Density Functional Study of
Elastic Properties of Metallic Alloys

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Abstract

Special quasi-random structure (SQS) and coherent potential approximation (CPA) are techniques widely employed in the first-principles calculations of random alloys. The aim of the thesis is to study these approaches by focusing on the local lattice distortion (LLD) and the crystal symmetry effects. We compare the elastic parameters obtained from SQS and CPA calculations. For the CPA and SQS calculations, we employ the Exact Muffin-Tin Orbitals (EMTO) method and the pseudopotential method as implemented in the Vienna Ab initio Simulation Package (VASP), respectively. We compare the predicted trends of the VASP-SQS and EMTO-CPA parameters against composition.

As a first case study, we investigate the elastic parameters of face centered cubic (fcc) Ti$_{1-x}$Al$_x$ (0 ≤ x ≤ 100 at.%) random solid solutions as a function of Al content (x). The EMTO-CPA and VASP-SQS results are in good agreement with each other. Comparing the lattice constants from SQS calculations with and without local lattice relaxations, we find that in Ti-rich (Al-rich) side the lattice constants remain almost unchanged (slightly increase) upon atomic relaxations. Taking local lattice distortions into consideration decreases the $C_{11}$ and $C_{44}$ elastic parameters, but their trends are not significantly affected. The $C_{12}$ elastic constant, on the other hand, is almost unchanged when atomic relaxations are included. In general, the uncertainties in the elastic parameters associated with the symmetry lowering in supercell studies turn out to be superior to the differences between the two alloy techniques including the effect of LLD.

We also investigate the elastic properties of random fcc Cu$_{1-x}$Au$_x$ (0 ≤ x ≤ 100 at.%) alloys as a function of Au content employing the CPA and SQS approaches. It is found that the CPA and SQS values for $C_{11}$ and $C_{12}$ are consistent with each other no matter whether the atomic relaxations are taken into account or not. On the other hand, the EMTO-CPA values for $C_{44}$ are slightly larger than those from SQS calculations especially for Cu-rich alloys which we ascribe to the differences in the DFT solvers rather than the differences between CPA and SQS.

The Perdew-Burke-Ernzerhof (PBE) approximation to the exchange-correlation term in density functional theory (DFT) is a mature approach and have been adopted routinely to investigate the properties of metallic alloys. In most of the cases, PBE provides theoretical results in good agreement with experiments. However, the ordered Cu-Au system turned out to be a special case where large deviations between the PBE predictions and observations occur. In this work, we make use of a recently developed exchange-correlation functional, the so-called quasi-non-uniform exchange-correlation approximation (QNA), to calculate the lattice constants and formation energies for ordered Cu-Au alloys as a function of composition. The calculations are performed using the EMTO method. We find that the QNA functional leads to excellent agreement between theory and experiment. The PBE strongly overestimates the lattice constants for ordered Cu$_{13}$Au, CuAu, CuAu$_{13}$ compounds and also for the pure metals which is nicely corrected by the QNA approach. The errors in the formation
energies of Cu$_3$Au, CuAu, CuAu$_3$ relative to the experimental data decrease from 38-45% obtained with PBE to 5-9% calculated for QNA.
Preface
List of included publications:

I Elastic constants of random solid solutions by SQS and CPA approaches: the case of fcc Ti-Al

II CPA description of random Cu-Au alloys in comparison with SQS approach
Li-Yun Tian, Li-Hua Ye, Qing-Miao Hu, Jijun Zhao, Börje Johansson and Levente Vitos, in manuscript.

III Density Functional description of Cu-Au Intermetallic Alloys
Li-Yun Tian, Henrik Levännäki, Kalevi Kokko and Levente Vitos, in manuscript.

Comment on my own contribution:

Paper I: part of calculations and data analysis, literature survey; the manuscript was written jointly.
Paper II: part of calculations, full data analysis, literature survey; the manuscript was written jointly.
Paper III: all calculations, full data analysis, literature survey; the manuscript was written jointly.

List of papers not included in the thesis:

I Ab initio study of the elastic properties of TiZrNbMo, TiZrVNb and TiZrNbMoV high-entropy alloys
Li-Yun Tian, Gui-Sheng Wang, Jijun Zhao, Börje Johansson and Levente Vitos, in manuscript.
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Chapter 1

Introduction

First-principles methods based on density functional theory (DFT) [1–3] are now adopted routinely to calculate the properties of materials. However, the application of these methods to random (disordered) alloys of technical importance is not straightforward. The prerequisite of a first-principles calculation is that one should know the atomic species on each crystal lattice site, which is not the case for random alloys, and, therefore, further approximations have to be made in order to describe the randomness. In this thesis, I calculate the elastic parameters and electronic density of states for disordered solid solutions by special quasi-random structure (SQS) [4, 5] and coherent potential approximation (CPA) [6, 7]. These approaches are frequently used in ab initio description of random alloys. The local lattice distortion (LLD) effect induced by local chemical environment is properly taken into account within the SQS. However, the LLD effect can not be considered by CPA within the single-site approximation, e.g. the A-A, A-B and B-B bonds are equal in binary $A_{1-x}B_x$ alloy. Nevertheless, CPA is a very successful mean-field approach for random alloys. Due to the single-site nature, the computational load increases linearly with the number of alloy components. Furthermore, in contrast to the SQS technique, the coherent Green function retains the symmetry of the alloy matrix. In applications to multi-component alloys, the size of the supercells is the SQS limiting factor.

Using the two random (disordered) Ti-Al and Cu-Au binary alloys as two examples, we demonstrate the SQS and CPA approaches by monitoring the trends of SQS and CPA bulk parameters against composition and the influence of local lattice relaxation. Both of these systems are considered in the face centered cubic (fcc) crystallographic lattice.

Previous studies of Cu-Au alloys mainly focused on the order-disorder transitions [8–10] and the properties of ordered phase [11]. For disordered Cu-Au alloys and the hypothetical random Ti-Al alloys, the elastic properties are scarce. Here we adopt the SQS and CPA methods to describe these alloys on an initio level. Furthermore, we give quantitative values for the effects of LLD and lattice symmetry of LLD on the formation energy and elastic constants of random Ti-Al and Cu-Au alloys.

The binary Cu-Au system has recently received a lot of attention because of the three ordered intermetallic compounds: $Cu_3Au$ (L1$_2$), $CuAu$ (L1$_0$) and
CuAu$_3$ (L1$_2$). Both experimentally and theoretically, the three ordered structures are stable with respect to the end-members having negative formation energies. In a recent investigation, it was found that the experimental formation energies are far lower than the theoretical values [12]. This finding has created some doubts concerning the scope of DFT and in particular of Perdew-Burke-Ernzerhof (PBE) [13] exchange-correlation functional for the Cu-Au system. Here we assess the Quasi-non-uniform exchange-correlation approximation (QNA) [14, 15], which is a new and improved approximation, producing excellent results for lattice constants. We show that QNA removes most shortcomings of PBE for the Cu-Au system.
Chapter 2

Theoretical Methodology

The mechanical properties of solid materials are investigated in this thesis using first-principles methods based on density functional theory (DFT). In a number of aspects of material properties, DFT can give accurate and reasonable results relative to experimental values. Today, DFT as the basic theory is widely used in computational material science.

Solids are composed of atoms. Each atom contains a nucleus with positive charge and electrons with negative charges \([16]\). In real materials, e.g. a multi-component many-body system, interactions exist in between the nuclei, the nuclei and electrons, and between electrons. A Hamiltonian describes all these interactions within the Schrödinger equation \([17, 18]\). Since this problem is usually not solvable, one should make several simplifications and approximations. The atomic-level properties of solid materials are determined by the behavior of the electrons moving within the field of rigidly displaced nuclei. In this chapter, we briefly introduce and discuss DFT.

2.1 The Hamiltonian of Electronic Structure

First-principles theory for a system of nuclei and electrons is based on solving the many body Schrödinger equation. The many body Schrödinger equation can be described as

\[
\hat{H}\Psi([\mathbf{R}_I, \mathbf{r}_i]) = E\Psi([\mathbf{R}_I, \mathbf{r}_i]),
\]

where \(\hat{H}\) is the Hamiltonian of the system, and \(E\) is the total energy. \(\Psi([\mathbf{R}_I, \mathbf{r}_i])\) is the many body wavefunction describing the state of the system; \(\mathbf{R}_I\) and \(\mathbf{r}_i\) are the positions of ions and electron \(i\).

The Hamiltonian contains the kinetic energy \(\hat{T}\) and the potential energy due to the interactions between the ions and the electrons (external potential \(\hat{V}\) and two-partial interaction \(\hat{W}\)).

\[
\hat{T} = -\sum_i \frac{\hbar^2}{2M_i} \nabla^2_{\mathbf{R}_i} - \sum_i \frac{\hbar^2}{2m_i} \nabla^2_{\mathbf{r}_i},
\]

where \(\hbar\) is the reduced Planck constant.
\[ \hat{W} = \frac{1}{2} \sum_{ij(i \neq j)} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{1\leq l < j} \left( Z_k Z_j e^2 \frac{1}{|R_l - R_j|} \right) \equiv V_{\text{ext}} \quad (2.3) \]

where \( h \) is the Planck’s constant divided by \( 2\pi \); \( e \) is the electron charge; \( Z_k \) is the charge of the ion; \( M_i \) is the mass of ion and \( m_i \) is the mass of the electron.

The motion of the ion should be separated from that of the electrons which was proposed by Born and Oppenheimer in 1927 [19]. If we neglect the motion of ion due to the huge relatively mass, this is called Born-Oppenheimer approximation [20]. Then the many-body wavefunction depends on the electronic degrees of freedom only. In addition, the term of ion-ion interaction potential is neglected, because it is simply a constant [21]. Therefore, the Hamiltonian of the simplified system becomes

\[ \hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}}(r) + \frac{1}{2} \sum_{ij(i \neq j)} \frac{e^2}{|r_i - r_j|} \quad (2.4) \]

Unfortunately, since there is a large number of electrons in a solid solving the electronic problem still remains which leads us to further simplifications and approximations.

### 2.2 Density Functional Theory

#### 2.2.1 Hartree-Fock approximation

In Eq. 2.4, the electronic wave-function depends on the spatial coordinates of the electrons. If we assume the particles in the system do not interact, so the individual electron wave-functions can be expressed by

\[ \Psi(\{r_i\}) = \psi_1(r_1)\psi_2(r_2) \ldots \psi_N(r_N) \quad (2.5) \]

This approach was originally proposed by Hartree in 1928 [22]. This leads to the Hartree scheme which is the simplest approximation the full wave-function. However, the antisymmetry of the many-fermion wave function can not be contained in Hartree approximation due to the distinguishable particles. This means the description of Eq.2.5 is incomplete.

Hartree-Fock theory [23, 24] is a frequently used approximation to the Schrödinger equation. In this theory, the fermionic nature of electrons is incorporated. The Hartree-Fock wave-function which is built up by one electron functions is defined as a antisymmetric Slater determinant [25]. In line with the Pauli principle, the determinant will change sign when interchanging the coordinates of arbitrary two electrons. The one electronic Hartree-Fock wave-function is solution for the equation

\[ \left[ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + V_{\text{ext}}(r) + V_{\text{eff}}(r) \right] \psi_i(r) - \frac{e^2}{2} \sum_{j \neq i} \left| \frac{1}{|r - r'|} \right| \psi_j(r) = \epsilon_i \psi_i(r) \quad (2.6) \]
where $e^2 \sum_{j \neq i} \langle \psi_j | \frac{1}{|r - r_j|} | \psi_i \rangle \psi_j(r)$ is the “exchange” term describing the effects of exchange between electrons. Here $V^H_i(r)$ is the Hartree potential expressing the Coulomb field created by the electronic density. One of the limiting factor of the Hartree-Fock approximation is computational cost due to that takes into account higher order electron-electron correlations.

### 2.2.2 Hohenberg-Kohn Theorem

In 1964, Hohenberg and Kohn introduced the fundamentals of density functional theory [26]. The two theorems are the central concept of DFT. Different from the Hartree-Fock theory, the wave-function of DFT is set by the ground states density $n(r)$. Theoretically the corresponding ground state energy and density can be determined.

**Theorem 1**: For a system of interacting electrons in an external potential, the potential is uniquely determined by the electron density $n(r)$.

**Corollary**: The Hamiltonian and the ground state energy are also determined uniquely in terms of the electron density.

**Theorem 2**: The ground state density minimizes the total energy functional of the system $E(n)$.

The ground state of the system is described in the following way:

$$E(n) = F(n) + \int V_{\text{ext}}(r)n(r)dr \tag{2.7}$$

where $F(n)$ is a universal functional of the electron density $n(r)$ and the second term is the interaction energy with the external potential.

### 2.2.3 Kohn-Sham Theory

The single-particle density and the total densities of the system were defined by Kohn and Sham [2] as

$$n_i(r) = |\Psi_i(r)|^2, \tag{2.8}$$

and

$$n(r) = \sum_i^N n_i(r). \tag{2.9}$$

According to Eq.2.8 and Eq.2.9, the total energy functional can be expressed by Hohenberg-Kohn theorem (HK) in terms of the single electron wave functional:

$$E = -\frac{\hbar^2}{2m} \sum_i^N \int \nabla \psi_i \nabla \psi_i \Psi_i(r) d^3r + \int V(r)n(r)d^3r + \int n(r)n(r') \frac{1}{|r - r'|} d^3rd^3r' + E_{ xc}(n), \tag{2.10}$$

where $E_{ xc}(n)$ is the exchange-correlation functional which includes all the quantum mechanical effects.
Unfortunately, so far the minimum of the total energy functional could not be established directly because the form of the kinetic energy functional is still unknown. Furthermore, the true form of the exchange-correlation energy functional is not known either. A practical way to overcome this problem is to use the Kohn and Sham scheme. The Kohn-Sham equations are single-electron equations, viz
\[
-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}} \psi_i(r) = \epsilon_i \psi_i(r).
\]
(2.11)
These equations differ from Eq. 2.6 in the non-local Hartree-Fock term. The single-electron wave function only depends on the effective potential \( V_{\text{eff}} \) and \( \psi_i(r) \). The effective potential \( V_{\text{eff}} \) is given by
\[
V_{\text{eff}} = V_{\text{ext}}(r) + V_H(r) + V_{\text{xc}}(r).
\]
(2.12)
\( V_H(r) \) is Hartree potential describing the Coulomb repulsion. The form is
\[
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3 r'.
\]
(2.13)
\( V_{\text{xc}} \) is exchange-correlation potential defined by
\[
V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}(n(r))}{\delta n(r)}.
\]
(2.14)

### 2.2.4 Exchange-Correlation functional

In fact, the exchange-correlation functional is not known although the existence of \( V_{\text{xc}} \) is guaranteed by HK theorem. Several approximations have been developed during the last decades. The simplest one is when the electron density is assumed to be constant around a particular point in space. This is the homogeneous electron gas approximation (HEG) [1]. In this case, the exchange-correlation functional can be derived exactly. The exchange-correlation potential at each position, based on the uniform electron gas, is known
\[
V_{\text{xc}}(r) = V_{\text{HEG}}^{\text{xc}}[n(r)].
\]
(2.15)
Because the approximation is valid at the area of local electron density, it is called the local density approximation (LDA) proposed by Kohn and Sham [2]. The exchange-correlation approximation based on LDA can be expressed as
\[
E_{\text{xc}} \approx E_{\text{xc}}^{\text{LDA}}(n) = \int n(r) e_{\text{xc}}(n(r)) dr,
\]
(2.16)
where \( e_{\text{xc}} \) is the exchange-correlation energy density per particle. The LDA gives us a way to completely define the Kohn-Sham equations. Despite its simplicity, the LDA was found to reproduce the ground properties of many systems with high accurate, such as bulk properties of 4\textit{d} and 5\textit{d} transition metals, surface properties of metals [27, 28].

To address the issue of inhomogeneities in the electronic density, it is crucial to develop new functionals that more accurately represent the exact functional and implement it in a mathematical form that can be efficiently solved for systems
2.3 Exact Muffin-Tin Orbitals Method

with a large number of electrons. The best known beyond-LDA functional is the generalized gradient approximation (GGA) [13, 29, 30]. GGA is more accurate than LDA, because GGA includes more physical information about the local electron density \( n(\mathbf{r}) \) and the local gradient in the electron density \( \nabla n(\mathbf{r}) \). It must be noted that GGA is also not always right. The exchange-correlation energy for GGA is written as

\[
E_{xc} \approx E_{xc}^{\text{GGA}} = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r} .
\]

(2.17)

Based on the characteristics of gradients in the electron density, there are a lot of distinct GGA functionals which can reproduce accurately physical properties of real materials. Perdew-Wang functional (PW91) [31] and the Perdew-Burke-Ernzerhof functional (PBE) [13] are the most widely used functionals for solid materials. In Chapter 5, we will show an example about Cu-Au alloys where large differences in physical properties with different GGA can be obtained.

2.3 Exact Muffin-Tin Orbitals Method

The Exact Muffin-Tin Orbitals (EMTO) [32–35] method is an improved screened Koringa-Kohn-Rostoker method (KKR) [36], which offers a very efficient scheme for solving the Kohn-Sham equations. The main idea of the EMTO approach is to use optimized overlapping Muffin-Tin (OOMT) potential spheres instead of non-overlapping ones which greatly improves the representation of the full potential. More detail and useful information about the EMTO method can be found in the Ref. [35].

Within the EMTO method, the effective single-electron potential \( V_{MT} \), as it appears in the Kohn-Sham equation 2.12, is approximated as

\[
V_{\text{eff}}(\mathbf{r}) \approx V_{\text{MT}}(\mathbf{r}) = V_0 + \sum_R [V_R(\mathbf{r}_R) - V_0] ,
\]

(2.18)

where \( V_R(\mathbf{r}_R) \) is the spherical potential centered at lattice sites \( R \) in the MT spheres, \( V_0 \) is a constant potential, called muffin-tin zero. By definition \( V_R(\mathbf{r}_R) \) becomes equal to \( V_0 \) outside the potential sphere of radius \( s_R (R \geq s_R) \). In Eq. 2.18, \( \mathbf{r}_R = \mathbf{r} - \mathbf{R} \), \( \mathbf{r}_R = |\mathbf{r}_R| \).

For fixed potential spheres, \( V_R(\mathbf{r}_R) \) and \( V_0 \) are determined by optimizing the mean of the squared deviation between \( V_{\text{MT}}(\mathbf{r}) \) and \( V(\mathbf{r}) \), which can be expressed as

\[
F_V([V_R], V_0) \equiv \int_\Omega \{ V(\mathbf{r}) - V_0 - \sum_R [V_R(\mathbf{r}_R) - V_0] \}^2 d\mathbf{r} ,
\]

(2.19)

where \( \Omega \) is the region of the potential optimization. The minimum conditions for the functional of the spherical potentials \( F_V \) are

\[
\int_\Omega \delta V_R(\mathbf{r}) \frac{\delta F_V([V_R], V_0)}{\delta V_R(\mathbf{r})} d\mathbf{r} = 0 \quad \text{for any } R ,
\]

(2.20)

and

\[
\frac{\delta F_V([V_R], V_0)}{\delta V_0} = 0 .
\]

(2.21)
From Eq. 2.20 and 2.21, we can obtain the optimal $V_R(r_R)$ and $V_0$. The solution for the above equations leads to the optimized overlapping muffin-tin (OOMT) potential.

To solve the single-electron Schrödinger equation, we could construct the KS orbital $\psi_i(r)$ in terms of exact MT orbitals $\bar{\psi}_{RL}(\epsilon_i, r_R)$. The form of KS orbital $\psi_i(r)$ is

$$\psi_i(r) = \sum_{RL} \bar{\psi}_{RL}(\epsilon_i, r_R) \psi_{RL,i},$$  \hspace{1cm} (2.22)

where $\psi_{RL,i}$ are the expansion coefficients, determined by demanding that the solutions are smooth functions in the entire space. $L = (l, m)$ represents a multi-index, denoting the set of the orbital ($l$) and magnetic ($m$) quantum numbers, respectively.

The exact muffin-tin orbits consist of two parts with different basis functions. Inside the potential spheres at $s_R$, the partial waves $\varphi_{RL}(\epsilon, r_R)$ are defined for any real or complex energy $\epsilon$ and inside the OOMT potential sphere $r_R \leq s_R$. In the interstitial region, the screened spherical waves $\psi_{RL}(\epsilon - v_0, r_R)$ are used as basis functions, where the potential is approximated by $v_0$. Combining the screened spherical waves and the partial waves, it can accurately describe the single-electron overlapping potential.

In fact, accurate potential spheres should overlap, however, a screened spherical wave behaves only on its own $a$-sphere. Therefore, an additional free-electron function $\varphi_{RL}(\epsilon, r_R)$ has to be introduced, which connects the screened spherical wave and the partial wave.

Finally, the EMTOs are constructed using different basis functions in the different regions:

$$\bar{\psi}_{RL}(\epsilon, r_R) = \varphi_{RL}(\epsilon, r_R) + \psi_{RL}(\epsilon - v_0, r_R) - \varphi_{RL}(\epsilon, r_R).$$  \hspace{1cm} (2.23)

By solving the so-called kink-cancellation equation related to the boundary condition in the region $s_R \leq r_R \leq s_R$, we can find the solution of the KS equation.

### 2.4 Coherent Potential Approximation

In this section, I will introduce the coherent potential approximation (CPA) [37–40], a very powerful technique that describes the properties of multicomponent alloys. The CPA is based on the assumption that the alloy may be replaced by an ordered effective medium, and the parameters are determined self-consistently. Unlike SQS, CPA does not use a supercell but treats the impurity problem within the single-site approximation, implemented within the framework of EMTO theory. An uniform effective medium is introduced to place the single impurity. There are two main approximations within the CPA: 1) Within an alloy the local potentials around a certain type of atom are the same; 2) The site independent coherent potential $\tilde{P}$ of a monoatomic describes the system.

Next we will take arbitrary binary alloys $A_{1-x}B_x$ as an example to give detail informations for CPA. Here $x$ stands for the fractions of the $B$ atom. $A$ and $B$ atoms are assumed to be randomly distributed on a crystal structure. It should be noted that within CPA, the short- or long-range order effects are neglected. In additional since we have no information about the local environment, the
2.4 Coherent Potential Approximation

effect of atomic relaxation is also neglected. The main steps to construct the CPA effective medium are as follows.

Within the KKR, Linear Muffin-Tin Orbital (LMTO) [41–43] or EMTO methods, the coherent Green function \( \tilde{g} \) has the form

\[
\tilde{g} = [S - \tilde{P}]
\]

where \( S \) is the structure constant matrix and \( \tilde{P} \) is the coherent potential.

The Green functions of the alloy compositions, \( g_i \), is determined by the real atomic potential \( P_i \) by solving the Dyson equation in real space.

\[
g_i = \tilde{g} + \tilde{g}(P_i - \tilde{P}) \quad , \quad i = A, B.
\]

Finally, the average of the individual Green functions should reproduce the single-site part of the coherent Green function

\[
\tilde{g} = (1 - x)g_A + xg_B ,
\]

where \( g_A \) and \( g_B \) are the single-site Green function for the atoms A and B. The above three equations are solved iteratively, and the output \( \tilde{g} \) and \( g_i \) s are used to determine the electronic structure, charge density and total energy of the random alloy.

2.4.1 Quasi-non-uniform gradient-level approximation

In the local density approximation (LDA) [2, 44], the interactions are described by the electron density \( n(r) \) mapping the system into a series of homogeneous electron gas [26]. The gradient-level density functional goes beyond LDA, by considering so-called density gradient-corrected functionals which introduced by Gross and Dreizler [29] and further developed by Perdew [30]. Subsystem functional approach (SFA) [45] is another gradient-level approximation based on various models, including the Airy gas model [46]. The local Airy gas functional [32], based on the linear potential approximation, has a number of advantages over GGA functions, such as, the properties of edge region. The main idea of SFA is to divide a system into subsystem and apply different functional to different parts. Furthermore, Airy gas approximation, the linear potential approximation, is simplest model of SFA based on a second-order gradient expansion. Vitos et al [47] have developed a functional, Local Airy gas (LAG) functional using the Airy gas exchange energy per particle and the LDA correlation energy per particle in the edge region.

The LAG exchange energy per electron may be written in the form

\[
\varepsilon_{x}^{LAG}(n, s) = \varepsilon_{x}^{LDA}(n)F_{x}^{LAG}(s(\zeta)),
\]

where \( F_{x}^{LAG}(s(\zeta)) \) is the enhancement function, \( \zeta \) is dimensionless parameter.

However, most of approximation density functionals include exchange and correlation energies, \( \varepsilon_{xc}(n, r) = \varepsilon_{x}(n, r) + \varepsilon_{c}(n, r) \). The total enhancement function can be expressed as

\[
F_{xc}(s) = (\varepsilon_{x}(n, r) + \varepsilon_{c}(n, r))/\varepsilon_{x}(n) .
\]
Combining Eq. 2.27, the total LAG enhancement function becomes
\[ F^{LAG}_{xc}(s) = F^{LAG}_x(s) + \frac{\epsilon^{LDA}_c(n)}{\epsilon^{LDA}_x(n)}, \]  
which \( s < 1 \) is a slowly varying electron density.

Based on above basic theory, QNA is developed with the two parameters \( \{\mu, \beta\} \) from the PBE/PBEsol approximations by Levämaäki et al. [14, 15]. In an attempt to find the "best" \( \{\mu, \beta\} \) combined the absolute relative error for the equilibrium volume and the bulk modulus
\[ f(^*args) = W_a \frac{|a_0(^*args) - a_{expt}|}{a_{expt}} + W_B \frac{|B_0(^*args) - B_{expt}|}{B_{expt}}. \]
In this way, the unique "optimal" \( \{\mu, \beta\} \) parameters are determined.

For metals, the truly gradient-sensitive region is always localized around the atomic sites and the region in between the sites is less sensitive to the details of the density functional approximation. Based on the SFA, QNA functional can be expressed as
\[ E^{QNA}_{xc}(n) = \sum_q \int_{\Omega_q} d^3 r LDA(n) F^{opt}_q(r, s), \]  
where \( F^{opt}_q(r, s) \) is the PBE/PBEsol enhancement function based on \( \{\mu, \beta\}_{opt_q} \) optimized for the alloy component \( q \).
Elastic Properties of Materials

Elastic properties of solid materials are important to describe various fundamental characteristics. The elastic constants are essential parameters providing a detailed information on the mechanical properties of materials, such as Poisson’s ratio, specific heat, sound wave velocities, Debye temperature and thermal expansion, etc. The elastic properties of single crystals are described by the elements $C_{\alpha\beta}$ of the elastic tensor.

### 3.1 Single-Crystal Elastic Constants

When solid materials are subject to small stresses, the crystals deform almost in a linear elastic manner and the deformation is homogeneous and elasticated. In general, the stress is described by the stress tensor $\sigma$. Similarly, the deformations of crystals caused by the small stress are described by the elastic strain tensor $\varepsilon$. The linear relationship between the stress tensor $\sigma$ and the strain tensor $\varepsilon$ is provided by the well-known Hooke’s law,

$$\sigma_{ij} = \sum_{k,l=1}^{3} C_{ijkl} \varepsilon_{kl} ,$$

(3.1)

where $i, j, k$ and $l$ are from 1 to 3, each $C_{ijkl}$ corresponds to the single-crystal elastic constant. Due to symmetry arguments $C_{ijkl} = C_{ijlk} = C_{jikl} = C_{klij}$, the number of 81 ($3^4$) elastic constants is reduced to a total of 21. It is arranged in a symmetric $6 \times 6$ matrix, $C_{\alpha\beta} = C_{\beta\alpha}$ ($\alpha, \beta$ running from 1 to 6 according to the sequence $xx, yy, zz, yz, xz, xy$). Eq. 3.1 can also be written as

$$\sigma_{\alpha} = \sum_{\beta=1}^{6} C_{\alpha\beta} \varepsilon_{\beta} .$$

(3.2)

Additionally, the number of independent parameters required to specify the tensor $C_{\alpha\beta}$ depends on the symmetry of the system. For example, it is $C_{\alpha\beta} \neq$

0 for lower symmetry of single-crystal materials, whereas for a material with cubic symmetry, there is only three independent elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$. The matrix for cubic material is described as:

$$
\begin{pmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{pmatrix}.
$$

(3.3)

The strain matrix can be defined as:

$$
D(\varepsilon) = \begin{pmatrix}
\varepsilon_1 & \frac{1}{2}\varepsilon_6 & \frac{1}{2}\varepsilon_5 \\
\frac{1}{2}\varepsilon_6 & \varepsilon_2 & \frac{1}{2}\varepsilon_4 \\
\frac{1}{2}\varepsilon_5 & \frac{1}{2}\varepsilon_4 & \varepsilon_3
\end{pmatrix}.
$$

(3.4)

For an adiabatic formation [48], the stress tensor is obtained by

$$
\sigma_\alpha = \left[ \frac{1}{V} \frac{\partial E}{\partial \varepsilon_\alpha} \right]_{\varepsilon=0}. 
$$

(3.5)

The second-order elastic constants can be expressed

$$
C_{\alpha\beta} = \left[ \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_\alpha \partial \varepsilon_\beta} \right]_{\varepsilon=0}.
$$

(3.6)

For a small deformation, the total energy can be Taylor expanded in powers of the component of the strain matrix with respect to the initial energy of the unstrained crystal in the following way

$$
E(V, \varepsilon_\alpha) = E(V_0, 0) + V_0 \sum_{\alpha=1}^{6} \sigma_\alpha \varepsilon_\alpha + \frac{V_0}{2} \sum_{\alpha,\beta=1}^{6} C_{\alpha\beta} \varepsilon_\alpha \varepsilon_\beta + \mathcal{O}(\{\varepsilon_\alpha\}^3)
$$

(3.7)

where $V_0$ is equilibrium volume and $\sum_{\alpha=1}^{6} \sigma_\alpha \varepsilon_\alpha = 0$ according to Eq. 3.6. Here $\mathcal{O}(\{\varepsilon_\alpha\}^3)$ stands for the neglected terms, which are of order of $\varepsilon^3$ or higher. The total energies in CPA are usually computed for six distortions $\varepsilon$ running from 0 to 0.05 with step of 0.01.

According to the specific distortions, we obtain a series of energy differences $\Delta E$. We fit the relation of $\Delta E$ and $\varepsilon^2$, then the elastic constants $C_{\alpha,\beta}$ are
obtained from the second order coefficient. For a cubic system, the energy change is

\[
\frac{E}{V} = \frac{1}{2} C_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + \frac{1}{2} C_{44} (\varepsilon_{23}^2 + \varepsilon_{31}^2 + \varepsilon_{12}^2) + C_{12} (\varepsilon_{11}\varepsilon_{22} + \varepsilon_{33}\varepsilon_{22} + \varepsilon_{11}\varepsilon_{33}) + O(\varepsilon^3).
\]

(3.8)

3.1.1 Stress-strain relations

The stress-strain approach can be directly used to calculate the stress tensor by means of VASP. The elastic constants matrix also can be derived according to Eq. 3.1. Because we have three independent elastic constants \( C_{11}, C_{12} \) and \( C_{44} \), the three distortions are used in the Stress-strain calculations and every strain matrix is symmetrical [49].

In this thesis, the stress-strain (\( \sigma - \varepsilon \)) relation was used to fit the elastic constants when using SQS. The symmetry of the SQS supercell is generally very low due to the quasi-random distribution of the atoms. This makes the calculations of some symmetry dependent properties inconvenient. In particular, the number of independent elastic constants \( C_{ij} \) increases greatly due to the lowering of the lattice symmetry.

For a perfect cubic system, the three independent elastic constants may be obtained by fitting the (\( \sigma - \varepsilon \)) relationship under only one strain tensor.

\[
\begin{pmatrix}
1 + \varepsilon & 0 & 0 \\
0 & 0 & 1 + \frac{1}{2} \varepsilon \\
0 & 1 + \frac{1}{2} \varepsilon & 0
\end{pmatrix},
\]

(3.9)

\[\sigma_1 = C_{11}\varepsilon; \sigma_2 = \sigma_3 = C_{12}\varepsilon; \sigma_4 = C_{44}\varepsilon.\]

(3.10)

However, since the cubic symmetry is broken for the SQS supercells, the strain tensors with different orthogonal direction, i.e.

\[
\begin{pmatrix}
0 & 0 & 1 + \frac{1}{2} \varepsilon \\
0 & 1 + \varepsilon & 0 \\
1 + \frac{1}{2} \varepsilon & 0 & 0
\end{pmatrix},
\]

(3.11)

and

\[
\begin{pmatrix}
0 & 1 + \frac{1}{2} \varepsilon & 0 \\
1 + \frac{1}{2} \varepsilon & 0 & 0 \\
0 & 0 & 1 + \varepsilon
\end{pmatrix},
\]

(3.12)

must be used, where the strains \( \varepsilon \) varied from -0.004 to 0.004 in steps of 0.002. To obtain the elastic constants of such random system, one generally averages the
relevant elastic parameters [50–52]. For a cubic system, the three independent elastic constants are obtained according to the following average relations:

\[ C_{11} = \frac{1}{3}(C_{11} + C_{22} + C_{33}); \]
\[ C_{12} = \frac{1}{3}(C_{12} + C_{23} + C_{13}); \]

and

\[ C_{44} = \frac{1}{3}(C_{44} + C_{55} + C_{66}). \] (3.13)

### 3.1.2 Energy-strain relations

In this thesis, the elastic constants are fitted by the energy-strain relation for all CPA calculations. The elastic constants were obtained from the total energies computed as a functional of small strains. We used volume-conserving orthorhombic and monoclinic deformations to the fcc unit cell as described by

\[
\begin{pmatrix}
1 + \varepsilon_o & 0 & 0 \\
0 & 1 - \varepsilon_o & 0 \\
0 & 0 & 1/(1 - \varepsilon_o^2)
\end{pmatrix},
\] (3.14)

and

\[
\begin{pmatrix}
1 & \varepsilon_m & 0 \\
\varepsilon_m & 1 & 0 \\
0 & 0 & 1/(1 - \varepsilon_m^2)
\end{pmatrix}.
\] (3.15)

The strains \( \varepsilon_o \) and \( \varepsilon_m \) vary between 0 and 0.05 with step of 0.01. The changes in total energy are obtained by applying a series of small strains at the equilibrium lattice. The elastic constants are deduced by the deformations. The elastic constants are identified as proportional to the second order coefficient in a polynomial fit of the total energy as a function of the distortion parameter \( \varepsilon \). The cubic shear elastic constants \( C' \) and \( C_{44} \) were evaluated by fitting the associated total energies against the distortions, namely

\[ E(\varepsilon_o) = E(0) + 2V_0 C' \varepsilon_o^2 + \mathcal{O}(\varepsilon_o^4), \] (3.16)

and

\[ E(\varepsilon_m) = E(0) + 2V_0 C_{44} \varepsilon_m^2 + \mathcal{O}(\varepsilon_m^4), \] (3.17)

respectively. Here \( \mathcal{O}(\varepsilon_m^4) \) stands for the neglected terms, which are of order of \( \varepsilon^4 \). For cubic system, we define the bulk modulus

\[ B = \frac{1}{3}(C_{11} + 2C_{12}) \] (3.18)

and the tetragonal shear modulus

\[ C' = \frac{1}{2}(C_{11} - C_{12}). \] (3.19)
Combining eq. 3.18 with 3.19, we can obtain $C_{11}$ and $C_{12}$.

The theoretical equilibrium volume and the bulk modulus were determined from an exponential Morse-type function \[53\] fitted to the \textit{ab initio} total energies of cubic structures calculated for nine different atomic volumes. The bulk modulus is calculated from the volume derivative of the pressure as

$$B(V) = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E(V)}{\partial V^2}.$$  

\[3.20\]

### 3.2 Elastic Modulus

The polycrystalline elastic modulus for metallic alloys can be determined from the three independent elastic constants for cubic materials. There are two approximation methods to calculate the elastic modulus: a uniform strain for Voigt averaging method \[54\] and a uniform stress for Reuss method. For cubic crystals, within the Voigt approach, the bulk and shear moduli can be expressed as

$$B_V = \frac{C_{11} + 2C_{12}}{3},$$  

and

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}.$$  

\[3.21\]

\[3.22\]

While within the Reuss approximation, the expressions are

$$B_R = B_V,$$  

and

$$G_R = \frac{5(C_{11} - C_{12}C_{44})}{4C_{44} + 3(C_{11} - C_{12})}.$$  

\[3.23\]

\[3.24\]

According to the Hill averaging method \[55\], Voigt-Reuss-Hill (VRH) average, the arithmetic average for the bulk and shear moduli can be estimated from Voigt and Reuss bounds

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2}.$$  

\[3.25\]

The Young’s modulus ($E$) and the Poisson ratio($v$) are connected to $B$ and $G$ by the following relationships

$$E = \frac{9BG}{3B + G},$$  

and

$$v = \frac{3B - 2G}{6B + 2G}.$$  

\[3.26\]

\[3.27\]

The elastic anisotropy is expressed by $A_{VR}$ \[56\] and $A_{Z}$ \[57\] characterized the polycrystalline solids. It is useful to measure

$$A_{VR} = \frac{G_V - G_R}{G_V + G_R},$$  

and the Zener ratio

$$A_{Z} = \frac{2C_{44}}{C_{11} - C_{12}}.$$  

\[3.28\]

\[3.29\]

For isotropic crystals, $A_{VR} = 0$ and $A_{Z} = 1$. 

Chapter 4

Relaxation effect on the Elastic properties of Ti-Al alloys

In this chapter, I discuss the lattice parameters and the elastic constants of the random fcc binary alloys $\text{Ti}_{1-x}\text{Al}_x$ ($0 \leq x \leq 100$ at.%) as a function of composition. All calculations are based on DFT and adopt the EMTO and VASP solvers.

4.1 Lattice constant

The equilibrium lattice constants of random $\text{Ti}_{1-x}\text{Al}_x$ are shown in Fig. 4.1 as functions of Al composition, $x$. As seen from the figure, they deviate significantly from Vegard's law. The lattice constants decrease linearly with $x$ up to 37.5 at.%, reach a minimum in between 75 at.% and 87.5 at.%, and then increase with further increasing $x$.

The SQS and CPA lattice constants are in good agreement with each other, the largest error being of the order of 0.2%. In fact, this difference appears already for pure fcc Ti, and represents the characteristic deviation between EMTO and VASP results for monoatomic systems.

Comparing the lattice constants from SQS calculations with and without atomic relaxations, we find that the lattice constants remain almost unchanged at Ti-rich side upon LLD. At Al-rich side, the lattice constants with atomic relaxation are only slightly larger than those with fixed atom positions.

4.2 Elastic properties

In this section, we investigate the effect of local lattice distortion on the elastic constants of $\text{Ti}_{1-x}\text{Al}_x$ based on the corresponding equilibrium lattice constants. The individual single elastic constants and some of the strain tensors from SQS calculations with and without atomic relaxation are calculated, and these data
Figure 4.1: Theoretical lattice constants for fcc-Ti_{1-x}Al_{x} alloys (0 \leq x \leq 100 \text{ at.\%}) plotted as a function of Al contents. Results are shown for both SQS (relaxed and unrelaxed) and CPA calculations. The dash lines denote the trend according to Vegard’s law.

are shown in my first paper. The symmetry of the supercell is broken by the randomness of the alloys, therefore the number of elastic constants for each composition is increased and the values are quite scattered. The largest difference is about 20 GPa for C_{11} at x = 75 \text{ at.\%} calculated with atomic relaxation. This represents about 16% of the corresponding mean C_{11} value. In general, the individual SQS elastic constants with and without atomic relaxations present similar level of scattering.

In Fig. 4.2, we plot the average elastic constants \overline{C}_{ij} from SQS calculations with and without atomic relaxation. As seen from the figure, both C_{11} and C_{44} decrease with x ranging from 25 \text{ at.\%} to 75 \text{ at.\%} due to the atomic relaxation. However, comparing the C_{12} from SQS calculations with and without atomic relaxation, we find that C_{12} has almost not changed and that means that the LLD effect on C_{12} is negligible. Taking the local lattice distortion into account, the C_{11} is reduced by a maximum 12 GPa (corresponding to \sim 11\%) at x = 62.5 \text{ at.\%}. The biggest difference for C_{11} is greater than that of C_{44} with a maximum 7 GPa (\sim 12 \%) at x = 75 \text{ at.\%}. However, the trends of the average elastic constants against the composition x are not heavily altered by the LLD even for C_{11}. It is noted that, in general, the scattering of the elastic constants associated with the symmetry lowering is superior to the difference induced by the LLD. In addition, the trend of the individual C_{ij}(x) for most of the strain tensors deviates significantly from that of the average elastic constant \overline{C}_{ij}(x). Therefore, one particular strain tensor is not enough to determine the composition dependence of the elastic constants of random Ti_{1-x}Al_{x}.

We also compare the elastic constants from SQS and CPA calculations without relaxing the atomic positions in Fig. 4.2. One can see from the figure, at Ti-rich side, C_{11} from CPA calculations is about 15 GPa lower than that
4.2 Elastic properties

Figure 4.2: Single crystal elastic constants of fcc-Ti$_{1-x}$Al$_x$ alloys as functions of composition. Results are shown for both SQS (unrelaxed) and CPA calculations. The dashed lines are the EAM predictions by Pezold et al [50].

From SQS calculations, whereas at the Al-rich side, CPA $C_{12}$ is about 10 GPa lower than the SQS one. CPA $C_{44}$ is larger than that from SQS calculations in the whole composition range. Since the above differences are to a large extent present also for the pure end members, they should be ascribed to the differences in the EMTO and VASP methods rather than to the difference in the corresponding alloy formalism. Nevertheless, CPA and SQS elastic constants show very similar composition dependence. $C_{11}$ decreases with $x$ at the Ti-rich side up to about 50 at.% and a bump occurs at the Al-rich side. $C_{12}$ and $C_{44}$ from both CPA and SQS calculations show a maximum at $x \approx 37.5$ at.%. The consistent trends of the elastic constants against the composition from CPA and SQS calculations indicate that both techniques catch reliably the chemistry
CHAPTER 4. RELAXATION EFFECT ON THE ELASTIC PROPERTIES OF TI-AL ALLOYS

behind the composition dependence of the elastic constants.

The elastic constants of fcc-Ti$_{1-x}$Al$_x$ have also been calculated by Pezold et al. [50] using molecular dynamic (MD) simulation with semi-empirical EAM potential. Their results are plotted in Fig. 4.2 by dashed lines for comparison. $C_{11}$ deviates substantially from our first-principles CPA and SQS calculations: we get a minimum $C_{11}$ at $x \sim 62.5$ at.\% whereas EMA calculations generated a maximum at $x = 50$ at.\%. The maximum $C_{12}$ and $C_{44}$ from the EAM calculations occur also at $x = 50$ at.\%, however, they are at $x \sim 37.5$ at.\% from the first-principles CPA and SQS calculations. Since those authors employed a semi-empirical method and our results are based on ab initio theory, we tend to believe that the true trends are more accurately represented by the present data. Since SQS and CPA $C_{ij}$ values follow very similar variations as a function of concentration (Fig. 4.2), in the following we focus on the CPA results and make an attempt to give a plausible explanation for the predicted trends based on the electronic structure.

4.3 Elastic parameters versus chemical composition

According to the present calculations (Fig. 4.1), the lattice parameter of Al decreases upon Ti addition up to $\sim 25$ at.\% Ti, which results in a pronounced negative deviation relative to Vegard’s rule. For the anomalous lattice contraction with alloying, in principle, one could adopt a similar procedure as in Ref.[58] to estimate the alloying effects in the lattice constant of Ti-Al. However, in the present system we have metallic bonds ranging from pure transition-metal-type (Ti) to $p$-metal-type (Al) and hence the alloying effects are expected to manifest in complex bonding properties. Titanium is an early transition metal with two $s$ electrons and two $d$ electrons. In general, $s$ electrons give rise to a broad band and stabilize a large lattice parameter dictated mainly by the balance between the repulsive kinetic energy of the average electron density and the attractive exchange-correlation hole. In contrast, the $d$ states are more short-ranged than the delocalized $s$ states and prefer small lattice constants. As a result, the equilibrium volume of Ti is obtained as an interplay between the homogeneous positive $s$ pressure $p_s(n_s/V)$ and the negative $d$ pressure $p_d(n_d,V)$. Here $n_s$ and $n_d$ denote the number of $s$ and $d$ electrons, respectively, and $V$ is the atomic volume. The presence of an attractive $d$ pressure in Ti is also reflected by the $\sim 35\%$ decrease of the Wigner-Seitz radius as we go from Ca to Ti. Similarly to the $d$ electrons in Ti, the $p$ electron in Al also gives rise to an attractive pressure $p_p(n_p,V)$ which shrinks the Wigner-Seitz radius of Al by $\sim 12\%$ compared to that of Mg. For details about the pressure expressions, the reader is referred to Refs. [59, 60]. Here we recall that the $s$ partial pressure depends on the average $s$ electron density, whereas the other partial pressures depend on the actual number of the electrons and volume.

In Ti$_{1-x}$Al$_x$ alloys, the partial $s$, $p$ and $d$ pressures vary continuously with composition from their values in pure Ti to those in pure Al. Since the change in the equilibrium volume with alloying is relatively small, one can assume that $p_s$ is proportional to the number of $s$ electrons. In addition, since both $p$ and $d$ states are bonding (less than half-filled bands), one may consider that $p_p$ and
4.3 Elastic parameters versus chemical composition

Figure 4.3: $s$, $p$ and $d$ electron numbers $n$ of fcc-Ti$_{1-x}$Al$_x$ alloys as a function of composition $x$. The electron numbers are plotted relative to the concentration weighted average of the values calculated for pure Ti and Al.

$p_d$ also scale with the number of $p$ and $d$ electrons, respectively. In Fig. 4.3, we plotted the changes in $n_s$, $n_p$ and $n_d$ relative to the linear trend corresponding to $(1-x)n_o(Ti) + xn_o(Al)$ ($o$ stands for $s$, $p$ or $d$). It is found that $n_d$ shows only a weak deviation relative to the linear mixing, meaning that the attractive $p_d$ pressure is removed from the system nearly linearly upon Al addition. However, both $n_s$ and $n_p$ show strong deviations from the linear trend. The positive deviation for $n_p$ suggests additional attractive $p_p$ pressure compared to that corresponding to the linear increase of the Al content. The negative deviation for $n_s$, on the other hand, signals a lowering of the repulsive $s_p$ pressure. Both of these mechanisms lead to a lattice contraction relative to Vegard’s rule, in line with Fig. 4.1. The change in the $s-p$ hybridization (increasing $s \rightarrow p$ electron transfer with Ti addition) turns out to be more pronounced in the Al-rich end, which explains why the equilibrium volume has the negative slope as a function of Ti-content in the Al-rich alloys.

The composition dependence of the $s$, $p$ and $d$ occupation numbers has implications on the trends obtained for the elastic parameters as well. The negative deviation of the equilibrium lattice parameter relative to Vegard’s rule (Fig. 4.1) is consistent with the positive deviation of the bulk modulus plotted in Fig. 4.4 (b). We recall that lower volume usually results in increased bulk modulus and vice versa. Combining now the bulk modulus and the tetragonal shear modulus, we get $C_{11} = B + 4/3C'$ and $C_{12} = B - 2/3C'$. Since for most of the alloys considered here $C' << B$, the trend obtained for $B$ should be dominating in both $C_{11}$ and $C_{12}$. This is indeed the case for $C_{12}$ in the whole concentration range and very roughly also for $C_{11}$ (Fig. 4.2). However, in Al-rich alloys, we find a clear local maximum in $C_{11}$ around $x = 80$ at.% and a local minimum near $x = 50$ at.%. In addition, $C_{11}$ has negative slope as a function of $x$ in Ti-rich alloys as compared to the positive slope found for $B$. We point out that
CHAPTER 4. RELAXATION EFFECT ON THE ELASTIC PROPERTIES OF Ti-Al ALLOYS

Figure 4.4: Tetragonal electric constant $C'$ (a) and bulk modulus $B$ (b) of fcc-Ti$_{1-x}$Al$_x$ as a function of composition $x$. The open squares in (a) represent $C'$ obtained at volumes corresponding to Vegard’s law. The dashed lines show the linear rule of mixing.

This non-monotonic behavior of $C_{11}$ as a function of Al content is to a large degree missing from the previous EAM data but it is present in both SQS and CPA results (although the minima are at somewhat shifted position).

The non-monotonic trend of $C_{11}$ is due to the strongly nonlinear behavior of $C'$ plotted in Fig. 4.4 (a). In Al-rich alloys, $C'$ increases with Ti addition and shows a local maximum near 80 at.% Al. At larger Ti content, $C'$ decreases and drops below the linear mixing value. We notice that the effect of $C'$ is somewhat weaker in $C_{12}$ than in $C_{11}$ manifesting in the nearly linear trend of $C_{12}$ in Al-rich alloys. In Fig. 4.4 (a), a few $C'$ values obtained for volumes estimated based on Vegard’s rule are shown. The small deviation between the two sets of $C'$ values indicates a more profound electronic structure origin behind the non-linear trend than the simple volume effect. A similar effect on $C'$ was found in the case of Al-Mg alloys as well, where a very strong positive deviation of $C'$ relative to the trend corresponding to the linear mixing was predicted [61]. In the Ti-rich side, gradually removing the bonding $d$ electrons results in a substantial drop in $C'$. The $s \to p$ charge transfer in Al-rich alloys turns the system more Al-like. This explains why $C'$ is relatively large in these alloys and thus $C_{11}$ exhibits a local maximum near 20 at.% Ti.
Chapter 5

Ab Initio Study of Cu-Au Alloys

5.1 Formation energy of ordered Cu-Au alloys

5.1.1 Lattice constant

The Cu-Au system shows three intermetallic compounds at the compositions of 25 at.% (Cu$_3$Au), 50 at.% (CuAu) and 75 at.% (CuAu$_3$) possessing the $L_1_2$,$L_1_0$ and $L_1_2$ crystal structures[62–64], respectively. In this chapter, I evaluate the relative merits of PBE and QNA [14, 15] approximations within the framework of density functional theory in the case of ordered Cu$_3$Au, CuAu and CuAu$_3$ alloys and pure fcc Cu and Au by comparing their performances for the equilibrium lattice constants and the formation energies. All PBE and QNA calculations are performed within the EMTO scheme.

Firstly, I compare the present lattice constants of Cu, Cu$_3$Au, CuAu, CuAu$_3$ and Au with the previous theoretical values and the available experimental data. We find that the PBE lattice constants are good agreement with the former Projector Augmented Wave (PAW) [65, 66] and the Linear Muffin-Tin Orbitals (LMTO) [67] results, however, they are overestimated relative to the experiment [68, 69]. Additionally, the lattice constants are also consistent with the theoretical results obtained using the Augmented Spherical Wave (ASW) method [70]. QNA can give excellent results: the QNA lattice constants are extremely closed to the experimental values. In this work, the c/a of $L_1_0$-CuAu alloy is 0.915 consisted with the theoretical values (0.915) [71] and the experimental data (0.926) [68].

In Fig. 5.1, we show the PBE and QNA lattice parameters errors relative to the experimental values. It is clearly seen that PBE strongly overestimates the lattice constants with 1.91% average absolute error. A smaller absolute error ~0.18% is obtained by QNA. For pure Cu and Au, as shown in Fig. 5.1, the results are also good agreement with the previous values calculated by Levämäki et al [14, 15].

Based on the above discussion, it is easy to believe that the exchange functional with large errors on volume will result in the change of other properties,
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Figure 5.1: Lattice Constant differences between theoretical predictions and experimental values in ordered Cu-fcc, Cu$_3$Au-L1$_2$, CuAu-L1$_0$, CuAu$_3$-L1$_2$ and Au-fcc. The red bars represent PBE and the blue bars refer to the QNA results. The present results are shown by solid bars whereas those calculated by Levämäki et al [15] by patterned bars.

The present results are shown by solid bars whereas those calculated by Levämäki et al [15] by patterned bars.

e.g. the formation energy, which is sensitive to the variation of volume. Therefore, the formation energies of ordered Cu-Au alloys should be calculated by the exchange correlation functional PBE and QNA.

5.1.2 PBE and QNA formation energy

In Fig. 5.2, the PBE and QNA excess energies of ordered Cu-Au alloys are plotted as a function of Wigner-Seitz radius ($sws$) (or volume). They are fitted to find the equivalent volume using Mose-type function [53]. The excess energy of ordered Cu-Au can be expressed as

$$\Delta E = E(sw) - (1 - x)E_{Cu}(sw_{Cu}) - xE_{Au}(sw_{Au})$$  \hspace{1cm} (5.1)

where $E(sw)$ is the total energy per atom of the alloys as a function of Wigner-Seitz radius. $E_{Cu}(sw_{Cu})$ and $E_{Au}(sw_{Au})$ represent the total energy per Cu and Au atom at equilibrium volume, respectively.

In Fig. 5.2 (a), the PBE excess energies are calculated at PBE and QNA volume $sw_{PBE}$ and $sw_{QNA}$, respectively. As shown in panel (a), the lowest excess energies for per alloy, defining the formation energies, are obtained at PBE volumes. The difference of excess energy at QNA and PBE volumes is slightly more pronounced with increasing the Au composition. However, they are close to each other when using the formation energy description (Fig. 5.3 (a)).
5.1 Formation energy of ordered Cu-Au alloys

QNA excess energies are lower with smaller volumes than those of PBE [Fig. 5.2 (b)]. From the figure, we find the difference magnitude of PBE (QNA) excess energies between the PBE and QNA volumes are consistent with the deviation of PBE and QNA lattice constants (Fig. 1 in paper III).

Here the formation energy is defined as

\[ \Delta H = E(V_{eq}) - (1-x)E_{Cu}(V_{Cu}) - xE_{Au}(V_{Au}) \]  

with \( E(V_{eq}) \) being the total energy per atom of the alloys at equilibrium volume and \( E_{Cu}(V_{Cu}) \) and \( E_{Au}(V_{Au}) \) the energy per atoms of Cu and Au in fcc equilibrium volume.

In Fig. 5.3, the present PBE and QNA formation energies for ordered Cu-Au (a) and Pd-Au (b) are displayed. The experimental values are also shown. For Cu-Au system, as shown in the figure, PBE formation energies are much higher than the experimental values [12], and QNA formation energies show excellent agreement with the experiment. For QNA, the errors in \( \Delta H \) are 4.73%, 6.67%, 5.38% for ordered Cu\(_3\)Au, CuAu and CuAu\(_3\), respectively. However, the PBE results have large deviations compared to the experimental values: namely the errors are 39.32%, 38.49% and 37.95%, respectively. This failure of PBE for the Cu-Au system has previously been demonstrated by Zhang et al [12] and Ozoliš [10]. The energies of ordered Cu-Au alloys are nearly a factor of 2 smaller in magnitude than experimental values.

As we known, QNA is designed to describe lattice constants, or volumes, very accurately and high accuracy in volume is expected to improve the description of other quantities as well. Here we show the so called “volume effect” on the formation energies. We calculate the formation energies at the PBE equilibrium volumes using QNA energies. Similarly, the PBE formation energies are calculated at the QNA equilibrium volumes. The results are shown in Fig. 5.2 and
Figure 5.3: Formation energies of two alloy systems [Cu-Au (a) and Pd-Au (b)] using different methods (PBE and QNA). The solid red circles and solid blue squares represent the EMTO calculations using PBE and QNA, respectively. The open red circles denote the calculations by PAW method. The open blue squares denote experimental values of ordered Cu-Au [12] and Pd-Au [72]. The cross circles (square) represent the formation energies at PBE (QNA) equilibrium volumes.

5.3. It is seen that the “volume effect” cannot explain the large improvement of the QNA results with respect to the PBE results. Further research is needed to understand the true reason behind this interesting effect.

In order to verify that the ordered Cu-Au system is not a special case, we also calculate the formation energies of Pd$_3$Au, PdAu-L1 and PdAu$_3$ (Fig. 5.3 (the lower panel)) using PBE and QNA methods. The Pd-Au system also shows $L1_2$-$L1_0$-$L1_2$ as stable ordered phases. The PBE and QNA formation energies are in good agreement with each other, and both are in line with the experiment [72]. Based on the two cases, we can get the conclusion that QNA can always give highly accurate formation energy.
5.2 Elastic properties of disordered Cu$_{1-x}$Au$_x$ alloys

5.2.1 Lattice parameters

In the Figure 5.4, we show the lattice constants of random Cu$_{1-x}$Au$_x$ (0 ≤ $x$ ≤ 100 at.%) alloys as a functional of Au concentration. Calculations were done using CPA and SQS approaches, respectively. It is found that the lattice constants of random Cu$_{1-x}$Au$_x$ alloys increase almost linearly with Au concentration. The calculated trends are consistent with Vegard’s law (shown by dashed lines), considering that the atomic radium of Au is bigger than that of Cu.

Next we address the question of the atomic relaxation effect on the lattice constants in the solid solutions. The CPA and SQS lattice constants without relaxation are in excellent agreement with each other, with the largest error being 0.1% at both ends. When atomic relaxations are performed in the SQS calculations, the lattice constants are slightly decreased between $x = 12.5$ at.% and $x = 87.5$ at.% upon allowing the SQS cell to relax. The maximum deviation is about 0.56% at $x = 37.5$ at.%. This may be regarded a small effect and in most of the case can be neglected.

For the two cases of Ti-Al and Cu-Au alloys, the trends of lattice constants show very different behaviors. Unlike Cu-Au alloys, the Ti-Al lattice param-
eters exhibit an opposite trend relative to Vegard’s rule in the Al-rich side. Furthermore, the formation energies for the two cases with distinct mismatch show different behaviors with and without relaxations. The mismatch in atomic radius is approximately 1.6% for Ti-Al alloys, however, up to about 12.2% for Cu-Au alloys. Therefore, some distinct characteristics are shown out for the two cases.

5.2.2 Formation energy

Next I turn to the formation energy of Cu$_{1-x}$Au$_x$ random solid solution. The formation energies are calculated according to Eqn. 5.2. All energies are computed at the corresponding theoretical equilibrium volumes. In Fig. 5.5, the formation energies are shown as functions of composition obtained by CPA and SQS methods. One can see that the calculated energies from CPA and SQS are in good agreement with each other when the atomic positions are not relaxed. The maximum of $\Delta E$ is approximately 52.72 meV/atom at $x = 37.5$ at.%. In figure, I also display previous theoretical results \cite{10, 67, 70, 73} for random Cu$_3$Au, CuAu and CuAu$_3$ obtained by different methods. There is a general good agreement between various theoretical predictions for rigid fcc lattice.

As shown in Fig. 5.5, the relaxed formation energies are lower substantially relative to the unrelaxed data. The largest reduction is about 52.79 meV/atom at $x = 37.5$ at.%. At $x = 50$ at.%, $\Delta E$ shows minimum at about -7.1 meV/atom, meaning that the relaxed random CuAu is stable with respect to the end members. We notice that our relaxed energies for Cu$_3$Au and CuAu$_3$ are about 0.38 meV/atom and -3.83 meV/atom which are consistent with 5.5 meV/atom and -5.2 meV/atom obtained by Ozoliņš \cite{10}, respectively. The large difference between relaxed and unrelaxed formation energies is connected to the large elastic strain energy that develops in rigid fcc lattice due to the large volume mismatch between Cu and Au atoms.

5.2.3 Single-crystal elastic constants

For a perfectly cubic lattice, the number of independent elastic constants is three ($C_{11}$, $C_{12}$ and $C_{44}$). This should be the case for a perfectly random structure when considering on a relatively large length scale. However, due to the small size of the SQS supercells, the symmetry is usually broken and thus the number for the elastic constants is increased. Similar to the Ti-Al random alloys, the symmetry for the elastic tensor by making an average between individual elastic parameters. All the individual elastic constants of random Cu$_{1-x}$Au$_x$ alloys are calculated by SQS. The data of $C_{ij}$ are collected in the manuscript of disordered Cu-Au alloys (paper II). The individual elastic constants are quite scattered due to the low symmetry of the present SQS structures. The largest difference between the three $C_{12}$ values is about 20 GPa at $x = 50$ at.%. This scatter accounts to a relative error of $\sim 17\%$. There is no systematic trend based merely on individual elastic constants.

The average elastic constants $\overline{C}_{ij}$ calculated by SQS with and without LLD are shown in Figure 5.6. In the thesis, $C_{11}$, $C_{12}$ and $C_{44}$ in SQS calculations refer to the averaged elastic constants. One can see that in general both $\overline{C}_{ij}$ show a much smoother variation with composition compared to the individual
5.2 Elastic properties of disordered Cu$_{1-x}$Au$_{x}$ alloys

Figure 5.5: Formation energies for random Cu$_{1-x}$Au$_{x}$ alloys plotted as a function of composition. Results are shown for both SQS (relaxed and unrelaxed) and CPA calculations. Separate symbols show previous theoretical results from Refs. [10, 67, 70, 73]

Figure 5.6: Elastic constants of random Cu$_{1-x}$Au$_{x}$ as a function of composition. Results are shown for both SQS (relaxed and unrelaxed) and CPA calculations.
elastic constant. The trends followed by the relaxed and unrelaxed parameters are relatively close to each other. Nevertheless, compared to the alloying effects and compared to the differences between the individual elastic constants, the effect of local lattice distortion on the single-crystal elastic constants seems to be relatively small.

The single crystal elastic constants of random Cu$_{1-x}$Au$_x$ (0 $\leq$ x $\leq$ 100 at.%) alloys obtained from CPA calculations are also plotted in Figure 5.6. In general, the elastic constants calculated from CPA total energies are in good agreement with $C_{11}$ and $C_{12}$ obtained by averaging the SQS results. The CPA $C_{44}$ is also quite substantial and comparable with that from the SQS calculations, although there is a little larger at the Cu-rich side. The biggest deviation for $C_{44}$ between CPA and SQS is about 18.9 GPa at x = 12.5 at.%. Nevertheless, the elastic constants obtained from CPA and SQS show very similar composition dependence. As noticed above, the SQS results remain almost unchanged when taking local lattice relaxations into consideration. Based on the consistency of the trends obtained with both techniques CPA and SQS, one can see that our results catch in a reliable way the chemistry behind the composition dependence of the elastic constants.

5.2.4 Electron density of states

In this section, I compare the electronic density of states (DOS) calculated using CPA and SQS. In Fig. 5.7, we show that the total DOS for random fcc Cu$_{1-x}$Au$_x$ alloys at compositions 25 at.%, 50 at.%, 75 at.%, as well as those obtained for the end numbers. These alloy systems have been extensively studied in the framework of CPA and SQS with and without relaxing atomic positions. As can be seen the results for DOS are in overall agreement.

The DOS for the fcc Cu calculated in the framework of EMTO and VASP are in good agreement. However, in comparison to the Au DOS calculated by VASP, the CPA DOS bandwidth becomes wider by about 0.2 eV. The reason for the discrepancy is the spin-orbit coupling effect (SOC). The impacts of SOC is large on the DOS of the heavy 5$d^-$Au, but negligible for the lighter 3$d$ Cu. We notice that the effect of SOC is not to be taken into account within the present EMTO calculations. The results for Cu and Au obtained by VASP are consistent with the previous calculations [74]. In addition, the bandwidth of Au was found to be larger than that of Cu. This indicates that the Cu-Cu atomic interaction is stronger than that of Au-Au, which is indeed the case as reflected e.g. by the bulk moduli of these two metals.

For random Cu$_3$Au, CuAu and CuAu$_3$ alloys, the CPA and SQS DOS are in line with each other. The more localizing 3$d$ orbital for Cu is insensitive to the local environment, whereas the 5$d$ orbital of Au is delocalized and varies easily with the local environment. In the Cu-Au alloys, the charges are transferred from 5$d$ Au atoms to 3$d$ Cu atoms (lower electron density).

The DOS bandwidths of random Cu$_3$Au, CuAu and CuAu$_3$ alloys become narrower due to the local lattice relaxation. From the viewpoint of bond strength, the narrower bandwidth shows the stronger interatomic interaction due to the lattice relaxation. It is consistent with changes in the lattice constants (Fig. 5.4). The bandwidth narrowing is in good agreement with the previous theoretical values determined by the local Au DOS [75].
5.2 Elastic properties of disordered Cu$_{1-x}$Au$_x$ alloys

Figure 5.7: Total electronic density of states from SQS and CPA calculations: (a) $x = 0.00$; (b) $x = 25$ at.%; (c) $x = 50$ at.%; (d) $x = 75$ at.%; (e) $x = 100$ at.%. For pure Cu and Au, the DOS was calculated by EMTO.
The variations for the electron density of states is similar between order structure and disorder alloys [11, 75]. The lattice constants of Cu$_{1-x}$Au$_x$ affect the variation of band position and widths. The atomic radius of Au is bigger than that of Cu, therefore, it will broaden the $d$ bands.
Chapter 6

Concluding Remarks and Future Work

In this thesis, first principles calculations based on coherent potential approximation (CPA) and special quasi-random structure (SQS) have been performed to investigate the elastic properties of disordered (random) metallic alloys. *Ab initio* total energies are obtained within the framework of Exact Muffin-Tin Orbitals (EMTO) and Vienna *Ab initio* Simulation Package (VASP).

The effect of local lattice distortion on the lattice constants, elastic constants and density of states is considered. The corresponding electronic structures and bonding characteristic with and without atomic relaxation are discussed.

Based on the results presented in this thesis, we can conclude the following: (a) the calculated results for CPA and SQS are consistent with each other; (b) the influence of local lattice relaxation on the lattice constants is negligible. For random Ti-Al alloys, the lattice constants increase slightly between 37.5 at.% and 87.5 at.% Al when taking the relaxation into account, however, for random Cu-Au, the relaxed lattice constants have a small reduction; (c) comparing the energies without relaxation, the relaxed formation energies usually decrease. The deviations between relaxed and unrelaxed energies are large for random Cu-Au. That means that the relaxation effect is strong for large atomic mismatch systems, e.g. about 12.2% for Cu-Au; (d) the results show that the relaxation effects on the elastic constant are negligible. Furthermore, we calculate the formation energies of ordered Cu-Au system. It shows that QNA gives excellent values compared with experimental results, whereas a large deviation arises for PBE.

In my future work, I will focus on the formation energy and elastic parameters of other alloy systems, for example, I want to investigate the influence of magnetism on the elastic properties of alloys, etc. I will extend the present study to more complex paramagnetic alloys including some high-entropy alloys. A more comprehensive assessment of the QNA for metallic alloys will also be part of my future efforts.
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