The Effect of Long Range Order on Elastic Properties of Alloys

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Abstract

*Ab initio* alloy theory, formulated within the exact muffin-tin orbitals method in combination with the coherent-potential approximation, is used to determine the effect of long range order on the elastic properties. The lattice parameters and single-crystal elastic constants of Cu$_3$Au are calculated for different partially ordered structures ranging from the fully ordered $L1_2$ to the random face centered cubic lattice. Special attention is put on the chemical and magnetic effects and on the interplay between these two degrees of freedom.

For non-magnetic Cu$_3$Au, it was found that the lattice parameters and single-crystal elastic constants follow a clear trend with the degree of chemical order: namely, $C_{11}$ and $C_{12}$ decrease slightly, whereas $C_{44}$ remains nearly constant with increasing disorder. As none of the single-crystal elastic constants were modified significantly due to the long-range-order, the polycrystalline elastic moduli of Cu$_3$Au also keep nearly constant upon ordering. The Debye temperature does not show a strong chemical order dependence either. Using the calculated Debye temperatures, we find that for the entropy change upon order-disorder transition varies between $-0.018 \, k_B$ and $0.022 \, k_B$, the upper value being surprisingly close to $0.023 \, k_B$ observed in experiments.

However, some of the elastic constants of ferromagnetic Ni$_3$Fe, adopting the same crystal lattice as Cu$_3$Au, were affected considerably. For the lattice parameter $a$, the main effect of magnetism is concentrated in the chemically disordered region, with long-range order parameter $S$ below $\sim 0.6$ and the effect gradually disappears with increasing $S$. In the ferromagnetic state, the lattice parameter is almost constant as a function of the degree of order. Out of the three single-crystal elastic constants, only $C_{11}$ and $C_{12}$ are found to be affected by magnetism in the ordered state, however, their combined effect results in a nearly constant bulk modulus as a function of $S$. $C_{44}$ changes slightly with $S$ and magnetic state. The tetragonal shear elastic constant $C'$, the Young’s modulus $E$ and the shear modulus $G$ increase significantly with the degree of order in the ferromagnetic state, but the effect becomes weak as the system approaches the random regime. Especially the $C'$ shear elastic constant depends strongly on the magnetic state and the degree of order. As a result, the Zener anisotropy ratio $C_{44}/C'$ and the Possion’s ratio are strongly affected by the long-range order in the ferromagnetic state. Nevertheless, the actual values for the Pugh ratio and the Cauchy pressure remain far from their critical values, indicating that the ductility of Ni$_3$Fe is not influenced by the chemical/magnetic ordering. Interestingly, the ferromagnetic $L1_2$ system possesses $\sim 5.4\%$ larger elastic Debye temperature than the paramagnetic one, which in turn has similar $\Theta_D$ as the chemically disordered face centered cubic phase being in either ferro- or paramagnetic state. The implications of the chemical/magnetic order on the mechanical properties and order-disorder transition is discussed.
Preface

List of included publications:

I The effect of long range order on the elastic properties of Cu$_3$Au

II *Ab initio* investigation of the elastic properties of Ni$_3$Fe

III Large magneto-chemical-elastic coupling in highly magnetostrictive Fe-Ga alloys

Comment on my own contribution:
Paper I: all calculation and data analysis, literature survey; the manuscript was written jointly.
Paper II: all calculation and data analysis, literature survey; the manuscript was written jointly.
Paper III: part of calculations and data analysis, literature survey; the manuscript was written jointly.

List of paper not included in the thesis:

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Chapter 1

Introduction

The elastic properties play an indispensable role in the application of an alloy. The elastic performance is sensitive to various internal and external conditions, such as alloying addition, temperature, applied force, fatigue, ordering and so on. In this thesis, we focus on the ordering effect which are important for the obvious reason namely that ordering rearranges the atomic positions. Ultimately, it is the interaction between the individual atoms that determines the elastic properties. Therefore, shedding light on how elastic constants respond to the ordering effect is particularly important. On the other hand, the coupling between magnetic moment and ordering effect make this problem more complex. In the Ni$_3$Fe system, Himuro et al. [1] reported that the magnetic ordering increases the stability of the $L1_2$ phase and the chemical ordering stabilizes the ferromagnetic state. Likewise, the coupling between magnetic and chemical ordering also affects the mechanical properties of FeGa system. Ref. [2] shows B$_2$-like chemical ordering of FeGa was thought to be the primary reason for the strong enhancement of magneto-elastic coupling.

It is well known that multi-component systems forming a random solid solution at high temperature may transform to an ordered single phase upon lowering the temperature. Some experimental [3, 4] and theoretical [5] works have shown that the ordering transformation may have sizable effects on the basic properties of alloys ranging from the electronic structure to macroscopic observable quantities [6].

The above question is highly relevant for both experimental and theoretical research. A rapidly cooled sample not reaching its thermodynamic equilibrium can very well possess a significant degree of disorder even at low temperatures. As a result, the measured elastic parameters can differ for quenched and annealed cases. A significant ordering effect in the elastic constants (ultimately in the phonon spectra) could alter the measured intrinsic temperature and alloying effects and affect the chemical order-disorder transition [7, 8]. On the theoretical side, most of the available ab initio calculations of the elastic properties have been performed for ordered structures, and thus their relevance for the actual partially or fully disordered solids is questionable. However, the ordering degree is difficult to control and to measure accurately in experiment. In theoretical simulation, the disordered alloys may be represented by big super cells containing minimum hundreds to thousands atoms. Further, it is difficult to define the
ordering degree in super cells calculations. Based above difficulties, the ordering effect on the mechanical properties are still not clear. Fortunately, with the advent of the modern \textit{ab initio} computational alloy theory [9–12], one is now able to model the random regime as well. Numerous applications demonstrate the success of this approach when focusing on chemically and magnetically disordered solid solutions [10, 13–24]. However, the complete ignorance of the ordering effects in such alloy studies may also lead to inconsistences between theory and observations. One question of particular interest is to what extent the mechanical characteristics of metallic alloys are influenced by the degree of chemical ordering, and to what extent the magnetic effect would change the ordering effect.

The present thesis aims to provide a comprehensive understanding on the ordering effect and give a systematic theoretical assessment in combination with some previous studies. In Chapter 4, the effect of long range order on the elastic constants of Cu$_3$Au is discussed. For non-magnetic material, ordering only have second order effect on the mechanical properties. In Chapter 5, we introduce the magnetic influence through studying the elastic properties of Ni$_3$Fe. The results show that in magnetic alloys the effect of long range order on the elastic constants follows a more complex picture. In addition, we show that in the FeGa system, $C'$ is very sensitive to magnetic state on the ordering effect.
Chapter 2

Elastic Properties of Materials

Elastic properties are characterized by single-crystal and poly-crystalline elastic constants. In *ab-initio* calculation, single-crystal elastic constants can be extracted from constitutive stress-strain relations or internal energy-strain relations. In this thesis, the latter one is applied. Polycrystalline elastic constants are estimated from single-crystal elastic constants by some effective theoretical averaging methods [12, 25]. In ab initio studies, the effect of temperature, local disorder (only long range disorder is considered using CPA which would be referred in the following chapters), and local lattice relaxations are often omitted.

2.1 Single-Crystal Elastic Constants

The adiabatic elastic constants are expressed as the second order derivatives of the internal energy with respect to the components of the strain tensor $\varepsilon_{kl}(k, l = 1, 2, 3)$, viz.,

$$C_{ijkl} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}},$$

(2.1)

where $E$ stands for the internal energy and $V$ denotes the atomic volume. The elastic constants form a fourth-rank tensor, which can be arranged in a $6 \times 6$ matrix with maximum 21 independent elements [26, 27]. In a cubic lattice there are only three independent elastic constants which are $C_{11}$, $C_{12}$, and $C_{44}$. $C_{11}$ and $C_{12}$ are connected to the bulk modulus ($B$) as

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

(2.2)

and to the tetragonal shear constant ($C'$) as

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

(2.3)

Therefore, we are free to choose any three independent ones out of $C_{11}, C_{12}, C_{44}, C'$ and $B$. In the present thesis, we choose $B$, $C'$ and $C_{44}$, then the other two ($C_{11}$ and $C_{12}$) can be extracted using the equations (2.2) and (2.3).
Figure 2.1: Illustration of the orthorhombic and monoclinic distortion of the fcc structure. oabc represents the fcc coordinate system. The orthorhombic distortion was applied through changing the length of a, b, and c. Monoclinic distortion was accomplished as an orthorhombic one in (a’b’c’)coordinate system by changing the length of a’, b’, and c’.

The bulk modulus and the equilibrium volume are derived from the equation of state, obtained by fitting the total energy data calculated for seven different cubic lattice constants (a) by a Morse-type of function [28]. Since the total energy depends on volume much more strongly than on small lattice strains, volume-conserving distortion applied on the unstrained conventional cubic unit cell are usually more appropriate to calculate $C'$ and $C_{44}$. Here, we employ the following orthorhombic distortion ($D_o$) for $C'$ calculations:

$$D_o + I = \begin{pmatrix} 1 + \delta_o & 0 & 0 \\ 0 & 1 - \delta_o & 0 \\ 0 & 0 & \frac{1}{1 - \delta_o} \end{pmatrix},$$

(2.4)

which leads to the energy change

$$\triangle E(\delta_o) = 2V C' \delta_o^2 + O(\delta_o^4),$$

(2.5)

where $O$ stands for the neglected terms. The shear modulus $C_{44}$ can be obtained
2.2 Polycrystalline Elastic Constants

Polycrystalline materials in which the single crystal grains are randomly oriented, can be considered as quasi-isotropic or isotropic from the point of view of macroscopic statistics. Due to the limitation of \textit{ab initio} simulations on polycrystalline materials, we deduce these parameters from the obtained single-crystal elastic constants using some theoretical averaging methods \cite{25}. One of the most

from the monoclinic distortion

\[
D_m + I = \begin{pmatrix}
1 & \delta_m & 0 \\
\delta_m & 1 & 0 \\
0 & 0 & \frac{1}{1-\delta_m^2}
\end{pmatrix}, \quad (2.6)
\]

and

\[
\triangle E(\delta_m) = 2VC_{44}\delta_m^2 + O(\delta_m^4). \quad (2.7)
\]

Both distortions are schematically shown in Fig. 2.1. In order to suppress the error, the total energy \(E(\delta)\) are computed for six small distortions \(\delta = 0, 0.01, ..., 0.05\). Then the elastic constants are extracted by linear fitting of internal energy \(E\) with respect to \(\delta^2\).

Bulk modulus and equilibrium volume is derived from the equation of state. In my works, the total energies are fitted by an exponential Morse function

\[
E(\omega) = a + be^{-\lambda\omega} + ce^{-2\lambda\omega} \quad (2.8)
\]

in which \(\omega\) is the average Wigner-Seitz radius and \(\lambda, a, b,\) and \(c\) are Morse fitting parameters which are independent of each other. For \(V = 4\pi\omega^3/3\), the pressure \(P\) can be expressed by

\[
P = -\frac{\partial E(V)}{\partial V} = \frac{1}{4\pi\omega^2} \frac{\partial E}{\partial \omega} = \frac{x\lambda^3}{4\pi(\ln x)^2} (b + 2cx), \quad (2.9)
\]

where

\[
x = e^{-\lambda\omega}. \quad (2.10)
\]

The equilibrium Wigner-Seitz radius, defined by \(V_0 = 4\pi\omega_0^3/3\), is obtained from the condition \(P(\omega_0) = 0\) as

\[
\omega_0 = -\frac{\ln x_0}{\lambda} \quad \text{with} \quad x_0 = -\frac{b}{2c}. \quad (2.11)
\]

From Eq. (2.9), we get the bulk modulus as a function of the Wigner-Seitz radius as

\[
B(\omega) = -\frac{x\lambda^3}{12\pi \ln x} [(b + 4cx) - \frac{2}{\ln x}(b + 2cx)] \quad (2.12)
\]

which gives the equilibrium state bulk modulus at \(\omega_0\)

\[
B_0 = -\frac{cx_0^3\lambda^3}{6\pi \ln x_0} \quad (2.13)
\]

2.2 Polycrystalline Elastic Constants
effective and widely used method is the Hill average which takes the arithmetic average of the results of Voigt, and Reuss estimation,

\[ B_H = \frac{B_V + B_R}{2}, \quad \text{and} \quad G_H = \frac{G_V + G_R}{2}, \quad (2.14) \]

where

\[ B_V = \frac{C_{11} + 2C_{12}}{3}, \quad \text{and} \quad B_R = B_V, \quad (2.15) \]

and

\[ G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad \text{and} \quad G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}, \quad (2.16) \]

where subscripts H, V and R represent Hill, Voigt, and Reuss average method. For an isotropic polycrystalline material, only two independent elastic constants are used to characterize its elastic properties. Young’s modulus (\(E\)) and Poisson’s ratio (\(\nu\)) can be expressed by

\[ E = \frac{9GB}{3B + G}, \quad \text{and} \quad \nu = \frac{3B - 2G}{6B + 2G}. \quad (2.17) \]

In an isotropic polycrystalline material, the sound velocity is isotropic except that the longitudinal branch and two transversal branches are different. The longitudinal velocity can be expressed by \(G\) and \(B\)

\[ \rho v_L^2 = B + \frac{4}{3}G, \quad (2.18) \]

and the transversal velocity is related to the polycrystalline \(G\)

\[ \rho v_T^2 = G, \quad (2.19) \]

where \(\rho\) is the density. These velocities are used in the conventional Debye model with Debye temperature defined as

\[ \Theta_D = \frac{\hbar}{k_B} \left( \frac{18\pi^2}{V} \right)^{1/3} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{-1/3}, \quad (2.20) \]

\(\hbar\) and \(k_B\) are the reduced Planck constant and the Boltzmann constant respectively.

### 2.3 The Definition of Long-range-order Degree

In the ordered \(L1_2\) structure, there are three A atoms sitting at the face centered positions and one B atom located at the origin. In partially ordered structures, the degree of long-range order is controlled by changing the composition at the face centered positions as \(A_{1-x}B_x\) and at the origin as \(A_{3x}B_{1-3x}\), represented by the formula unit \((A_{1-x}B_x)3(A_{3x}B_{1-3x})\). Accordingly, we changed \(x\) from 0 (corresponding to \(A_3B\) in the structure of \(L1_2\)) to 0.25 (corresponding to the completely disordered \(A_{0.75}B_{0.25}\) alloy in the fcc structure). In my work, we focus on the theoretical study of cubic systems which have fcc sites occupation
in the completely disordered state, and $L1_2$ structure in the fully ordered state. First, we define the degree of order $S$,

$$S = (p - r) / (1 - r)$$ \tag{2.21}$$

$$p = 1 - 3x$$ \tag{2.22}$$

where $r$ is the concentration of B atoms in the system, and $p$ represents the probability of finding an B atom at corner sites in the $L1_2$ structure.

### 2.4 Order-disorder Transition Temperature

In the completely disordered system, the fcc sites are occupied by A and B atoms with probabilities $3/4$ and $1/4$, respectively; in the ordered $L1_2$ structure, the corner sites are occupied by atom A and the face centered sites by atom B. The order-disorder transition temperature ($T_o$) can be estimated using the Bragg-Williams-Gorsky approximation [29]. According to that, the degree of order $S$ could be expressed as

$$S(U,T) = 1 - \frac{[4p(1 - r)(e^p - 1) + 1]^{1/2} - 1}{2r[1 - r(e^p - 1)]}, p = U/k_BT,$$ \tag{2.23}$$

where $T$ is the temperature and $U$ is an average increment in the potential energy when one B atom is interchanged with a A atom (interchange will not affect the degree of order $S$). Assuming a linear relationship between the order parameter and the energy cost $U$, viz. $U = U_0S$, where $U_0$ is the maximum interchange energy corresponding to $S = 1$, one can solve Eq. (2.23) for a given $T$. For the critical temperature of the order-disorder transition (where $S$ vanishes) we get

$$T_o \approx 0.21U_0/k_B.$$
Chapter 3

Theoretical Methodology

3.1 First-Principles Theory of the Electronic Structure

Solids are composed of numerous positively charged nuclei and negatively charged electrons and the interactions among these particles mainly decide most of the properties of materials. In order to understand materials properties by calculating the interaction energy, one first has to solve the multi-particle time-independent quantum-mechanical Schrödinger equation

\[ \hat{H}\Psi = E\Psi, \] (3.1)

where \( \Psi = \Psi(r_1, \ldots, r_N, R_1, \ldots, R_M) \) denotes the many-body wave function for \( N \) electrons and \( M \) nuclei with positions \( r_i, i = 1 \ldots N, \) and \( R_j, j = 1 \ldots M, \) respectively.

The many body Hamiltonian \( \hat{H} \) is \([30]\)

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla^2 r_i - \frac{\hbar^2}{2M} \sum_{j=1}^{M} \nabla^2 R_j - \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{e^2 Z_j}{|r_i - R_j|} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j}^{M} \frac{e^2 Z_i Z_j}{|R_i - R_j|}, \] (3.2)

where \( \hbar \) stands for the reduced Planck constant, \( e \) denotes the elementary charge, \( m_e \) is the mass of electrons and \( M_j \) are the masses of the nuclei with the atomic number \( Z_j \). The first term and the second term in the previous equation are the kinetic energy operators for electrons and nuclei, respectively. The third term describes the interaction between electrons and nuclei (Coulomb potential). The last two terms express the electron-electron and nucleus-nucleus interactions.

If we want to directly solve this equation, we would meet two main problems. One is that we have roughly \( 10^{22} \) nuclei and \( 10^{23} \) electrons even in a solid material with the volume of \( 1 \text{cm}^3 \). The other serious one arises from the two body interaction term which rules out the method of separation of variables. Therefore, we have to apply some approximations and simplify the many-body
equation. The first step to overcome these obstacles is given by the Born-Oppenheimer (BO) approximation [31]. Given that nuclei, which are much heavier than electrons ($M_j \gtrsim 1000 m_e$), move so slow that all electrons can respond to the nuclei moving instantaneously. We can assume that on the timescale of nuclear motion, electrons are moving around some fixed nuclei. Based on this assumption, we will take the variable separation

$$\Psi = \Psi(r_1, \ldots, r_N, R_1, \ldots, R_M) \approx \Psi(r_1, \ldots, r_N) \Theta(R_1, \ldots, R_M), \quad (3.3)$$

Substitute Eq. (3.3) into Eq. (3.1), we got

$$\left( -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_r^2_{r_i} + \sum_i^N \sum_j^M e^2 Z_j \left| \frac{1}{r_i - R_j} \right| \right) \Psi = (\hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}) \Psi = E \Psi, \quad (3.4)$$

where the operators $\hat{T}$, $\hat{V}_{\text{ext}}$ and $\hat{V}_{\text{ee}}$ denote the kinetic energy, electron-nucleus interaction energy, and electron-electron interaction energy, respectively. The wave function $\Psi$ in the previous expression depends only parameterically on $R_j$.

After solving the equation (3.4), the nucleus Schrödinger equation can be dealt with the potential energy $V = U_{R_i R_j} + E$.

### 3.2 Density Functional Theory

Even for a system of $N$ interacting electrons moving in a static external potential (Eq. (3.4)), it is rather difficult to solve the Schrödinger equation directly. The very powerful tool to solve Eq. (3.4) for the ground state is by means of density functional theory (DFT). Nowadays, most of the electronic structure calculation for solids are based on density functional theory, which was contributed by Hohenberg, Kohn and Sham [30, 32]. Atomic units ($\hbar = m_e = e = 1$) are used throughout. Within DFT, the many-electron problem is reduced to an effective single-electron problem and the electron density $n(r)$ as the functional variable is introduced. DFT is based on two important theorems, which were formulated by Hohenberg and Kohn (HK) [33]:

**Theorem I:** For any system of interacting particles in an external potential $V_{\text{ext}}(r)$, the potential is determined uniquely, except for a constant, by the ground state density $n_0(r)$.

**Theorem II:** A universal functional for the energy $E(n(r))$ in terms of the density $n(r)$ can be defined, valid for any external potential $V_{\text{ext}}(r)$. For any particular $V_{\text{ext}}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$.

The first theorem indicates that there is a one-to-one mapping between the ground state electron density and state ground state wave function and the second one shows that if we know the true functional form, then the ground
state energy could be got by variational principle. Using the HK theorems, the energy functional can be written as

\[ E(n(r)) = F(n(r)) + \int V_{\text{ext}}(r)n(r)dr. \] (3.5)

The two terms on the right hand side are the universal functional of the electron density and the Coulomb interactions between the electrons and the nuclei. The Hohenberg-Kohn functional \( F(n(r)) \) is called universal functional because it does not depend on the particular form of \( V_{\text{ext}} \).

Although HK theorems give us a powerful navigation from Schrödinger equation to its answer, we still don’t know the explicit form of the functional \( F(n(r)) \). A practical way to write down the functional is in terms of the single-electron wave functions, \( \Psi_i(r) \) which are connected with electron density in the form

\[ n(r) = \sum_i |\psi_i(r)|^2. \] (3.6)

Then the energy functional can be expressed as

\[ E[\Psi_i] = E_{\text{known}}[\Psi_i] + E_{\text{XC}}[\Psi_i], \] (3.7)

where the known part \( E_{\text{known}}[\Psi_i] \) includes kinetic energy, the Hartree energy and external potential of a non-interacting system of electrons. And \( E_{\text{XC}}[\Psi_i] \) is everything else, which mainly contains two parts, kinetic energy correction due to the independent electron approximation and exchange correlation corrections between electrons. Sometimes, electron self interaction correction is also included into \( E_{\text{XC}}[\Psi_i] \). By applying the variational principle, the famous KS single-particle equations are obtained [30]

\[ \left[ -\frac{1}{2} \nabla_i^2 + V_{\text{eff}}(n(r); r) \right] \psi_i(r) = \epsilon_i \psi_i(r). \] (3.8)

The effective potential is

\[ V_{\text{eff}} = V_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|} dr' + V_{\text{xc}}(r), \] (3.9)

where the exchange-correlation potential is defined as \( V_{\text{xc}} = \frac{\delta E_{\text{xc}}(n(r))}{\delta n(r)} \).

The electronic energy (total energy) is given by

\[ E = \sum_i \epsilon_i - E_H + E_{\text{xc}} - \int V_{\text{xc}}(r)n(r)dr. \] (3.10)

To this step, the only difficulty left is how to specify the exchange-correlation energy functional defined in Eq. (3.7). In fact, although the existence of exchange-correlation is guaranteed by the Hohenberg-Kohn theorem, we still don’t know its true form due to its complexity. Fortunately, there is one special situation where the exchange-correlation could be produced exactly: the uniform electron gas. In this case, the electron density is constant everywhere. It seems too imagination to approximate the real materials electron distribution. However,
this model provides a practical way to solve the Kohn-Sham equation finally. In order to do this more reasonably. The exchange-correlation potential at each \( r \) is approximated from the uniform electron gas model using the same electron density at this point of the uniform gas density

\[
V_{xc}(r) \approx V_{xc}^{\text{electron gas}}[n(r)].
\]  

For a non-spin-polarized system, the local-density approximation (LDA) for the exchange-correlation energy is written as

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

where \( \epsilon_{xc} \) is the exchange-correlation energy density. The LDA gives us a useful way to completely define the Kohn-Sham equation, but it is crucial to remember that the results from these equations do not exactly solve the true Schrödinger equation because we are not using the true exchange-correlation functional [33]. However, LDA was still found to reproduce the ground properties of many systems with high accuracy. Especially for some bulk properties of 4d and 5d transition metals and oxides, first-principle calculation based on LDA can give a very good description [30, 32]. Based on LDA, many kinds of generalized gradient approximation, which include the information about the local electron density and the local gradient in the electron density \( \nabla n(r) \), have been developed:

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

According to our tests, for most of the Fe-based alloys, GGA produced much better results than LDA. The LDA in the parameterization of Perdew and Wang [34] and the GGA in the parameterization of Perdew, Burke and Ernzerhof [35] are two widely used exchange-correlation functionals.

### 3.3 Exact Muffin-Tin Orbitals Method

Based on DFT with some reasonable approximations, the many-body Schrödinger equation is finally transferred into the single-electron KS equation with effective potential. In order to solve KS equation, lots of methods were developed. Exact Muffin-Tin Orbitals (EMTO) method, as the 3rd generation Muffin-Tin method, was applied in the present thesis. The EMTO method is an improved screened Korrninga-Kohn-Rostoker (KKR) method [36], where the full potential is represented by overlapping MT potential spheres. Inside these spheres, the potential is spherically symmetric and constant in between.

Within the overlapping muffin-tin approximation, the effective single-electron potential, referred to as MT potential \( V_{MT} \), is approximated by spherical potential wells \( V_R(r_R) - V_0 \) centered on lattice sites \( R \) with potential radius \( s_R \) plus a constant potential \( V_0 \) (muffin tin zero),

\[
V_{eff} \approx V_{MT} = V_0 + \sum_R [V_R(r_R) - V_0],
\]
3.4 Coherent Potential Approximation

with the notation \( r_R = r - R, r_R = |r_R| \). For the above MT potential, to solve the KS equations, we expand the KS orbital \( \psi_i(r) \) in terms of exact MT orbitals \( \psi_{RL}(\epsilon_i, r_R) \), viz.

\[
\psi_i(r) = \sum_{RL} \overline{\psi}_{RL}(\epsilon_i, r_R) v_{RL,i}^\alpha, \tag{3.15}
\]

where \( v_{RL,i}^\alpha \) are expansion coefficients which are determined from the condition that the expansions are the solution of the KS equations (Eq. (3.8)) in the entire space. \( L \) represents a multi-index, \( L = (l, m) \), where \( l \) and \( m \) are the orbital and magnetic quantum numbers, respectively.

The exact MT orbitals are constructed using different basis functions at different regions of space. Inside the MT potential spheres (\( r_R \leq s_R \)), the partial waves \( \phi_{RL}^\alpha(\epsilon_i, r_R) \) are chosen as the basis functions, which are solutions of the radial scalar-relativistic Dirac equation. In the interstitial region, the screened spherical waves \( \psi_{RL}^\alpha(\epsilon_i-v_0, r_R) \) are employed as basis functions, which can be obtained from the solution of the Schrödinger equation at constant potential \( v_0 \). The boundary condition for the Schrödinger equation are given in conjunction with non-overlapping spheres (hard spheres) centered at lattice sites \( R \) with radii \( a_R (a_R < s_R) \). By means of hard spheres, screened spherical waves are localized in space. The partial waves and screened spherical waves must be connected smoothly. This was accomplished by introducing an extra free-electron wave functions with pure \( lm \) character, by which the connection between the screened spherical waves and the partial waves is obtained. Finally, the exact muffin-tin orbitals are constructed as the superposition of the screened spherical waves, the partial waves and the free electron solution,

\[
\overline{\psi}_{RL}^\alpha(\epsilon_i, r_R) = \phi_{RL}^\alpha(\epsilon_i, r_R) + \psi_{RL}^\alpha(\epsilon_i-v_0, r_R) - \varphi_{RL}^\alpha(\epsilon_i, r_R)Y_L(\hat{r}_R). \tag{3.16}
\]

The total density of the system is obtained by summations of one-center densities, which may be expanded in terms of real harmonics around each lattice site

\[
n(r) = \sum_R n_R(r_R) = \sum_{RL} n_{RL}(r)Y_L(\hat{r}_R). \tag{3.17}
\]

The total energy of the system is obtained via the full charge density (FCD) technique using the total charge density. The space integrals over the Wigner-Seitz cells in Eq. (3.10) is solved via the shape function technique. The FCD total energy is decomposed into the following terms

\[
E_{tot} = E_{kin}[n] + \sum_R (F_{intra}[n_R] + E_{xc}[n_R] + F_{inter}[n]), \tag{3.18}
\]

where \( E_{kin}[n] \) is the kinetic energy, \( F_{intra}[n_R] \) is the electrostatic energy due the charges inside the Wigner-Seitz cell, \( F_{inter}[n] \) is the electrostatic interaction between the cells (Madelung energy) and \( E_{xc}[n_R] \) is the exchange-correlation energy.

3.4 Coherent Potential Approximation

In order to effectively investigate the ordering effect on the elastic properties, one method to deal with the disordered alloys has to be used. At present, three
popular ways, coherent potential approximation (CPA) [37, 38], virtual crystal approximation (VCA) [39] and special quasirandom structures (SQS) [40] are used in lots of scientific studies. Compared to VCA and SQS, CPA has two useful merits which would be essential in my calculation. The first one is that alloys with any proportions of ingredients could be dealt with conveniently. Of course, SQS also can do this job, but relative big super-cell is needed which is unacceptable for people and computer due to its time-consuming. The second one directly asking me to choose CPA undoubtedly is that CPA can more conveniently and accurately reproduce the paramagnetic state comparing with VCA and SQS method.

The CPA was introduced by Soven for the electronic structure problem and by Taylor for phonon in random alloys. Later, Györfy formulated the CPA in the framework of the multiple scattering theory using the Green function technique. The CPA is based on the assumption that the alloy may be replaced by an ordered effective medium, the parameters of which are determined self-consistently. The impurity problem is treated in the single-site approximation. This means that one single impurity is replaced in an effective medium and no information is provided about the individual potential and charge density beyond the sphere or polyhedra around this impurity.

We consider a substitutional alloy $A_a B_b C_c$, where $a$, $b$, $c$ ... stands for the atomic fractions of the A, B, C, ... atoms respectively. The system can be characterized by the Green function $g$ and the alloy potential $P_{alloy}$. There are two main approximations within CPA. First, it is assumed that the local potentials around a certain type of atom from the alloy are the same. Second, the system is replaced by a monatomic set-up described by the site independent coherent potential $\tilde{P}$. According to Green functions, the true Green function $g$ is approximated by the coherent Green function $\tilde{g}$. For each alloy component $i = A, B, C, ...$ a single-site Green function $g_i$ is introduced.

The CPA effective medium was constructed as follows. First, the coherent Green function is calculated from the coherent potential with an electronic structure method

$$\tilde{g} = [S - \tilde{P}]^{-1}, \quad (3.19)$$

where $S$ refers to as the structure constant matrix corresponding to the underlying lattice. The Green functions of the alloy components $g_i$ are determined by substituting the coherent potential of the CPA medium by the atomic potential $P_i$, which is given by

$$g_i = \tilde{g} + \tilde{g}(P_i - \tilde{P})g_i, \quad i = A, B, C, ... \quad (3.20)$$

The previous equation is the Dyson equation in real space. At last, the average of the individual Green functions should reproduce the single-site part of the coherent Green functions, i.e.,

$$\tilde{g} = ag_A + bg_B + cg_C \quad (3.21)$$

Three equations are solved iteratively, and the output $\tilde{g}$ and $g_i$ are used to determine the electronic structure, charge density and total energy of random alloys. The implementation of the CPA in the EMTO method is described in Ref. [12].
Since the impurity problem is solved within the single-site approximation, the Coulomb system of a particular alloy component may contain a non-zero net charge. The effect of charge misfit was taken into account using the screened impurity model (SIM) [41, 42]. According to that, the additional shift in the one-electron potential,

$$\Delta v_{SIM,i}^{R} = -\frac{2\alpha_i}{w}(Q_{R}^{i} - \sum_i c_i Q_{R}^{i}), \quad (3.22)$$

is controlled by the dimensionless screening parameter $\alpha_i$. Here, $Q_{R}^{i}$ is the average number of electrons inside the potential spheres at $R$, $c_i$ the concentration of the alloy component $i$, and $w$ the average atomic radius. The parameter $\alpha_i$ is determined from the average net charges and electrostatic potentials of the alloy components obtained in regular supercell calculations [42]. The corresponding SIM correction to the total energy is

$$E^{SIM} = -\sum_i c_i \frac{\beta \alpha_i}{w} (Q_{R}^{i} - \sum_i c_i Q_{R}^{i})^2. \quad (3.23)$$

The second dimensionless parameter $\beta$ is determined from the condition that the total energy calculated within the CPA should match the total energy of the alloy obtained using the supercell technique. For most of the alloys, the suggested optimal values of $\beta$ and $\alpha_i$ are between $\sim 0.6$ and $\sim 1.2$ [41, 42]. Often, the two SIM parameters $\alpha_i$ and $\alpha \equiv \beta \alpha_i$ are chosen to be the same [12].

### 3.5 Disordered Local Magnetic Moment Model

Paramagnetic state of alloys was modeled applying the CPA technique which is referred to as Disordered Local Magnetic Moment (DLM) [37, 38] model. Within the DLM picture, a binary alloy $A_{1-c}B_c$, for example, in paramagnetic state is described as a four ingredients alloy

$$A_{1-c}B_c(\text{paramagnetic}) = A_{(1-c)/2}^\uparrow A_{(1-c)/2}^\downarrow B_{(1-c)/2}^\uparrow B_{(1-c)/2}^\downarrow, \quad (3.24)$$

where arrows represent different spins orientation. In this way, we could conveniently investigate the paramagnetic state.
Chapter 4

Ordering Effect on the Elastic Properties of Non-magnetic Materials

Ordering effect on the elastic properties largely depend on the magnetic state. In order to extract the pure ordering effect on the elastic properties, we first focus on non-magnetic intermetallic compounds. This Chapter is contributed by supplements I.

4.1 Assessing the Accuracy of the EMTO Method

According to previous study [22, 43], long range order effect on the elastic constants is predicted to be not significant. In order to grasp this minute influence, we establish the accuracy of the EMTO method for the present elementary fcc Cu and Au by comparing the EMTO results with those obtained by full-potential methods [44–49]. Because different exchange-correlation functionals can give quite different results, such comparison is meaningful only if the different methods employ the same exchange-correlation term. The theoretical results listed in Table 4.1 were obtained using PBE (EMTO, PAW, PP) or LDA (EMTO, FPLMTO, LAPW, PP, WIEN97). We find that for both Cu and Au, the present theoretical lattice parameters are in good agreement with those obtained in former calculations. The different sets of single-crystal elastic constants and bulk moduli are also in general close to each other. However, in some cases, like the LDA $C_{44}$ values for Au or the LDA $C_{11}$ values for Cu, the scatter of the theoretical predictions is somewhat more pronounced. We take as typical numerical errors associated with the elastic constant calculations the deviations between the quoted full-potential results obtained using the same exchange-correlation approximation. Within the so defined error bars, the EMTO method may be considered having similar accuracy as the full-potential methods.

Different implementations of the exchange-correlation approximation have significant impact on the calculated equilibrium properties. In order to decide
which functional is the most suitable for the present study, we calculated the equilibrium lattice parameter, bulk modulus and single-crystal elastic constants of fcc Au and fcc Cu using five different exchange-correlation approximations. The results are shown in Table 4.2. For comparison, some experimental values are quoted in the last column. In Table 4.2, the average errors ($\gamma$) of the three single-crystal elastic constants, defined according to

$$\gamma = \sqrt{\frac{\sum_{ij} (C_{ij}^{\text{(EMTO)}} - C_{ij}^{\text{(Expt.)}})^2}{3}} \quad (4.1)$$

are also listed.

A comparison between the calculated results and the experimental data in Table 4.2 shows that for Cu all gradient-level approximations yield results in reasonable agreement with the experimental values. This is due to the fact that the volume effect on elastic constants is generally quite significant. The lattice parameter obtained using LDA deviates from the experimental value by $\sim 2.1\%$, whereas the other approximations give lattice parameters close to the experiment. In the case of Au, the PBE results deviate most from the experimental values, the other functionals yield significantly better single-crystal elastic constants. This is due to the fact that PBE strongly overestimates the lattice parameter of Au. Based on the above analysis, PBEsol and AM05 are those approximations which give the smallest error in $C_{ij}$ and thus all of these approximations might be suitable for the present investigation. Considering, however, that PBEsol is a gradient-level functional designed especially for solids, we selected this approximation for the rest of our work.

### 4.2 The Determination of SIM Parameters

The SIM parameters were optimized within the framework of the same computational approach as the one employed for the CPA calculations. We adopted a Special Quasi-random Structure (SQS) [40, 53] for the Cu$_3$Au system containing 16 atoms per unit cell and computed the total energy for three different cubic (fcc) lattice constants ($a = 3.687, 3.764$ and $3.832$ Å) using the EMTO method. Then we compared the SQS total energy to those obtained by CPA using different SIM parameters. For this optimization, we adopted the PBEsol functional and for the sake of simplicity we assumed $\alpha_i = \alpha$. The results are summarized in Fig. 4.1. For the "optimal" SIM parameter we find $\alpha = 0.8865$ at $a = 3.697$ Å, $\alpha = 0.9041$ at $a = 3.764$ Å, and $\alpha = 0.9175$ at $a = 3.832$ Å. The SIM parameter linearly but weakly depends on the fcc lattice constant $a$

$$\alpha(a) \approx 0.0392 + 0.2294a, \quad (4.2)$$

where $a$ is expressed in units of Å and the two coefficients were obtained from the optimal $\alpha$ values calculated for different volumes according to Fig. 4.1. Equation of state calculations performed for $\alpha = 0.8865$ and $\alpha = 0.9041$ and employing the same exchange-correlation approximation lead to equilibrium lattice parameter $\sim 3.75$ Å. Therefore, we conclude that the above simple optimization process results in $\sim 0.9$ for the optimal value for $\alpha$ and $\alpha_i$. Incidentally, for the random Cu-Au system a supercell study, based on the locally self-consistent
4.3 Elastic Properties

Table 4.1: Theoretical lattice parameter \((a)\) (in units of Å) and single-crystal elastic constants \((\text{in units of GPa})\) for fcc Cu and Au obtained using PBE and LDA (shown in parentheses). The quoted theoretical methods are EMTO: present results; PP: ultrasoft pseudopotential method Ref. [46]; PAW: full-potential projector augmented wave method Ref. [47]; FPLMTO: full-potential linear muffin-tin orbitals method \(^a\) Ref. [44] and \(^b\) Ref. [49]; LAPW: full-potential linear augmented plane wave method [45]; and WIEN97: full-potential linear augmented plane wave method Ref. [48]. The FPLMTO\(^a\), LAPW and WIEN97 calculations were performed at the reported experimental lattice parameters.

<table>
<thead>
<tr>
<th>Method</th>
<th>(a)</th>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{44})</th>
<th>(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu EMTO (PBE)</td>
<td>3.639</td>
<td>162.3</td>
<td>124.5</td>
<td>85.7</td>
<td>137.1</td>
</tr>
<tr>
<td>PAW (PBE)</td>
<td>3.637</td>
<td>174.8</td>
<td>122.8</td>
<td>76.3</td>
<td>140.1</td>
</tr>
<tr>
<td>PP (PBE)</td>
<td>3.64</td>
<td>167.8</td>
<td>113.5</td>
<td>74.5</td>
<td>131.6</td>
</tr>
<tr>
<td>EMTO (LDA)</td>
<td>3.520</td>
<td>200.2</td>
<td>151.4</td>
<td>117.4</td>
<td>167.7</td>
</tr>
<tr>
<td>FPLMTO(^a) (LDA)</td>
<td>3.596</td>
<td>193</td>
<td>151</td>
<td>82</td>
<td>165</td>
</tr>
<tr>
<td>LAPW (LDA)</td>
<td>3.61</td>
<td>156</td>
<td>106</td>
<td>80</td>
<td>133</td>
</tr>
<tr>
<td>Au EMTO (PBE)</td>
<td>4.175</td>
<td>147.3</td>
<td>136.1</td>
<td>39.9</td>
<td>139.8</td>
</tr>
<tr>
<td>PAW (PBE)</td>
<td>4.175</td>
<td>159.1</td>
<td>136.7</td>
<td>27.6</td>
<td>137.6</td>
</tr>
<tr>
<td>EMTO (LDA)</td>
<td>4.067</td>
<td>198.2</td>
<td>184.6</td>
<td>55.5</td>
<td>189.1</td>
</tr>
<tr>
<td>PP (LDA)</td>
<td>4.07</td>
<td>202.1</td>
<td>174.2</td>
<td>37.9</td>
<td>183.5</td>
</tr>
<tr>
<td>FPLMTO(^a) (LDA)</td>
<td>4.062</td>
<td>209</td>
<td>175</td>
<td>31</td>
<td>186</td>
</tr>
<tr>
<td>FPLMTO(^b) (LDA)</td>
<td>4.066</td>
<td>201.3</td>
<td>176.1</td>
<td>36.9</td>
<td>184.5</td>
</tr>
<tr>
<td>WIEN97 (LDA)</td>
<td>4.062</td>
<td>190.4</td>
<td>162.8</td>
<td>27.4</td>
<td>172.0</td>
</tr>
<tr>
<td>LAPW (LDA)</td>
<td>4.06</td>
<td>200</td>
<td>173</td>
<td>33</td>
<td>182</td>
</tr>
</tbody>
</table>

Greens function method [54], gave \(\alpha_1 = 0.74\) and \(\beta = 1.16\) [55]. In the present study for Cu\(_3\)Au, two sets of parameters were considered and compared.

4.3 Elastic Properties

In Fig. 4.2, the effect of long-range-order on the lattice parameter and elastic modulus is shown. The results indicate that the lattice parameter decreases and bulk modulus increases with increasing the degree of long-range-order. Similar trends were reported in experiments as well [43], although the experimental changes for both \(a\) and \(B\) are smaller than those predicted by the present theory. Usually the changes in the bulk modulus correlate well with the changes in the equilibrium volume. Namely, larger volume corresponds to smaller bulk modulus and vice versa. In our case, the large negative slope of \(B(x)\) can be ascribed to the overestimated positive slope of \(a(x)\). The room-temperature experimental lattice parameters obtained for the ordered and disordered phases are 3.7426 Å and 3.749 Å, respectively [43]. The corresponding low-temperature (4.2 K) experimental values are 3.7303 Å and 3.7367 Å, the prior being estimated from the room-temperature data using the same linear thermal expansion as the one reported for the disordered phase. The present PBEsol values deviate
CHAPTER 4. ORDERING EFFECT ON THE ELASTIC PROPERTIES OF NON-MAGNETIC MATERIALS

Figure 4.1: Total energies of fcc Cu$_3$Au random alloy calculated using the EMTO-CPA method in combination with PBEsol as a function of SIM parameter $\alpha$. The energies are plotted relative to the total energy of an SQS supercell containing 16 sites. Results are shown for three different lattice constants.

Figure 4.2: Lattice parameter ($a$) and bulk modulus ($B$) of partially ordered Cu$_3$Au as a function of the degree of long-range-order. Theoretical results are shown for $\alpha = 0.9$ and $\alpha = 0.74$. The low-temperature (4.2 K) experimental data are from Ref. [43].
4.3 Elastic Properties

Table 4.2: Lattice parameter ($a$) (in the unit of Å), bulk modulus and single-crystal elastic constants (in the unit of GPa) for fcc Cu and Au using five different exchange-correlation functionals. The experimental data are indicated in the last column. The average estimated errors ($\gamma$) are also given in the table.

<table>
<thead>
<tr>
<th>System</th>
<th>LDA</th>
<th>PBE</th>
<th>PBEsol</th>
<th>AM05</th>
<th>LAG</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B$</td>
<td>167.7</td>
<td>137.1</td>
<td>154.6</td>
<td>152.4</td>
<td>146.3</td>
</tr>
<tr>
<td></td>
<td>$C_{11}$</td>
<td>200.2</td>
<td>162.3</td>
<td>184.2</td>
<td>182.4</td>
<td>174.6</td>
</tr>
<tr>
<td></td>
<td>$C_{12}$</td>
<td>151.4</td>
<td>124.5</td>
<td>139.8</td>
<td>137.4</td>
<td>132.2</td>
</tr>
<tr>
<td></td>
<td>$C_{44}$</td>
<td>117.4</td>
<td>85.7</td>
<td>103.8</td>
<td>105.2</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>$\gamma$(%)</td>
<td>29</td>
<td>8.3</td>
<td>16.0</td>
<td>15.7</td>
<td>10.6</td>
</tr>
<tr>
<td>Au</td>
<td>$a$</td>
<td>4.067</td>
<td>4.175</td>
<td>4.101</td>
<td>4.095</td>
<td>4.126</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>189.1</td>
<td>139.8</td>
<td>171.7</td>
<td>169.0</td>
<td>156.8</td>
</tr>
<tr>
<td></td>
<td>$C_{11}$</td>
<td>198.2</td>
<td>147.3</td>
<td>180.6</td>
<td>178.7</td>
<td>165.1</td>
</tr>
<tr>
<td></td>
<td>$C_{12}$</td>
<td>184.6</td>
<td>136.1</td>
<td>167.2</td>
<td>164.1</td>
<td>152.7</td>
</tr>
<tr>
<td></td>
<td>$C_{44}$</td>
<td>55.5</td>
<td>39.9</td>
<td>50.6</td>
<td>52.9</td>
<td>45.8</td>
</tr>
<tr>
<td></td>
<td>$\gamma$(%)</td>
<td>10.6</td>
<td>37.0</td>
<td>12.6</td>
<td>14.3</td>
<td>23.2</td>
</tr>
</tbody>
</table>

Figure 4.3: Single-crystal elastic constants of partially ordered Cu$_3$Au as a function of the degree of disorder. Theoretical results are shown for $\alpha = 0.9$ and $\alpha = 0.74$. The low-temperature (4.2 K) experimental data are from Ref. [43].

from the above low-temperature experimental data by $-0.14\%$ and $+0.30\%$, respectively. Fig. 4.3 exhibits the results of $C'$ and $C_{44}$ with respect to the degree of long-range-order. Both of them produce negligible change upon the ordering effect. Comparing with experimental results, our theoretical study
clearly reproduces the ordering effect. However, the present value underestimate the $C'$ and overestimate the $C_{44}$. The effects of long-range-order on the three elastic constants are about 2% for $C_{11}$, $C_{44}$ and 3% for $C_{12}$, which are shown in Fig. 4.4. These theoretical findings support the experimental observation that the influence of the long-range order on the elastic constants of Cu$_3$Au is very small. Polycrystalline elastic constants are derived from single-crystal elastic constants. So small change in single-crystal elastic constants upon the degree of long-range-order, all of the polycrystalline elastic constants doesn’t show sizable change due to the long-range-order effect.

### 4.4 Debye Temperature

Long-range-order obviously changes the neighbours of the atoms. Therefore, the phonon vibrations associated with the interaction between atoms could be modified. The Debye temperature is an essential quantity which is closely related to the phonon vibrations. The present theoretical Debye temperatures are based on the elastic constants and thus respect the so called elastic Debye temperatures. These Debye parameters are often employed in simple models of phonon vibrations, although they might not necessarily coincide with those corresponding to the full phonon spectrum (and thus account properly for the vibrational term). Nevertheless, using the calculated Debye temperatures, we can estimate the entropy change upon order-disorder transition. According to the high-temperature expansion of the harmonic phonon entropy [26], for the entropy change upon the order-disorder transition we have $\Delta S_{ph}^{d-o} \approx 3k_B \ln \Theta_D/\Theta_D$. In
4.4 Debye Temperature

Figure 4.5: The Debye temperature of partially ordered Cu₃Au as a function of the degree of long-range-order. Theoretical results are shown for $\alpha = 0.9$, $\alpha = 0.74$, and dynamic $\alpha$ which depends on the lattice parameter $a$. The low-temperature (4.2 K) experimental data are from Ref. [43].

Fig. 4.5 the Debye temperature $\Theta_D$ is shown as a function of $S$. The results show that the degree of long-range-order has a relatively small effect on $\Theta_D$. Using the present results, we find that the theoretical $\Delta S_{ph}^{\alpha-d}$ varies between $-0.018k_B$ and $0.022k_B$. The upper value of this prediction is surprisingly close to $0.023k_B$ derived from the measured elastic parameters [43]. As seen from Fig. 4.5, it seems that $\Theta_D$ rest on the choice of SIM parameter. Namely, $\alpha = 0.9$ leads to slightly decreasing and $\alpha = 0.74$ to slightly increasing $\Theta_D$ with increasing $S$. But, if we include the $\alpha(a)$ dependence on the lattice parameter $a$, a steady Debye temperature line as a function of the degree of long-range-order can be obtained, in which case the results are similar with that of $\alpha = 0.74$. 
Chapter 5

Ordering Effect on the Elastic Properties of Ferromagnetic Materials

In this chapter, we consider further the effect of long-range-order on the elastic constants, in the presence of magnetic effects. The coupled effect of magnetic moment and long-range-order on the elastic properties produces completely different picture from the pure chemical order effect. In this chapter, we focus on the study of elastic properties of the ferromagnetic alloy Ni$_3$Fe. The accuracy of EMTO-CPA for iron and nickel, both essential and widely used elements in modern alloy industries, were tested in related simulations. The SIM parameter was optimized to be 0.9 for Ni$_3$Fe using the same method with that of Cu$_3$Au. Similar work will not be repeated here. This Chapter is contributed by supplements II and III.

5.1 Single-crystal Elastic Constants

In Fig. 5.1, we parallel our results for the lattice parameter $a$ with the experimental values [56–59] and the former theoretical result [60]. The results indicate that for the ferromagnetic state of Ni$_3$Fe, the lattice parameter change is less than $10^{-3}$ Å, which can, in fact, be ignored within the present estimated error bar associated with the numerical fit of the equation of state. For the paramagnetic state Ni$_3$Fe, about $4.5 \times 10^{-3}$ Å was modified, which is slightly larger than the one obtained for the ferromagnetic state and it might have some effect on the volume-sensitive physical properties. That means magnetic state mainly affects the lattice parameter in the random solid solution, and this effect almost disappears as the system approaches the ordered state. The present result for the chemically ordered $L1_2$ phase turns out to be in good agreement with most of the experimental data. We also notice that on the average the agreement with experiments is better for the EMTO results than for the FLAPW results [60]. Comparing the quoted experimental values, we observe that the milling method slightly overestimates the lattice parameter as compared to the other values.
Figure 5.1: (Color online) Lattice parameter as a function of the degree of the long-range order $S$ for the ferromagnetic and paramagnetic states of Ni$_3$Fe. The experimental results are from Ref. [56] ($^a$), Ref. [57] ($^c$), Ref. [58] ($^d$) and Ref. [59] ($^e$). The quoted theoretical value (FLAPW) for the ordered ferromagnetic state is from Ref. [60] ($^f$). All experimental results refer to the ferromagnetic state.

Chinnasamy et al. [58] reported lattice parameters between 3.563 and 3.587 Å, depending on the milling time.

Single-crystal elastic constants for para- and ferromagnetic state are shown in Fig. 5.2. First, we can have a bird view of this figure. All lines representing the paramagnetic state lie horizontally, however, the lines representing the ferromagnetic state are bend. That indicates that the elastic constants respond much stronger on the long-range order in ferromagnetic state than in paramagnetic state. Specifically, $C_{11}$ increases by 8.3% with increasing $S$ from 0 to 1. At the same time, $C_{12}$ slightly decreases and $C_{44}$ increases with $S$. However, these latter changes are substantially smaller in absolute value than that of $C_{11}$. In the paramagnetic state, all elastic constants remain almost constant as a function of $S$. That is, the single-crystal elastic constants are not affected by the degree of long-range order in the magnetically disordered state. This finding is in accordance with the results reported for the non-magnetic cases. Therefore, different magnetic states lead to markedly different behavior of the elastic constants as a function of the long-range chemical order. On the other hand, different degrees of chemical order produce quite different dependence of the single-crystal elastic constants on the magnetic state. In particular, $C_{11}$ and $C_{12}$ have much bigger response to the magnetic ordering effect in the chemically ordered state than in the disordered state. But $C_{44}$ behaves in the opposite way, it has bigger response to the magnetic effect in the chemically disordered state. When $S \lesssim 0.4$, the magnetic effect on $C_{12}$ may be ignored, but it has sizable impact on $C_{44}$. When $S \gtrsim 0.4$, the magnetic effect in $C_{12}$ becomes important, but $C_{44}$ keeps almost the same value for the two magnetic states.
5.2 Polycrystalline Elastic Constants

The polycrystalline elastic parameters are summarized in Fig. 5.3. The present bulk modulus $B$ and shear modulus $G$ are in line with the experimental and the former theoretical values. The exception is the paramagnetic $L1_2$ phase, for which the EMTO bulk modulus differs considerably from the FLAPW result, which was reported to be substantially higher (by $\sim 20$ GPa) than that of the ferromagnetic state. That is because in Ref. [60] the nonmagnetic calculations were used to model the paramagnetic state, ignoring the effect of disordered local magnetic moments on the bulk properties. In the ferromagnetic state, the Young’s modulus $E$ increases nonlinearly as the degree of order $S$ increases. However, for the paramagnetic state, $E$ is almost constant with $S$. The dependence of the shear modulus $G(S)$ on the long-range order for two different magnetic state is similar to that of $E(S)$. Close to the ordered state, the ferromagnetic Ni$_3$Fe is much stiffer than in the paramagnetic one. Close to the disordered state, the effect of magnetism almost disappears. The trend of the bulk modulus is totally different from those of $E(S)$ and $G(S)$. Namely, $B(S)$ has a weak dependence on the degree of the long-range order and magnetism. This may be understood from the trends of $C_{11}$ and $C_{12}$ in Fig. 5.2. The ordering-induced increase of $C_{11}$ is to large extent canceled by the ordering-induced decrease of $C_{12}$ in $B = (C_{11} + 2C_{12})/3$. For all cases, the magnitude of the Pugh ratio of $B/G$ is much bigger than the critical value 1.75 for the ductile/brittle transition [65]. On this ground, we may conclude that the long-range order and magnetism do not affect the ductility of Ni$_3$Fe system.

Figure 5.2: (Color online) Single-crystal elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ plotted as a function of the degree of order $S$ for the ferromagnetic and paramagnetic states of Ni$_3$Fe. For comparison, we included the available experimental data for Ni$_{77.82}$Fe from Ref. [61] (a) (room temperature data) and Ni$_{79.19}$Fe from Ref. [62] (b) (extrapolated from lower temperature values to 0 K). All experimental results refer to the ferromagnetic state.
 CHAPTER 5. ORDERING EFFECT ON THE ELASTIC PROPERTIES OF FERROMAGNETIC MATERIALS

Figure 5.3: (Color online) The tetragonal shear elastic constant \( C' \) and polycrystalline elastic moduli \( B, G \) and \( E \) as a function of the degree of order \( S \) for the ferromagnetic and paramagnetic states of Ni\(_3\)Fe. For reference (see the text), \( C' \) obtained for the hypothetical nonmagnetic (NM) systems are also shown. For comparison, the values from Ref. [63] \(^{(a)}\), Ref. [64] \(^{(b)}\), Ref. [60] \(^{(c)}\) and Ref. [64] \(^{(d)}\) are shown.

Figure 5.4: (Color online) The degree of order \( S \) plotted as a function of \( g \equiv (G - G_d)/G_d \), where \( G \) is the partially ordered and \( G_d \) the fully disordered shear modulus.
Poisson’s ratio $\nu$ and the Cauchy pressure $(C_{12} - C_{44})$ change slightly and all of them are far form their critical ductile/brittle values. Hence, magnetism and the degree of order have negligible influence on the ductile/brittle property of Ni$_3$Fe alloys.

Given the strong elastic-chemical coupling in the ferromagnetic state, we suggest that one can estimate the degree of order $S$ using the measured elastic modulus. Fig. 5.4 gives the relationship between the degree of order $S$ and the reduced shear modulus $g$ defined as $g \equiv (G - G_d)/G_d$, where $G_d$ is the shear modulus of the fully disordered phase. We find that a simple power fit function can accurately reproduce the calculated data. For instance, the trial function $S(g) = ag^b$ with $a = 0.30559$ and $b = 0.46063$ reproduces well the $S(g)$ curve up to $g \sim 10\%$. Then one can find the actual degree of order $S$ by measuring the shear modulus and comparing that to the fully disordered value.

Now, we turn to discuss the tetragonal shear elastic constant $C' = (C_{11} - C_{12})/2$. The bulk modulus does not produce a large change upon long range-order even in ferromagnetic state, $C_{44}$ also gives a minute increase in the ferromagnetic state and almost keep constants in the paramagnetic state. According to the linearly dependence from equations (2.2) and (2.3) among these single-crystal elastic constants, we can conclude that the $C'$ was modified significantly in some way. For convenient of constructing figure, $C'$ is shown in the left upper corner of Fig. 5.3 along with one experimental value reported for the disordered FM state [63]. The results indicate that in the ferromagnetic state, $C'$ increases by $\sim 25\%$ when going from the disordered to the ordered state. This change is very large, which shows that the ordered state is significantly more stable mechanically than the disordered state. In the paramagnetic state, $C'$ changes only by $\sim 3.6\%$ as $S$ increase from 0 to 1. Therefore, magnetism affects $C'$ and thus the elastic anisotropy $(C_{44}/C')$ in a very different way at different degrees of order. In the chemically ordered state, the magnitude of $C'$ raises from 37.1 GPa to 49.9 GPa ($\sim 35\%$) upon magnetic ordering. The effect is diminished as the degree of order gradually decreases. This confirms that magnetism stabilizes dynamically the ordered state.

So as to get more evidence on the surprising effect of long-range-order on the tetragonal shear modulus $C'$, our attention was given to another magnetic system Fe$_{0.75}$Ga$_{0.25}$. The structure and chemical order dependence of $C'$ of Fe$_{75}$Ga$_{25}$ were studied for A2, B2 and DO$_3$ lattices for the nonmagnetic, paramagnetic and ferromagnetic states. The results are shown in Fig. 5.5. All elastic constants were computed at the same volume to exclude the volume effect. The total energies of NM B2 and DO$_3$ are very close to each other, suggesting that the interaction between Ga atoms prevents them occupying the first nearest neighbors in the bcc lattice. In the FM state, however, magnetic ordering repulse Ga atoms to third nearest neighbors to form the DO$_3$ structures. More strikingly, $C'$ of NM Fe$_{0.75}$Ga$_{0.25}$ increases with the chemical order from a negative value for the A2 phase (dynamically unstable) to a large positive value for the NM DO$_3$ (Fig. 5.5a). When spin-polarization is considered, $C'_{DO3}$ decreases monotonically with magnetism to a small nonzero value (Fig. 5.5b). At the same time, magnetism will increase $C'_{A2}$ to a positive value and stabilize the system dynamically. Namely, magnetism stabilizes A2 but destabilizes the DO$_3$, ordering stabilizes NM but destabilizes FM. The large contributions from ferromagnetism $\Delta C'_{Mag} = C'_{FM} - C'_{NM}$ and chemical ordering $\Delta C'_{Ord} = C'_{DO3} - C'_{A2}$
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Figure 5.5: (Color online) The effects of chemical ordering and magnetism on the tetragonal shear modulus \( C' \) of stoichiometric Fe\(_{75}\)Ga\(_{25}\) alloy. Panel a: Long range chemical order dependence of \( C' \) calculated for ferromagnetic (FM, black squares) and nonmagnetic (NM, red circles) states. Panel b: Magnetic state dependence of \( C' \) calculated for random A\(_2\) (black squares) and ordered DO\(_3\) (red circles) phases. The magnetic \( \Delta C'_\text{Mag} = C'_{\text{FM}} - C'_{\text{NM}} \) and the chemical ordering \( \Delta C'_\text{Ord} = C'_\text{DO3} - C'_A \) contributions are also shown (blue triangles).

suggest a strong and complex interaction between chemistry and magnetism in stoichiometric Fe\(_{75}\)Ga\(_{25}\) alloy.

5.3 Debye Temperature and Order-disorder Transition Temperature

Fig. 5.6 illustrates the relationship between the elastic Debye temperature and the magnetic and chemical long-range order effects. The present results for \( \Theta_D \) is surprisingly close to the results by Turchi et al. [66] and Kanrar and Ghosh [62], both measurements obtained for FeNi\(_{79.19}\). According to the dependence of the Debye temperature on the Ni concentration as obtained in Ref. [62], the Debye temperature of the ferromagnetic disordered Ni\(_3\)Fe system should be about \( \sim 450 \)K, which is also close to the results of the present work. The difference between the Debye temperatures in the disordered and partially ordered states \( (S = 0.69) \) is reported to be 7.8K [67]. This is in accordance with the results of the present \( ab \) \textit{initio} calculations. Compared to the previous works on Cu\(_3\)Au, the above change may be considered large. Due to the magnetic effects, the long-range order contributes more in the Ni\(_3\)Fe system than in the nonmagnetic Cu\(_3\)Au to the vibration entropy change upon ordering. In the chemically disordered state, magnetic ordering changes the Debye temperature by \( \sim 1.2\% \) compared to 5.4\% (25.4 K) found for the ordered state. The entropy change due to order-disorder transition can be estimated from the present elastic Debye temperatures. According to the high-temperature expansion of the
harmonic phonon entropy [26], for the entropy change upon the order-disorder transition we have \( \Delta S_{ph}^{o-d} \approx 3k_B \ln \Theta_D^o/\Theta_D^d \). Using the present results, the theoretical \( \Delta S_{ph}^{o-d} \) changes from \( 0.024k_B \) to \( 0.147k_B \) due to the magnetic effects, which indicates that magnetism strengthens the vibrational entropy effect. The reason behind this effect is that the elastic constants depend differently on the degree of order \( S \) for the two magnetic states. The Fe atoms have totally different distributions for the completely disordered and the ordered structures. In the ordered structure, the Fe atoms sit in a simple cubic sub-lattice, but in the disordered structure, the Fe atoms occupy a face centered cubic structure.

5.4 Order-disorder Transition

Using the Bragg-Williams-Gorsky approximation [29], the transition temperature was roughly estimated. In the present work, we get \( U_0 = 0.034333 \) Ry which gives \( T_o = 1138 \) K. This value is very close to the Monte-Carlo result (1030 K) by Ekholm et al. [68]. According to the discussion in Ref. [68], when the temperature is close to the transition temperature, the magnetically ordered state is degenerated with the partially ordered magnetic state, and at the same time lattice parameter has the corresponding change. This would apparently decrease the value of \( U_0 \) and consequently decrease the estimated transition temperature.
5.5 Electronic Structure

In order to understand why the tetragonal shear elastic constant $C'$ (FM) exhibits fairly large relative change, the electronic total densities (DOSs) of ordered and disordered alloys in FM, PM and NM states of Ni$_3$Fe alloys are analyzed. They are shown in Fig. 5.7, upper, middle and lower panels, respectively. We included the DOSs for the undistorted fcc and $L_{12}$ lattices (red solid curves) and also for the orthorhombic lattices obtained by applying the $D_o$ distortion (Eq. (2.7)) with $\delta_o = 0.05$ (black dashed curves). This lattice distortion is used to compute $C'$. We observe that the large NM peak near the Fermi level ($\sim 33 - 37$ states/Ry) disappears in the FM and PM states, explaining the observed spontaneous spin polarization of the system in terms of the classical Stoner model. Furthermore, in the ordered FM state, the spin-up $d$ channel is fully occupied, whereas the spin-down channel shows a local minimum near the Fermi level. This indicates strong covalent type of bonds for the ordered FM system. The local minimum disappears in the disordered FM state, showing that this phase is thermodynamically less stable as compared to the ordered FM state. The occupied parts of the PM DOSs are very similar for the ordered and disordered cases.

Elastic distortion lowers the cubic symmetry and thus splits the degenerate $E_g$ and $T_{2g}$ states of the $d$ density of states. If the degenerate states are present around the Fermi level ($E_F$), the symmetry lowering deformation usually de-
5.5 Electronic Structure

creases the one electron energy and thus the kinetic energy of the system. That is because part of the split sub-bands move above the Fermi level and as a result the partial spectral weight decreases. According to this scenario, larger DOS peak at the Fermi level should yield larger negative kinetic energy change (in absolute value) and hence result in smaller elastic parameter. For instance, the body centered cubic Fe at high pressure is nonmagnetic and has a pronounced DOS peak at the Fermi level, which was used to explain the calculated large negative C′ elastic parameter [69]. We should point out that the above arguments hold assuming that the systems in question possess similar electrostatic and exchange-correlation energy change with lattice distortion. Otherwise, the force theorem fails [70], and the latter energy terms can very well overwrite the changes dictated merely by the kinetic energy. In the present case, we compare the ordered and disordered DOSs of various magnetic states to find out the ordering effect on C′. Here we assume that the average electrostatic and exchange-correlation energy terms in ∆E(δo) do not change upon chemical ordering and thus the leading energy term comes entirely from the one electron energy (i.e., the force theorem holds). We denote by D the DOS at the Fermi level. According to Fig. 5.7, D(NM)ord > D(NM)dis (the difference being about 3 states/Ry), suggesting C′(NM)ord < C′(NM)dis based on the above scenario. Next, we find that for the spin-down channels (the spin-up channels are very similar) D(FM)ord < D(FM)dis (the difference being about 5 states/Ry), indicating C′(FM)ord > C′(FM)dis. Finally, D(PM)ord < D(PM)dis (the difference being about 1 states/Ry) resulting in C′(PM)ord > C′(PM)dis. Moreover, considering the relative differences between the ordered and disordered DOSs at the Fermi level, we may conclude that the difference between the ordered-disordered C′s should be the largest for the FM state and the smallest for the PM state. All these predictions are in perfect agreement with the actual trends from Fig. 5.3. It is gratifying that the above simple arguments, based merely on the total electronic density of states, can account for the fully self-consistent results. Comparing the undistorted and distorted DOSs in Fig. 5.7, we can reveal some further details behind the calculated ordering effects in C′s. The large DOS peak for ordered NM Ni3Fe located right below EF (near −0.015 Ry) splits upon lattice distortion. Part of it moves to energies above and part of it below EF. This results in a small decrease of D(NM). No similar changes can be seen for the disordered NM phase, which explains why C′(NM)ord is smaller than C′(NM)dis. On the other hand, the spin-down D(FM) of ordered state slightly increases with lattice distortion as a result of splitting the DOS peaks above and below the Fermi level. Part of the local minimum is also filled up, indicating a substantial energy increase upon lattice distortion and thus a relatively large C′(FM)ord. For the PM state, no significant changes in the DOSs can be seen near the Fermi level, in accordance with the almost vanishing ordering effect in C′(PM).
Chapter 6

Concluding Remarks and Future Work

*Ab initio* alloy theory, formulated within the exact muffin-tin orbital method in combination with the coherent-potential approximation, was used to determine the elastic properties of ordered, partially ordered and random solid solutions. We investigate the effect of long range order on the elastic constants for non-magnetic and ferromagnetic materials.

For non-magnetic material, long range order has small (nearly insignificant) effect on the elastic constants. The tests for Cu$_3$Au showed that the ordering effect is about 2% for $C_{11}$, $C_{44}$ and 3% for $C_{12}$. These theoretical findings support the experimental observation that the influence of the long-range order on the elastic constants of Cu$_3$Au is very small. Our conclusion is in line with that reported for the Pd-Ag system as well as for some semiconductor alloys. Therefore, it seems that for non-magnetic systems, the chemical long-range order has only a higher order effect on the elastic parameters. This conclusion was also supported by the previous observation [26], namely that at high-temperature mass disorder has no effect on the phonon entropy difference between ordered and disordered phases. Therefore, for many practical cases, when screening the alloying or structural effects on the elastic properties, it is sufficient to perform calculations on completely random structures using well adapted alloy theory or on more complex ordered structures using e.g. full-potential techniques.

However, for magnetic materials, long-range order produces sizable effects on the elastic constants in the ferromagnetic state, but this kind of influence disappeared in the paramagnetic state. According to the results obtained for Ni$_3$Fe, we found that in the ferromagnetic state, out of the three single-crystal elastic constants, only $C_{11}$ and $C_{12}$ are affected by magnetism in the ordered state, however, their combined effect results in a nearly constant bulk modulus as a function of order parameter $S$. $C_{44}$ changes slightly with $S$ and magnetic state. The tetragonal shear modulus $C'$, the Young’s modulus $E$ and the shear modulus $G$ increase significantly with the degree of order in the ferromagnetic state, but the effect becomes weak as the system approaches the random regime. Especially the $C'$ shear modulus depends strongly on the magnetic state and the degree of order. As a result, the Zener anisotropy $C_{44}/C'$ and the Possion’s ratios are strongly affected by the long-range order in the ferromagnetic...
state. Nevertheless, the actual values for the Pugh ratio and the Cauchy pressure remain far from their critical values, indicating that the ductility of Ni$_3$Fe is not influenced by the chemical/magnetic ordering. For both ferromagnetic and paramagnetic states, the chemically disordered phase is elastically softer, which contributes by $0.024 - 0.147k_B$ to the ordering entropy, depending on the magnetic state. On the other hand, using a nonmagnetic approximation for the paramagnetic state, as often done in standard density functional calculations, would result in softer ordered phase and thus in negative ordering entropy. The calculated trends were explained using the electronic density of states of ordered and disordered nonmagnetic, ferromagnetic and paramagnetic Ni$_3$Fe alloys. We showed that the details of the DOSs can fully account for the calculated ordering effects in $C'$ and thus also in the Young's and shear moduli and Debye temperature. The present findings highlight the importance of the magnetic state in studying the chemical ordering and demonstrate that the magnetic effects can overwrite the chemical terms.

The present results offer a consistent starting point for further theoretical modeling of the micro-mechanical properties of technologically important transition metal alloys. Based on these achievements, we conclude that the EMTO-CPA approach provides an efficient and accurate theoretical tool to deal with the disordered alloys. In the next step, we will include the temperature effect to investigate the coupled effect of long range order, magnetic moment and temperature on the elastic properties.
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