weight $\exp(-\beta E(\xi))$, where $E(\xi)$ is the configurational energy, $\beta = 1/T$ the inverse temperature, and alloy properties can be obtained from the partition function in the canonical ensemble $[22, 23]$,

$$Z = \sum_\xi \exp(-\beta E(\xi)), \quad (2.2)$$

with the following constraints,

$$\frac{1}{N} \sum_i c_s^i = c^s, \quad \sum_s c^s = 1, \quad (2.3)$$

which fixes the concentration, $c^s$, of the alloy constituents; here, $N$ is the total number of atoms in the alloy.

In terms of Hamiltonian $H_{\text{alloy}}(\{c_s^i\})$, the partition function can be written as

$$Z = \text{Tr} \exp(-\beta H_{\text{alloy}}(\{c_s^i\})) \equiv \sum_{s, i, c_s^i=0,1} \exp(-\beta H_{\text{alloy}}(\{c_s^i\})) \quad (2.4)$$
2.2 Theoretical approach

with \( s = 1, ..., n_s - 1 \), where \( n_s \) is the number of atom sorts; the summation here is over all possible configurations, i.e. over all possible values of the occupation numbers \( c_s^i \).

From the partition function the free energy is calculated as usual,

\[
F(\beta, c^s) = -\frac{1}{\beta} \ln Z, \tag{2.5}
\]

and averages are given by

\[
\langle Q \rangle = \frac{1}{Z} \sum_\xi Q(\xi) \exp(-\beta E(\xi)) = \text{Tr} \rho Q \tag{2.6}
\]

\[
\rho(\{c^s_i\}) = \frac{1}{Z} \sum_\xi \exp(-\beta H_{\text{alloy}}(\xi)). \tag{2.7}
\]

To simplify the above mathematical representation, let us consider a homogeneous binary alloy \( A_{1-c}B_c \) consisting of \( N \) atoms of type A and B with corresponding occupation numbers \( c^A_i = c_i \) and \( c^B_i = 1 - c^A_i = 1 - c_i \). The concentrations of each component are \( c \equiv c^A = \langle c^A_i \rangle \) and \( c^B = (c^B) = 1 - c \).

In order to describe a phase transformation, occupation numbers themselves are not very handy, because they provide a way too much unnecessary information about exact atoms configurations underline lattice. Instead, correlation functions \( \langle c_ic_j...c_k \rangle \) are used to distinguish one phase from another. The correlation functions allow one easily to explain the local ordering phenomena depending on the sign of the nearest-neighbor (NN) pair correlation function \( \langle c_ic_j \rangle \):

- if, \( \langle c_ic_j...c_k \rangle = \langle c_i \rangle \langle c_j \rangle ... \langle c_k \rangle \), the configuration is statistically uncorrelated,
- there is a local decomposition if, \( \langle c^A_i c^A_j \rangle > \langle c^A_i \rangle \langle c^A_j \rangle \), or, in terms of the cumulant average \( \langle c^A_i c^A_j \rangle_{\text{cum}} = \langle c^A_i c^A_j \rangle - \langle c^A_i \rangle \langle c^A_j \rangle > 0 \)
- a negative value of the cumulant average \( \langle c^A_i c^A_j \rangle_{\text{cum}} < 0 \) marks a local ordering.

The correlation functions are experimentally measurable quantities. They can be measured as a direct result of, for instance, a neutron scattering experiment which yields the Fourier transforms of the short-range order (SRO) parameters, \( \alpha_m \), related to the correlation functions\[24, 25\]

\[
\alpha(k) = \sum_m \alpha_m \sum_{R_i \in CS_m} e^{-iKR_i}, \tag{2.8}
\]

where the first summation is over the coordination shell number, \( m \), and the SRO parameters \[26, 27\] can be defined in terms of the conditional probability,

\[
P_m = \frac{\langle (1 - c(R_i + r_m)c(R_i)) \rangle}{c} = 1 - \frac{\langle c(R_i + r_m)c(R_i) \rangle}{c}, \tag{2.9}
\]

17
2.2 Theoretical approach

of finding an atom B at the \(m\)-th coordination shell of an atom A, from which we have,

\[
\alpha_m \equiv 1 - \frac{p_m}{1 - c} = \frac{\langle c(R_i)c(R_i + r_m) \rangle_{cum}}{c(1 - c)},
\]

(2.10)

where \(c(R_i) \equiv c_i\), and \(r_m\) is a lattice vector belonging to the \(m\)-th coordination shell.

For a completely random alloy, \(\langle c_i c_j \rangle_{cum} = 0\), hence \(\alpha_m = 0\). In case of decomposition (clustering), the \(m\)-th coordination shell of each atom A is occupied only by A, and \(\alpha_m = 1\). The minimal value of a SRO parameter is, \(\alpha_m = -c(1 - c)\), and corresponds to full ordering. Note, that the extreme values may be unattainable due to geometric constraints. At large distances, the correlations disappear and \(\alpha_m \to 0\) as \(m \to \infty\).

2.2.2 Cluster expansion

Cluster expansion is a formalism for calculating configuration dependent properties of random alloys such as energy. In the energy expression, any configuration of a cluster \(f = i, j, ..., k\) consisting of sites \(i, j, ..., k\) is unambiguously defined by a relation \(c_i^{s_1} c_j^{s_2} ... c_k^{s_n} = 1\) whenever the cluster sites are occupied by atoms of sorts \(s_1, s_2, ..., s_k\).

Let us introduce spin-like variables \(\sigma_i = 2c_i - 1\) which take on values 1 or -1 depending on whether site \(i\) is occupied by an atom A or B, respectively. Obviously, the \(N\)-vector \(\sigma = \sigma_1, \sigma_2, ..., \sigma_N\) defines the alloy configuration unambiguously. A basis set can be introduced in terms of the characteristic functions \(\Phi_{(n)}^f(\sigma)\) of \(n\)-clusters \(f\), \([28, 29, 30]\)

\[
\Phi_{(n)}^f(\sigma) = \prod_{i \in f} \sigma_i.
\]

(2.11)

The corresponding inner product is given by

\[
\langle \langle \Phi_{(n)}^f(\sigma) \Phi_{(n)}^g(\sigma) \rangle \rangle = \frac{1}{2N} \sum_\sigma \Phi_{(n)}^f(\sigma) \Phi_{(n)}^g(\sigma) = \delta_{f,g},
\]

(2.12)

where the sum is over all configurations. The characteristic functions \(\Phi_{(n)}^f(\sigma)\) along with the inner product \(\langle \langle \ldots \rangle \rangle\) constitute an orthonormal basis set, and any function of the configuration can therefore be expanded in this basis set,

\[
F(\sigma) = \sum_f F_f(\sigma) \Phi_{(n)}^f(\sigma),
\]

(2.13)

where the summation is over all possible clusters \(f\), and the coefficients are

\[
F_f(\sigma) = \langle \langle F(\sigma), \Phi_{(n)}^f(\sigma) \rangle \rangle.
\]

(2.14)
In particular, the energy of an alloy can be expanded as

\[ V_f^{(n)} = \langle \langle E_{\text{conf}}(\bar{\sigma}), \Phi_f^{(n)}(\bar{\sigma}) \rangle \rangle, \tag{2.15} \]

and with that, the Hamiltonian \( H_{\text{alloy}}(\xi) = H_{\text{alloy}}(\bar{\sigma}) \) is defined as

\[ H_{\text{alloy}}(\bar{\sigma}) = \sum_n \sum_{i,j,...,k \in f} V_f^{(n)} \sigma_i \sigma_j, ... \sigma_k. \tag{2.16} \]

### 2.3 Coherent Potential Approximation

In the case the disordered systems the main thrust goes to obtain the configurationally average quantities. Therefore the main aim is to determine the configurationally average Green’s function a disordered system. The coherent potential approximation (CPA) was introduced simultaneously by Soven\(^\text{[31]}\) in connection with disordered electronic systems and Taylor\(^\text{[32]}\) in connection with the lattice dynamics of mass disordered alloys in 1967. In the case of totally random alloys their basic idea was to obtain a translationally symmetric effective Hamiltonian \( (H_{\text{eff}}) \) and its representation in terms of Green’s function \( G_{\text{eff}} \). If we write the total Hamiltonian as \( H = H_0 + V \) where \( V = \sum_i V_i \) is the superposition of the real individual site potential \( V_i(z) \) then in terms of self-energy operator \( \Sigma(z) \) one can write the average Green’s function as:

\[ \langle G(z) \rangle = ((z - H)^{-1}) = [z - H_0 - \Sigma(z)]^{-1} \tag{2.17} \]

In a translationally invariant medium \( \Sigma(z) \) the total Hamiltonian can be written as

\[ H(z) = H_{\text{eff}}(z) + V(z) - W(z) \quad \text{with} \quad H_{\text{eff}}(z) = H_0(z) + W(z) \]
2.3 Coherent Potential Approximation

where \( W(z) = \sum_i W_i(z) \) is the translationally invariant site-dependent quantities \( W_i(z) \). Defining \( \mathcal{V}(z) = \sum_i (V_i - W_i) \) and \( G^{e\!f\!f}(z) = (z - H^{e\!f\!f})^{-1} \) we can express the resolvent \( G(z) \) and corresponding \( T \) operator \( T(z) \) as:

\[
G(z) = G^{e\!f\!f} \left[ 1 - \mathcal{V}(z)G^{e\!f\!f} \right] \\
T(z) = \mathcal{V}(z) + \mathcal{V}(z)G^{e\!f\!f} \mathcal{V}(z) \\
G(z) = G^{e\!f\!f} + G^{e\!f\!f} T(z) G^{e\!f\!f}
\]

Clearly \( G^{e\!f\!f} \) is translationally symmetric and therefore the average \( \langle G(z) \rangle \) becomes

\[
\langle G(z) \rangle = G^{e\!f\!f}(z) + \langle G^{e\!f\!f}(z) \rangle G^{e\!f\!f}(z)
\]

and hence to get the average Green’s \( \langle G(z) \rangle \) function as the effective Green’s function \( G^{e\!f\!f}(z) \) i.e.

\[
\langle G(z) \rangle = G^{e\!f\!f}(z).
\]

We need to satisfy

\[
\langle T(z) \rangle = 0.
\]

Now the self-energy becomes

\[
\Sigma(z) = z - H_0(z) - [\langle G(z) \rangle]^{-1} \\
= W(z) + \langle T(z) \rangle \left[ 1 + G^{e\!f\!f}(z) \langle T(z) \rangle \right]^{-1} = W(z) + \Sigma_1(z).
\]

With the help of \( t \)-matrix, we can write

\[
\langle T(z) \rangle = \sum_i \langle Q_i(z) \rangle,
\]

where \( \langle Q_i \rangle \) can be represents as

\[
\langle Q_i \rangle = \langle t_i(z) \rangle \left[ 1 + G^{e\!f\!f}(z) \sum_{i \neq j} \langle Q_j(z) \rangle \right] + \left[ \langle t_i(z) \rangle - \langle t_i(z) \rangle \right] G^{e\!f\!f}(z) \sum_{i \neq j} \left[ Q_j(z) - \langle Q_j(z) \rangle \right].
\]

The first term of the above expression contains only the single-site quantities but the second one is a kind of a correlation term. The CPA, the second term is neglected and therefore it is the single-site approximation. But neglecting the second term means excluding the local environmental effect like short-ranged ordering. So in the CPA \( \langle Q_i(z) \rangle \) becomes

\[
\langle Q_i(z) \rangle = \langle t_i \rangle \left[ 1 + G^{e\!f\!f}(z) \sum_{j \neq i} \langle Q_j(z) \rangle \right].
\]
2.3 Coherent Potential Approximation

In the single-site coherent potential approximation condition in equation \((2.20)\) namely \(\langle T(z) \rangle = 0\) reduces to

\[
\langle Q_i(z) \rangle = 0 = \Rightarrow \langle t_i(z) \rangle = 0 \quad \text{for all } i.
\]

This condition implies that the average scattering on a site is zero. It is possible to prove that this approximation preserves the analytic properties of the Green’s function and gives the first eight moments of the density of state exactly. It is also reproduces several limiting cases like the dilute limit where it is exact up to the first order. In the atomic limit, it can be shown that the CPA is exact up to the second order term by using the locator formalism.

### 2.3.1 Scattering path operators

Using the CPA, one attempts to calculate the electronic structure of a random alloy. The scattering properties of alloy components are given by a \(\tau\)-matrix. The CPA effective medium is given by a coherent \(\tau\)-matrix on each site, \(\tau_c\). Then the corresponding scattering path operator \(\tilde{\tau}_c(\epsilon)\) is

\[
\tilde{\tau}(\epsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} dK \frac{1}{\tau^{-1}_c(\epsilon) - G(k, \epsilon)}.
\]

The CPA condition in Eq. \((2.23)\) demands the coherent path operator to be the average of the components, which for binary alloys is expressed as follows,

\[
\tilde{\tau}(\epsilon) = c\tau^A(\epsilon) + (1 - c)\tau^B(\epsilon),
\]

where the single-site green’s functions for the components, \(\tau^A, \tau^B\), are determined self-consistently via a single-site Dyson equation,

\[
\tau^s(\epsilon) = \frac{1}{1 + \tilde{\tau}(\epsilon)(P^s(\epsilon) - P)} \tilde{\tau}(\epsilon),
\]

with \(s = A, B\), and \(P^s\) are the potential functions defined as \(P = \tau^{-1}\).

The CPA is one of the most extensively used methods in the study of electronic structure of disordered solids.
2.4 Generalized perturbation method

The generalized perturbation method (GPM) allow one to calculate effective cluster interactions of Ising-like Hamiltonian for the atomic degree of freedom. It has been shown in Section 2.2.2 that the configurational energy of a binary alloy can be expanded in terms of cluster interactions shown in Fig. 2.4:

\[ E_{\text{conf}}(\sigma) = \sum_{i,j,k \in f} V_f^{(n)}(\sigma_i \sigma_j \sigma_k). \] (2.27)

For a fixed concentration, the configurational energy of the alloy can also be expressed in terms of fluctuations of concentrations variables, \( \delta c_i = c_i - c \):

\[ E_{\text{conf}} = \sum_{i,j,k \in f} \tilde{V}_f^{(n)}(\delta c_i \delta c_j \delta c_k). \] (2.28)

Here \( \tilde{V}_f^{(n)} \) are the cluster interactions in the concentration-variable basis, which are connected to the interactions on the spin-variable basis as \( \tilde{V}_f^{(n)} = 2^n V_f^{(n)} \).

The cluster interactions can be rewritten in a slightly different form as suggested by Berera et al [34, 35]

\[ V_f^{(n)} = \frac{1}{2^n} \sum_{\sigma_1, \ldots, \sigma_n = -1, 1} v_f^{(n)}(\sigma_1, \sigma_2, \ldots, \sigma_n) \prod_{i=1}^{n} \sigma_i, \] (2.29)

where \( v_f^{(n)}(\sigma_1, \sigma_2, \ldots, \sigma_n) \) are the \( n \)-body potentials of cluster \( f \) composed of atoms A and B in the configuration \( \sigma_1, \sigma_2, \ldots, \sigma_n \), and the summation is over all possible occupations of this cluster. The \( n \)-body potentials are determined by

**Figure 2.4: Cluster** - A schematic representation of a pair, 3-site and 4-site interactions in the bcc structure.

\[ v_f^{(n)}(\sigma_1, \sigma_2, \ldots, \sigma_n) = \frac{1}{z} \sum_{\bar{\sigma}} E(\sigma_1, \sigma_2, \ldots, \sigma_n; \bar{\sigma}) \] (2.30)
2.4 Generalized perturbation method

where \( E(\sigma_1, \sigma_2, ..., \sigma_{nf}; \bar{\sigma}) \) is the energy of a system having configuration \( \sigma_1, \sigma_2, ..., \sigma_n \) in the cluster \( f \) and the summation is over the rest of the system \( \bar{\sigma} \); \( z \) is the total number of configurations.

The energy \( \upsilon^{(n)}_f(\sigma_1, \sigma_2, ..., \sigma_n) \) of cluster \( f \) embedded in the CPA effective medium can be calculated using a so-called embedded cluster method (ECM) \[36\]. The cluster interactions \( V^{(n)}_f \) are then obtained using Eq. (2.29). Noticing that the sign of the spin product in Eq. (2.29) is determined by whether there is an odd or even number of atoms A in the cluster, one can obtain a general relation for the cluster interactions \[37, 38\],

\[
V^{(n)}_f = \frac{1}{2^n} \left( E_{A-even} - E_{A-odd} \right)
\]

(2.31)

where \( E_{A-even} \) and \( E_{A-odd} \) are the total energies of the systems containing clusters \( f \) with only an even or odd number of atoms A, respectively.

The energy of embedding a cluster into the effective medium can be calculated using the force theorem. One should note that the embedding of a cluster into the medium leads to the change in the local charge density, resulting in an additional electrostatic contribution to the pair interaction energy. The pair interaction energy can then be written as a sum of two parts, one-electron \( V^{(2)-one-el} \), and electrostatic \( V^{(2)-scr} \), the latter actually representing the screened electrostatic interaction,

\[
V^{(2)} = V^{(2)-one-el} + V^{(2)-scr},
\]

(2.32)

Effective interactions for clusters containing more than two sites, there is only the one-electron contribution, which can be obtained according to the force theorem as,

\[
V^{(n)-one-el}_f = -\frac{1}{2^n} \frac{1}{\pi} \text{Im} \int_{E_f} \text{Tr} \ln \left[ \prod_{p \in A-even} Q_p \left( \prod_{p \in A-odd} Q_p \right)^{-1} \right],
\]

(2.33)

with the cluster matrices \( Q_p \) defined as

\[
Q_{ij} = \delta_{ij} - \tau^i \tilde{\tau}_{ij} \left( 1 - \delta_{ij} \right)
\]

(2.34)

where the coherent path operator of the reference system, \( \tilde{\tau}_{ij} \), gives scattering between sites \( i \) and \( j \) in the cluster; \( \tau^i \) are the single-site scattering matrices determined from the coherent potential function \( \tilde{P} \) and the on-site path operator \( \tilde{\tau}_0 \),

\[
\tau^i = \frac{\tilde{P} - P^i}{1 + (\tilde{P} - P^i)\tilde{\tau}_0}
\]

(2.35)
The potential function is \( P^i = P^A, P^B \) depending on whether site \( i \) is occupied by atom A or B. It can easily be shown using Eqs. (2.25), (2.26) that \( \tau^i \) satisfy the CPA self-consistency equation.

\[
c(\tau^A) + (1 - c)(\tau^B) = 0 \tag{2.36}
\]

Finally, the interactions within the GPM are obtained by expanding the logarithm in Eq. (2.33),

\[
V^{(n)-GPM}_f = \frac{-1}{2 n \pi} \int_{E_f} \sum_{p \in f} \text{Tr} \left( \Delta \tau^i \tilde{\tau}_{ij} \Delta \tau^j ... \Delta \tau^k \tilde{\tau}_{ki} \right) f \tag{2.37}
\]

where \( \Delta \tau^i = \tau^A - \tau^B \), and the summation is performed over all irreducible paths starting and ending on the same site and passing only once through each site.

The electrostatic part \( V^{(2)-scr} \) comes from the screened Coulomb interaction of the charges inside the atomic spheres (or, generally, cells) of the atoms entering corresponding pair clusters. To be more precise, if one considers the expression Eq (2.31) for a cluster interaction with two atoms A and B, then the pair interaction is written as,

\[
V^{(2)} = \frac{1}{4} (E^{AA} + E^{BB} - E^{AB} - E^{BA}). \tag{2.38}
\]

When space is divided into atomic spheres, each sort of atoms embedded into the effective medium is associated with a charge \( q_X \) (X = A,B), there is a screening charge \( -\rho_{scr}^X \) distributed in the effective medium outside the given atomic sphere. This charge comes from a response of the system to introducing an excess charge at a given site. Then, the electrostatic contribution for a cluster XY (X,Y = A,B) of two atoms separated by vector \( \mathbf{R} \) is given by,

\[
E_{el}^{XY} = \frac{1}{2} q_X \left( \frac{q_Y}{R} - \int_{s_R}^{\infty} \rho_{scr}^Y(r) \frac{dr}{|r - \mathbf{R}|} \right) \tag{2.39}
\]

from which we have the total electrostatic contribution to pair cluster interactions,

\[
V^{(2)-scr}(\mathbf{R}) = \frac{1}{8} \left( q_A - q_B \right) \frac{2 \alpha_{scr}(\mathbf{R})}{s_R} \tag{2.40}
\]

where in the equality we assume that screening can be described within linear response with the screening charge proportional to the bare charge with the material specific constant of proportionality \( \alpha_{scr}(\mathbf{R}) \) (screening constant) depending on distance, and generally varying with the alloy concentration and volume. The screening constant can be established in a supercell calculation in which electrostatics is correctly taken into account, provided that the supercell is sufficiently large.
Chapter 3

Order-Disorder Phase Transition of FeCo alloys

3.1 Introduction

FeCo alloys possess a unique combination of magnetic and mechanical properties, which make them indispensable as materials for advanced motors and electrical generators in aviation and special power applications [39]. In particular, they are characterized by exceptionally high saturation magnetization, low coercivity and high Curie temperature (> 820°C). The elevated Curie temperatures of the alloys makes them especially attractive for various high temperature applications. However, at around 730°C, the disordered body-centered cubic Fe\textsubscript{x}Co\textsubscript{1−x} alloys undergo an ordering phase transition into the B2 structure (space group Pm3m) in the composition range \(0.3 \leq x \leq 0.7\) [40, 41, 42, 43], which significantly affects their magnetic and mechanical properties.

There exist numerous investigations of phase equilibria in the Fe-Co system; in particular, the order-disorder phase transition [41]. This has been observed for the first time by Seehra and Silinsky [40], who measured the electrical resistivity in FeCo alloys and found near \(T_c = 1006K\) a change in the slope of the temperature dependent resistivity curve indicating an order-disorder phase transition. Oyedele and Collins [41] investigated the order-disorder phase transition in FeCo alloys by the neutron-powder diffraction techniques for the composition range of 30 to 70 at.% of Co. Montano and Seehra [42] used Mössbauer spectroscopy to identify the order-disorder phase transition. They found the transition temperature about \(T_c = 1006K\) for the equiatomic composition. Ohnuma et al. [44] investigated the phase equilibria in the Fe-Co system both experimentally, using transmission electron microscopy for thin-film samples and
3.1 Introduction

X-ray and electron diffractometer for the bulk system, and theoretically by the CAL-PHAD method, which was modified by considering chemical interactions dependent on the magnetic state.

The coupling of magnetism and atomic short-range order (SRO) in Fe-Co, up to 25 at.% of Co, have been investigated experimentally by Pierron-Bohnes et al.\cite{45,46,47} using neutron diffuse scattering and nuclear magnetic resonance techniques. For the first time, the influence of the magnetism on the atomic SRO was clearly evident from an abrupt change in the temperature dependence of the local order at the Curie temperature. The theoretical analysis of the coupling between the magnetic and chemical degrees of freedom based on the mean-field approximation of a combined Ising-Heisenberg Hamiltonian was done by Pierron-Bohnes et al.\cite{45}. They have shown that the magnetic contribution to the effective interactions should be roughly proportional to the square of the magnetization.

The FeCo system has been theoretically studied by using a wide variety of phenomenological methods as well as with first principles techniques. In an early phenomenological treatment of the A2-B2 transition, Beinenstock and Lewis \cite{48} employed a low temperature expansion of the Ising model to calculate a phase diagram with non-magnetic components. This phenomenological approach resulted in a B2 phase field symmetric about the 50-50 composition and somewhat narrower than that found experimentally. Real space renormalization group was used by Racz and Collins \cite{49} to study the slight asymmetry in the A2-B2 phase boundary. In the context of a non-magnetic nearest-neighbor Ising model, they found that a small three-body interaction could account for the experimentally observed asymmetry.

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3.2 Methodology

3.2.1 Effective cluster interactions for finite magnetization

The PDLM state, which represents the partially ordered magnetic state for a given global magnetization \( m \), can be introduced as a straightforward generalization of disordered local moment (DLM) \( [64, 65] \) model. The magnetic binary \( \text{Fe}_x\text{Co}_{1-x} \) alloy is described in terms of a four component alloy \( \text{Fe}^+_{dx}\text{Fe}^+_{dz}\text{Co}^+_{u(1-x)}\text{Co}^+_{d(1-x)} \), where \( u = (1 + m)/2 \) and \( d = (1 - m)/2 \), respectively. Fe and Co atoms with up and down spin...
orientation are distributed randomly relative to one another on the underlying lattice. In the adiabatic approximation adopted in this paper, the dynamics of the spins and its coupling with other types of thermal excitations has been neglected. One can see, that this model gives the ferromagnetic state for \( m = 1 \) and the DLM state for \( m = 0 \).

Using the fact that thermally induced fluctuations of the local magnetic moment orientations are much faster than the atom-vacancy exchanges associated with equilibrating the atomic short-range order, one can define “spin-averaged” effective pair interactions (EPI’s) for a binary \( \text{Fe}_x\text{Co}_{1-x} \) alloy in the PDLM states as

\[
< V_{ij}^{\text{FeCo}^\sigma} > = \frac{1}{16} \sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} p_{\sigma_1} p_{\sigma_2} p_{\sigma_3} p_{\sigma_4} V_{ij}^{\text{Fe}^{\sigma_1,\sigma_2}\text{Co}^{\sigma_3,\sigma_4}},
\]

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\[
< V_{ij}^{\text{FeCo}^\sigma} > = \frac{1}{16} \sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} p_{\sigma_1} p_{\sigma_2} p_{\sigma_3} p_{\sigma_4} V_{ij}^{\text{Fe}^{\sigma_1,\sigma_2}\text{Co}^{\sigma_3,\sigma_4}},
\]

### 3.2.2 Details of the first principles calculations

We have used three related first-principles techniques for our calculations:

(i) the Korringa-Kohn-Rostoker Green function method in the atomic sphere approximation (KKR-ASA). This was used for the calculation of the densities of states and magnetic moments of the alloys at different compositions;
3.2 Methodology

(ii) the locally self-consistent Green’s function (LSGF) method [69, 70] based on the KKR-ASA method for the determination of the on-site and inter-site screening constants needed for the electrostatic part of the screened generalizied perturbation method (SGPM) effective pair interactions; and

(iii) the exact muffin-tin orbital (EMTO) method within the full charge density formalism [19] for the total energy and cluster interaction calculations.

Randomness has been treated using the coherent potential approximation (CPA) [31, 68, 69, 71]: the KKR-ASA-CPA and the EMTO-CPA. The local density approximation (LDA) [72] has been used for the exchange-correlation potential.

The KKR-ASA Green function and LSGF methods have been used to determine the screening constants which enter the DFT-CPA formalism in the single-site approximation (in the so-called “isomorphous” CPA model). In this formalism, the on-site screened electrostatic potential \( V_{scr}^i \) and energy \( E_{scr}^i \) are determined as suggested by Ruban [73] and Ruban et al. [74]:

\[
V_{scr}^i = -e^2 \alpha_{scr} q_i / S \\
E_{scr}^i = -e^2 \frac{1}{2} \alpha_{scr} \beta_{scr} q_i^2 / S.
\] (3.3)

Here, \( q_i \) is the net charge of the atomic sphere of the \( i \)th alloy component, \( S \) the Wigner-Seitz radius, \( \alpha_{scr} \) and \( \beta_{scr} \) the on-site screening constants. Their values, which are \( \alpha_{scr} = 0.81, 0.84, 0.88 \) and \( \beta_{scr} = 1.15, 1.17, 1.18 \), have been determined from the corresponding supercell LSGF calculations of random Fe\(_{30}\)Co\(_{70}\), Fe\(_{50}\)Co\(_{50}\) and Fe\(_{70}\)Co\(_{30}\) alloys, respectively.

The screening charge has also been used to determine the inter-site screening constants, \( \alpha_{scr}(R) \), needed in the calculations of the electrostatic part of the SGPM effective pair interactions [73, 75], the intersite screened Coulomb interactions for the \( i \) and \( j \) sites, which in the case of a binary A-B alloy can be defined as

\[
V_{ij}^{scr} = e^2 \alpha_{scr}(R_{ij}) q_{eff}^2 / S,
\] (3.4)

where \( q_{eff} = q_A - q_B \) is the effective charge transfer in the case of a binary alloy and \( R_{ij} \) is the vector connecting sites \( i \) and \( j \). The whole SGPM interaction is then

\[
V_{ij}^{(2)} = V_{ij}^{one-el} + V_{ij}^{scr},
\] (3.5)

where \( V_{ij}^{(2)} \) is the SGPM interaction at the \( i \)th coordination shell and \( V_{ij}^{one-el} \) the one electron contribution to the SGPM interaction.
Experimental lattice parameters [43] have been used in the first-principles calculations of the electronic structure and effective interactions of Fe\textsubscript{x}Co\textsubscript{1−x} alloys. The Monkhorst-Pack grid[76] with subdivisions along each reciprocal lattice vector 31×31×31 has been used for integration over the Brillouin zone in the LDA self-consistent and SGPM calculations.

### 3.3 Results and discussion

#### 3.3.1 Electronic structure and magnetic properties of Fe-Co alloy

The electronic structure and magnetic properties of Fe-Co alloys have been calculated previously by MacLaren et al.[77] by the KKR-CPA method. In this paper we use a similar Green’s function KKR-ASA-CPA method [67, 68] for the calculations of the electron density of states (DOS) and magnetic moments. The experimental[43] lattice spacing varying with composition from a=2.835 Å to 2.863 Å has been used in our LDA self-consistent calculations. In Fig. 3.1 we show the electronic density of states

![DOS plot](image_url)

**Figure 3.1:** DOS - Density of states of bcc Fe, Co, and ordered B2-FeCo alloy.

(DOS) of pure bcc Fe and Co as well as B2-ordered FeCo alloy calculated for the
same lattice parameter, $a = 2.86 \text{ rA}$. The majority bands of pure Fe and Co are shifted relative each other, which is a consequence of the fact that this band is filled in Co but unoccupied to some degree in Fe. The completely filled majority d-band in Co becomes inert or non-bonding and moves down with energy closer to the bottom of the valence band. There is also a substantial difference in the position of the minority band of Co and Fe, which is due to the difference in the number of the occupied states in this band.

What may however seem a bit unusual is the fact that the position and the form of the majority and minority bands of the ordered B2-FeCo almost coincide with those of bcc Co almost up to the Fermi energy. Only approximately 0.05 eV below the Fermi energy, the minority band of FeCo becomes different from that of Co by forming a an additional valley and redistributing the states above the Fermi energy. To explain the electronic structure of the B2-FeCo, it is useful to see what happens with electronic states at the local level, inside atomic spheres of Fe and Co.

In Fig. 3.2a we show the local DOS of Co and Fe atoms in the ordered B2-FeCo alloy. The local DOS of the majority Fe and Co states are practically the same. The difference in the minority DOS of Fe and Co is more pronounced, although they still have a similar form and position up to the Fermi energy. Such a strong similarity of the local Fe and Co bands can be understood, in its turn, in terms of the average bond model, proposed by Ruban et al. [78].

Let us note first that the B2 structure is quite special in respect that every Fe atom is completely surrounded by Co atoms at the first coordination shell and vice versa. In this case, the Fe and Co nearest neighbors form a common bond between themselves due to the strong hybridization of the d-states. Since the d-states are quite localized, the influence of more distant coordination shells on the electronic structure is small, and thus the DOS of the ordered alloy is vey similar to that of pure metals, as has been demonstrated by Ruban et al. [78] for the case of non-magnetic 4d-metal alloys. The position of majority and minority states in the B2-FeCo can be then explained by the shift of the majority d-band of FeCo due to its complete filling and the consequent hybridization of the minority band with the majority one. Such a coherent behaviour of the local DOS of Fe and Co appears to be disturbed by the randomness in random alloys, which can be clearly see in Fig. 3.2b, where we present the local DOS of random Fe$_{0.5}$Co$_{0.5}$ alloy. The positions of the peaks of the local DOS of Fe and Co atoms are shifted relative to each other, which is a manifestation of the fact the they have on average equal number of Fe and Co atoms at the first coordination shell. In particular, the minority DOS of Co strongly increases at the Fermi energy, as it should be when Co atoms has Co nearest neighbors at the fist coordinations shell (see the DOS of pure Co in the bcc structure in Fig. 3.1). This makes such an atomic configuration unfavorable.
3.3 Results and discussion

compared to the ordered B2 structure and this is the main source origin of the ordering behaviour of Fe-Co alloys.

Now, it is easy to understand the reason for the changes of the DOS with variations of the composition of random alloys, which is shown in Fig. 3.2c and d for Fe$_{0.25}$Co$_{0.75}$ and Fe$_{0.75}$Co$_{0.25}$ alloys, respectively. In the case of Fe$_{0.25}$Co$_{0.75}$ alloy (Fig. 3.2c), the average number of Fe atoms surrounded each Fe atom decreases, and the local DOS of Fe mainly follows that of Co, especially in the case of the majority band. At the same time, the average number of Co atoms surrounded each Co atom increases, and this again leads to the increase of the Co minority DOS at the Fermi energy. Vice versa, in the case of the Fe$_{0.75}$Co$_{0.25}$ alloy, the effective number Fe atoms at the first coordination shell of increases thereby pushing the Fe majority band to the Fermi energy as in pure bcc Fe (see Fig. 3.1 for Fe). At the same time, Co atoms become surrounded mostly by Fe atoms and this makes possible to rearrange their minority band in a way to have a valley at the Fermi energy similar to the case of the B2 phase.

The concentration dependence of the average magnetic moment of Fe-Co alloys exhibit the Slater-Pauling behavior and it was discussed in details by MacLaren et al.\textsuperscript{[77]}. In Fig. 3.3 we compare our results for the average and local magnetic moments in Fe-Co random alloys with the first-principles calculations by MacLaren et al.\textsuperscript{[77]}

**Figure 3.2:** DOS - DOS of Fe and Co in ordered-B2 and random alloys.
and experimental data [81]. One can see that our results follow the same trend as MacLaren et al. [77], but closer to the experimental data. The difference arises due to the use of different lattice spacings, since we have used experimental data. Our calculated magnetic moments a bit lower than the experimental data. The reason for the this discrepancy is most probably related to atomic short range order effects neglected in our single-site CPA calculations, and which may exist and be pronounced in the experimental samples. Let us also note, that Co-rich FeCo alloys are not a good candidates for neutron experiments [84], first, because of their higher neutron absorption cross-section and also because of their high magnetic anisotropy. FeCo alloys exhibit the weakest environment effects compared to other Fe-based alloys. In addition Co has small but significant orbital magnetism that makes the system more complicated.

According to the neutron-diffraction studies [81], the complete occupation of the majority band of Fe by the addition of Co leads to a maximum mean magnetic moment 2.45 $\mu_B$ per atom at the composition $c_{Co}=0.3$. Fig. 3.3 shows that our the KKR-CPA calculations reproduce well the experimental trend of magnetization with composition. One can notice quite a peculiar behaviour of the local magnetic moments. The local moment on the Co atom remains nearly the same in the whole concentration range. At the same time, the local magnetic moment of Fe increases with increasing Co concentration from 2.2$\mu_B$ in bcc Fe to the unusually large magnitude of about 2.62 $\mu_B$ at $c_{Co}=0.5$ and then remains almost constant. The addition of Co to Fe leads to a redistribution of the electrons such that the total system becomes a strong ferromagnet. The local moment of Fe is environment dependent. It increases with the number of Co nearest neighbors and takes its maximum value when all eight nearest neighbor sites have been occupied by Co. This happens in the B2 structure.

### 3.3.2 Effective cluster interactions and ordering energies in the FM state

The effective cluster interactions in this work has been determined by the SGPM method. This method yields only a "chemical" contribution to the effective interactions, which determine the configurational energetics on a fixed ideal lattice. The contribution related to the possible local lattice relaxations should however be small in the Fe-Co alloys due to small atomic size mismatch of Fe and Co. We have also ignored contribution from lattice vibrations, which we expect to be insignificant in this system at least relative to quite large chemical interactions.
3.3 Results and discussion

Figure 3.3: Magnetic Moments - Magnetic moments of FeCo alloys. The experimental data have taken from Bardos et al. [83] and Collins et al. [81] and the theoretical data have taken from MacLaren et al. [77].

The SGPM interactions are concentration and volume dependent. In Fig. 3.4 we show the EPI for three different alloy compositions: Fe$_{0.3}$Co$_{0.7}$, Fe$_{0.5}$Co$_{0.5}$, and Fe$_{0.7}$Co$_{0.3}$ in the FM state. As one can see, the strongest EPI is at the first coordination shell for all the alloy compositions. Other significant interactions are at the first five coordination shells and at the eleventh coordination shell, which is in the closed-packed [111] direction. One can also notice that the nearest neighbor EPI is changing almost by a factor of two in the concentration range of 0.3 $< c_{Co} < 0.7$, decreasing for Co-rich alloys. It is clear, that such a dependence should affect the order-disorder transition temperature too.

We have also calculated the three- and four-site interactions. In Fig. 5.10, 5.11 we show some of the strongest multisite interactions in Fe$_{0.5}$Co$_{0.5}$ alloy in the ferromagnetic state. The interaction index is given by the coordination shell numbers of the sides of the corresponding cluster. In the case of the four-site interactions, the order of indexes matters, so the choice is the following: the first four indexes are the coordination shells of the sides of a closed loop through all the four sites, and the last two are the coordination shells of remaining sides of the cluster. It is clear that many-body interactions do not vary systematically, however in most cases the strongest multisite
interactions are along the line in the close-packed direction such as, for instance, \( V_{1-1-5}^{(3)} \) in the case of 3-site interactions and \( V_{1-5-11-1-5-1}^{(4)} \) in the case of four-site interactions. The discussion of the trends for multisite ECI can be found in Ref. [85].

In order to check the validity of the SGPM effective cluster interactions, we have calculated the ordering energy of a set of ordered structures \( \alpha \), determined as the difference of the total energies of the ordered random alloys, \( \Delta E_{\text{ord}} = E_{\text{ord}} - E_{\text{random}} \) from both the direct total energy calculations using this formula as well as from the SGPM interactions. In Table 3.1 we show the ordering energies of FeCo for four different ordered phases: A11, B11, B2 and B32. The agreement seems to be quite good, especially taking into consideration the fact that the SGPM interactions are obtained in the random state, where magnetic state, including, for instance, the local magnetic moments of Fe and Co atoms, is different from those in the ordered structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>SGPM (mRy)</th>
<th>Total energy (mRy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A11</td>
<td>-0.231</td>
<td>-0.639</td>
</tr>
<tr>
<td>B11</td>
<td>0.200</td>
<td>0.649</td>
</tr>
<tr>
<td>B2</td>
<td>-5.051</td>
<td>-4.614</td>
</tr>
<tr>
<td>B32</td>
<td>0.634</td>
<td>0.509</td>
</tr>
</tbody>
</table>

Table 3.1: The ordering energy calculated from the SGPM ECI and from the direct total energy calculations.
3.3 Results and discussion

Figure 3.5: ECI - Three-site ECI for Fe$_{0.5}$Co$_{0.5}$ alloy in the FM state.

Figure 3.6: ECI - Four-site ECI for Fe$_{0.5}$Co$_{0.5}$ alloy in the FM state.
3.3 Results and discussion

3.3.3 Order-disorder phase transition in the reduced ferromagnetic state

Accurate phase equilibria calculations in magnetic systems becomes highly non-trivial at temperatures close to the point of a phase transition when magnetic and configurational interactions are of the same order, i.e. when magnetic and configurational degrees of freedom becomes strongly coupled and complexly interconnected. In Fe-Co alloys the order-disorder phase transition is only 100 C below the magnetic phase transition, which means that magnetic thermal excitations should affect the order-disorder phase transition.

Unfortunately, there is no simple and accurate first-principles based approach to the description of the thermally excited ferromagnetic state of the itinerant magnets, like Fe-Co alloys. Thus, the only way to proceed is to use a simplified model, hopefully not too simple, to the description of the magnetic state. As has been mentioned above, we use the PDLM model for treating the alloy in the ferromagnetic state with a reduced magnetization. Since the magnetic excitations are much faster than atomic configurational, which are connected to the quite slow process of the atomic diffusion, we can separate out the magnetic degree of freedom. In the single-site mean field consideration adopted in this work, the magnetic state is given by the reduced magnetization $m$.

![Figure 3.7: EPI - The magnetization dependent EPI's of Fe$_{0.3}$Co$_{0.7}$ (upper panel) and Fe$_{0.5}$Co$_{0.5}$ (lower panel) alloys.](image)
The variation of the EPI with magnetization from the DLM state \((m = 0)\) to the FM state is shown in Fig. 3.7 for two different alloy compositions. It is clear that the mostly affected EPI’s are for the first and second coordination shells. This is so since the connection between interactions in different magnetic states is roughly determined by the magnetic exchange interaction parameters, which have approximately the same hierarchy as the chemical interactions \([57]\). One can also see that the nearest neighbor EPI changes non-monotonically with magnetization. The most dramatic change with the magnetization is however for the next nearest neighbor EPI: it changes the sign from negative in the FM state to positive in the DLM state. In fact, this change in the EPI for the next nearest neighbor affects very strongly the order-disorder transition temperature. The order-disorder transition temperatures in Fe-Co alloys in the concentration range of \(0.3 < c_{Co} < 0.7\) has been determined in the Monte Carlo simulations. The following ECI have been used in this case: The EPI at the first 30 coordination shells, 13 for three-site and 10 four-site strongest ECI. In Fig. 3.8 we show the calculated order-disorder transition temperature of Fe_{0.5}Co_{0.5} as a function of magnetization together with the EPI at the first five coordination shells. It is clear, that transition temperature is very sensitive to the magnetization. One can also see, that
the dependence of the transition temperature from the magnetic state is not entirely related to the magnetization dependence of the EPI at the first coordination shell. In fact very strong increase of the transition temperature close to the FM state is also related to the decrease of the EPI at the second coordination shell. This is so, since the second coordination shell in the B2 structure consists of the atoms of the same type, and therefore negative interaction at this coordination shell is stabilizing the B2 structure. Finally, in Fig. 3.9 we show the calculated order-disorder transition temperature for several values of magnetization as function of alloy composition together with the experimental data. The experimental transition temperature is close to the theoretical prediction for magnetization $m = 0.8$. There are very few experimental data for the magnetization close to the ordering transition. According an early experimental study by Clegg and Buckley and a Mössbauer study by Montano and Seehra, the magnetization at the temperature of the ordering transition is $m \approx 0.83$ for the equiatomic alloy composition. Thus, one can conclude that our results are in very good agreement with experimental data.

Of course, such agreement can to some degree be fortuitous, and further investigations are apparently needed concerning the description of the magnetic state and probably some other contributions, neglected in this work. In particular, a drawback of our model is that it neglects longitudinal spin fluctuations expected to be important for Co-rich alloys. However, it is clear that our calculations confirm quite strong dependence of the ordering effects on the degree of magnetization, similar to the cases of fcc Fe-Ni and bcc Fe-Cr alloys considered lately.
Chapter 4

Temperature dependence of stacking-fault and anti-phase boundary energies in Al$_3$Sc from *ab initio* calculations

4.1 Introduction

Al-Sc alloys represent a new generation of high performance alloys for aerospace and automotive applications [88, 89]. Superior mechanical properties of these alloys are mainly due to precipitation hardening that results in the formation of Al$_3$Sc phase having the L1$_2$ crystal structure [90, 91], which interact with dislocations in Al matrix [92, 93, 94, 95]. One of the possible results of such interaction is a formation of superdislocations, which are two partial dislocations connected either by a stacking fault or an anti-phase boundary (APB) [96, 97]. Thus, the energetics of the stacking fault and antiphase boundaries are important parameters, which can be responsible for mechanical properties of Al-Sc alloys.

Both these defects are planar but one of them is related to the change of the structure of the underlying lattice, while the other to a change of the ideal atomic configuration. In particular, the stacking fault is formed by removing one layer from the fcc-type $ABC$-sequence of the \{111\} layers, $...ABCABCABC...$, so it becomes locally, for instance, $ABAB$, $...ABCAB|ABC...$, as is in the case of the hcp structure. The APB preserves the underlying fcc structure, but disrupts the long-range order. In the case of the L1$_2$ structure, it can be formed by translating one part of the crystal
with respect to the other by the [0.5 0.5 0] vector within the (001) plane \[22 \text{,} 98\]. This type of the APB is called conservative as it conserves the composition.

The defect energies can be obtained in several ways by first-principles methods. First of all, the direct calculations are possible either by the surface Green’s function technique \[96 \text{,} 97\] in the semi-infinite geometry or by a supercell approach where the crystal with a defect is modeled by a finite slab in the direction perpendicular to the defect. Alternatively, cluster expansion type phenomenological models can be used. In particular, the axial Ising model (AIM) and its particular approximation, axial next nearest neighbor Ising (ANNNI) model \[99 \text{,} 100\] are frequently used in the calculations of the SFEs as well as APBEs, although an Ising model on the underlying lattice may suffice in the case of the APBEs.

There exist several theoretical investigations of the SFE and APBE in the ordered Al\(_3\)Sc. Fu et al. \[101 \text{,} 102\] calculated the SFE and APBE from first principles more than 20 years ago by the full-potential linearized augmented plane-wave method. Hyland et al. \[103\] employed a semi-empirical embedded atom method. Recently, Wu et al. \[104\] have performed first-principles calculations of the generalized planar fault energy in the Al\(_3\)Sc and Al\(_3\)Mg using a 12-layer-slab model. However, all these calculations were performed at 0 K. At the same time, some experimental data \[105 \text{,} 106\] suggest the existence of quite strong temperature dependence of the SFE in the Al\(_3\)Sc.

If this is indeed the case, the temperature dependence of the defect energies cannot be neglected in the theoretical modeling. Therefore, in this paper, we investigate the effect of temperature on the SFEs and APBEs in the Al\(_3\)Sc. This is done by including the one-electron and lattice vibration excitations together with the thermal lattice expansion. To obtain the last one we use the Debye-Grüneisen model while the contribution from lattice vibrations is calculated in the harmonic approximation from the dynamical matrix of the corresponding systems. We also compare different methods in order to establish their relative accuracy.

### 4.2 Methodology

#### 4.2.1 The supercell approach

Within the supercell approach, the SFE, \(\gamma_{SF}\), is obtained from the total energy calculations of sufficiently large supercells representing an ideal lattice and a lattice with a defect. In this case, the SFE is:

\[
\gamma_{SF} = (E_{sf} - \tilde{E}_{id})/A, \tag{4.1}
\]
where the $A$ is the interface area; $E_{sf}$ and $\tilde{E}_{id}$ are total energies of the supercell with and without the defect, respectively. The last one is normalized on the number of atoms in the supercell with the defect (or the number of planes, which is equivalent).

### 4.2.2 Phenomenological models

Phenomenological models are based on the use of certain type of an Ising Hamiltonian, parameter of which describe either the interaction of planar defects as in the AIM or effective interactions of alloy components on the underlying lattice of an alloy.

#### 4.2.2.1 Axial Ising model

In the AIM, the crystal is represented by a sequence of planes along a certain direction. The correct sequence of the $i$th plane is described by positive spin-variable $\sigma_i = +1$. If the sequence is incorrect $\sigma_i = -1$. Assuming that there are only pairwise interactions between planar defects, the corresponding Hamiltonian is

$$H = \sum_{i,n=1,N} J_n \sigma_i \sigma_{i+n},$$

where $J_n$ are the interaction parameters or coupling energy parameters for two planes separated by $n$ planes and $i$ is the plane index. The fcc intrinsic SFE, $\gamma_{SF}$, is then

$$\gamma_{SF} = 4(J_1 + J_2 + J_3 + \ldots)/A. \tag{4.3}$$

Interaction parameters can be obtained by a structure inversion method using the total energies of some predefined structures with defects and an expansion of the these energies in terms of the corresponding Hamiltonian (4.2). For instance, if one assumes that the dominating interactions in the system are the nearest and next-nearest-neighbor interactions, $J_1$ and $J_2$, these parameters can be obtained from the total energies of the fcc (ABC stacking), hcp (ABAB stacking), and double-hcp (ABAC) structures. This is the so-called ANNNI model. The first and the second order SFE within the AIM are defined as follows [107, 108]:

$$\gamma_{SF}^{(1)} = 4J_1/A = 2(E_{hcp} - E_{fcc})/A$$

$$\gamma_{SF}^{(2)} = 4(J_1 + J_2)/A = (E_{hcp} + 2E_{d-hcp} - 3E_{fcc})/A, \tag{4.4}$$
4.2 Methodology

where $\gamma^{(2)}_{SF}$ corresponds to the ANNNI model and $E^{fcc}$, $E^{hcp}$ and $E^{dhcp}$ are the total energies of the fcc (ABC stacking), hcp (ABAB stacking), and double-hcp (ABAC) structures, respectively.

Hamiltonian \((4.2)\) can be also used in the calculations of APBEs. For instance, the APBE in the (001) plane of the L12 structure is expressed \([109, 110, 111, 112]\) in terms of interaction parameters between layers, $\tilde{J}_n$, as

$$
\gamma^{(001)}_{APB} = -(2\tilde{J}_1 + 4\tilde{J}_2 + 6\tilde{J}_3 + \ldots)/A. \quad (4.5)
$$

The (001) APBs can be also introduced using long period superstructures (LPS). The LPS with modulation length $m$ in the [001] direction, LPS-m, (≡ LPS-(10x)) has an additional superstructure vector $k = 2\pi/a(10x)$, where $x = 1/2m$ \([22]\). In these terms, the DO22 structure is just LPS-1 and DO23 structure is LPS-2, while the L12 structure corresponds to the LPS-$\infty$ with infinite modulation length. Using this definition of the LPS-m, one can formulate the AIM for the (001) APBEs in the L12 structure \([112, 113]\):

$$
\gamma^{(001)}_{APB}(m) = m \left( E^{LPS-m} - E^{L12} \right)/A. \quad (4.6)
$$

Here, $\gamma^{(m)}_{APB}$ is the APBE of order $m$, $E^{L12}$ and $E^{LPS-m}$ are the total energies per atom of the L12 and LPS-m structures, respectively, and $A$ is the surface area. By taking limit $m \to \infty$ in Eq. \((4.6)\), one finds the energy of the isolated APB. The ANNNI model for the APBEs \([107, 113]\) corresponds to the case of $m = 2$.

### 4.2.2.2 Ising Hamiltonian on the underlying lattice

The APBE can be also calculated from the effective cluster interactions of the Ising alloy Hamiltonian on the underlying lattice:

$$
H = \frac{1}{2} \sum_p V_p^{(2)} \sum_{i,j \in p} \delta c_i \delta c_j + \\
\frac{1}{3} \sum_t V_t^{(3)} \sum_{i,j,k \in t} \delta c_i \delta c_j \delta c_k + \\
\frac{1}{4} \sum_q V_q^{(4)} \sum_{ijk \ell \in q} \delta c_i \delta c_j \delta c_k \delta c_\ell. \quad (4.7)
$$

Here, $V_s^{(n)}$ are the $n$-site effective cluster interactions for the cluster of an $s$-type; $\delta c_i$ are the concentration fluctuations at sites $i$: $\delta c_i = c_i - c$, where $c_i$ is the occupation number at site $i$, taking on values 1 or 0 if site $i$ is occupied by Al or Sc atom, respectively, and $c$ is the concentration of Al. The summation in Eq. \((5.1)\) is carried out over all sites.
In this case, the APBE, $\gamma_{APB}$, is equal to the change of the ordering energy $\Delta E_{ord}$ of the alloy due to the presence of a defect divided by the area of an APB plane per atom $A$ \cite{114,115,116}:

$$\gamma_{APB} = \Delta E_{ord}(c)/A. \quad (4.8)$$

The advantage of this method is that it allows one to avoid spurious interactions between the antiphase boundaries, which can exist in the case of direct supercell calculations due to translational periodicity. In general, the knowledge of the effective interactions is important for establishing the range of the defect-defect interactions.

Using the AIM definition for the (001) APBE (4.6), one can actually find an analytical expression for the contribution of the effective pair interactions to the (001) APBE:

$$\gamma_{APB}^{(001)} = \frac{1}{2A} c(1-c) \sum_p z_p V_p^{(2)} \left( \alpha_p^{LPS-\infty} - \alpha_p^{LPS-k_p} \right), \quad (4.9)$$

where $z_p$ is the coordination shell number, and $\alpha_p$ are the Warren-Cowley short-range order (SRO) parameters. The $k_p$ is the index of the LPS structure, which is either $\infty$, as for instance in the case of the first coordination shell, $p = 1$, or the first LPS-$m$ with increasing $m$, when $\alpha_p^{LPS-m}$ is no longer equal to $\alpha_p^{LPS-\infty} (\equiv \alpha_p^{L1_2})$. For instance, $k_p = 1$ for $p = 2, 3, 4, 6, 7, \ldots$, $k_p = 2$, for $p = 8, 9, 15, \ldots$ and so on.

In the explicit form, the (001) APBE can be expressed in terms of the first several pair, three-, and four-site interactions as

$$\gamma_{APB}^{(001)} = \frac{1}{8A} \left(-2V_{(2)}^2 + 8V_{(2)}^3 - 8V_{(4)}^2 - 8V_{(6)}^{(2)} + 16V_{(2)}^{(2)} - 4V_{(3)}^2 + 16V_{(9)}^{(2)} - 24V_{(11)}^{(2)} + 8V_{(12)}^{(2)} - 32V_{(13)}^{(2)} + 32V_{(15)}^{(2)} + 16V_{(16)}^{(2)} - 16V_{(17)}^{(2)} + 16V_{(18)}^{(2)} - 40V_{(20)}^{(2)} - 6V_{(21)}^{(2)} + 16V_{(22)}^{(2)} + 24V_{(23)}^{(2)} + \ldots \right) + \frac{1}{16A} \left(6V_{(3)}^2 - 12V_{(3)}^3 + 6V_{(4)}^{(3)} + 12V_{(6)}^{(3)} - 24V_{(7)}^{(3)} - 6V_{(8)}^{(3)} - 24V_{(9)}^{(3)} + 24V_{(10)}^{(3)} + \ldots \right) + \frac{1}{32A} \left(-4V_{(4)}^{(4)} - 2V_{(3)}^{(4)} + 4V_{(4)}^{(4)} + 16V_{(4)}^{(4)} - 16V_{(7)}^{(4)} + 16V_{(8)}^{(4)} - 24V_{(9)}^{(4)} + \ldots \right). \quad (4.10)$$

Analytical expressions of the APBE in terms of effective pair interactions only has also been derived by Turchi et al. \cite{117}, Barrachim et al. \cite{118} and Kentzinger et al. \cite{119} up to the 8th coordination shell.
4.2 Methodology

4.2.3 Electronic structure calculations

Present electronic structure calculations are based on density functional theory (DFT) \cite{120} and have been performed by two complementary first-principles techniques: the exact muffin-tin orbitals (EMTO) method \cite{17, 18, 19} and projector augmented wave (PAW) \cite{127, 128} method as implemented in the Vienna \textit{ab initio} simulation package (VASP) \cite{129}. The PAW calculations yield the most accurate results and should be considered as standard.

In the EMTO calculations, the substitutional disorder in random Al\textsubscript{0.75}Sc\textsubscript{0.25} alloys has been treated using the coherent potential approximation (CPA) \cite{31, 33}. In this case, additional electrostatic contributions to the one-electron potential of alloy components and the total energy should be taken into consideration in the single-site DFT formalism \cite{121}. The on-site screened Coulomb interaction, $V^i_{\text{scr}}$, which contributes to the one-electron potential, and the corresponding electrostatic energy $E^i_{\text{scr}}$ are \cite{121}

$$V^i_{\text{scr}} = -e^2 \alpha_{\text{scr}} \frac{q_i}{S},$$

$$E^i_{\text{scr}} = -e^2 \frac{1}{2} \alpha_{\text{scr}} \beta_{\text{scr}} \frac{q^2_i}{S}. \tag{4.11}$$

Here $e$ is the electron charge, $S$ is the Wigner-Seitz (atomic sphere) radius, and $q_i$ is the average net charge (inside the atomic sphere) of the $i$th alloy component. Screening parameters $\alpha$ and $\beta$ were evaluated from supercell calculations using the locally self-consistent Green’s function (LSGF) technique \cite{69, 70}. The values of $\beta$ and $\alpha$ parameters were found to be $\beta = 1.15$ and $\alpha = 0.772$.

The effective cluster interactions of the Ising Hamiltonian have been calculated by the screened generalized perturbation method (SGPM) \cite{37}, \cite{22}. The pair effective interaction (EPI) for the $p$-th coordination shell is defined in the SGPM as:

$$V^{(2)}_p = V^\text{one-el}_p + V^\text{scr}_p, \tag{4.12}$$

where $V^{(2)}_p$ is the total effective interaction, $V^\text{one-el}_p$ the one electron contribution, or GPM interaction, and $V^\text{scr}_p$ the contribution from the screened Coulomb interaction, which can be determined as

$$V^\text{scr}_p = e^2 \alpha_{\text{scr}} \frac{q^2_{\text{eff}}}{S}. \tag{4.13}$$

where $q_{\text{eff}} = q_A - q_B$ is the effective charge transfer. The inter-site screened Coulomb constants $\alpha_{\text{scr}}$ were determined in the supercell calculations by the LSGF method as described in Ref. \cite{121}. For that purpose a 864-atom supercell modeling random Al\textsubscript{0.75}Sc\textsubscript{0.25} alloy has been used.
The total energies were calculated using the local density approximation (LDA)\cite{123}, the generalized gradient approximation (GGA)\cite{124}, and the local Airy gas approximation (LAG)\cite{125} to the exchange-correlation energy within the full charge density (FCD) formalism\cite{126}. All the self-consistent EMTO-CPA calculations were performed using an orbital momentum cutoff of $l_{\text{max}} = 3$ for partial waves. The effective cluster interactions in this work have been calculated by the SGPM within the EMTO-CPA method. The integration over the Brillouin zone for $\text{Al}_{0.75}\text{Sc}_{0.25}$ random alloy has been performed using a $31 \times 31 \times 31$ grid of special $k$-points determined according to the Monkhorst-Pack scheme.\cite{76} In the case of ordered alloys, the $k$-point grid has been rescaled from $31 \times 31 \times 31$ according to the tetragonality ratio, such as, for instance it has been $31 \times 31 \times 31$, $31 \times 31 \times 17$, $31 \times 31 \times 9$, and $31 \times 31 \times 35$ for the $\text{L}_12$, $\text{DO}_{22}$, $\text{DO}_{23}$, and $\text{DO}_{19}$ structures, respectively.

To include the effect of local lattice relaxations and thermal lattice vibrations we have carried out the corresponding supercell calculations by the PAW method\cite{127, 128} method as implemented in the VASP code\cite{129}. The local ionic positions have been relaxed by using a conjugate-gradient algorithm. The VASP has been also used to obtain a dynamical matrix of supercells using the linear-response method based on density functional perturbation theory (DFPT)\cite{130}. The dynamic matrix of the supercells then have been used in the vibrational free energy calculations using the PHONOPY code\cite{131}. The convergence tolerance for the total energy was $10^{-7}$ eV/atom, while $10^{-4}$ eV/\AA for the forces during ionic relaxations.

In the supercell SFE calculations, we have used two $\text{L}_12$-structure-based supercells with ABCABCABC and ABCABCA sequences of four-atom (111) layers. The (111) APBE has been modeled by a similar $\text{L}_12$-structure-based supercell consisting of 12 (111) layers. Assuming that the interplane distance remain the same in the case of the SFE and APBE creating by two partials, we have relaxed only local atomic positions in the corresponding first-principles calculations. Integration over the Brillouin zone in this case has been done using a $15 \times 15 \times 5$ Monkhorst-Pack grid.

### 4.2.4 Temperature-dependent properties

We have included the effect of thermal electronic and vibrational excitations in the calculations of the SFE, so instead of the total energy, the free energy have been obtained at the volume, $V$, found in the Debye-Grüneisen model calculations:

$$ F(V, T) = E_{\text{el}}(V) + F_{\text{el}}(V, T) + F_{\text{vb}}(V, T). $$  \hspace{1cm} (4.14)
Here, $F_{el}(V, T)$ is the thermal electronic contribution to the free energy and $F_{vib}(V, T)$ is the vibrational contribution to the free energy, which has been obtained in the harmonic approximation as described above.

The electronic contribution to the free energy is

$$F_{el}(V, T) = E_{el}(V, T) - T S_{el}(V, T),$$

where the energy $E_{el}(V, T)$ includes the contribution from thermal electronic excitation:

$$E_{el}(V, T) = \int N(\epsilon, V) f(\epsilon, T)\epsilon d\epsilon - \int \epsilon^F N(\epsilon, V)\epsilon d\epsilon.$$

Here, $N(\epsilon, V)$ is the electronic density of states, $\epsilon_F$ is the Fermi energy, and $f$ is the Fermi-Dirac distribution function

$$f(\epsilon, T) = \left(1 + e^{(\epsilon - \epsilon_F)/k_B T}\right)^{-1}.$$

The electronic entropy $S_{el}$ is

$$S_{el}(V, T) = -k_B \int N(\epsilon, V) \left( f(\epsilon, T) \ln(f(\epsilon, T)) + (1 - f(\epsilon, T)) \ln(1 - f(\epsilon, T)) \right) d\epsilon.$$

In order to obtain the thermal lattice expansion and the corresponding finite temperature lattice constants of the Al$_3$Sc, the quasiharmonic approximation within Debye-Grüneisen model has been used [214]. The free energy in the Debye-Grüneisen model is determined as

$$F(V, T) = E_{el}(V) - k_B T \left( D(\Theta_D/T) + 3 \ln(1 - e^{-\Theta_D/T}) + \frac{9}{8} k_B \Theta_D \right),$$

(4.15)

where $E_{el}(V)$ is the energy of the static lattice at a given volume determined from first-principles calculations, $k_B$ is the Boltzmann constant; $D(\Theta_D/T)$ and $\Theta_D$ are the Debye function and Debye temperature. The latter is obtained from the first-principles total energy as is describe in Ref. [214]. The free energy is minimized with respect to the volume for given $T$.

4.3 Results and discussion

4.3.1 Ground state and thermal properties of Al$_3$Sc

In Fig. 4.1 we show the LDA total energies of random Al$_{0.75}$Sc$_{0.25}$ alloy as well as the L1$_2$, DO$_{22}$, DO$_{23}$, and DO$_{19}$ ordered structures as a function of the Wigner-Seitz radius. It is clear that the L1$_2$ structure is by far the most stable one, with the ordering
energy, defined as the difference of the total energies of the random and ordered alloys, of about 20 mRy if the local lattice relaxation effects are neglected and about 18.5 mRy if local lattice relaxations in random alloys are taken into consideration. The energy of local lattice relaxations have been determined in the PAW calculations for a 64-atom supercell modelling random Al$_{0.75}$Sc$_{0.25}$ alloy at the equilibrium atomic volume. Such a large ordering energy means that one can practically neglect the disordering effects up to 1500 K in this phase.

Let us note that in the case of the DO$_{22}$ and DO$_{23}$ structures the lattice relaxation energy was found to be 2.5 and 1.7 mRy/atom, respectively. In the case of the DO$_{22}$ structure, this is actually the energy of the tetragonal distortion. The DO$_{19}$ structure is the hcp-based ordered structure with ordering in the (0001) plane similar to that in the (111) plane of the L1$_2$ structure. According to (4.4), the double difference of the total energies the DO$_{19}$ and L1$_2$ structures is the SFE of the first order in the AIM model.

Figure 4.1: Equation of states - Total energy as a function of Wigner-Seitz radius for random fcc, L1$_2$, DO$_{22}$, DO$_{23}$, and DO$_{19}$ structures. The total energy zero is set to $E_0 = -746.375Ry$.

The calculated ground state properties of the L1$_2$ Al$_3$Sc are presented in Table 4.1 where they are compared with the experimental data [133, 134, 135, 136] and the previous theoretical calculations [101, 137, 138, 139, 140]. The Grüneisen constant, $\gamma$,..
4.3 Results and discussion

Table 4.1: Calculated and measured properties of the Al\textsubscript{3}Sc. \(a_0\) is the lattice parameter, \(B_0\) is the bulk modulus, \(\gamma\) is the Gruneisen parameter, and \(\alpha\) is the thermal expansion coefficient.

<table>
<thead>
<tr>
<th>References</th>
<th>(a_0) (\text{Å})</th>
<th>(B_0) (GPa)</th>
<th>(\gamma)</th>
<th>(\alpha) (10(^{-6})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (LDA)</td>
<td>4.05 (0 K)</td>
<td>95 (0 K)</td>
<td>1.56</td>
<td>15.7 (800 K)</td>
</tr>
<tr>
<td>This work (LDA)</td>
<td>4.06 (300 K)</td>
<td>93 (300 K)</td>
<td>1.56</td>
<td>15.7 (800 K)</td>
</tr>
<tr>
<td>This work (GGA)</td>
<td>4.13 (0 K)</td>
<td>86 (0 K)</td>
<td>1.60</td>
<td>16.9 (800 K)</td>
</tr>
<tr>
<td>This work (GGA)</td>
<td>4.14 (300 K)</td>
<td>84 (300 K)</td>
<td>1.60</td>
<td>16.9 (800 K)</td>
</tr>
<tr>
<td>This work (LAG)</td>
<td>4.10 (0 K)</td>
<td>88 (0 K)</td>
<td>1.56</td>
<td>16.4 (800 K)</td>
</tr>
<tr>
<td>This work (LAG)</td>
<td>4.11 (300 K)</td>
<td>86 (300 K)</td>
<td>1.56</td>
<td>16.4 (800 K)</td>
</tr>
<tr>
<td>Asta et al. [138] (LDA)</td>
<td>4.01-4.05 (0 K)</td>
<td>94, 96 (0 K)</td>
<td>1.60</td>
<td>14.3 (800 K)</td>
</tr>
<tr>
<td>Ozolins et al. [139] (LDA)</td>
<td>4.01 (0 K)</td>
<td>96 (0 K)</td>
<td>1.60</td>
<td>14.3 (800 K)</td>
</tr>
<tr>
<td>Fu et al. [131] (LDA)</td>
<td>4.04 (0 K)</td>
<td>92 (0 K)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Xu et al. [140] (LDA)</td>
<td>4.05 (0 K)</td>
<td>93 (0 K)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Experimental data</td>
<td>4.10 [134]</td>
<td>92 [135, 99]</td>
<td>–</td>
<td>16.0 [133]</td>
</tr>
<tr>
<td></td>
<td>(300 K)</td>
<td>(300 K)</td>
<td></td>
<td>(298K-1173 K)</td>
</tr>
</tbody>
</table>

has been obtained by using a polynomial fit of the 5th order to the corresponding total energy data. Let us note that the thermal expansion coefficient calculated in this work using the Debye-Grüneisen model is in good agreement with the available experimental data as well as with the other theoretical calculations [137, 138, 139], where it has been determined in the first-principles phonon calculations in the quasiharmonic approximation. This allows us to use the Debye-Grüneisen model for the thermal lattice expansion in this alloy.

In Fig. 4.2 we show our theoretical results obtained within different approximations for the exchange-correlation energy for the thermal expansion coefficient and the lattice parameter as a function of temperature. The thermal expansion coefficient was measured by Harada et al. [133, 134], who reported an average value of 16.0 × 10\(^{-6}\)K\(^{-1}\) between 300 and 1173K. This is very close to our LDA result, which is 15.7 × 10\(^{-6}\)K\(^{-1}\) at 800 K, while the GGA and LAG slightly overestimate the thermal expansion coefficient. At the same time, the LAG seems to work best for the equilibrium lattice constant of Al\textsubscript{3}Sc.

4.3.2 Effective cluster interactions and APBE

Effective cluster interactions were calculated by the SGPM for a random Al\textsubscript{0.75}Sc\textsubscript{0.25} alloy at the 0 K LDA lattice constant. They are presented in Fig. 4.3. The nearest neighbor interaction of about 20 mRy is obviously dominant. However, the next several
interactions are also quite large, which is an indication of a very strong ordering tendency in Al-Sc alloys. The EPI quite slowly decay with the distance, and, for instance, the EPI at the 46th coordination shell, $V_{653}^{(2)}$, is still $−0.0112$ mRy. This shows that long-range interactions have to be taken into account for the accurate description of the system.

The three-site and four-site interactions calculated at $T = 0$ are shown in Figs. 4.5 and 4.6 respectively. The interaction index is given by the coordination shell numbers of the sides of the corresponding cluster. In the case of the four-site interactions, the order of indexes matters, so the choice is the following: the first four indexes are the coordination shells of the sides of a closed loop through all the four sites, and the last two are the coordination shells of remaining sides of the cluster. A few examples of the three-site and four-site clusters are shown in Fig. 4.4.

It is clear that multisite interactions are sizable in this system, and they should be taken into consideration in the accurate numerical modelling. Although, the multisite ECIs do not vary systematically, in most cases, the strongest multisite interactions correspond to an atomic chain aligned in the close-packed direction such as, for instance, $V_{1−1−4}^{(3)}$ in the case of the 3-site interactions (4.88 mRy) and $V_{1−4−10−1−4−1}^{(4)}$ (1.9 mRy).
4.3 Results and discussion

Figure 4.3: EPI - The EPIs in the Al$_{0.75}$Sc$_{0.25}$ random alloy at 0K determined in the SGPM calculations.

Figure 4.4: Cluster - A schematic representation of some 3-site and 4-site clusters. The maximum energy clusters are aligned along the closed packed direction ([110] in the fcc structure). Numbers denote coordination shells of the edges of the clusters.
in the case of the 4-site interactions (see Fig. 4.4). The discussion of the trends for multisite ECIs can be found in Ref. [85].

![Figure 4.5: ECI: 3-site](image)

Figure 4.5: ECI: 3-site - Three-site ECIs in the Al0.75Sc0.25 alloy.

The SGPM interactions produce quite well the ordering energies. The ordering energy of the L12 structure is $-19.4$ mRy from the SGPM interactions, which include the first 75 coordination shells of pair interactions, 50 three-site, and 25 four-site interactions. It is in very good agreement with the value of direct total energy calculation of $-20.6$ mRy. Let us note that the contribution of the multisite interactions to the ordering energy of the L12 phase is about -2 mRy, which comes in fact mostly from three-site interactions.

Further, we have also calculated the ordering energies of several LPS–m structures using the SGPM interactions up to $m=15$ and the EMTO total energies up to $m=10$. The difference between these energies and the ordering energy of the L12 structure yields the (001) APBE of order $m$ (see Eq. (4.6)). These results are presented in Fig. 4.7 together with the results for $\gamma_{APB}^{(111)}(m)$, obtained from the SGPM interactions and in the PAW supercell total energy calculations. In this case, the antiphase boundary is created by a shift of half of the crystal by $(\frac{1}{2} \frac{1}{2} \frac{1}{2})a$ vector in the (111) plane in every 3m layer for parameter $m$.

As one can see, the EMTO and SGPM results are in good agreement for $\gamma_{APB}^{(001)}$, and therefore we believe that the SGPM interactions are accurate enough for the description of the APBE in this system if the relaxations are neglected. We also find similar very
4.3 Results and discussion

Figure 4.6: ECI: 4-site - Four-site ECIs in the Al<sub>0.75</sub>Sc<sub>0.25</sub> alloy.

good agreement between the SGPM and total energy PAW supercell calculations shown in Fig. 4.7. In this case, since the SGPM yields chemical interactions on a fixed fcc underlying lattice, the SGPM results correspond to the unrelaxed case. Let us note that the contribution from the three-site interactions is about 3 mRy, which is a relatively large value. However, such a contribution is still less than the one from the local lattice relaxations, which has turned out to be quite substantial, almost 5 mRy per atom in the (111) plane, which is about 25% of the unrelaxed value.

4.3.3 Temperature dependence of the APBE

As has been mentioned above, to take temperature dependence of the defect formation energies into consideration, we use lattice constants, which correspond to given temperature, we use the Fermi-Dirac distribution function in the electronic structure calculations [141, 142], and we also obtain free energy of lattice vibrations at the corresponding temperature. In the present work, we use the LDA results for the lattice constant shown in Fig. 4.2 (bottom panel).

In order to analyze the lattice constant dependence, in Fig. 4.8 we show the temperature dependence of the strongest EPI in Al<sub>0.75</sub>Sc<sub>0.25</sub> at the first four coordination shells. One can see that the EPI at the first and third coordination shells, \( V^{(2)}_{110} \) and \( V^{(2)}_{211} \), decrease while those at the second and fourth coordinations shells, \( V^{(2)}_{200} \) and \( V^{(2)}_{220} \),
4.3 Results and discussion

Figure 4.7: Convergence - The APBE multiplied by the corresponding surface area per atom, $A$, as a function of period $m$, which in the case of the $(001)$ APB determines the period of the LPS, and in the case of the $(111)$ APB, the number of $(111)$ layers in the supercell modelling the APB, which is $3m$.

increase with temperature (or lattice constant). In fact, they all are weakening as temperature increases since their absolute value decreases.

This means that the ordering tendency should also be weakening with the temperature, which can indeed be seen in Fig. 4.9 where we show the ordering energies of the $L_{12}$, $DO_{22}$, and $DO_{23}$ structures obtained both in the direct total energy calculations and from the SGPM ECI. It is therefore quite expected that the APBEs decrease as the temperature increases. This is in fact seems to be a general tendency: a number of $L_{12}$-ordered alloys have been found in transmission electron microscopy investigation \[\text{[114]}\] where the APBEs decrease with increasing temperature.

In Fig. 4.10 we show our results for $\gamma_{APB}^{(001)}$ and $\gamma_{APB}^{(111)}$ obtained by different methods. One can see that $\gamma_{APB}^{(001)}$ calculated from the EMTO total energies within the AIM and from the ordering energies using the SGPM interactions are in good agreement, although these results are substantially lower than those obtained by Fu et al. \[\text{[101]}\] and Hyland et al. \[\text{[103]}\]. We do not know the reason for this disagreement. Let us note that these results include only temperature dependence due to the thermal lattice expansion and one-electron excitations.

The most interesting case, however, is the $(111)$ APBEs, $\gamma_{APB}^{(111)}$, which are relevant for mechanical properties, and for which there is experimental data. As one can notice,
4.3 Results and discussion

Figure 4.8: EPIs - The SGPM EPI parameters as a function of temperature in the $\text{Al}_{0.75}\text{Sc}_{0.25}$ random alloy. The temperature dependence have been taking into consideration only by using the temperature dependent lattice constant and the Fermi-Dirac distribution function in the electronic structure calculations.

Figure 4.9: Ordering energy - The ordering energies as a function of temperature. The temperature dependence have been taking into consideration only by using the temperature dependent lattice constant and the Fermi-Dirac distribution function in the electronic structure calculations.
the zero K results are quite scattered: between 433.9 and 670 mJ/m$^2$ obtained by Hyland et al. [103] and Fu et al. [101], respectively. Our PAW unrelaxed result obtained in the 12-layer ($m=4$) supercell calculations, is about 607 mJ/m$^2$ which is in good agreement with the SGPM results. Taking local lattice relaxations into consideration significantly reduces this energy to 460 mJ/m$^2$. This energy is additionally reduced by about 14 % at 1350 K due to thermal lattice expansion and further by about 14 % due to the vibrational free energy contribution, which have been obtained from the dynamical matrixes of the supercells with and without APB at the lattice parameter of 4.1 Å.

So, in the end, the theoretical (111) APBE at 1350 K turns out to be 327 mJ/m$^2$, which is very close to the experimental data, 313 mJ/m$^2$ by George et al. [136]. As one can see in Fig. 4.10, the contribution from free energy of thermal lattice vibrations plays crucial role in this case. This result shows, that the vibrational free energy contribution is indeed very important in the high-temperature thermodynamics of Al-Sc system, the fact which has been demonstrated earlier by Ozolins and Asta [139].

![Figure 4.10: APBEs - The APBES as a function of temperature. The experimental data by George et al. [136]; the theoretical results of the APBE are taken from Ref. [101, 103]](image)

4.3.4 Temperature dependence of the SFE

The SFEs have been obtained by the supercell approach and using the AIM within the first and second order approximations (see Eq. (4.4)) as described above. The results are presented in Fig. 4.11. Assuming that the supercell approach provides most accurate results, one can see that the first order AIM slightly underestimates the SFE,
while the second order AIM, which is the ANNNI model, slightly overestimates the SFE. Let us note that our results for the SFE are in fair agreement with other theoretical calculations, also shown in the figure. However, this agreement becomes much worse if the local lattice relaxations are considered. They lower the SFE of the Al$_3$Sc by about $-70$ mJ/m$^2$, which is a significant shift from $225$ mJ/m$^2$ at 0K.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sfe_temperature}
\caption{SFE - The SFE as a function of temperature. The experimental data are taken from Ref. \cite{105,106}, the theoretical results from Ref. \cite{101,103,104}.}
\end{figure}

The temperature dependence of the SFE has been considered as in the case of the APBE by taking into consideration the thermal lattice expansion, one electron excitations and the free energy of lattice vibrations in the harmonic approximation, as is described above. For that purpose, the dynamical matrixes of supercells with and without stacking fault have been calculated at the lattice parameter of 4.1 Å. Then the corresponding phonon density of state have been used in order to get the vibrational free energy in the whole temperatures range.

As can be seen in Fig. 4.11, both, the effect of the thermal lattice expansion and the vibrational free energy, decrease the SFE with temperature. The vibrational free energy contribution is again quite substantial and comparable with that from the thermal lattice expansion. Let us note that a similar decrease of the interfacial energy of Al/Al$_3$Sc has been found by Asta et al. \cite{137,144}.

On the contrary, the experimentally determined SFEs show a dramatic increase with temperature \cite{105,106}. Unfortunately, we don’t know for sure the reason for this discrepancy. Nevertheless, our results and the experimental estimate are in very good
agreement at 200 K, which is, of course, can be coincidental. To resolve this issue more elaborate experimental and theoretical studies are needed.

4.3.5 Conclusions

The SFEs and APBEs in the Al$_3$Sc and their temperature dependence have been investigated in the first-principles calculations. The supercell approach and AIM method have been used to model these defects. We have also calculated the effective cluster interactions by the SGPM, which allows to single out the important chemical interactions and determine their convergence, which, in the end, also determines which size of the supercell provides accurate modeling of the APBEs. According to these results a 12-layer slab is enough to determine the (111) APBE accurately and LPS-3 structure should proved accurate model for the (001) APBE.

The temperature effects have been included in the calculations of the defect formation energies using the contributions from the one-electron excitations, free energy of lattice vibrations and thermal lattice expansion. The latter has been obtained in the Debye-Grüneisen model. The calculations show that both the thermal lattice expansion and the free energy of lattice vibrations leads to a practically linear and quite significant decrease of the APBEs and SFE with temperature. However, if both these contributions are almost equal in the case of the SFE, the vibrational contribution is larger than that one from the thermal lattice expansion in the case of the (111) APBE.

Our results for the (111) APBE at 1350 K are in good agreement with existing experimental data. This is not, however, the case of the results for the temperature dependence of the SFE, which are varying with the corresponding experimental data [105, 106], where the SFE rapidly increases with temperature. At this moment, we do not know the reason for this disagreement. First-principles calculations can hardly be in large error, since there are no strongly correlated electronic states in Al$_3$Sc alloy, for which the used approximations for the exchange-corrrelation energy might fail. There can be another physical mechanism involved in the temperature behavior of the SFE, which is not accounted in our work, however, this needs further investigation. Nevertheless, the PAW results, which include the relaxation and vibrational contributions, present the best possible theoretical answer for the APBEs and SFE we could get in this investigation.
Chapter 5

First-principles study of atomic ordering in fcc Ni-Cr alloys

5.1 Introduction

Ni-Cr alloys form solid solutions over a wide range of composition and temperature on the fcc lattice. They have an excellent combination of mechanical strength and high-corrosion resistance at elevated temperature, which make them attractive in a variety of applications such as aircraft gas turbines, steam turbine power plants, chemical and petrochemical industries. At the same time, it is established that some properties, for instance, electrical resistivity and ductility are connected to atomic ordering in this system, which exhibits quite unusual properties.

At low temperatures, fcc Ni-rich random alloys become unstable and a first-order phase transition occurs to the Pt$_2$Mo-type ordered structure with the highest transition temperature of 863 K at the stoichiometric alloy composition, Ni$_2$Cr. It is characterized by a superstructure reflections at the $(\frac{2}{3}, \frac{2}{3}, 0)$ (or $\frac{1}{3}(1, 1, 0)$) reciprocal space positions. The fact that the latter is shifted from the $(1, 1, 0)$ symmetry special point position, where the diffuse scattering SRO maxima of random Ni-Cr alloys is observed, has attracted much interest to the mechanism of the phase transformation in Ni-Cr and other similar systems.

The atomic SRO in fcc Ni-Cr random alloys has been extensively studied experimentally. Diffuse neutron scattering technique was used by Vintaykin et al. for Ni$_{0.67}$Cr$_{0.33}$ alloys and by Caudron et al. for Ni$_{0.67}$Cr$_{0.33}$ and Ni$_{0.75}$Cr$_{0.25}$. Schönfeld et al. and Schweika and Haubold studied the atomic SRO and static atomic displacements in Ni$_{0.8}$Cr$_{0.2}$ and Ni$_{0.89}$Cr$_{0.11}$ using the diffuse neutron scattering and synchrotron radiation. They also evaluated effective pair interactions...
5.2 Methodology

in this system using both the Krivoglaz-Clapp-Moss equations and the inverse Monte Carlo method.

As for theoretical investigations, there exist two \textit{ab initio} studies of the SRO in Ni-Cr alloys.\cite{169, 170} However, their results are quite controversial. Turchi \textit{et al.}\cite{169} calculated effective cluster interactions (ECI) by the generalized perturbation method (GPM) implemented in the first-principles framework of the Korringa-Kohn-Rostocker (KKR) method and the coherent potential approximation (CPA). They got negative nearest neighbor effective pair interaction, which lead to a phase separation instead of ordering.

Staunton \textit{et al.}\cite{170}, who used the $S^{(2)}$-formalism within the same KKR-CPA method for the effective interactions and the mean-filed approach with Onsager cavity correction for the statistical consideration, demonstrated that the problem with interactions in the calculations by Turchi \textit{et al.}\cite{169} was related to the neglect of charge transfer in the GPM calculations. At the same time, although the problem with a phase separation trend was solved in Ref. \cite{170}, the resulting theoretical diffuse intensity map in the reciprocal space had additional ($\frac{2\sqrt{3}}{3}, 0$) peaks at variance with the existing experimental data.

In this work, we apply different theoretical tools in order to solve a long-standing problem with \textit{ab initio} description of atomic ordering in fcc Ni-Cr alloys. In particular, we use the SGPM,\cite{37, 121} which is a GPM method adopted to the DFT first-principles calculations by including screened Coulomb interaction contribution,\cite{22, 121} to determine the chemical part of effective cluster interactions (ECI) and the full-potential PAW method\cite{171} for calculating strain-induced interactions. The statistical modeling is done by the Monte Carlo method and using ring mean-field approximation.\cite{172, 173, 174} Here, we present a generalized RMFA for random binary alloys that incorporates effect of multi-site interactions.

5.2 Methodology

5.2.1 Configurational Hamiltonian

In this work, we use an Ising Hamiltonian for a statistical thermodynamic description of alloy energetics on a lattice, which presents the configurational energy of an alloy in terms effective cluster interactions:

$$E_{\text{conf}} = \frac{1}{2} \sum_p V_p^{(2)} \sum_{i,j \in p} \delta c_i \delta c_j +$$
5.2 Methodology

\[
\frac{1}{3} \sum_t V_t^{(3)} \sum_{i,j,k \in t} \delta c_i \delta c_j \delta c_k + \\
\frac{1}{4} \sum_q V_q^{(4)} \sum_{ijk \in q} \delta c_i \delta c_j \delta c_k \delta c_\ell
\]  

(5.1)

Here, \(V_s^{(n)}\) are the \(n\)-site ECI for the cluster of an \(s\)-type; \(\delta c_i\) are the concentration fluctuations at sites \(i\): \(\delta c_i = c_i - c\), where \(c_i\) is the occupation number at site \(i\), taking on values 1 or 0 if the site \(i\) is occupied by Ni or Cr atom, respectively, and \(c\) is the concentration of Ni. The summation in (5.1) is carried out over all sites.

The contribution of effective pair interactions (EPI) to the ordering energy can be expressed as

\[
\Delta E_{\text{ord}}(c) = \frac{1}{2} c(1-c) \sum_p z_p V_p^{(2)} \alpha_p
\]  

(5.2)

where \(\alpha_p = (\langle c_i c_j \rangle - c^2)(c(1-c))^{-1}\) is the Warren-Cowley short-range order parameter and \(z_p\) is the coordination number of the \(p\)-th coordination shell.

5.2.2 Static Concentration Wave method

The static concentration wave method is a powerful tool to study ordering phenomena using reciprocal space representation. According to this method, any arrangement of atoms on a Bravais lattice can be expressed as a superposition of static concentration waves

\[
c_i \equiv c(R) = c + \frac{1}{2} \sum_q \left( c_q e^{iqR} + \text{c.c.} \right),
\]  

(5.3)

where \(q\) is a non-zero wave vector defined in the first Brillouin zone with \(c_q\) being the amplitude of the concentration wave, which is the Fourier transform of concentration fluctuations:

\[
c_q = \sum_i \delta c_i e^{-i q R_i}.
\]  

(5.4)

The spectrum of concentration waves determines the distribution of alloy components on the lattice, and in completely ordered alloys it reduces just to one or several superstructure vectors. In the case of Ni\(_2\)Cr alloy, having Pt\(_2\)Mo structure, there is only one superstructure vector, which is \((\frac{2}{3} \frac{2}{3} 0)\) (or equivalently \(\frac{4}{3}(1 \frac{1}{2} 0)\)). That is, the Ni\(_2\)Cr ordered structure can be represented by the stacking of either (420) or (220) planes with every third plane containing only Cr and two others only Ni atoms.
The \( \text{Cr-Ni-Ni-Cr} \) stacking of the (420) or (220) planes is shown in Fig. 5.1. In the completely ordered state, the site occupation in the Pt\(_2\)Mo structure is determined by the following equation:\[ c(R) = \frac{1}{3} + \frac{2}{3} \cos \left( \frac{4\pi}{3} \left( x + \frac{1}{2} y \right) \right) \] (5.5)

where \( R \) is the fcc lattice vector, and \( x \) and \( y \) are \( x - \) and \( y - \)components of \( R \) in units of the lattice constant.

As has been noted, the superstructure vector of Ni\(_2\)Cr structure, \((\frac{2}{3} \frac{2}{3} 0)\), does not coincide with the position of the atomic SRO diffraction maxima at \((1 \frac{1}{2} 0)\) observed in the experiment for different alloy compositions in Ni-rich NiCr alloys.

### 5.2.3 Ring mean-field approximation

Accurate mean-field theories (MFTs) are valuable theoretical tools in statistical modeling allowing one not only to avoid time-consuming Monte Carlo simulations but also to get thermodynamic properties of metastable systems and a qualitative picture of ordering phenomena. In particular, as far as atomic short-range order in binary alloys
concerns, a MFT by Krivoglaz, Clapp and Moss (KCM) [25, 26, 27] presently known as the KCM formula, establishes a simple relation between the experimentally observed diffuse scattering and the Fourier transform of the effective pair interactions thereby elucidating the driving force for a specific type of ordering.

In recent years, a number of advanced MFTs have been developed, which have a substantially improved accuracy compared to the KCM theory. Among them, one of the most successful is the ring-mean-field approximation (RMFA), [172, 173, 174, 180, 181, 182] which provides an analytical solution of the SRO in reciprocal space using thermodynamic fluctuation in binary random alloys. More recently Udyansky et al. [183] and Bugaev et al. [184] have given a general formulation of to the analytical method for solving the SRO in random binary alloys.

In the RFMA, the energy of a random binary alloys is presented as

\[ E_{\text{conf}} = E_{\text{rand}}(c) + \frac{1}{2N} \sum_{k} \tilde{V}_k c_k c_k^* \tag{5.6} \]

Here, the first term is the energy of a random alloy, which can be expressed in terms of the effective interactions as

\[ E_{\text{rand}}(c) = \frac{c^2}{2} V^{(2)}_{k=0} + \frac{c^3}{3} V^{(3)}_{k=0,0} + \frac{c^4}{4} V^{(4)}_{k=0,0,0} + \ldots \tag{5.7} \]

where \( V^{(n)}_{k_1,k_2,\ldots,k_{n-1}} \) and \( c_k \) is the Fourier transforms of \( V^{(n)}_{R_1,R_2,\ldots,R_{n-1}} \)

\[ V^{(n)}_{k_1,k_2,\ldots,k_{n-1}} = \sum_{R_1,R_2,\ldots,R_{n-1}} V^{(n)}_{R_1,R_2,\ldots,R_{n-1},0} \exp \left[ -i \sum_{l=1}^{n-1} k_l R_l \right] . \tag{5.8} \]

The second term in (5.6) is the ordering energy defined here in terms of the Fourier transform of the renormalized effective pair interactions:

\[ \tilde{V}_k = V^{(2)}_k + cV^{(3)}_{k,0} + \frac{c^2}{2} V^{(4)}_{k,0,0} + \ldots, \tag{5.9} \]

and it is equivalent to (5.2) if only effective pair interactions are considered. However, in this particular case, an average contribution from multisite interaction is also included due to renormalization (5.9).

The product \( c_k c_k^* \) satisfies the sum rule:

\[ \frac{1}{N} \sum_k c_k c_k^* = c(1 - c) \tag{5.10} \]
and thus the properly normalized solution, given by $c_k$ and can be obtained by a minimization of the free energy functional with the respect to the corresponding Lagrange multiplier, $\mu$:

$$E_{\text{ord}} = \frac{1}{2N} \sum_k \tilde{\mathcal{V}}_{\mathbf{k}} c_k c_k^* + \frac{\mu}{2N} \left[ \sum_k c_k c_k^* - c(1 - c) \right]$$

The free energy of a random alloy within the RMFA is defined as

$$F = E_{\text{rand}}(c) - T S_{\text{rand}}(c) + \Delta F_{\text{ord}}$$

where

$$S_{\text{rand}}(c) = k_B \left[ c \ln c + (1 - c) \ln(1 - c) \right]$$

and the contribution from the atomic SRO to the free energy in the RMFA is then determined as

$$\Delta F_{\text{ord}} = \frac{1}{2N} \sum_k \left[ \tilde{\mathcal{V}}_{\mathbf{k}} + \mu + \frac{k_B T}{c(1 - c)} \right] c_k c_k^*$$

The correlation functions or Fourier transforms of the Warren-Cowley SRO parameters can be obtained within the thermodynamic fluctuation method as

$$\alpha_k = \left[ 1 + \frac{c(1 - c)}{k_B T} \left( \mu + \tilde{\mathcal{V}}_{\mathbf{k}} \right) \right]^{-1}.$$  

(5.13)

The Lagrange multiplier, $\mu$, has the meaning of the chemical potential and is determined from the sum rule (5.10), which is for $\alpha_k$:

$$\frac{1}{N} \sum_k \alpha_k = 1$$

For $\mu = 0$, Eq. (5.13) is reduced to the KCM formula. Finally, the Warren-Cowley short-range order parameter, $\alpha_p$, is determined as:

$$\alpha_p = \frac{1}{N} \sum_k \alpha_k e^{i \mathbf{R}_p},$$

(5.15)

where lattice vector $\mathbf{R}_p$ belongs to the $p$–th coordination shell.
5.2 Methodology

5.2.4 First-principles calculations

*Ab initio* calculations have been done by the exact muffin-tin orbitals (EMTO) [17, 18, 19] and PAW [171, 185] methods using density functional theory (DFT) [120]. The CPA [31, 33] has been used in the EMTO calculations of random alloys. In this case, additional electrostatic contributions to the one-electron potentials of alloy components and to the total energy should be taken into consideration in the single-site DFT formalism [121]. In this formalism, the on-site screened Coulomb interaction, $V_{\text{scr}}^i$, which contributes to the one-electron potential, and the corresponding electrostatic energy $E_{\text{scr}}^i$ are

$$
V_{\text{scr}}^i = -e^2 \alpha_{\text{scr}}^i \frac{q_i}{S},
$$

$$
E_{\text{scr}}^i = -e^2 \frac{1}{2} \alpha_{\text{scr}}^i \beta_{\text{scr}}^i \frac{q_i^2}{S}.
$$

(5.16)

Here, $q_i$ is the net charge of the atomic sphere of the $i$th alloy component, $S$ the Wigner-Seitz radius, $\alpha_{\text{scr}}$ and $\beta_{\text{scr}}$ the on-site screening constants.

The screening parameters, $\alpha$ and $\beta$, were evaluated from 864-atom supercell calculations of random Ni$_x$Cr$_{1-x}$ alloys using the locally self-consistent Green’s function (LSGF) method [122]. Their values are $\alpha_{\text{scr}} = 0.794, 0.785, 0.773$ and $\beta_{\text{scr}} = 1.15, 1.147, 1.144$, for random Ni$_{0.67}$Cr$_{0.33}$, Ni$_{0.75}$Cr$_{0.25}$ and Ni$_{0.8}$Cr$_{0.2}$ alloys, respectively.

The effective cluster interactions of the Ising Hamiltonian have been calculated by the SGPM [22, 37, 121]. The effective pair interactions (EPI) for the $p$-th coordination shell is defined in the SGPM as:

$$
V_p^{(2)} = V_{p-\text{el}} + V_p^{\text{scr}},
$$

(5.17)

where $V_p^{(2)}$ is the total effective interaction, $V_{p-\text{el}}$ the one electron contribution, or GPM interaction, and $V_p^{\text{scr}}$ the contribution from the screened Coulomb interaction, which can be determined as

$$
V_p^{\text{scr}} = e^2 \alpha_p^{\text{scr}} \frac{q_{\text{eff}}^2}{S},
$$

(5.18)

where $q_{\text{eff}} = q_A - q_B$ is the effective charge transfer. The inter-site screened Coulomb constants $\alpha_p^{\text{scr}}$ were determined in the supercell calculations by the LSGF method as described in Ref. [121].

The local density approximation (LDA) [123] has been used for the exchange-correlation potential in the DFT self-consistent calculations, while the total energy has been calculated in the generalized gradient approximation [186]. All the EMTO-CPA calculations were performed using an orbital momentum cutoff of $l_{\text{max}} = 3$ for
5.2 Methodology

partial waves. The experimental lattice parameters\cite{43, 147, 157, 188, 189} have been used in the calculations of the ECI.

The integration over the Brillouin zone for Ni\textsubscript{x}Cr\textsubscript{1−x} random alloys has been performed using a $31 \times 31 \times 31$ grid of special $k$-points determined according to the Monkhorst-Pack scheme.\cite{76} In the case of ordered alloys, an equivalent grid of $k$-points has been used in the corresponding Brillouin zone.

The PAW method\cite{171} as is implemented in the Vienna \textit{ab initio} simulation package (VASP)\cite{185} has been used in the calculations of enthalpies of formation of ordered alloys, relaxation energies of random alloys, and forces and local lattice relaxations needed to determine strain-induced interactions as described below. The GGA\cite{186} has been used for the exchange-correlation energy and potential. The energy cutoff was 300 eV.

5.2.5 Microscopic elastic theory within \textit{ab initio} calculations

The PAW method\cite{171, 185} was employed to obtain forces and local atomic displacements needed in the microscopic elastic theory formalism for the strain-induced interactions.\cite{190, 191, 192} Within this formalism, the strain-induced interactions can be determined from the Hellmann-Feynman (Kanzaki) forces, $F_i$, (before relaxation) and local displacements, $u_i$, (after relaxations) of the host atoms in single-impurity calculations. It can be done either in the real space\cite{193} or equivalently by using the Fourier transform of the strain-induced interactions, which in the microscopic theory of elasticity are given by

$$V(q) = u(q)F^*(q),$$  \hspace{1cm} (5.19)

where $u(q)$ and $F(q)$ are the Fourier transforms of $F_i$ and $u_i$, respectively. Then the strain-induced interactions in the real space are

$$V^{si}(R_p) = \frac{1}{N_q} \sum_q V(q) \exp(iqR_p),$$  \hspace{1cm} (5.20)

where $N_q$ is the number of $q$ points in the summation.

The Kanzaki (or equivalently Hellmann-Feynman) forces and local lattice displacements have been obtained in the dilute limit of Cr in Ni. For that purpose a single impurity of Cr in a 256-atom fcc supercell built upon 4-atom fcc cubic unit cell ($4 \times 4 \times 4 \times 4$) of Ni has been calculated by the PAW\cite{171} as is implemented in the Vienna \textit{ab initio} simulation package (VASP).\cite{185} The integration over the Brillouin zone has been done using the the $4 \times 4 \times 4 \times 4$ Monkhorst-Pack grid.\cite{76}
5.3 Results and discussion

Let us note that although it is less accurate method compared to their direct calculations, as has been done, for instance, in Ref. [194], it allows to get a long-range tail of the strain-induced interactions, which is important in this case. In fact, due to a small size mismatch of Ni and Cr atoms, the strain-induced interactions give relatively little, although important, contribution to the total effective pair interactions.

In Fig. 5.2 we show the calculated strain-induced interactions. Let us note that this formalism is valid if the concentration of one of the alloy components is small. However, we assume that strain-induced interactions do not depend much on the alloy composition. The point is that this seems to be the only feasible way to get strain-induced interactions from first-principles calculations at the moment.

![Figure 5.2: Strain-induced interactions obtained in the dilute limit of Cr in Ni using Eq. (5.20).](image)

5.3 Results and discussion

5.3.1 Electronic structure of random NiCr alloys

In spite of its many desirable properties, the CPA, as a single-site theory, suffers from various limitations, such as its inability to account for the effects of short-range order and the effect of many-site statistical fluctuations. The latter are usually important in systems where partial bands of alloy components have a restricted overlapping, which is just the case of Ni and Cr d-bands in NiCr alloys. Therefore in order to test the
5.3 Results and discussion

accuracy of the CPA for Ni-Cr alloys we have calculated the density of state (DOS) of a random Ni$_{0.67}$Cr$_{0.33}$ alloy using the CPA and the LSGF method.

The LSGF method is an accurate first-principles tool for the total energy and electronic structure calculations of random alloys. Using an enough big supercell one can take care of the most important atomic distribution correlation functions within the needed range and then calculate its electronic structure. The local interaction zone (LIZ) in the LSGF method allows one effectively to cut the long-range (infinite in fact) interactions thereby retaining the correct properties of electronic spectrum of random alloys. On the other hand, all the local environment effects are taken into consideration within the LIZ, which also allows one to consider systems with atomic SRO.

In Fig. 5.3, we compare the DOS of a random Ni$_{0.67}$Cr$_{0.33}$ alloy obtained in the CPA and 864-atom LSGF calculations with LIZ=3, which means that the electronic correlations within the first two coordination shells are taken into account. The experimental lattice parameter, 3.566 Å [43, 147] was used for the calculation of the DOS. As can be seen in Fig. 5.3, the local environment effects are indeed quit important in Ni-Cr alloys: the DOS obtained within the CPA and using LSGF differ in the energy range close to the Fermi energy.

![Figure 5.3: DOS - Density of states in Ni$_{0.66}$Cr$_{0.33}$ random alloy obtained using the CPA and in the 864-atom supercell LSGF calculations. Ni and Cr partial density of states are shown by dashed and dashed-dotted lines, respectively.](image)

The origin of the local environment effects, as has been mentioned above, is a quite distant position of Ni and Cr d-states relative each other, as one can see in Fig. 5.3. Local fluctuations of composition in this case lead to the appearance of new features,
which are not properly presented in the single-site approximation, where the local environment is fixed to the average one. Nevertheless, we proceed with calculations of effective interactions within the CPA, since the CPA DOS deviates insignificantly from the accurate one.

![Graph showing DOS comparison with and without SRO](image)

**Figure 5.4: DOS** - Density of states in Ni$_{0.66}$Cr$_{0.33}$ random alloy obtained from the LSGF with and without considering the atomic SRO.

Finally, we would like to demonstrate the effect of the atomic SRO on the DOS. For that purpose we calculate the DOS of a random Ni$_{0.67}$Cr$_{0.33}$ alloy with non-zero Warren-Cowley SRO parameters at the first two coordination shells, which are approximately equal to -0.1 and 0.1 using the LSGF method with LIZ=3. The latter corresponds to the atomic SRO in this alloy at about 1000 K. As one can see in Fig. 5.4, such an atomic SRO leads to a more pronounced pick close to the Fermi level, however, the effect of the SRO on the DOS is relatively small.

### 5.3.2 Effective cluster interactions, ordering energies and enthalpies of formation

The chemical part of the ECI in Ni-Cr alloys was obtained by the SGPM in the EMTO-CPA calculations. Since Ni and Cr have quite different d-band fillings, one can expect the existence of a strong concentration dependency of the ECI. To demonstrate such a dependence, we calculate the Fourier transforms of the SGPM interactions, $V(q)$, on the
5.3 Results and discussion

fcc lattice for three different alloy compositions: Ni$_{0.2}$Cr$_{0.8}$, Ni$_{0.5}$Cr$_{0.5}$, and Ni$_{0.8}$Cr$_{0.2}$.

The results are shown in Figs. 5.5, 5.6, and 5.7.

Indeed, one can see that not only the value of $V(q)$ differs in all three cases, but, more importantly, the minimum of $V(q)$ moves with concentration. This means that the type of ordering should also be changing with alloy composition: in the Cr-rich and equiatomic alloys, the chemical EPI should induce a (100)-type ordering, while in Ni-rich alloys, an ordering associated with (0.7, 0.7, 0) point of the fcc Brillouin zone. In fact, the transition between these two types of ordering occurs somewhere close to 45 at.% of Cr.

The latter result is obviously at variance with the existing experimental data, where the (1120)-type of ordering is observed in the random state. However, it is consistent with the results of Staunton et al.[170], who found an additional pick close to the ($\frac{2}{3}\frac{2}{3}0$) position in the $S^{(2)}(q)$, which has the same meaning as $V(q)$, as well as in the diffuse scattering calculations for alloy compositions within concentration range of 11 - 33 at.% Cr. The fact that our and Ref. [170] results agree is not surprising since the methods of calculations are similar.

Of course, the difference between $V(q)$ at $q = (1\frac{1}{2}0)$ and (0.7, 0.7, 0) is very small, and it turns out that the balance in favor of (1120) is shifted when the strain-induced interactions are taken into consideration. In Fig. 5.8 we show the Fourier transform of

\[\text{Figure 5.5: Contour - Fourier transform of the chemical EPI for Ni}_{0.2}\text{Cr}_{0.8} \text{ alloy in the (001) plane.}\]
5.3 Results and discussion

Figure 5.6: Contour - Fourier transform of the chemical EPI for Ni$_{0.2}$Cr$_{0.8}$ alloy in the (001) plane.

Figure 5.7: Contour - Fourier transform of the chemical EPI for Ni$_{0.2}$Cr$_{0.8}$ alloy in the (001) plane.
5.3 Results and discussion

the total EPIs, which consist of the chemical contribution from the SGPM interactions and the strain-induced contribution, for Ni\(_{0.2}\)Cr\(_{0.8}\) alloy in the (001) plane. It has minimum at the \((1\frac{1}{2}0)\) point, as one can see in Fig. 5.8, which is consistent with the experimental data for diffuse neutron scattering data.

![Figure 5.8: Contour - Fourier transform of the total EPI for Ni\(_{0.2}\)Cr\(_{0.8}\) alloy in the (001) plane.](image)

The real space total and SPGM EPI for Ni\(_{0.8}\)Cr\(_{0.2}\) are shown in Fig. 5.9. Interactions are determined for the lattice constant of 3.565 Å, which corresponds to the temperature of 828 K for this alloy composition.\(^{157, 188, 189}\) As one can see the contribution from the strain-induced interactions is indeed small, but it is important since the difference between \(V(q)\) at \((1\frac{1}{2}0)\) and \((0.7, 0.7, 0)\) points is also small. Exactly the same shift of the minimum of \(V(q)\) due to the strain-induced interaction is also observed for Ni\(_{0.67}\)Cr\(_{0.33}\) and Ni\(_{0.75}\)Cr\(_{0.25}\) alloys.

We also compare our results with other GPM calculations\(^{169}\) and deduced from experimental ASRO.\(^{166, 167}\) The agreement is quite good between all the results, except for the nearest-neighbor pair interaction in the earlier GPM calculations,\(^{169}\) which is quite underestimated due to the missing electrostatic contribution, as has been discussed in Ref. \(^{170}\). Note however that we have chosen one set of "experimental" values, although there is quite a substantial scattering of the experimental EPI for different samples\(^{166}\) and also due to differences in the approximations and models used in the fitting.\(^{167}\)
5.3 Results and discussion

Figure 5.9: EPIs - EPIs in Ni$_{0.8}$Cr$_{0.2}$ obtained in this worked, in earlier calculations by Turchi et al. [169] and fitted to the experimental ASRO by Schönfeld et al. [166]

In Figs. 5.10 and 5.11 we show three- and four-site interactions in Ni$_{0.8}$Cr$_{0.2}$ obtained in the corresponding SGPM calculations. One can see that especially strong multisite interactions are for the clusters containing the sides along the closed-packed [110] direction, i.e. for the first, (110), fourth, (220), ninth, (330), and so on coordination shells. In particular, the strongest 3-site interaction is $V^{(3)}_{1-1-4}$, (-4.7 mRy) and four-site interact $V^{(4)}_{1-4-9-1-4-1}$ (4.04 mRy), which are both just segments in the closed-packed direction. Let us note that this is a very general feature of the ECI in transition metal alloys, which is discussed in Ref. [85].

To demonstrate the impact of multisite interactions upon atomic ordering in NiCr, we calculate the ordering energy of some fcc-based structures relevant for the present consideration. In Table 5.1 we show the ordering energies of the A2B2, L1$_0$, Pt$_2$Mo, L1$_2$, DO$_{22}$, DO$_{60}$, and D1$_a$ structures obtained using the strongest ECIs, which include the first 30 coordination shells, 75 three-site, and 26 four-site SGPM interactions and determined in the direct total energy calculations, as the energy difference of these structures and the corresponding random alloys on the ideal fcc underlying lattice. The multisite interactions have been chosen for the clusters within of a certain range of diameter, with the exception for those which are on the line in the closed-packed direction (like $V^{(4)}_{1-4-9-1-4-1}$). Of course, it does not guarantee that we have chosen all the most important interactions, nevertheless, we believe that our choice is good enough to reproduce qualitative picture of ordering in the system.

As one can see in Table 5.1 the L1$_0$ structure, which is of the (001) type, is more stable than A2B2, which is of the (1 1 0) type, for equiatomic alloy composition, Ni$_{0.5}$Cr$_{0.5}$. One can also note that the 4-site interactions yield practically the same contribution as...
5.3 Results and discussion

Figure 5.10: ECI: 3-site - Calculated three-site ECIs in Ni$_{0.8}$Cr$_{0.2}$ random alloy.

Figure 5.11: ECI: 4-site - Calculated four-site ECIs in Ni$_{0.8}$Cr$_{0.2}$ random alloy.
5.3 Results and discussion

Table 5.1: Ordering energies (in mRy/atom) of Ni$_x$Cr$_{1-x}$ alloys. In the case of SGPM results we also show the contributions from pair, 3-site, and 4-site interactions.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Structure</th>
<th>EMTO Total</th>
<th>SGPM Total</th>
<th>2-site</th>
<th>3-site</th>
<th>4-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>A2B2</td>
<td>1.61</td>
<td>−0.4</td>
<td>−3.4</td>
<td>0.0</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>L1$_0$</td>
<td>−1.58</td>
<td>−4.14</td>
<td>−4.18</td>
<td>0.0</td>
<td>0.04</td>
</tr>
<tr>
<td>0.67</td>
<td>Pt$_2$Mo</td>
<td>−5.45</td>
<td>−6.18</td>
<td>−3.29</td>
<td>−3.30</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>L1$_2$</td>
<td>5.99</td>
<td>0.97</td>
<td>−2.01</td>
<td>2.51</td>
<td>0.47</td>
</tr>
<tr>
<td>0.75</td>
<td>DO$_{22}$</td>
<td>−1.89</td>
<td>−3.21</td>
<td>−2.82</td>
<td>−0.10</td>
<td>−0.21</td>
</tr>
<tr>
<td></td>
<td>DO$_{60}$</td>
<td>−3.03</td>
<td>−3.92</td>
<td>−2.31</td>
<td>−1.44</td>
<td>−0.18</td>
</tr>
<tr>
<td>0.80</td>
<td>D1$_a$</td>
<td>−2.12</td>
<td>−3.11</td>
<td>−2.14</td>
<td>−0.65</td>
<td>−0.32</td>
</tr>
</tbody>
</table>

pair interactions, but with the opposite sign in the case of A2B2 structure, practically compensating it. At the same time, in the case of an Ni$_{0.75}$Cr$_{0.25}$ alloy, the situation is completely the opposite. The L1$_2$ structure of the (001) type is highly unstable. Although the SGPM interactions obviously underestimate its very large ordering energy, they yield very interesting qualitative picture: the strong destabilization of the L1$_2$ structure is largely an effect of three-site interactions.

The DO$_{22}$ structure, which is usually considered as (1$rac{1}{2}$0)-type, but in fact it has a bit of the (001) type too, is substantially more stable than the L1$_2$. However, even more stable is the DO$_{60}$ structure, which is of (1$rac{1}{2}$0)-type. Again, in the last case, the 3-site interactions yield a substantial contribution, which stabilizes the DO$_{60}$ against the DO$_{22}$. There is a similar strong stabilizing contribution from the 3-site interactions in the case of D1$_a$ structure, which is of the $\frac{4}{3}(1\frac{1}{2}0)$ type.

The most interesting result is however for the ordering energy of the Pt$_2$Mo structure, which is of the $\frac{4}{3}(1\frac{1}{2}0)$, or, equivalently, (2$\frac{2}{3}$0) type. It has the lowest ordering energy, almost twice as low as that of the DO$_{60}$ structure. The EPI and three-site interactions contribute equally large to the ordering energy. The strong stabilization of this structure is consistent with the fact that the global minimum of $V(q)$ for this alloy composition is at (0.71, 0.71, 0) position, which is very close to (2$\frac{2}{3}$0), similar to the case of the $V(q)$ in Ni$_{0.8}$Cr$_{0.2}$ alloy.

In order to determine which of those phases presented in Table 5.1 structures can be stable, we have calculated their enthalpies of formation in the non-magnetic state relative to bcc Cr and fcc Ni using PAW method, as described above. The results are presented in Fig. 5.12. Let us note that there exist a number of first-principles results for the formation enthalpy of Ni$_2$Cr in the Pt$_2$Mo structure, which are scattered from
−6.62 to −11.59 [197] kJ/mole, and which are collected in Ref. [198]. The experimental enthalpy at 773 K is expected to be higher than that at 0 K due to incomplete long range order.

![Figure 5.12](image-url) Enthalpy - Calculated 0 K enthalpies of formation of Ni-Cr alloys in the Pt$_2$Mo, DO$_{22}$, DO$_{60}$, and D1$_a$ ordered structures (by PAW) and random alloys (by EMTO-CPA). The experimental data for Pt$_2$Mo at 773 K are taken from Ref. [199] and for random alloys at 1538 K from Ref. [200].

The interesting point is that it seems that D1$_a$ structure should be stable in this system for alloy compositions close to 20 at.% Cr, at least above the Curie temperature. This is very similar to the Ni-Mo system, which is isoelectronic to the Ni-Cr. However, the ordering transition temperatures are much lower in the Ni-Cr alloys and this can be the reason why D1$_a$ phase is not observed in this system.

In Fig. 5.12 we also show the enthalpy of formation of random Ni-Cr alloys at 0K determined in the EMTO-CPA calculations. They do not include the contribution from local lattice relaxations. However, in separate 64-atom supercell calculations for random alloy configurations up to the 8th coordination shell by PAW method we have found that they are -0.5 kJ/mole for Ni$_{0.75}$Cr$_{0.25}$ and -1.11 kJ/mole for Ni$_{0.5}$Cr$_{0.5}$. In other words, they produce just a little correction to the CPA results. In this figure, we also show the experimental data from Ref. [200]. However, they are for quite high temperature of about 1500 K, and thus it is expected that they can differ from theoretical results.

The important message is that the enthalpy of formation of random alloys in this
5.3 Results and discussion

system exhibits a quite strong deviation from the usual parabolic-like behavior. This explains the relative low enthalpy of formation of the D1\textsubscript{a} structure, although its ordering energy is much less than that of the Pt\textsubscript{2}Mo ordered structure. As one can see, the enthalpy of formation of random Ni\textsubscript{0.67}Cr\textsubscript{0.33} alloy is quite high. So in the end, the enthalpies of formation of Ni\textsubscript{2}Cr and D1\textsubscript{a}-Ni\textsubscript{4}Cr are very close to each other.

5.3.3 Statistical thermodynamic simulations of atomic ordering in Ni\textsubscript{2}Cr

Atomic ordering in Ni\textsubscript{2}Cr have been investigated by Monte Carlo (MC) and RMFA methods. MC calculations have been done using an 18 × 18 × 18 simulation box of the fcc unit cell. We have performed 6000 MC steps per atom with 3000 steps for thermodynamic averaging to equilibrate the alloy configuration at the corresponding temperature. The ECI for these calculations have been determined for the lattice constant of 3.596 Å, which corresponds to 1073 K. The contribution from electronic excitations is included via the Fermi-Dirac distribution. In the RMFA calculations, we have used the same sets of the ECIs as in the MC simulations, which consisted of 25 pair, 15 three-site, and 13 four-site strongest interactions. The Brillouin zone integration in the RMFA calculations has been done using 19×19×19 the Monkhorst-Pack grid.

In Fig. 5.13 we show the real space SRO parameters of Ni\textsubscript{0.67}Cr\textsubscript{0.33} random alloy compared with experimental data from Caudron et al. One can see that theoretical RMFA and MC results are
5.3 Results and discussion

in excellent agreement. This is due to the fact that the RMFA always satisfies the normalization conditions Eq. (5.14) using a self-consistent procedure. As a result, the RMFA, despite the simplicity of its analytic form, is an accurate approximation for random alloys with correlated distributions of atoms.

One can also see that the agreement between theoretical results and experimental data is very good, although the theoretical SRO parameters at the first two coordination shells are larger in absolute value, which also leads to a larger variations of their Fourier transform as one can see in Fig. 5.14 where we show $\alpha(q)$ in the (001) plane.

![Contour](image)

**Figure 5.14: Contour** - Calculated SRO parameters in Ni$_{0.67}$Cr$_{0.33}$ random alloy compared with experimental data from Caudron et al. [164]

It is important that the theory can now correctly reproduce the position of the scattering maximum or $\alpha(q)$, which is $(1 \frac{1}{2} 0)$. After the first order phase transition to the Pt$_2$Mo structure, the minimum is going to be in the $(\frac{2}{3} \frac{2}{3} 0)$ point. However, such a shift seems to have very little with the ECI, it originates from simple geometrical rules, as the only way to have the (420) stacking for this particular alloy composition (for a thorough discussion see Ref. [158, 159, 160, 201, 202, 203, 204]).

Using these ECI we determine the order-disorder transition temperature in MC simulations by cooling the system from high temperatures and monitoring the discontinuity in the average energy and peak in the heat capacity. The theoretical result is found to be 880 K, which is in very good agreement with the experimental value of 863 K. [147, 153, 154, 155, 156, 157] Let us note that in spite of good agreement we believe that results presented here are still insufficiently accurate because we have
5.3 Results and discussion

not considered possible contributions from thermal magnetic excitations and lattice vibrations. The latter however is quite non-trivial task especially if they should be considered together.

Figure 5.15: Ordering energy - Calculated the energy of atomic SRO in Ni$_{0.67}$Cr$_{0.33}$ random alloy.

The results of MC simulations have also allowed us to test the accuracy of the RMFA used for the energy of atomic SRO in the random state. In Fig. 5.15, we show the ordering energy of a random Ni$_{0.67}$Cr$_{0.33}$ alloy obtained in the MC simulations and within the RMFA closely reproduces the ordering energy of the MC simulations. The agreement between two results is excellent in spite of the fact that the effects of the 3- and 4-site ECIs are taken into account in the RFMA through a renormalization of EPIs Eq. (5.9). The obvious advantage of the RMFA, apart from its extreme efficiency when it comes to numerical calculations, is that it in principle allows one to get the energy and entropy related to the atomic SRO in random alloys even if they are in metastable state.

5.3.4 Atomic short-range order in Ni$_{0.75}$Cr$_{0.25}$ and Ni$_{0.8}$Cr$_{0.2}$ alloys

Finally, we calculate ASRO in Ni$_{0.75}$Cr$_{0.25}$ and Ni$_{0.8}$Cr$_{0.2}$ alloys at 993 and 828 K, respectively, using the corresponding ECI determined for the experimental lattice parameters[157, 188, 189] which are 3.578 Å for Ni$_{0.75}$Cr$_{0.25}$ at 993 K and 3.565 Å for Ni$_{0.8}$Cr$_{0.2}$ at 828 K. The calculated SRO parameters in real space are presented in Figs. 5.16 and 5.17 together with the experimental data.[164, 166]

Again, as in the case of Ni$_{0.67}$Cr$_{0.33}$, the theoretical SRO parameters, $\alpha_{lmm}$, have a larger amplitude at the first two coordination shells. At the same time, it is worth
mentioning that $\alpha_{000}$ in the experiment are 0.935, 0.843, and 0.9274 in Ni$_{0.67}$Cr$_{0.33}$, Ni$_{0.75}$Cr$_{0.25}$, and Ni$_{0.8}$Cr$_{0.2}$ alloys, respectively, which is noticeably less than 1, which is required by normalization condition (5.14). The later indicates that the experimental values of $\alpha(q)$ could be underestimated.

Figure 5.16: SRO - Calculated SRO parameters in Ni$_{0.75}$Cr$_{0.25}$ random alloy compared with experimental data from Caudron et al. [164]

In Fig. 5.18, we compare the theoretical and experimental diffuse intensity map, $\alpha(q)$, of Ni$_{0.80}$Cr$_{0.20}$ random alloy at 828 K in the (001) plane. As one can see, they are in good agreement and both have maximum at the (1$\frac{1}{2}$0) special point. Discussing the SRO diffuse intensity distribution in Ni$_{0.8}$Cr$_{0.2}$ alloys, it is worth noting that the diffuse peaks are roughly triangular shaped with the edges extending towards the neighboring D1$_a$ superlattice $\frac{4}{5}(1\frac{1}{2}0)$ positions. Thus, this structure can potentially be formed at
lower temperatures during the first order phase transition as in the case of the Ni$_2$Cr alloy.

Unfortunately, we could not calculate such a transition, which could take place according our results for the formation energies presented in Fig. 5.12. In our MC calculations, we observe actually the formation of Pt$_2$Mo ordered structure. One of the possible reasons is that we consider only configurational part of the energy of an alloy. At the same time, as we have demonstrated above, the relatively low enthalpy of formation the D1$_a$ phase, compared to the Ni$_2$Cr phase is mainly due to the low enthalpy of formation of a random Ni$_{0.8}$Cr$_{0.2}$. This is not accounted for in the Monte Carlo simulations.

### 5.4 Conclusions

In this work, we have attempted to solve a long-standing problem of qualitatively accurate description of ordering in Ni-rich Ni-Cr alloys using the-state-of-the-art *ab initio* methods. We have found out that the chemical interactions, which are very close to those obtained long time ago by Turchi *et al.* [169] and Staunton *et al.* [170], cannot be alone responsible for the observed in the experiment ASRO in random alloys at high temperature, although they apparently yield the strongest dominating contribution.
It has turned out that the correct qualitative picture of the ASRO in Ni-rich Ni-Cr alloys is restored only when relatively small strain-induced interactions are taken into consideration. In order to get quantitatively accurate results, one need to address some issues of the methods used in work, starting from the CPA. Moreover, we have not included in our consideration the effect of thermal magnetic and lattice vibration excitations. The latter is a highly nontrivial task, which cannot be efficiently address at the present time.

Finally, we have demonstrated that the RMFA is able to provide accurate results for energetics and atomic distribution correlation functions in alloys. It is a powerful tool in the statistical mechanics investigations, which can take care of multisite interactions on one hand and, on the other hand, very efficiently get accurate information about all the energy related properties even in the metastable state.
Chapter 6

Finite temperature elastic properties of B2-FeCo alloy: A first-principles study

6.1 Introduction

Fe-Co alloys exhibit high saturation magnetization, high Curie temperatures (1288K), high relative permeability, good strengths which are ideally suited for high temperature applications.\cite{39,205,206} However, the applications of FeCo alloys have been widely limited due to its poor mechanical properties, and in particular their brittleness,\cite{207} which makes them difficult to handle. Poor mechanical properties are connected to a precipitation of B2-FeCo ordered phase,\cite{208} which is formed at 1006 K near the stoichiometric composition.\cite{40,41,42,43,44}

There can be different source of brittleness, however, the most difficult to overcome is the so-called intrinsic one, which is directly connected with elastic properties of material. Although such information is available for Fe and Co over wide range of temperatures\cite{209,210}, data on the elastic properties of FeCo alloys are limited. There are no published experimental data on the elastic constants of the B2-FeCo.

A feasible alternative is theoretical calculations. The first-principles calculations based on density functional theory (DFT) have been remarkably successful in reproducing and explaining a wide variety of materials phenomena. Many first-principles calculations have also been performed to determine the thermodynamic properties of the ordered phase B2-FeCo. In particular, extensive first-principles calculations of the B2-FeCo alloy were conducted by Liu et al.\cite{213} who also determined elastic prop-
6.2 Methodology

6.2.1 Temperature-dependent properties

In this study, we assume that the thermal lattice expansion produces the main effect on the temperature dependence of the elastic constants. In order to determine the elastic properties of the B2-FeCo at finite temperatures, we calculate the lattice constant of the B2-FeCo within a quasiharmonic approximation using the Debye-Gr"uneisen model, and linear-response theory. In this case, the Helmholtz free energy, $F(V, T)$ at volume, $V$ and temperature $T$ is determined as:

$$F(V, T) = F_{el}(V, T) + F_{vib}(V, T). \quad (6.1)$$

Here, $F_{el}(V, T)$ is the free energy electronic subsystem, which is obtained using the Fermi-Dirac distribution function

$$f(\epsilon, T) = \left(1 + e^{(\epsilon - \mu(T))/k_B T}\right)^{-1}$$

in the self-consistent DFT calculations and the corresponding the electronic entropy $S_{el}$

$$S_{el}(T) = -k_B \int n(\epsilon) \left[ f(\epsilon, T) \ln (f(\epsilon, T)) \right. + \left. (1 - f(\epsilon, T)) \ln (1 - f(\epsilon, T)) \right] d\epsilon$$

where $\mu(T)$ is the electronic chemical potential and $n(\epsilon)$ is the electronic density of states.
6.2 Methodology

6.2.1.1 Vibrational contribution from DFPT

Linear response method based on density functional perturbation theory (DFPT) \[130\], vibrational modes with wave vectors at arbitrary points in the Brillouin zone can be accurately and efficiently computed without using large supercells, allows us to calculate the dynamical matrix related to the interatomic force constants. Using the linear response method, as the atom of mass \(M_i\) is displaced from its equilibrium position, a restoring force, \(f\), is exerted on it

\[
f(i) = \Phi(i, j) \delta u(j).
\]

where \(\Phi(i, j)\) represents \(3 \times 3\) matrices, called force constant tensors, that establish the force exerted on atom \(i\), as atom \(j\) is displaced from its equilibrium position by vector \(\delta u_j\). The force constant tensor, \(\Phi(i, j)\), has its origin in the harmonic approximation of the Hamiltonian of the system:

\[
\Phi_{\alpha\beta}(i, j) = \frac{\delta^2 E}{\delta u_{\alpha}(i) \delta u_{\beta}(j)}. \tag{6.2}
\]

The force constant tensor, \(\Phi(i, j)\), can be used to determine the dynamical matrix, \(D = \frac{\Phi(i, j)}{\sqrt{(M_i M_j)}}\), whose eigenvalues yield frequencies of the allowed modes of oscillation for the structure. The distribution of these frequencies, \(g(\nu)\) yields the vibrational free energy of the structure

\[
F_{\text{vib}}(T) = k_B T \int_0^\infty \ln \left[ 2 \sinh \left( \frac{h \nu}{2 k_B T} \right) \right] g(\nu) d\nu \tag{6.3}
\]

The harmonic approximation can be improved by making the phonon density of states (DOS), \(g(\nu)\), volume dependent, which can be easily done by calculating, within the harmonic approximation, the phonon DOS for several volumes. This approach is called the quasi-harmonic approximation.

6.2.1.2 Vibrational contribution from the Debye-Grüneisen model

For the sake of simplicity, the vibrational contribution to Helmholtz free can be estimated using the Debye-Grüneisen model (DG).\[214\] The Helmholtz free energy in the DG model is determined as

\[
F(V, T)_{\text{vib}} = E_{el}(V) - k_B T \left[ D(\Theta_D/T) + 3 \ln(1 - e^{-\Theta_D/T}) \right] + \frac{9}{8} k_B \Theta_D, \tag{6.4}
\]
where \( E_{el}(V) \) is the energy of the static lattice at a given volume determined from first-principles calculations, \( k_B \) is the Boltzmann constant; \( D(\Theta_D/T) \) and \( \Theta_D \) are the Debye function and Debye temperature. The latter is obtained from the first-principles total energy as described in Ref. [214]. The free energy is minimized with respect to the volume for a given \( T \).

### 6.2.2 Elastic Constants

Elastic constants are determined by straining the equilibrium lattice at fixed volumes, using volume-conserving strains and then computing the free energy as a function of strain. The lattice distortion transforms the primitive vectors \( \mathbf{a} \) into the new vectors \( \mathbf{a}' \).

\[
\mathbf{a}' = (\epsilon(\delta) + I)\mathbf{a}
\]

The internal energy of a crystal under a general strain \( \delta \) can be expressed by expanding the internal energy \( E(V, \{\delta\}) \) of the deformed crystal with respect to the strain tensor, in terms of the Taylor’s series, as

\[
E(V, \{\delta\}) = E(V, 0) + V \sum C_i \delta_i + \frac{V}{2} \sum C_{ij} \delta_i \delta_j + O(\delta^3) \quad (6.5)
\]

The symmetry of the crystal lattice reduces the number of independent elastic constants \( C_{ij} \). For the cubic lattice, there are only three independent elastic constants \( C_{11}, C_{12} \) and \( C_{44} \), which enable to describe the elastic anisotropy completely. The energetic response of the atomic systems to hydrostatic, monoclinic and orthorhombic displacements in Fig. 6.1 were employed to determine the elastic constants of the FeCo alloy. Two of the elastic constants are derived from the bulk modulus.

**Figure 6.1: Elastic Constants** - Hydrostatic, orthorhombic and monoclinic distortions used to determine the three symmetry-inequivalent elastic constants \( (C_{11}, C_{12} \) and \( C_{44} \)) in cubic FeCo alloy.
6.2 Methodology

\[ B = \frac{1}{3} (C_{11} + 2C_{12}) \]

and the tetragonal share modulus

\[ C' = \frac{1}{2} (C_{11} - C_{12}) \]

The share modulus \( C' \) is determined from volume-conserving orthorhombic strain,

\[ \epsilon(\delta_0) = \begin{pmatrix} \delta_0 & 0 & 0 \\ 0 & -\delta_0 & 0 \\ 0 & 0 & \frac{\delta_0^2}{1-\delta_0^2} \end{pmatrix} \]

The Helmholtz free energy related to this strain is defined as

\[ F(V, \delta_0) = F(V, 0) + 2VC'\delta_0^2 + O(\delta^4) \quad (6.6) \]

The share modulus \( C_{44} \) is calculated from volume-conserving monoclinic distortion,

\[ \epsilon(\delta_m) = \begin{pmatrix} 0 & \frac{\delta_m}{2} & 0 \\ \frac{\delta_m}{2} & 0 & 0 \\ 0 & 0 & \frac{\delta_m^2}{1-\delta_m^2} \end{pmatrix} \]

which leads to the free energy change

\[ F(V, \delta_m) = F(V, 0) + \frac{V}{2} C_{44}\delta_m^2 + O(\delta^4) \quad (6.7) \]

Finally, the elastic anisotropy of Zener is defined as

\[ A_Z = \frac{2C_{44}}{C_{11} - C_{12}} \quad (6.8) \]

In principle, the temperature dependence of the elastic constants is determined by combination of the volume dependence of elastic constants and the temperature dependence of volume from the minimization of Helmholtz free energy \((6.1)\) at a given temperature. The equilibrium volume at various temperatures is determined from Eq. \((6.1)\) with both lattice vibrational and thermal electronic contributions included. The combination of \( C_{ij}(V(T)) \) and \( V(T) \) leads to the temperature dependence of the elastic constants \( C_{ij}(T) \).
6.3 Results and discussion

6.2.3 Details of the first-principles and phonon calculations

The first-principle calculations performed in this work are based on density functional theory[120] and were carried out using the EMTO[17, 18, 19] and PAW[127] methods. The generalized gradient approximation (GGA) [124] has been used for the exchange-correlation potential.

All the self-consistent EMTO calculations were performed using an orbital momentum cutoff of $l_{\text{max}} = 3$ for partial waves. The Brillouin zone was sampled employing the Monkhorst-Pack grid[76] with a $33 \times 33 \times 33$ subdivision along each reciprocal lattice vector.

The phonon calculations were carried out by the linear-response method within the framework of the DFPT implemented in the VASP code.[129] The electron-ion interactions are described by the full-potential frozen-core PAW method[127, 128] as implemented in the VASP code.[129] The kinetic energy cutoff was 300 eV and a uniform $26 \times 26 \times 26$ grid of $k$-point. The energy convergence criterion for electronic self-consistency was $10^{-7}$ eV/atom. The PHONOPY code [131] was used to determine the phonon frequencies and vibrational free energy. For the quasi-harmonic approximation, we have calculated $F_{\text{vib}}(V,T)$ at twelve different volumes. The equilibrium volume at temperature $T$, $V(T)$ and bulk moduli are obtained by minimizing the free energy as implemented in the PHONOPY code.

6.3 Results and discussion

6.3.1 Thermal lattice expansion of B2-FeCo

The equilibrium lattice constant at each temperature was obtained by minimizing the free energy (6.1) with the vibrational contribution either from the Debye-Grüneisen model and electron free energy obtained in the EMTO calculations (EMTO-DG) or with the free electron energy from the PAW calculations and the free electron energy from PHONOPY calculations according to the quasiharmonic model (PAW-QH). In Table 6.1, we compare results for the lattice constant and bulk modulus of B2-FeCo obtained in the EMTO-GD and PAW-QH calculations with other ab initio calculations by the general-potential linearized augmented plane wave (LAPW)[213] and augmented spherical wave (ASW) methods[80, 217] and experimental data.[43, 211] As one can see, the LSDA significantly underestimates the lattice constant and overestimates the bulk modulus, while GGA provides reasonably accurate description of these properties. Let us note that slightly different LSDA results obtained by the ASW method[80, 217] are
6.3 Results and discussion

Table 6.1: Theoretical and experimental lattice parameter, $a_0$, bulk modules, $B_0$, and partial magnetic moments, $m_{Fe}$ and $m_{Co}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{xc}$</th>
<th>$T$</th>
<th>$a_0$ (Å)</th>
<th>$B_0$ (GPa)</th>
<th>$m_{Fe}$ ($\mu_B$)</th>
<th>$m_{Co}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMTO</td>
<td>LSDA</td>
<td>0 K</td>
<td>2.77</td>
<td>249</td>
<td>2.65</td>
<td>1.70</td>
</tr>
<tr>
<td>EMTO-DG</td>
<td>LSDA</td>
<td>300 K</td>
<td>2.777</td>
<td>242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EMTO</td>
<td>GGA</td>
<td>0 K</td>
<td>2.85</td>
<td>188</td>
<td>2.84</td>
<td>1.73</td>
</tr>
<tr>
<td>EMTO-DG</td>
<td>GGA</td>
<td>300 K</td>
<td>2.86</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAW</td>
<td>GGA</td>
<td>0 K</td>
<td>2.848</td>
<td>189</td>
<td>2.79</td>
<td>1.77</td>
</tr>
<tr>
<td>PAW-QH</td>
<td>GGA</td>
<td>300 K</td>
<td>2.854</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LAPW[213]</td>
<td>LSDA</td>
<td>0 K</td>
<td>2.77</td>
<td>247</td>
<td>2.84</td>
<td>1.81</td>
</tr>
<tr>
<td>ASW[217]</td>
<td>LSDA</td>
<td>0 K</td>
<td>2.83</td>
<td>226</td>
<td>2.69</td>
<td>1.67</td>
</tr>
<tr>
<td>ASW[80]</td>
<td>LSDA</td>
<td>0 K</td>
<td>2.814</td>
<td>272</td>
<td>2.72</td>
<td>1.69</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>300 K</td>
<td>2.857</td>
<td>187.86[211]</td>
<td>2.92[218]</td>
<td>1.62[218]</td>
</tr>
</tbody>
</table>

Figure 6.2: thermal expansion - Lattice constant (lower panel) and thermal expansion coefficient (upper panel) of B2-FeCo.
6.3 Results and discussion

probably due to inaccuracies connected with the use of the spherical approximation for one-electron potential and density in this method.

In the upper panel of the Fig. 6.2, we show the thermal lattice expansion coefficient and the temperature-dependent lattice constant (lower panel) of the B2 FeCo alloy obtained in the DG model and first-principles DFPT calculations. One can see that the agreement between two results is very good, in spite of the fact that the DG model is applied here on average using virtual crystal approximation, i.e. disregarding ordering and assuming that the mass of virtual atoms is just the average of those of Fe and Co. The temperature effects on the bulk modulus is shown in Fig. 6.3. Again, one can see that the DG and DFPT agree quite well. At the same time, they are somewhat different from the experimental data, especially at low temperatures, although at temperatures above 500-600 K they agree quite well. The reason for the overestimated low-temperature bulk modulus in the first-principles GGA calculations is not clear. Nevertheless, the overall agreement between theory and experiment is fair, and thus we believe that our results for the temperature dependence of the elastic constants should be enough accurate to make qualitative conclusions.

6.3.2 Elastic properties of FeCo

In Table 6.2 we present the calculated zero K elastic constants, $C_{ij}$, and anisotropy coefficient, $A_z$. The agreement between LSDA results obtained in this work and the previous LAPW calculations is excellent. However, the results are very sensitive
to the approximation for the exchange-correlation energy: The GGA results differ from the LSDA as is also the case of the lattice constant and bulk modulus. Let us note that in fact this difference originates from the different equilibrium lattice constants in the LSDA and GGA. It is also clear that the requirement of the mechanical stability given by the following conditions for the elastic constants: $C_{11} - C_{12} > 0$, $C_{11} > 0$ and $C_{44} > 0$, is satisfied in the B2-FeCo.

The temperature dependence of the elastic constants is mainly due to the thermal lattice expansion, while the thermal electronic excitations play a minor role. In Fig. 6.4 we show the calculated elastic and anisotropy constants of completely ordered B2-FeCo in the ferromagnetic state as a function of temperature, disregarding the effects of magnetic and atomic thermal induced disorder, which should be relatively small up to 800 K.

As one can see the elastic constants change essentially linearly with temperature. At least this is the case of $C_{11}$ and $C_{12}$, which are gradually decreasing. At the same

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**Figure 6.4: Elastic Constants** - Temperature dependence of elastic constants of B2-FeCo. The experimental data is taken from Clark et al. [212]
6.3 Results and discussion

Table 6.2: Calculated elastic $C_{ij}$ (in GPa) and anisotropy constants, $A_z$, for B2-FeCo at 0 K.

<table>
<thead>
<tr>
<th>Method</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$A_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMTO (LSDA)</td>
<td>321</td>
<td>211</td>
<td>158</td>
<td>2.86</td>
</tr>
<tr>
<td>EMTO (GGA)</td>
<td>263</td>
<td>152</td>
<td>108</td>
<td>1.95</td>
</tr>
<tr>
<td>LAPW (LSDA)</td>
<td>317</td>
<td>209</td>
<td>158</td>
<td>2.93</td>
</tr>
</tbody>
</table>

time, $C_{44}$ remains almost constant, not exhibiting visible temperature dependence. The reason for such a difference is the fact that $C_{11}$ and $C_{12}$ are associated not only with the change of the shape of the crystal, but also its volume, while $C_{44}$ is related to the volume-conserving deformation. Thus, the change of the volume with temperature directly affects the $C_{11}$ and $C_{12}$ elastic constants.

As for the Zener anisotropy constant, $A_z$, its temperature dependence mainly comes from the temperature dependence of the difference of $C_{11}$ and $C_{12}$. Since both these elastic constants are changing approximately with the same rate with the temperature, the overall temperature dependence of $A_z$ is relatively small. In order to investigate

\[ \text{Figure 6.5: Young's modulus} \] Calculated directional dependence of the Young’s modulus of B2-FeCo at $T = 300$K.
the anisotropy of the elastic properties of the B2-FeCo further, we calculate and plot a three-dimensional orientation dependence of the Young modulus, $E$. The latter can be obtained from the elastic compliance coefficients $S_{ij}$. For the case of cubic system, the Young’s modulus in any direction is given by a combination of the three elastic compliance coefficients and the direction cosines of the corresponding crystallographic direction:

$$
\frac{1}{E} = S_{11} - 2 \left[(S_{11} - S_{12}) - \frac{1}{2} S_{44}\right] \left(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2\right),
$$

where $l_1, l_2$ and $l_3$ are direction cosines and $S_{11}$, $S_{12}$, and $S_{44}$ are obtained from relationships $C_{11} = 1/S_{11}$, $C_{11} - C_{12} = 1/(S_{11} - S_{12})$, and $C_{11} + 2C_{12} = 1/(S_{11} - 2S_{12})$.

In Fig. 6.6 we show the orientation dependence of the Young’s modulus for the B2-FeCo at 300 K. The highest Young’s modulus is for the [111] direction, which is 267.8 GPa, and it is about two times as large as that for the [100] direction, which is 147.91 GPa. The projections of the Young’s modulus at 300 K is presented in Fig. 6.6. The variation in magnitude of the Young’s modulus with respect to the direction would indicate the overall anisotropy exhibited by the B2-FeCo.

Figure 6.6: Young’s modulus - Calculated projections of the directional dependence of the Young’s modulus of B2-FeCo at 300 K.
6.3 Results and discussion

6.3.3 Conclusion

We have performed first-principles calculations of thermal and elastic properties of the B2-FeCo using various techniques. Our results are in good agreement with previous calculations for the same exchange-correlation potential. We find that the GGA removes most of the errors found in the previous LSDA calculations yielding lattice parameters and bulk moduli in good agreement with experimental data.

We find that the $C_{11}$ and $C_{12}$ elastic constants decrease almost linearly with the temperature, while $C_{44}$ practically remains constant. The Zener anisotropy constant, $A_z$ varies little with temperature between 1.95 and 1.92 in the temperature interval between 0 and 800 K. A similar, relatively large, anisotropy exhibits the the Young’s modulus, which is found to be 267.8 GPa in the [111] direction and 147.91 GPa in the [100] direction.
Chapter 7

Conclusion and future directions

7.1 General Conclusions.

In this thesis a combination of model and first-principles calculations have been performed to investigate a couple of the long standing problems related to ordering, thermodynamics, mechanical and elastic properties of binary alloys.

We have found that the order-disorder transition is strongly affected by the development of magnetic moments in Fe-Co alloys. The variation of transition temperature with magnetization is quite large and systematic, and has not been reported so far for this system. The most important aspect of this study is that using the disordered local moment model we have showed that the magnetic disorder influences the chemical interactions. We have suggested that the itinerancy of the 3d electrons is crucial for this behavior. It turns out that the ferromagnetic states give the highest ordering temperature in the FeCo alloys.

Based on first-principles quasiharmonic approach by considering both the vibrational and thermal electronic contributions, the predicted intrinsic stacking-fault and anti-phase boundary energies of Al$_3$Sc have been extended to finite temperatures. Both intrinsic stacking fault and anti-phase energies decrease with increasing temperature. It therefore offers a unified picture of the planer defects in the Al$_3$Sc within the theoretical framework.

We have conducted first-principles calculations of fcc NiCr alloys which are of interest as local atomic ordering is observed experimentally for a wide range of compositions. The results of the present study clearly demonstrate that computed the short-range order parameters are sensitive to small change in the values of the SGPM effective cluster interactions. The results showed that both the Monte Carlo and ring mean field approximation are well suited for investigating the SRO in alloys.
Using EMTO method we have presented the thermodynamic and temperature dependent elastic properties of B2 FeCo alloy. The elastic constants are calculated through strain energy approach and used the thermal expansion of lattice constants with electronic excitation to obtain their temperature dependence. The elastic constants decrease with increasing temperature and satisfy the stability conditions for B2 structure.

7.2 Future directions.

In this thesis different types of binary alloy systems were investigated with regard to their electronic, magnetic and thermodynamic properties using first-principles calculations. The results that have been obtained give rise to a better understanding of the different ordering in binary alloys.

We think that with this work an important step toward a systematical study of ordering in binary alloys was done. We see, however, itinerant magnets both transverse and longitudinal spin fluctuations are very important for description of thermodynamic properties. The magnetic excitations have to be taken into account in order to correctly describe the ordering that are taking place in alloys. In addition, the magnetic short-range order influences the magnetic and structural phase transitions in transition metals and alloys.

Physical models of these phenomena remain the subject of intense research and, often, dispute. The mathematical properties of the models have to be studied rigorously. Besides electronic structure for ground states at zero temperature. It is necessary to introduce thermodynamic models coupled with first-principle techniques in order to analyze temperature dependent properties.

A PhD. program is always time bound and a person’s thirst for knowledge may not find it’s fulfillment in this limited span of time. But this endeavor may be considered as a training ground for research and it does elevate his thirst for more. I cannot assess how much knowledge of disorder physics I have been able to pick up, but I sincerely believe that this work with all its limitations will encourage me to go on working in this vastly exciting area of materials studies.
ACKNOWLEDGMENTS

There are many people I would like to thank for their support and guidance throughout my doctoral studies.

First and foremost, I would like to express my sincere gratitude to my supervisor Prof. Andrei Ruban. His patience and persistence, insights into various problems, critical thinking and insistence on clarity have been most useful and inspiring. Working with him has been a rich and rare experience and I am indebted to him for reasons much beyond the pages of this thesis.

I would like to thank Prof. Börje Johansson for giving me an opportunity to be a graduate student of your group. In addition, he found financial support which enabled me to work on the thesis.

I am also very happy to express my gratitude to Prof. Abhijit Mookerjee. I am grateful to you for all time you spent explaining me various aspects of physics. I am really appreciate your interest in my scientific development and your care about my future career.

Further, I would like to thank Prof. Pavel Korzhavyi for serving as a co-supervisor, who cooperated on the significant part of the work. He also stimulated the work with fruitful discussion and comments.

The Swedish Research Council, the Swedish Institute (SI) and the European Research Council are acknowledged for financial supports. The Swedish National Infrastructure for Computing (SNIC) and MATTER Network are acknowledged for providing computing resources.

I would like to thank my colleagues: Oleg, Volya, Vitaly, Hossein, Johan, Mikael, Andreas, Stephan, Lorand and Erna of our group. I have had a nice time with many friends in the department - have been particularly close. It has been fun interacting with them and other students over all these years.

Last, but not least, my sincerest thanks go to my parents, sister and especially to my wife for sharing my dreams and for giving me encouragement to work for my goal.
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[195] The interaction index is given by the coordination shell numbers of the sides of the corresponding cluster. In the case of the four-site interactions, the order of indexes matters, so the choice is the following: the first four indexes are the coordination shells of the sides of a closed loop through all the four sites, and the last two are the coordination shells of remaining sides of the cluster. 73

[196] An example of strong three-site interactions for a relatively large clusters are, for instance, $V_{4\ldots 17}^{(3)}$ and $V_{3\ldots 9\ldots 17}^{(3)}$, which are 0.43 and 0.46 mRy, respectively, in Ni$_{0.4}$Cr$_{0.2}$ alloy. Here the 17th coordination shell is (440). Let us note that the pair effective interaction at the 17th coordination shell is $\sim 0.15$ mRy. 73


107
REFERENCES


