ABSTRACT

NIU, CHANGNING. First Principles Studies of NiFeCrCoMn High Entropy Alloys. (Under the direction of Douglas L. Irving.)

Density functional theory (DFT) tools have been applied for theoretical studies of the high entropy alloy (HEA) system of quaternary NiFeCrCo and quinary NiFeCrCoMn with equiatomic and non-equatomic concentrations. Phase formation influenced by local chemistry and mechanical properties of these HEAs have been investigated, divided into four studies. First, in contrast to the common understanding that equiatomic NiFeCrCo HEA is a random solid solution, predictions that a $L_1_2$-like lattice with Cr ordering is more thermodynamically stable and that this partially ordered phase has a lower magnetic moment are made by DFT calculations and confirmed by experiments. Second, for non-equatomic random-solid-solution NiFeCrCo HEAs, composition-dependent properties are calculated with each component ranging from 10 to 40 atomic percent. Elemental effects on these properties, i.e., mixing enthalpy, lattice parameter, bulk modulus $B$, shear modulus $G$, are predicted for the guidance of HEA design. Equations to conveniently estimate mixing enthalpy and bulk modulus from binary alloy calculations are proposed and evaluated. Third, stacking fault energy (SFE) of equiatomic NiFeCrCo is studied by two complementary computational toolsets and two modeling methods for SFE. SFEs from the EMTO-CPA calculations based on the supercell method are compared to experimental results. The VASP calculations based on the supercell method show that the formation of stacking faults causes high energy fluctuation in small regions because of chemical complexity, overwhelming structural energetic compensation. All the other calculations based on the axial interaction model (AIM) show that the hexagonal close-packed (hcp) phase is more stable than the face centered cubic (fcc) phase at 0 K. Calculations of vibrational entropy show that the fcc phase is stabilized at high temperatures by energetic contribution from vibrational
entropy. Because of energy scattering, an accurate SFE from the AIM method needs more vibrational calculations, which are computationally demanding. Finally, the well-established toolsets have been applied to the study of NiFeCrCoMn HEAs. It is found that partial ordering of Cr and Mn is also energetically preferred to the random solid solution phase.
First Principles Studies of NiFeCrCoMn High Entropy Alloys

by
Changning Niu

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Materials Science and Engineering

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APPROVED BY:

__________________________    ____________________________
Carl C. Koch                  Srikanth Patala

__________________________    ____________________________
Mohammed A. Zikry            Douglas L. Irving
Chair of Advisory Committee
DEDICATION

To my parents, who have believed in and supported me unconditionally through the years, and

my wife, whose love is the best thing that ever happened to me.
BIOGRAPHY

The author was born in Binzhou, China.

He attended University of Science and Technology Beijing (USTB) in Beijing, China and obtained his bachelor’s degree in Materials Physics in 2011. In the same year, he travelled to Raleigh, U.S. to study Materials Science and Engineering at NC State with Professor Douglas L. Irving.
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The work in this dissertation has been in close collaboration with experimental groups led by Professor Carl Koch and by Professor James LeBeau. Besides the two professors, I am also very grateful for the collaboration with their group members: Alex Zaddach, Adedapo Oni, Xiahan Sang, Everett Grimley, and Khaled Youssef. I would like to thank Professor Levente Vitos for sharing his EMTO-CPA code with our group.

I would like to thank my committee members for generously spending time and giving feedback for my projects and this dissertation: Carl Koch, Srikanth Patala, Mohammed Zikry, and Douglas Irving.

Most of all, I wish to thank my parents and my wife for their love and support.

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Chapter 1

Introduction

About 2300 years ago, the philosopher Han Fei (Han is his family name) was born in ancient China. He wrote a story that is known by many Chinese today. The story goes that there was once a merchant selling spears and shields, who declared that his spears were the sharpest and could penetrate any shield, and that his shields were the strongest and could defend from any spear. Eventually, someone asked him this question: what if your spears were used against your shields? The merchant was speechless. Because of this story, a new word, spear-shield, was created and has become popular in the Chinese language. If two properties are mutually exclusive, they are a spear-shield.

In materials science and engineering, situations of spear-shield are very common. A killer property of a material often comes at the expense of some other desirable properties. Examples of spear-shield properties include strength vs. ductility, strength vs. density, etc. Materials scientists and engineers are like the merchant. They want to combine two seemingly exclusive properties into one material. They search for new materials, study the science behind them, and engineer them for optimal performance. So, when the idea of a new type of alloy that enables unlimited possibilities for alloy design was discovered, it easily attracted the interest of
materials researchers. These so-called high entropy alloys (HEA) have exhibited many great properties and excellent potential. They are regarded by many as a good starting point towards solving the spear-shield situation of materials.

This study aims at studying a HEA system using computational tools to shine light on properties of this HEA system which otherwise are difficult to investigate experimentally. Insight into the properties studied in this dissertation leads to better understanding of HEAs and suggests predictive high entropy alloying strategies. Methodologies established in this dissertation may be extended to other HEA systems so that the exploration of HEAs can be greatly accelerated via predictive calculations. What is learned from this study cannot provide direct solutions to the spear-shield dilemma in materials science and engineering, but can nonetheless be very helpful towards finding better performance in HEAs.

In this chapter, the first section gives a general background of HEAs. The second section is an introduction to the latest research about the HEA system of NiFeCrCoMn. At the end the goals of this research, the structure of the book, and discoveries from this dissertation work are summarized.

1.1 High-Entropy Alloy (HEA)

In 2004, Yeh et al. [1] and Cantor et al. [2] published their mutually independent work on multi-component alloys with equal atomic ratios, some of which they found were single-phase solid solutions. In contrast to conventional alloys that have one or two major components with additional elements in small concentrations, these multi-component alloys have five or more elements in nearly equal concentrations.
Configurational entropy of an ideal solid solution is given by

$$S_{\text{conf}} = -R \sum_{i} c_i \ln c_i$$

(1.1)

where $R$ is the gas constant, $n$ is the number of components, and $c_i$ is the atomic ratio of each component. As demonstrated in Fig. 1.1, the configurational entropy of a ternary solid solution is highest in the center of the alloying map. Similarly, this new type of alloy discovered by Yeh and Cantor has a higher entropy than conventional alloys. Yeh gave these alloys the name high-entropy alloy [1], which has been widely used. These high entropy alloys are believed to be thermodynamically stabilized because the Gibbs free energy $G$ is reduced by entropy $S$:

$$G = H - TS$$

(1.2)

where $H$ is the enthalpy of formation and $T$ is the temperature.
Additionally, high-entropy alloys greatly expand the availability of recipes for alloy design. Since they were introduced in 2004, research into high-entropy alloys has been an active topic in materials science. As an indication of the continuously increasing interest in this research field, the number of Google Scholar searching results of the term "high entropy alloys" per year is plotted in Fig. 1.2. The data points for the year of 2015 is estimated as a double of current results on July 8, 2015. Hundreds of HEA systems have been manufactured and studied so far. This section aims to be a general introduction to the recent advances of high-entropy alloys.
1.1.1 Overview

Current HEAs are mostly based on transition metals including Ni, Fe, Cr, Co, Mn, Zn, Au and Cu, or refractory metals such as V, Ti, Mo, Nb, Ta, W, Zr and Hf. Al is often added into transition metal HEAs with varying concentrations to tune the structural or mechanical properties. Recently, a few low-density HEAs that are composed of light metals have also been reported. [3, 4] Other elements, such as Sn and Bi, are also found in a few HEA studies. Elements involved in high entropy alloys are marked in Fig. 1.3. [5]

![Figure 1.3 Elements involved in high entropy alloys. Green: transition metal HEAs. Blue: refractory metal HEAs. Yellow: others.](image)

While the concept of HEAs is based on the idea that phase stabilization is realized by high configurational entropy in ideal random solid solutions with multiple components, single-phase HEAs turn out to comprise only a small part of all multi-component alloys, i.e., mixing
several elements usually does not lead to a single-phase solid solution alloy. However, these single-phase HEAs are among the most interesting alloys with very attractive properties. On the other hand, for the multiphase HEAs, there are unique opportunities to engineering properties through microstructure control.

Table 1.1 Single-phase HEAs from the literature. fcc: face centered cubic; bcc: body centered cubic.

<table>
<thead>
<tr>
<th>HEA</th>
<th>Phase(s)</th>
<th>Ref</th>
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<tr>
<td>NiFeCrCo</td>
<td>fcc</td>
<td>[6–14]</td>
</tr>
<tr>
<td>NiFeCr_xCo</td>
<td>fcc</td>
<td>[15]</td>
</tr>
<tr>
<td>NiFeCrCoMn</td>
<td>fcc</td>
<td>[2, 6, 16–22]</td>
</tr>
<tr>
<td>NiFeCoCu</td>
<td>fcc</td>
<td>[23]</td>
</tr>
<tr>
<td>NiFeCrCoCu</td>
<td>fcc</td>
<td>[1, 24, 25]</td>
</tr>
<tr>
<td>NiFeCrCoCuAl_x</td>
<td>fcc/bcc</td>
<td>[1, 24, 26]</td>
</tr>
<tr>
<td>NiFeCrCoAl_x</td>
<td>fcc/bcc</td>
<td>[11, 27, 28]</td>
</tr>
<tr>
<td>NiFeCrCoPd_x</td>
<td>fcc</td>
<td>[7]</td>
</tr>
<tr>
<td>NiFeCrCoMo_x</td>
<td>fcc</td>
<td>[10, 27]</td>
</tr>
<tr>
<td>NiFeCrCoTi_x</td>
<td>fcc</td>
<td>[29]</td>
</tr>
<tr>
<td>NbHfZr</td>
<td>bcc</td>
<td>[30]</td>
</tr>
<tr>
<td>NbZrTiV</td>
<td>bcc</td>
<td>[4, 31]</td>
</tr>
<tr>
<td>NbHfZrTiV</td>
<td>bcc</td>
<td>[32]</td>
</tr>
<tr>
<td>NbZrTiMoV_x</td>
<td>bcc</td>
<td>[33]</td>
</tr>
<tr>
<td>NbTiTaVAL_x</td>
<td>bcc</td>
<td>[34]</td>
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</table>

Some typical single-phase HEAs are listed in Table 1.1. Transition metal HEAs are mostly in a simple fcc lattice. Addition of Al, which has a larger atomic radius, can change the lattice to bcc. Refractory metal HEAs are usually bcc crystals. However, this trend in the phase formation of single-phase HEAs is not a reliable rule. Studies of phase prediction for HEAs will be further discussed in section 1.1.2. More examples of single-phase HEAs may be found in Table 1 of Ref [35], Table 1 of Ref [5], and Table 1 of Ref [36].
The research on HEAs has not been limited to single-phase solid solutions. While multiphase HEAs have a lower entropy than single-phase solid solutions do, the entropy is still on a high level because of the large number of components. In this dissertation, all alloys having four or more components with atomic ratios of 10-40% are regarded as HEAs. The multiphase HEAs have a greater number than single-phase HEAs, and their categorization is more difficult. The list of multiphase HEAs can be found in Table 1 of Ref [36] and Table 1 of Ref [37]. Phases of these HEAs mostly include combinations of body centered cubic, face centered cubic, hexagonal close packed, σ, compounds, and Laves phase.

Structural materials require a combination of beneficial mechanical properties, such as strength and ductility. As reviewed by Zhang et al., HEAs exhibit high hardness and high specific strength (ratio of yield strength over density) that are better than many conventional structural materials, and a wide range of Young’s modulus with a high specific strength. The yield strength of HEAs at room temperature varies from 300 MPa, found in the fcc NiFeCrCoCuTi_x system [38], to about 3000 MPa, found in the bcc AlNiFeCrCoTi_x system [25]. Refractory VNbMoTaW has a high strength at elevated temperatures up to 1800 K. [39] Al_{0.5}NiFeCrCoCu HEAs has great fatigue resistance that outperforms conventional alloys including titanium alloys, steels, and bulk metallic glasses. [40] The wear resistance of NiFeCrCoTi and AlNiFeCr-CoTi HEAs are found to be better than that of conventional wear-resistant steels. [41]

1.1.2 Phase Prediction

The Gibbs phase rule predicts the number of phases of a material: \( P = C + 2 - F \), where \( P \) is the maximum number of phases at equilibrium, \( C \) is the number of components, and \( F \) is the degree of freedom of the system. For example, water at a free temperature and a fixed pressure (ambient pressure) has \( P = C + 2 - F = 1 + 2 - 1 = 2 \) phases at equilibrium at most, that is,
at 0 °C or 100 °C. The Gibbs phase rule works well for conventional alloys. According to this rule, a high-entropy alloy is anticipated to have many phases, which often is not desirable for practical engineering requirements. After the discovery of single-phase high-entropy alloys, researchers would love to see if more multi-component alloys are stable as a single-phase material. Existing studies show that high-entropy alloys manufactured by casting through rapid quenching or ball milling are inclined to keep simple crystal lattices, including body-centered cubic (bcc), face-centered cubic (fcc), hexagonal close-packed (hcp), etc., and that processing at elevated temperatures, such as annealing and aging, in some cases introduces additional phases. [3, 42–44] It is unclear how single-phase HEAs are stabilized from separating into multiple phases. Many theories of HEA phase formation have been proposed.

Valence electron concentration (VEC) was proposed as a guide to predict whether a single-phase HEA will form as a fcc or bcc. [45] VEC is defined as the average valence electron of the alloy, given by

\[
\text{VEC} = \sum n_i^V c_i
\]  

(1.3)

where \( n_i^V \) and \( c_i \) are the number of valence electrons and the atomic ratio of each constituent element, respectively. Generally, a single-phase HEA prefers the bcc lattice when \( \text{VEC} \leq 6.87 \), the fcc lattice when \( \text{VEC} \geq 8.0 \), and a mixture of bcc and fcc lattices when \( 6.87 \leq \text{VEC} \leq 8.0 \).

Yang and Zhang proposed two parameters to predict whether a HEA is a solid solution, an intermetallic compound, or a metallic glass. [36] The two parameters are defined by:

\[
\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}, \quad \delta = \sqrt{\sum c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}
\]  

(1.4)

where \( T_m = \sum c_i T_i^m \) is the average melting temperature weighted by composition \( c_i \), \( \Delta S_{\text{mix}} = -R \sum c_i \ln c_i \) is the entropy of mixing as a random solid solution, \( \Delta H_{\text{mix}} = \sum 4c_i c_j \Delta H_{\text{mix}}^{AB} \) is the average enthalpy of mixing calculated from binary enthalpies, and \( \bar{r} = \sum c_i r_i \) is the average
atomic radius. Formation of solid-solution HEAs requires that $\Omega \geq 1.1$ and $\delta \leq 6.6\%$. The two parameters are based on general physics. The parameter $\Omega$ requires that the enthalpy of mixing must be close enough to zero in order to be overcome by entropy to form a random solid solution. If the enthalpy of mixing is strongly positive, phase separation or segregation is likely to occur. If the enthalpy of mixing is strongly negative, intermetallic compounds may form. The second parameter $\delta$ requires that the atomic size mismatch in the solid solution must be small enough; otherwise, the crystal lattice can be distorted to form a metallic glass. The two parameters are generally successful in phase prediction of a random solid solution for many HEAs. They are also the earliest to offer a physically reasonable criterion for the prediction of HEA phases. However, they are not fully predictive and require further theoretical support. First, the equations to calculate the averaging melting temperature ($T_m$) and the averaging enthalpy of mixing ($\Delta H_{\text{mix}}$) are unproven estimations. Second, the average atomic radius ($\bar{r}$) is based on the Vegard’s law, which is not entirely reliable for the prediction of alloyed lattice spacing in most alloys.

Otto et al. reported the influence of binary enthalpies on HEA phase formation. [17] They prepared a single-phase fcc solid-solution HEA NiFeCrCoMn along with five derivatives by replacing one element of the alloy at a time with similar elements according to the Hume-Rothery rules, i.e., elements with similar atomic size, electronegativity, crystal structure, and valency. The six alloys were: NiFeCrCoMn (base), NiFeMoCoMn, NiFeVCoMn, NiVCrCoMn, NiFeCrTiMn, and CuFeCrCoMn. Their $\Omega$ parameters are 4.9, 5.6, 2.3, 2.3, 1.6, and 4.6, respectively. Their $\delta$ parameters are 3.3, 4.2, 3.4, 3.3, 6.6, and 3.1%, respectively. All of them satisfy the solid-solution criterion ($\Omega \geq 1.1$ and $\delta \leq 6.6\%$). However, Otto et al. found that only the NiFeCrCoMn had a single phase while all other five alloys had multiple phases. They concluded that individual binary enthalpies contributed to the formation of secondary phases.

There have been other efforts to predict the phase formation of HEAs, such as a geometry
parameter [37]. These studies are less widely used than the previous ones and also cannot accurately predict the phase of HEAs. HEA phase prediction remains an unsolved problem so far. In Chapter 5, a DFT study to predict the phase formation of NiFeCrCo HEA by revealing the magnetic theories behind such phase transformation will be given.

1.2 NiFeCrCoMn HEAs

As one of the most important single-phase HEA systems, NiFeCrCoMn HEAs, including NiFe-CrCo and NiFeCrCoMn, have exhibited interesting physical properties in recent reports.

1.2.1 Mechanical Properties

Equiatomic NiFeCrCo and NiFeCrCoMn both form single-phase fcc solid-solution phases before and after annealing. Salishchev et al. [46] prepared equiatomic NiFeCrCo and NiFeCr-CoMn using arc-melting/casting followed by annealing at 1000°C for 24h. They measured Vickers microhardness as well as tensile properties (yield strength, ultimate yield strength and elongation) for the two alloys before and after annealing (Table 1.2). Their results showed that the five-component HEA had slightly higher strength but also became less ductile than the four-component alloy. Gali et al. [21] used the same method as by Salishchev et al. [46] to produce the same two equiatomic alloys. They measured tensile strength with temperature ranging from 77 K to 1273 K. Their results at 297 K and 77 K are listed in Table 1.2, which is relatively close to the measurements by Salishchev et al. [46]. They also found that the ductility of both NiFeCrCo and NiFeCrCoMn got increased as temperature decreased. Gludovatz et al. [22] manufactured equiatomic NiFeCrCoMn using arc-melting/casting and recrystallization processing. They measured the tensile strength of this HEA at 297 K and 77 K and obtained much higher yield strength and ultimate yield strength than the results of Salishchev et al. [46]
and Gali et al. [21]. This is most likely due to smaller grain sizes caused by the lack of grain growth in the recrystallization processing. The room temperature yield strength of NiFeCr-CoMn was 410 MPa with an ultimate yield point at 763 MPa. At 77 K its ultimate strength exceeded 1.2 GPa. They also measured the initiation fracture toughness to be 191 MPa m$^{1/2}$, which indicated that equiatomic NiFeCrCoMn HEA could be highly fracture-resistant at cryogenic temperatures. Zaddach et al. [6] prepared equiatomic NiFeCrCo and NiFeCrCoMn using ball-milling and casting, and observed hardness as high as 642 HV and 795 HV in as-milled NiFeCrCo and NiFeCrCoMn samples, respectively. After annealing, these samples exhibited similar hardness as previous results by Salishchev et al. [46]. All data reported in Table 1.2 shows that NiFeCrCoMn HEAs have good strength with excellent performance in ductility.

Table 1.2 Properties of equiatomic NiFeCrCo and NiFeCrCoMn from literature

<table>
<thead>
<tr>
<th></th>
<th>Hardness (HV)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate yield strength (MPa)</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFeCrCo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFeCrCoMn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>642.4 ± 10.2 [6]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFeCrCoMn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>144.8 ± 3.1 [6]</td>
<td></td>
<td></td>
<td>40% (297K) [21]</td>
</tr>
<tr>
<td></td>
<td>410 ± 21 (297K) [22]</td>
<td></td>
<td>763 ± 32 (297K) [22]</td>
<td>61% (77K) [21]</td>
</tr>
<tr>
<td></td>
<td>759 ± 67 (77K) [22]</td>
<td></td>
<td>1280 ± 59 (77K) [22]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 (297K) [21]</td>
<td>600 (297K) [21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>420 (77K) [21]</td>
<td>1100 (77K) [21]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zaddach et al. [6] obtained the stacking fault energy (SFE) by combining experimental and computational results of NiFeCrCoMn HEAs and observed a low SFE, which was used to explain the balanced performance in strength and ductility. In an alloy with a low SFE, a
pair of partial dislocations separate further apart, making it more difficult to slip across grain boundaries. Therefore the strength of this low-SFE alloy is improved. Meanwhile, twinning is more likely to occur in this low-SFE alloy, producing more storage space for dislocation accumulation, making the alloy more ductile.

Exploration for off-stoichiometric NiFeCrCoMn HEAs reveals even greater potential of this single-phase solid-solution HEA system. Zaddach et al. [6] found a Ni$_{14}$Fe$_{20}$Cr$_{26}$Co$_{20}$Mn$_{20}$ HEA that had an extremely low SFE of 3.5 mJ/m$^2$, which implied that this HEA may have even better performance in strength and ductility. Yao et al. [47] prepared a Ni$_{26}$Fe$_{40}$Cr$_2$Co$_5$Mn$_{27}$ alloy and confirmed that the Ni-Fe-Cr-Co-Mn system remained in the fcc solid-solution phase even without a high configurational entropy. They found this alloy also exhibited good tensile ductility ($\sim 60\%$). Tasan et al. [48] from the same research group confirmed Yao’s conclusion by showing that Fe$_{37}$Cr$_9$Co$_9$Mn$_{45}$ formed fcc single-phase solid solution as well. They concluded that well-controlled compositional variations could be considered not only to decrease the processing and alloying costs but also to explore improved mechanical property combination.

1.2.2 Theoretical Study

To continue searching for off-stoichiometric NiFeCrCoMn HEAs that have excellent mechanical performance, a theoretical understanding of the deformation mechanism in this system is desirable. There have been several attempts to study the deformation mechanism in the NiFe-CrCoMn HEA system. In Yao et al.’s report [47], they observed that the Ni$_{26}$Fe$_{40}$Cr$_2$Co$_5$Mn$_{27}$ alloy was dominantly deformed by dislocation slip and not by twinning. They also proposed that the planar slipping should be promoted by strong friction stress on dislocation motion that arose from lattice distortion, not by short-range ordering or reduction of stacking fault energy.
Zhu et al. [49] conducted instrumented nano-indentation on an equiatomic NiFeCrCoMn alloy to characterize the nature of incipient plasticity. They calculated the activation energy and volume of the onset of plasticity to be $1.72 \pm 0.35 \text{ eV}$ and $34 \pm 7 \text{ Å}^3$, respectively, which indicated that vacancy-mediated heterogeneous dislocation nucleation was favored as the mechanism for the onset of plasticity in NiFeCrCoMn. They also concluded that the higher activation energy and volume in the current NiFeCrCoMn alloy in comparison with that obtained from conventional fcc metals suggested that vacancy migration in HEAs was not a traditional process of direct atom-vacancy exchange, but involved the cooperative motion of several atoms. Tsai et al. [18] measured the diffusion parameters of Ni, Fe, Cr, Co and Mn in NiFeCrCoMn HEAs. Their results showed that the diffusion coefficients in NiFeCrCoMn were lower than those in various conventional fcc metals. Sluggish diffusion in NiFeCrCoMn with higher activation energy was found to be caused by the greater fluctuation of lattice potential energy and more significant atomic traps and blocks. Computational investigation has been reported to explore the deformation theory in HEAs. Middleburgh et al. [50] examined the ease of vacancy formation in equiatomic NiFeCrCo using first-principles modeling. They found that the formation energy of a vacancy on Ni/Fe/Co sites was positive while negative on Cr sites. They concluded that Cr was not thermodynamically stable in NiFeCrCo and that Cr may segregate into precipitates in the bulk or migrate to the surface. This work showed that chemical complexity in NiFeCrCo may have an influence on the phase stability and defects formation. Such influence may be even greater in NiFeCrCoMn HEAs with higher chemical complexity.

1.3 Motivation and Road Map

This dissertation aims at studying the NiFeCrCoMn HEA system using computational tools to develop a mechanistic understanding of properties which otherwise are difficult to investigate
experimentally. Specifically, it seeks to work out the following questions:

1. What properties that are important for HEAs can be investigated by computational tools? And how to best proceed?

2. What practical issues are there that need to be taken care of with HEA calculations?

3. Do we have the correct understanding of structure and phase formation in the simpler HEA, NiFeCrCo?

4. What can we find in composition-dependent maps of properties for NiFeCrCo HEAs?

5. Can we calculate the stacking fault energy of HEAs? What difficulties need to be solved?

6. Can we extend these computational methods and conclusions to more complex systems, like NiFeCrCoMn HEAs?

Answers to the questions above can provide useful information to both theoretical and experimental researchers in this area. These questions are studied each in an individual chapter from Chapter 3 to Chapter 8. Chapter 2 introduces the theoretical background of first-principles methods and density functional theory methods.

Through the computational studies in this dissertation, it has been found that

1. The stable phase of equiatomic NiFeCrCo is an L12 type lattice with Cr ordering due to the decrease in enthalpy when antiferromagnetic Cr atoms avoid direct bonding with each other. This DFT prediction is confirmed by experimental magnetic measurements and electronic microscopy observation.

2. Properties of NiFeCrCo HEAs with varying compositions are mainly controlled by one or two elements, e.g., enthalpy of mixing is almost entirely dependent on Cr concentration, lattice parameter on Co and Cr, bulk modulus $B$ on Fe, shear modulus $G$ on Co, and
$B/G$ ratio on Cr. The enthalpy of mixing and bulk modulus can be estimated with some errors via equations that only use input data from binary alloy calculations.

3. Two complimentary computational methods and two modeling methods for stacking fault energy (SFE) are investigated for the equiatomic NiFeCrCo HEA. The supercell model with EMTO-CPA method leads to reasonable SFE results. The axial interaction model from both EMTO-CPA and VASP calculations show that hcp is more stable than fcc at 0 K. Calculations of vibrational entropy show that the fcc phase is stabilized at high temperatures. Accurate calculation of SFE needs more vibrational calculations, which are computationally demanding.

4. The well-established toolsets have been applied to the study of NiFeCrCoMn HEAs. It is found that partial ordering of Cr and Mn is also energetically preferred to the random solid solution phase.
Chapter 2

Density Functional Theory (DFT)

This dissertation focuses on first-principles studies. The term "first-principles" comes from philosophy, meaning a statement is simply assumed and needs no reasoning. In physics, a first-principles calculation starts directly from physical theories and is not fitted to reproduce experiment. Theories that do fit to available experimental data are known as empirical methods. First-principles methods and empirical methods have their own pros and cons and serve for different purposes, e.g., the former reveal more atomistic-level details in a material but also have stricter size limitations. This dissertation work uses first-principles methods because (1) the materials it studies have limited experimental database and (2) parameter-fitting in empirical calculations of multi-component alloys is a non-trivial task. The first section of this chapter covers fundamentals of first-principles methods.

There are many theories available for first-principles calculations, and density functional theory (DFT) is most popular for condensed systems. As a first-principles tool, DFT provides a convenient means to calculate the system energy from only electronic density. The background of DFT will be given in the second section as well as some practical issues and corresponding solutions. Two DFT software used in this dissertation will also be introduced.
DFT calculations are computationally expensive and have a size limitation. This size limitation is usually not a problem for simulations of ordered bulk crystals. Nevertheless, when it comes to disordered structures, DFT simulation becomes complicated: the requirement of disorder conflicts with the periodic boundary condition in plane wave DFT. In the third section, two techniques that assist DFT simulation of disordered structures are introduced.

2.1 First-Principles Methods

First-principles calculations are rooted in modern physics developed after the early 1900s. Milestones of the development of first-principles methods include:

- the Schrödinger equation that builds the foundation of quantum mechanics
- the variational principle that approximates the ground state solution using a trial solution
- the Born-Oppenheimer approximation that allows separation of the electronic and nuclear terms

2.1.1 The Schrödinger Equation

The Schrödinger equation is the foundation of quantum mechanics. It is simply proposed without theoretical support, yet has been working like a charm. The inspiration for the Schrödinger equation is symmetry principle – if it works this way, it perhaps works in the opposite direction. One application of the symmetry principle is the derivation of wave-particle duality by Louis de Broglie. If wave has particle-like properties as proposed by Einstein to explain the photoelectric effect (1905), it is perhaps true that matter also has wave-like properties. Based on this hypothesis, de Broglie made his big discovery (1924): \[ p = \frac{h}{\lambda}. \] The Schrödinger equation can also be understood in a similar way. It is symmetric to an equation in classical mechanics.
Let’s start from the plane wave function in the complex form:

\[ \Psi(r, t) = Ae^{i(k \cdot r - \omega t)} \quad (2.1) \]

The idea behind choosing the plane wave function is that a universal equation must work for any situation, so it makes perfect sense to start with a convenient one. The plane wave function is the simplest wave function that satisfies the Bloch’s theorem. Our target is to find a solvable equation containing the wave function and other basic properties (mass, potential, etc.). We need to pick an equation from classical mechanics and then substitute its classical terms with quantum mechanics equivalents which contain the wave function only. Since the target is a master equation in quantum mechanics, it is reasonable to assume that its equivalent in classical mechanics is the most important one, law of energy conservation:

\[ E = \frac{p^2}{2m} + U(r, t) \quad (2.2) \]

Now the problem is how to express \( E \) and \( p \) in Eq. 2.2 as a function of the plain wave function \( \Psi \).

Substituting \( k \) and \( \omega \) in Eq. 2.1 with momentum \( p \) and energy \( E \) yields

\[ \Psi(r, t) = Ae^{\frac{i}{\hbar}(p \cdot r - Et)} \quad (2.3) \]

The first-order partial derivatives of Eq. 2.3 with respect to space and time are

\[ \nabla \Psi(r, t) = \frac{i}{\hbar} p \Psi(r, t) \quad (2.4) \]
and

\[ \frac{\partial \Psi(r,t)}{\partial t} = -i\frac{E}{\hbar} \Psi(r,t) \]  \hspace{1cm} (2.5)

respectively. Multiplying both sides of Eq. 2.2 by \( \Psi \) and inserting Eq. 2.4 and Eq. 2.5 to substitute \( E \) and \( p \) yield:

\[ i\hbar \frac{\partial}{\partial t} \Psi(r,t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r,t) + U(r,t)\Psi(r,t) \]  \hspace{1cm} (2.6)

Eq. 2.6 is known as the time-dependent Schrödinger equation. Its general form is

\[ i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \]  \hspace{1cm} (2.7)

where \( \hat{H} \) is the Hamiltonian operator which characterizes the energy term \( E \), given by

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U \]  \hspace{1cm} (2.8)

The time-dependent Schrödinger equation describes the wave function \( \Psi(r,t) \) of a system. \(|\Psi(r,t)|^2\) after normalization means the probability density of finding a particle in a given place at a given time. Solving the time-dependent Schrödinger equation is not an easy task, even for the simplest system. To simplify this problem, let’s assume the system is in stationary states where its potential is independent from time. Then we can factorize the wave function between space and time:

\[ \Psi(r,t) = \psi(r) \cdot T(t) \]  \hspace{1cm} (2.9)

Inserting Eq. 2.9 into Eq. 2.6 yields

\[ i\hbar \frac{\partial T(t)}{\partial t} \frac{T(t)}{T(t)} = -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + U(r)\psi(r) \]  \hspace{1cm} (2.10)
The left side of Eq. 2.10 only has the variable $t$, while the right side only has the variable $r$. This implies that both sides must equal a constant in order to make Eq. 2.10 always true. This constant turns out to be the system energy $E$. The right side of Eq. 2.10 becomes the time-independent Schrödinger equation:

$$\frac{\hbar^2}{2m} \nabla^2 \psi(r) + U(r) \psi(r) = E \psi(r)$$

(2.11)

It also has a general form:

$$\hat{H} \psi = E \psi$$

(2.12)

The time-independent Schrödinger equation can be applied for standing waves, such as atomic orbitals and molecular orbitals.

We can use a brute-force approach to get analytical solutions of the time-independent Schrödinger equation. First, specify the potential of the system. This potential term completes the time-independent Schrödinger equation, which then becomes a differential equation to solve. Second, solve the equation and obtain solutions. Several sets of solutions may be obtained. Then evaluate boundary conditions to screen these solutions. Finally, normalize solutions that pass the boundary condition test. The real challenge of solving the time-independent Schrödinger equation comes from the potential term. Only a few systems have been solved analytically, e.g., a free particle, a finite potential well, and a hydrogen atom (which is non-trivial already). For complex systems in the real world, solving the Schrödinger equation analytically by applying the brute-force approach is a mission impossible.
2.1.2 The Variational Principle

The variational principle provides an alternative route to solving the time-independent Schrödinger equation. After determining the Hamiltonian of a system, we can guess a normalized trial wave function and use that trial wave function to obtain a trial energy. The variational principle proves that this energy is always higher than the ground state energy of the given system. If the trial energy equals the ground state energy, it means the trial wave function is actually the ground state wave function.

\[ \int_{-\infty}^{\infty} \psi_T^* \hat{H} \psi_T \, dr = E_T \geq E_{GS} \] (2.13)

The variational principle is the base of many modern techniques developed to solve the Schrödinger equation. It implies that we can start from a trial solution and continue searching for a better one which gives a lower energy. Whichever normalized wave function gives the lowest energy is closest to the ground state wave function.

2.1.3 The Born-Oppenheimer Approximation

The first step to apply the variational principle for a complex system is to determine the Hamiltonian. The Hamiltonian of a system with \( N_\mu \) nuclei and \( N_e \) electrons is

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \frac{1}{2M_i} \sum_{i=1}^{N_\mu} \nabla_i^2 - \sum_{i,j}^{N_e,N_\mu} \frac{Z_i}{|R_i - r_j|} + \sum_{i>j}^{N_e,N_\mu} \frac{1}{|r_i - r_j|} + \sum_{i>j}^{N_\mu,N_\mu} \frac{Z_i Z_j}{|R_i - R_j|} \] (2.14)

which can be written in a compact form as

\[ \hat{H} = T_e(\mathbf{r}) + T_\mu(\mathbf{R}) + V_{e-\mu}(\mathbf{r}, \mathbf{R}) + V_{e-e}(\mathbf{r}) + V_{\mu-\mu}(\mathbf{R}) \] (2.15)
where \( e \) and \( \mu \) denote electron and nucleus, respectively, \( r \) and \( R \) are electronic and nuclear coordinates, respectively, \( T \) is kinetic energy, and \( V \) is potential energy. Because nuclei are much heavier than electrons, the Born-Oppenheimer approximation assumes that the nuclei are clamped down at a fixed position while the electrons instantaneously relax to their positions. Hence, the Hamiltonian is simplified as

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i,j}^{N_e,N\mu} \frac{Z_j}{|R_j - r_i|} + \sum_{i>j}^{N_e,N_e} \frac{1}{|r_i - r_j|}
\]

\( = T_e(r) + V_{e-\mu}(r; R) + V_{e-e}(r) \)

The Born-Oppenheimer approximation (Eq. 2.16) reduces the Hamiltonian into three parts: the kinetic energy of electrons, the attraction between electrons and the nucleus, and the repulsion between electrons. The significance of the Born-Oppenheimer approximation (Eq. 2.16) is that it allows splitting the wave function into an electronic term and a nuclear term: \( \psi(r, R) = \psi(r; R) \chi(R) \), where \( \psi(r; R) \) is the electronic wave function with a constant nuclear coordinates \( R \). The independence of the electronic wave function from the nuclear coordinate greatly simplifies the problem in that the trial wave function needs only to be a guess for the electronic wave function now:

\[
\frac{\int \text{d}r_1 \text{d}r_2 \ldots \text{d}r_{N_e} \psi_T^* \hat{H} \psi_T}{\int \text{d}r_1 \text{d}r_2 \ldots \text{d}r_{N_e} \psi_T^* \psi_T} \geq E_{GS} \quad \text{(2.17)}
\]

There exist several methods attempting to solve the electronic wave function problem (Eq. 2.17), such as the Hartree-Fock method that employs the expansion of the electronic wave function in Slater determinants. However, the Hatree-Fock method requires huge computational effort and ignores the correlation energy between electrons.
2.2 Density Functional Theory

Density functional theory provides an alternative route to solving Eq. 2.17 for the electronic wave function problem. Because of its accuracy and efficiency, this method has become the most popular first-principles method for the study of condensed systems. This section introduces the background of density functional theory. The Thomas-Fermi approach firstly proposed the concept of electron density to replace wave function when using the variational principle to get the lowest energy. The Hohenberg-Kohn theorems established a solid theoretical base for density functional theory.

2.2.1 The Thomas-Fermi Approach

The predecessor to DFT was the Thomas-Fermi approach. In 1927, Thomas and Fermi proposed to use electron density instead of wave functions to solve this problem. The electron density is given by

\[ n(r) = 2 \sum_{i}^{N} \phi_{i}^{*} \phi_{i} (2.18) \]

where \( N \) refers to the highest occupied orbital. It assumes two electrons with up and down spinning orientation at each orbital.

The kinetic energy term in the Born-Oppenheimer approximation (Eq. 2.16) is given by

\[ T_{TF}[n(r)] = \frac{3}{10} (3\pi^{2})^{\frac{2}{3}} \int n(r)^{\frac{5}{3}} \, dr \quad (2.19) \]

In the equation above, the kinetic energy is a function of the electron density, which is a function of the electron coordinates. A function of a function is called a functional. This is why the theory based on electron density is named density functional theory. Combining this kinetic
energy term with classical electrodynamics terms for electron-electron repulsion and electron-nuclear attraction yields the total energy:

\[
E[n(\mathbf{r})] = T_{\text{TF}}[n(\mathbf{r})] - Z \int \frac{n(\mathbf{r})}{r} \, d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (2.20)
\]

This Thomas-Fermi approach (Eq. 2.20) is much easier than the Hartree-Fock method, but is not accurate in that 1) \(T_{\text{TF}}\) is a very coarse approximation; 2) it misses any contribution from electron exchange or correlation energy. However, the idea of expressing the system energy in terms of electron density instead of wave functions led to the development of DFT.

### 2.2.2 The Hohenberg-Kohn Theorems

Two theorems proposed by Hohenberg and Kohn in 1964 build a solid theoretical base for DFT. The two theorems are:

I (Proof of Existence) For any ground state electron density \(n(\mathbf{r})\), there exist a unique external potential \(V_{\text{ext}}(\mathbf{r})\), to within a constant. This \(V_{\text{ext}}(\mathbf{r})\) defines a unique Hamiltonian, therefore also defines all properties of the ground state system.

II (Variational Principle) For any many-body system, there exist a unique electron density \(n(\mathbf{r})\) for its ground state. All other electron densities lead to a higher energy than the ground state energy.

Theorem I shows that any system energy \(E\) is a function of the electron density \(n(\mathbf{r})\). Recall the Born-Oppenheimer approximation (Eq. 2.16) which separates electronic wave function from nuclear wave function. Similarly, the ground state energy of the many-body system can be
written as a function of the ground state electron density $n_0$:

$$E[n_0] = T[n_0] + E_{e-e}[n_0] + E_{e-\mu}[n_0] \quad (2.21)$$

In Eq. 2.21, $T[n_0]$ is the ground state kinetic energy, $E_{e-e}[n_0]$ is the ground state energy of electron-electron interaction, and $E_{e-\mu}[n_0]$ is the ground state energy of electron-nucleus interaction. This equation can be broken into system-dependent and universal expressions:

$$E[n_0] = \begin{cases} n_0(r)V_{e-\mu}\,dr + T[n_0] + E_{e-e}[n_0] \\ \text{system dependent} & \text{universal} \end{cases} \quad (2.22)$$

The universal expression is independent from the system, i.e., external potential, and determined only by the electron density. It is called the Hohenberg-Kohn functional, $F_{HK}[n_0]$.

$$F_{HK}[n_0] = T[n_0] + E_{e-e}[n_0] \quad (2.23)$$

Although Theorem I proves that for any given electron density $n_0$ there exist a system energy, the two pieces in $F_{HK}[n_0]$ - the electronic kinetic energy term and the electron-electron interaction term - are not known exactly. The electron-electron interaction can be broken into a Coulombic part and non-classical contribution:

$$E_{e-e}[n_0] = \frac{1}{2} \int \frac{n_0(r_1)n_0(r_2)}{|r_1 - r_2|}\,dr_1\,dr_2 + E_{n-c}[n_0] \quad (2.24)$$

The non-classical term $E_{n-c}[n_0]$ includes all electron-electron interactions that are not captured in the Coulombic expression, including exchange and correlation, and self-interaction corrections.
While Theorem I states that electron density is the only information we need to get all properties of the system, we also need Theorem II that allows us to use the variational principle to solve for system energy. Any trial density $n_T(\mathbf{r})$ satisfies:

$$E_0 \leq E[n_T(\mathbf{r})] = T[n_T(\mathbf{r})] + E_{e-e}[n_T(\mathbf{r})] + E_{e-u}[n_T(\mathbf{r})]$$  \hspace{1cm} (2.25)

### 2.2.3 The Kohn-Sham Equation

As mentioned earlier in Eq. 2.24, we can break the electron-electron interaction into a Coulumbic part and non-classical contribution:

$$E_{e-e}[n_0] = J[n_0] + E_{n-c}[n_0]$$  \hspace{1cm} (2.26)

The non-classical piece is still unknown, but at least we can solve the Coulumbic term and approach the real value. The same idea is proposed by Kohn and Sham to approach the kinetic term by splitting it into a solvable piece describing a system of non-interacting electrons and whatever is not included. The non-interacting kinetic energy is expressed by a Slater determinant:

$$T_S[n_0] = -\frac{1}{2} \sum_{i=1}^{N_e} \langle \phi_i | \nabla^2 | \phi_i \rangle$$  \hspace{1cm} (2.27)

where $\phi_i$ is single-electron wave function of Kohn-Sham orbitals. The difference between the total kinetic energy $T[n_0]$ and $T_S[n_0]$ is a new quantity, $T_C$, which encapsulates the correlated motion of electrons:

$$T[n_0] = T_S[n_0] + T_C[n_0]$$  \hspace{1cm} (2.28)
If we replace the two parts in the Hohenberg-Kohn functional expression (Eq. 2.23) with Eq. 2.28 and Eq. 2.26, we have:

\[
F_{HK}[n_0] = T_S[n_0] + J[n_0] + T_C[n_0] + \underbrace{E_{n-c}[n_0]}_{E_{XC}[n_0]}
\] (2.29)

This new quantity, \(E_{XC}[n_0]\), collects all unknown terms in the Hohenberg-Kohn functional. It is called the exchange and correlation functional. The single-particle potential \(V_S\) for the Kohn-Sham orbitals is:

\[
V_S(r) = \int \frac{n(r_j)}{|r_i - r_j|} \, dr_j + V_{XC}(r) - \sum_A Z_A \frac{r_i A}{r_i A} \tag{2.30}
\]

The potential \(V_{XC}\) is the potential of exchange and correlation functional \(E_{XC}\):

\[
V_{XC} = \frac{\partial E_{XC}}{\partial n} \tag{2.31}
\]

2.2.4 Exchange and Correlation

The Kohn-Sham equation has grouped all unknown quantities in the Hohenberg-Kohn functional into the exchange-correlation functional. The real challenge in calculations is to express the exchange-correlation functional as a function of electron density. The only system whose exchange-correlation functional is certain is the uniform electron gas. So an initial approach to define the unknown exchange-correlation functional for any given system is to assume the unknown functional is equal to that of a uniform electron gas with the same local electron density:

\[
V_{XC}^{LDA} = V_{XC}^{\text{electron gas}}[n(r)] \tag{2.32}
\]

This approach is called Local Density Approximation (LDA). Despite its simple nature, LDA has a surprisingly good accuracy for many systems, especially those with a slowly-changing
electron density.

If the electron density of a system varies quickly, the simple assumption of LDA is insufficient. Instead, the value of local electron density, as well as how it varies in space, needs to be considered when designing an approximating method. This is called the Generalized Gradient Approximation (GGA), given by:

\[
V_{XC}^{\text{GGA}} = V_{XC}[n(r), \nabla n(r)]
\]  

(2.33)

2.2.5 Pseudopotentials

Once we have chosen the appropriate exchange-correlation functional approximation, we can solve the Kohn-Sham equation for each electron and obtain the system energy. For systems with a large number of electrons, the calculation can become very expensive. Alternatively, we can only consider the valence electrons that are the most important for electronic interactions and assume the core electrons are fixed. That is, all core electrons are frozen in the calculation while the valence electrons are allowed to relax. This approximation method can greatly reduce the number of active electrons in the calculation. Potentials describing the frozen core and valence electrons are called pseudopotentials. This approximation is physically justified because core electrons often are unchanged in condensed systems. One way of generating pseudopotentials is the projector-augmented wave (PAW) method. The use of pseudopotentials in density functional theory greatly accelerates the calculation while giving very similar results to those using full-electron potentials.
2.2.6 Plane-Wave Basis Sets

To solve the Kohn-Sham equation numerically, we need to select a basis set to decompose the Kohn-Sham wave functions. According to Bloch’s theorem, the wave functions of a periodic system need to satisfy:

\[ \phi_k(r) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(r) \]  

(2.34)

where \( u_k \) is a periodic function and \( e^{i\mathbf{k}\cdot\mathbf{r}} \) is a plane-wave function defined by real space coordinate \( r \) and reciprocal space coordinate \( \mathbf{k} \). The periodic function \( u_k(r) \) can then be expanded as a set of plane-wave functions. Ideally, the number of expansion plane-wave functions is infinite. However, plane-wave functions with higher kinetic energies have a much smaller contribution to the overall energy than those with lower kinetic energies. A cut-off energy, therefore, is used in practice to truncate the plane-wave expansion of the Kohn-Sham wave functions. Convergence tests are usually necessary to determine its exact value.

2.2.7 Exact Muffin-Tin Orbitals (EMTO)

As mentioned earlier, pseudopotential provides an efficient way to approximate the potential field by fixing core electrons. The computing speed of solving the Kohn-Sham equation is significantly higher in pseudopotential calculations. Another group of Kohn-Sham methods is based on the so-called muffin-tin approximation to describe the effective potential field and electron density. This approximation assumes that the atomic sites in a crystal lattice have spherically symmetric potentials centered on the atoms plus a constant potential in the interstitial space. The exact muffin-tin formalism was introduced in the early 1990s, allowing to solve the single-electron equations exactly for the muffin-tin potentials. While plane-wave basis sets are used to expand the single-electron wave functions within the constant interstitial potential,
the atom-centered muffin-tin orbitals are expanded in terms of spherical basis sets.

A key advantage of the exact muffin-tin orbitals method is that it can be combined with the coherent potential approximation technique to simulate random solid solutions. The coherent potential approximation will be discussed in section 2.3.2.

2.3 DFT with Chemical Disorder

DFT for condensed systems depends on the Bloch’s theorem to describe potentials for a periodic crystalline environment. When trying to solve the Kohn-Sham equations of single electrons, both the plane-wave basis sets and the muffin-tin orbitals are based on periodic boundary conditions. The periodic boundary conditions are the perfect choice for simulation of crystals, in which the alignment of atomic sites is periodic, too. However, in a crystal with chemical disorder, i.e., solid solution alloys, the periodic boundary condition brings some degree of order into the system. What’s more, the size of unit cell is usually limited by computer hardware. This leads to an avoidable problem in DFT simulation of solid solutions: the model is not disordered! In this section, two methods to assist DFT simulation of solid solutions are introduced. The first is based on atomic models, called special quasi-random structures (SQS). The second is a one-site approximation, called coherent potential approximation.

2.3.1 Special Quasi-random Structure (SQS)

Special quasi-random structure (SQS) is an essential tool in modeling disordered alloys with specific atomic resolution. Intuitively, to model a random solid solution, we can generate a large supercell and randomly distribute the solute and solvent atoms on its lattice sites. However, this brute-force approach would need very large supercells to adequately represent the statistics of random alloys and would therefore be computationally too expensive for DFT calculations. The
The concept of SQS is to build a special periodic structure with a small number of atoms per unit cell whose correlation functions for the first few nearest-neighbor shells are as close to those of a target random alloy as possible such that periodicity errors only exist between more distant neighbors. Because interactions between distant neighbors generally contribute much less to the system energy than between near neighbors, a SQS can be regarded as the best possible periodic unit cell representing a given random alloy.

The application of SQS to high-entropy alloys has some limitations that need to be considered. Three major questions need to be answered to obtain a SQS for HEAs. The first is to determine the size of desired SQS. Is it large enough to allow exploring aimed compositions with sufficient accuracy and small enough for DFT calculations within current hardware limitations? The second is to decide the criteria of clusters used in the calculations of correlation functions. Namely, what is the maximum distance for pairs and triplets that are considered in generating SQS? Is it always preferred to use strict criteria? The third is to determine when to stop the generation of SQS. Ideally, the generation of SQS will stop automatically after finding the perfect SQS. However, it is likely that a perfect SQS of a HEA can never be found, in which case the generation of SQS needs to be stopped by the user. There are no standard answers to the three questions. Rather, these questions are to remind researchers of what must be taken into consideration before and during the generation of SQS for their research projects.

The most convenient toolkit for generation of SQS is the Alloy Theoretic Automated Toolkit (ATAT) developed by Alex van de Walle and co-workers. [51, 52] Two utilities from ATAT, corrdump and mcsqs, are used to build an SQS. The utility corrdump is a convenient tool to obtain a cluster file that is needed by mcsqs. The utility mcsqs uses a Monte Carlo algorithm to find a SQS [53] and is preferred to an earlier code gensqs, another utility from ATAT. The full functionalities of ATAT can be found in the official manual. Based on the authors’ experience, it usually takes a few weeks to obtain an optimal SQS for HEAs with small
correlation function mismatch, e.g., all < 0.05.

2.3.2 Coherent Potential Approximation (CPA)

The coherent potential approximation works in a way that it replaces the alloy with effective medium of all atoms such that the alloy can be represented by a single site with the effective potential instead of a group of atoms. This approximation method makes it extremely fast to simulate random alloys because this method only needs to solve the Kohn-Sham equations for the effective sites. At the same time, this method neglects the difference between local potentials of the same type of atoms, i.e., the local chemical environment is regarded as the same. Consequently, atomic displacement is not captured in such approximation. The CPA technique has been implemented into the EMTO method by Vitos. [54] Although the one-site approximation in exact muffin-tin orbitals method ignores atomic displacement, this method has shown good accuracy for alloys with similar atomic sizes.
Chapter 3

Properties and Methodology

Properties studied in this dissertation are derived through thermodynamics. What DFT calculations generate is system energy at ground state, i.e., 0 K. Starting from these energies, we can then calculate many properties. This chapter aims at introducing how some properties can be obtained and their physical meanings.

3.1 Ground State

System energy from a DFT calculation is the lowest energy of that specific system at 0 K. This energy is not necessarily the ground state energy of the real material, which corresponds to the equilibrium volume with the lowest energy. This lowest system energy can be found automatically by volumetric relaxation with the highest degree of freedom in VASP calculations. However, other properties are also of interest that are not captured by knowing the ground state energy alone, e.g., the bulk modulus. Rather, the employment of equation of state provides a convenient means to finding the equilibrium energy and bulk modulus at the same time. What is more, the EMTO-CPA code does not have the function of automatic volumetric relaxation,
therefore it must be used with the equation of state to find the equilibrium state.

### 3.1.1 Equation of State and Bulk Modulus

The bulk modulus of a crystal is defined by

\[
B = -V \left( \frac{\partial P}{\partial V} \right)_T
\]  

(3.1)

An equation of state describes the relation between state variables of a system. We can use an equation of state to obtain the bulk modulus of a crystal. In this case, bulk modulus is one of the variables in the equation of state. The Birch-Murnaghan equation of state [55] is the most widely used equation of state by DFT users. It is based on Taylor expansion of the strain energy in terms of the finite strain in the crystal. The first-order Birch-Murnaghan equation of state reduces to the Murnaghan equation of state [56].

The Murnaghan equation of state assumes that the bulk modulus is a linear function of the pressure:

\[
B = B_0 + B'_0 P
\]  

(3.2)

Insert Eq. 3.1 into Eq. 3.2 and solve the differential equation:

\[
\begin{align*}
- V \frac{dP}{dV} &= B_0 + B'_0 P \\
\Rightarrow \quad \frac{dP}{B_0 + B'_0 P} &= \frac{dV}{-V} \\
\Rightarrow \quad \int_0^P \frac{1}{B_0 + B'_0 P} dP &= \int_{V_0}^V \frac{1}{-V} dV \\
\Rightarrow \quad \log \left( 1 + \frac{B'_0 P}{B_0} \right)^{1/B'_0} &= \log \left( \frac{V}{V_0} \right)^{-1} \\
\Rightarrow \quad V &= V_0 \left( 1 + \frac{B'_0 P}{B_0} \right)^{-1/B'_0}
\end{align*}
\]
We can also express the pressure depending on the volume:

\[ P(V) = \frac{B_0}{B'_0} \left( \frac{V}{V_0} \right)^{-B'_0} - 1 \]  

(3.3)

Inserting Eq. 3.3 into the relationship \( P = -\frac{dE}{dV} \) gives

\[ E(V) = E_0 + B_0 V_0 \left[ \frac{1}{B'_0 (B'_0 - 1)} \left( \frac{V}{V_0} \right)^{1-B'_0} + \frac{1}{B'_0 V_0} \frac{V}{B'_0 - 1} \right] \]  

(3.4)

Eq. 3.4 is the Murnaghan equation of state.

In the second-order form of the Birch-Murnaghan equation of state, the pressure is

\[ P(V) = \frac{3B_0}{2} \left( \eta^{-7} - \eta^{-5} \right) \]

where \( \eta = (V/V_0)^{1/3} \). The pressure is independent from \( B'_0 \), therefore the second-order form is rarely used.

The third-order form of the Birch-Murnaghan equation of state is indeed the most popular equation of state. It expresses the pressure as

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

(3.5)

Inserting Eq. 3.5 into the relationship \( P = -\frac{dE}{dV} \) leads to the third-order Birch-Murnaghan equation of state:

\[ E(\eta) = E_0 + \frac{9B_0 V_0}{16} (\eta^2 - 1)^2 \left[ 6 + B'_0 (\eta^2 - 1) - 4\eta^2 \right] \]  

(3.6)

where \( \eta = (V/V_0)^{1/3} \).
Another popular equation of state is the Vinet EOS, given by

\[
E(\eta) = E_0 + \frac{2B_0V_0}{(B'_0 - 1)^2} \left( 2 - [5 + 3B'_0(\eta - 1) - 3\eta]e^{-3(B'_0 - 1)(\eta - 1)/2} \right) \tag{3.7}
\]

While the Birch-Murnaghan equation of state is the most widely used equation of state in condensed matter physics, it is sometimes suggested to use the Vinet equation of state for better stability. [57]

### 3.1.2 Elastic Constants

We have discussed methods to calculate bulk modulus of a crystal using an equation of state in the previous part. However, knowing the bulk modulus is far from enough to characterize the elastic properties of a crystal. Elastic tensor, a 6 × 6 matrix, carries the full elastic information. Members in the matrix are called elastic constants, noted as \(C_{ij}:

\[
C_{\alpha\beta} = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{pmatrix} \tag{3.8}
\]

To calculate these 36 elastic constants for a random lattice is non-trivial. Fortunately, all HEAs in this dissertation work are fcc crystals, for which the elastic tensor is significantly
simplified due to lattice symmetry. The elastic tensor for fcc lattices is

\[ C_{\alpha\beta} = \begin{pmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{pmatrix} \] (3.9)

We only need to obtain three independent elastic constants, \( C_{11}, C_{12}, \) and \( C_{44}, \) to fully capture the elasticity of fcc HEAs. The crystal is mechanically stable only if

\[
C_{11} + 2C_{12} > 0 \\
C_{11} - C_{12} > 0 \\
C_{44} > 0
\] (3.10)

At least two methods are available to calculate the three elastic constants for fcc using DFT tools. The first one is an automatic derivation using internal strain and stress data implemented in VASP. It is recommended for small atomic models, though, because the number of displacements increases linearly as the cell has more atoms. A system with over a hundred atoms will not only have to relax over a hundred systems but also find each relaxation step more slowly. Another method is based on energy and strain relations. This volume-conserving deformation method has been developed by Mehl et al. [58] and widely used in first-principles studies [6, 54]. Compared to the stress-strain method, it at least avoids the linearly-increasing number of relaxations to run for each system.

The first step is to obtain the bulk modulus and the equilibrium lattice parameter. Then we
can apply the following deformation on the equilibrium structure:

\[
D_0 = \begin{pmatrix}
1 + \delta & 0 & 0 \\
0 & 1 - \delta & 0 \\
0 & 0 & (1 - \delta^2)^{-1}
\end{pmatrix}
\] (3.11)

where \( \delta \) is often in the range of 0.01 to 0.05. The deformation matrix \( D_0 \) does not change the volume of the structure. After running DFT calculations using these structures and collecting their energies, we can calculate the value of \( (C_{11} - C_{12}) \) from fitting the energy-strain data to the following equation:

\[
E = E_0 + V(C_{11} - C_{12})\delta^2
\] (3.12)

The bulk modulus is a function of \( C_{11} \) and \( C_{12} \):

\[
B_0 = (C_{11} + 2C_{12})/3
\] (3.13)

Combining Eq. 3.12 and Eq. 3.13, we can easily derive the values of \( C_{11} \) and \( C_{12} \). The calculation of \( C_{44} \) needs another deformation matrix, given by

\[
D_m = \begin{pmatrix}
1 & \delta & 0 \\
\delta & 1 & 0 \\
0 & 0 & (1 - \delta^2)^{-1}
\end{pmatrix}
\] (3.14)

Similarly, we need to fit the energy-strain data to this equation:

\[
E = E_0 + VC_{44}\delta^2
\] (3.15)
The $R$ values of the regression for both Eq. 3.12 and Eq. 3.15 are usually higher than 0.99. If the fitting is not close to a perfect match, it is very likely something just went wrong, such as some deformed structures did not converge to the lowest energy, or some converged to different magnetic states, which is most likely to occur in ferromagnetic systems consisting of iron or other strongly magnetic elements. While the fitting can be highly efficient via command line calculations without a graphic output, the fitted results cannot be regarded reliable unless the $R$ values have been checked or the fitting curves have been examined visually.

3.2 Entropy

3.2.1 Configurational Entropy

Configurational entropy is part of a system’s entropy related to the position of all constituent particles. It is defined by the Boltzmann entropy formula

$$S^{\text{conf}} = k_B \ln \Omega$$  \hspace{1cm} (3.16)

where $k_B$ is the Boltzmann constant and $\Omega$ is the number of possible configurations. The Boltzmann entropy formula is a straightforward expression with only one variable, but we need a more convenient equation to calculate the configurational entropy, one depending on variables easy to obtain, such as molar concentrations of an alloy.

3.2.1.1 Random solid solution

Let’s consider a 4-component solid solution system. The atomic ratio of each component is $c_i = N_i/N_A \ (i = 1, 2, 3, 4; \sum N_i = N_A)$, where $N_i$ is the number of atoms and $N_A$ is Avogadro
constant. The number of possible configurations of this system is

\[
\Omega = \frac{N_A!}{N_1! (N_A - N_1)!} \cdot \frac{(N_A - N_1)!}{N_2! (N_A - N_1 - N_2)!} \cdot \frac{(N_A - N_1 - N_2)!}{N_3! (N_A - N_1 - N_2 - N_3)!} = \frac{N_A!}{N_1! N_2! N_3! N_4!}
\]

(3.17)

where \( \binom{n}{r} = \frac{n!}{r!(n-r)!} \) is the number of possible combinations of \( r \) objects from a set of \( n \) objects.

Substituting the number of possible configurations \( \Omega \) in the Boltzmann entropy formula (Eq. 3.16) with Eq. 3.17 yields

\[
S_{\text{conf}} = k_B \ln \frac{N_A!}{N_1! N_2! N_3! N_4!}
\]

\[
= k_B (\ln N_A! - \ln N_1! - \ln N_2! - \ln N_3! - \ln N_4!)
\]

Here we need to replace the factorial terms using Stirling’s approximation (\( \ln n! \approx n \ln n - n \)):

\[
S_{\text{conf}} = k_B \left[ N_A \ln N_A - N_A - \sum_{i=1}^{4} (N_i \ln N_i - N_i) \right]
\]

\[
= -k_B N_A \left[ \sum_{i=1}^{4} (c_i \ln N_i) - \left( \sum_{i=1}^{4} c_i \right) \ln N_A \right]
\]

\[
= -R \sum_{i=1}^{4} c_i \ln \frac{N_i}{N_A}
\]

\[
= -R \sum_{i=1}^{4} c_i \ln c_i
\]

where \( R = k_B N_A \) is gas constant.

The equation above is for 4-component solid solution systems only. But we can easily
derive a similar equation for a \( n \)-component random solid solution:

\[
S^{\text{conf}} = -R \sum_{i=1}^{n} c_i \ln c_i
\]  

(3.18)

3.2.1.2 Solid solution with partial ordering

In the case of an alloy in which long-range ordering exists, we need another equation to calculate the configurational entropy rather than simply subtract the ordered components in Eq. 3.18 for solid solution systems.

Again, let’s consider a 4-component alloy in which one element has long-range order and three other elements have random positions. The number of atoms of the ordered element is \( N_1 \).

The number of possible configurations of this random alloy with partial ordering is

\[
\Omega = \frac{(N_A - N_1)}{N_2} \cdot \frac{(N_A - N_1 - N_2)}{N_3} \cdot \frac{(N_A - N_1 - N_2 - N_3)!}{N_3! (N_A - N_1 - N_2 - N_3)!} \\
= \frac{(N_A - N_1)!}{N_2! N_3! N_4!}
\]  

(3.19)

Inserting Eq. 3.19 into Eq. 3.16 gives

\[
S^{\text{conf}} = k_B \ln \left[ \frac{(N_A - N_1)!}{N_2! N_3! N_4!} \right] \\
= -k_B \left[ \ln N_2! + \ln N_3! + \ln N_4! - \ln (N_2 + N_3 + N_4)! \right] \\
= -k_B \left[ \sum_{i=2}^{4} (N_i \ln N_i - N_i) - \left( \sum_{i=2}^{4} N_i \right) \ln (N_A - N_1) + \sum_{i=2}^{4} N_i \right] \\
= -k_B \sum_{i=2}^{4} N_i \ln \frac{N_i}{N_A - N_1}
\]
For a \( n \)-component solid solution with one long-range ordered element \( k \), its configurational entropy becomes

\[
S^{\text{conf}} = -R \sum_{i=2}^{n} c_i \ln \frac{c_i}{1 - c_i}
\]

(3.20)

Eq. 3.20 reduces to Eq. 3.18 when \( c_k = 0 \). Actually, we can reach Eq. 3.20 in an easier way by assuming the alloy is rather a ternary random solid solution with fewer atoms. In the next part of discussion of more complicated situations, derivations from the Boltzmann entropy formula Eq. 3.16 are skipped and expressions like Eq. 3.20 are given directly.

3.2.1.3 Solid solution with partial ordering in sublattices

Configurational entropy of an ideal random solid solution is

\[
S_{\text{config}} = \sum c_i \ln c_i = \sum \frac{N_i}{N} \ln \frac{N_i}{N}
\]

(3.21)

If the alloy has two sub-lattice sites, A and B, on which elements \( a_1/a_2 \) and \( b_1/b_2 \) occupy randomly, respectively, then its configurational entropy is

\[
S_{\text{config}} = \frac{N_A}{N} \sum A \frac{N_{a_i}}{N_A} \ln \frac{N_{a_i}}{N_A} + \frac{N_B}{N} \sum B \frac{N_{b_i}}{N_B} \ln \frac{N_{b_i}}{N_B}
\]

(3.22)

Now we need to calculate the configurational entropy of NiFeCrCo transiting from the RSS to L12. The only variable is the concentration of Cr on the corner site, \( x \). Then the concentration of Ni/Fe/Co on the corner site is \( y = (1 - x)/3 \). The concentration of Cr on the face-center site is \( x' = (0.25 - 0.25x)/0.75 \). The concentration of Ni/Fe/Co on the face-center site is \( y' = \)
(1 - x')/3. For quick reference, we list the concentration expressions below:

\[ x = x \]  \hspace{1cm} (3.23)

\[ y = (1 - x)/3 \]  \hspace{1cm} (3.24)

\[ x' = (0.25 - 0.25x)/0.75 \]  \hspace{1cm} (3.25)

\[ y' = \frac{1 - (0.25 - 0.25x)/0.75}{3} \]  \hspace{1cm} (3.26)

First, we need to deal with the L1\(_2\) phase. It is simpler than all other phases that are composed with two sub-lattice sites with random alloying. For the L1\(_2\) phase, we can simply ignore the corner site because it’s entirely occupied by Cr only. Its configurational entropy is

\[ S_{\text{L1}_2\text{config}} = \frac{3}{4} \left( 3y' \ln y' \right) \]

\[ = \frac{3}{4} \left( 3 \times \frac{1 - (0.25 - 0.25x)/0.75}{3} \times \ln \frac{1 - (0.25 - 0.25x)/0.75}{3} \right) \]

The calculation of configurational entropy of RSS-L1\(_2\) transition needs the entire Eq. 3.22:

\[ S_{\text{trans.config}} = \frac{1}{4} (x \ln x + 3y \ln y) + \frac{3}{4} (x' \ln x' + 3y' \ln y') \]

\[ = \frac{1}{4} \left( x \ln x + 3 \times \frac{1 - x}{3} \times \ln \frac{1 - x}{3} \right) \]

\[ + \frac{3}{4} \left( \frac{0.25 - 0.25x}{0.75} \ln \frac{0.25 - 0.25x}{0.75} + 3 \times \frac{1 - (0.25 - 0.25x)/0.75}{3} \times \ln \frac{1 - (0.25 - 0.25x)/0.75}{3} \right) \]

Now, let’s test for the total RSS using the equation above using \( x = 0.25 \):

\[ x = 0.25 \]

\[ y = (1 - 0.25)/3 = 0.25 \]
\[ x' = (0.25 - 0.25 \times 0.25) / 0.75 = 0.25 \]
\[ y' = (1 - 0.25) / 3 = 0.25 \]
\[ S_{\text{config}}^{\text{RSS}} = \frac{1}{4} (0.25 \ln 0.25 + 3 \times 0.25 \ln 0.25) + \frac{3}{4} (0.25 \ln 0.25 + 3 \times 0.25 \ln 0.25) \]
\[ = 4 \times 0.25 \ln 0.25 \]

This result agrees with Eq. 3.21, an evidence of the validation of previous derivation.

### 3.2.2 Vibrational Entropy

Crystal lattice oscillates at some frequency. A phonon is a quantum mechanical description of such vibrational motions. Phonons are particularly important for thermal and electrical conductivity properties of crystals. In some cases, they also play an important role in the determination of crystal structures, e.g., when the ground state energy gap between two phases is too small such that other energetic contributors get a chance to dominate phase preference. For a harmonic crystal, the phonon entropy is calculated as

\[ S_{\text{vib}} = k_B \sum_i \left[ -\ln \left( 1 - e^{-\beta \epsilon_i} \right) + \frac{\beta \epsilon_i}{e^{\beta \epsilon_i} - 1} \right] \]  

(3.27)

where \( N \) is the number of atoms, \( k_B \) is the Boltzmann’s constant, \( \beta = (k_B T)^{-1} \), \( \epsilon_i = h \omega_i \) is energy of a phonon at the vibrational frequency \( \omega_i \). This simple harmonic model assumes the ideal conditions, such as constant specific heat and infinite thermal conductivity. Usually such rough estimation of vibrational entropy is enough to determine a phase preference. However, if the vibrational entropy with higher precision is necessary, it is necessary to employ the quasi-harmonic model, in which thermal expansion effect is considered.

In EMTO-CPA calculations, vibrational entropy is difficult to capture because of the one-
site approximation that neglects atomic displacement. In VASP calculations, phonons are fully stored in the atomic models. One of the software designed for phonon calculation is called phonopy. [59] It has an interface to VASP and also provides tools for quasi-harmonic phonon calculations. These vibrational calculations are usually computationally demanding.

3.2.3 Magnetic and Electronic Entropy

In paramagnetic materials, orientation of atomic spins is randomized with disorder. The disorder of atomic spins can be quantified by magnetic entropy and contributes to the system energy. In DFT calculations for magnetic entropy, the magnetic setup must be for a paramagnetic system. Simulation of paramagnetism by VASP has been a non-trivial problem. However, the CPA technique in the EMTO-CPA method can be combined with so-called disordered local moment (DLM) method [60] to approximate a paramagnetic random alloy. In the DLM method, each element in the random solid solution is split into two separate parts with up and down spins, respectively. For example, the magnetic setup for the quaternary NiFeCrCo random alloy is $\text{Ni}^{\uparrow}\text{Ni}^{\downarrow}\text{Fe}^{\uparrow}\text{Fe}^{\downarrow}\text{Cr}^{\uparrow}\text{Cr}^{\downarrow}\text{Co}^{\uparrow}\text{Co}^{\downarrow}$. Elements showing non-magnetism in the DLM model can be safely ignored, so this quaternary random alloy in EMTO-CPA calculations can be simplified as $\text{Fe}^{\uparrow}\text{Fe}^{\downarrow}\text{NiCrCo}$, given that the elements of Ni, Cr, and Co all have zero spin moments in the paramagnetic state. According to the mean field approximation [61], magnetic entropy for each element in the paramagnetic random alloy is given by

$$S_{\text{mag}} = k_B \ln (2m_i + 1)$$

(3.28)

where $m_i$ is the magnetic moment of the element in unit of Bohr magneton, $\mu_B$, and $k_B$ is the Boltzmann constant. The overall magnetic entropy of the paramagnetic alloy can then be calculated as the weighted sum of magnetic entropy of each component.
Electronic entropy is given by [62]:

\[
S_{\text{elec}} = -k_B \int n \left[ f \ln f + (1 - f) \ln (1 - f) \right] dE
\]

(3.29)

where \( n \) and \( f \) are the density of states and Fermi distribution function, respectively. Only electrons whose energy falls in \( \pm k_B T \) to the Fermi level make contributions to electronic excitations, so the magnetic entropy is usually small and can be ignored most of the time.

3.3 Phase Stability

A lattice phase is stable if its Gibbs free energy is the lowest among all possible phases. In solid state physics, enthalpy instead of Gibbs free energy is often used to describe energetics of a material because it is more closely connected to DFT outputs. It is quite convenient to get Gibbs free energy from enthalpy results. Definitions of enthalpy varies from liquid to solid, from chemistry to physics. Here we establish the language used in this dissertation of the calculated enthalpies.

3.3.1 Enthalpy of Formation

Enthalpy of formation is defined as the energy change to form a new alloy from pure elements in the stable phases. It is expressed as:

\[
\Delta H^f = E^\text{Alloy}_0 - \sum_{i=1}^{N} c_i E_i
\]

(3.30)

where \( E^\text{Alloy}_0 \) is the ground state energy of the alloy, \( c_i \) is the atomic concentration of each element, and \( E_i \) is the ground state energy of the pure element in its stable phase. All energies
in Eq. 3.30 must have the same unit, e.g., eV per formula unit.

It should be noted that enthalpy contains two parts: the internal energy, which is obtained from DFT calculations as in Eq. 3.30, and the external pressure contribution.

\[ \Delta H = \Delta U + P\Delta V \]  

(3.31)

In solid state physics, the \( \Delta V \) term is usually ignored due to the extremely small volumetric change. It is safe to assume that \( \Delta H = \Delta U \).

Enthalpy of formation can be used to determine if the formation of a certain phase is energetically preferred at ground state. Should its enthalpy of formation be negative, the new phase is favored because of energy release from the transformation from pure elements to the alloy. Such conclusions serve as phase predictions for the ground state, and may be extended to finite temperatures. In other cases, we need to use the free energy instead of enthalpy for phase prediction at higher temperatures. Gibbs free energy is defined by

\[ G = H - TS \]  

(3.32)

If we ignore the \( PV \) term in the enthalpy, it becomes the Helmholtz free energy \( A \):

\[ A = U - TS \]  

(3.33)

Both concepts of free energy have been used in computational studies of alloys. In most cases they are the same, although the latter is more accurate.
3.3.2 Enthalpy of Mixing

The concept of enthalpy of mixing comes from chemistry, where it describes the heat taken up or released when mixing two chemical substances in liquid. Materials scientists use it for metals and alloys in the liquid state above the melting point. By applying this concept to high entropy alloys in the solid state, we can express the enthalpy of mixing for solid HEAs by

$$\Delta H_{\text{mix}} = E_{0}^{\text{Alloy}} - \sum_{i} c_{i} E_{i}^{\text{same}}$$

(3.34)

where $E_{i}^{\text{same}}$ is the ground state energy of the pure element in the *same crystal structure* as the alloy. Eq. 3.34 allows us to focus on the energy change related to chemical disorder without structural factors. Validation of this equation will be given in Chapter 6.

3.4 Stacking Fault Energy

A dislocation in a fcc crystal can split into two partial dislocations, like:

$$\frac{a}{2}[10\bar{1}] \rightarrow \frac{a}{6}[2\bar{1}\bar{1}] + \frac{a}{6}[11\bar{2}]$$

The area between the two partial dislocations is a planar defect. In close-packed structures, the decomposition of a dislocation occurs first in the slip plane, i.e., the close-packed layers. The area between the two partial dislocations has a different stacking sequence from the other perfect regions, called a stacking fault. Energy change to form a stacking fault is called stacking fault energy.
The stacking sequence of a fcc crystal is written as:

\[ ABC,ABC,ABC \]

When a stacking fault forms on the fifth layer from left, \( B \), a partial dislocation passing through changes it to layer \( C \). It can’t become \( A \) because the layer on its left is \( A \) and two layers having the same stacking index can’t sit together. The perfect fcc stacking sequence after the shifting of the fifth layer then becomes:

\[
\begin{align*}
ABC, & \, A | \, CA, BCA \\
\text{hcp-like} & \quad \text{hcp-like}
\end{align*}
\]

where \( | \) is an intrinsic stacking fault. Intrinsic stacking fault is the most common in close packed structures. Should another pair of partial dislocations cause shifting on the sixth layer, the close-packed structure then becomes:

\[
\begin{align*}
ABC, & \, A | | \, CB, CAB \\
\text{hcp-like} & \quad \text{hcp-like}
\end{align*}
\]

where \( | | \) is an extrinsic stacking fault. One convenient method to tell whether it is an intrinsic or extrinsic stacking fault is to find whether it is equivalent to removing or inserting an extra layer into the perfect fcc stacking.

If the seventh layer also shifts on top of the sixth layer, the extrinsic stacking fault turns into a twin:

\[
\begin{align*}
ABC, & \, A | | \, -CB, A, BC \\
\text{hcp-like} & \quad \text{hcp-like}
\end{align*}
\]

When we talk about stacking fault energy, we mean the formation energy of an intrinsic stacking fault. This value is closely connected to the formation energy of twins. Therefore, in a material whose stacking fault energy is low, the energy to form twins is also low. A great number of twins are expected in low-SFE materials. Stacking fault energy has a large influence
on mechanical properties of crystals, such as tensile strength, ductility, work hardening rate, and wear resistance.

Two methods to calculate the stacking fault energy in fcc have been used in this dissertation. The first one is the supercell method:

\[ \gamma_{\text{SF}} = (E_{\text{SF}} - E_{\text{fcc}})/A \]  

(3.35)

where \( E_{\text{SF}} \) and \( E_{\text{fcc}} \) are the system energies of the stacking fault structure and the perfect fcc lattice with the same lattice spacing on the close-packed planes, and \( A \) is the area of the stacking fault.

Another method to calculate the stacking fault energy is based on the axial interaction model (AIM). [63, 64] This model assumes that the system energy of a close-packed structure can be represented by a function of orientation variables \( S_i \), where \( i \) is the layer index.

\[ E = - \sum_i \sum_n J_n S_i S_{i+n} \]  

(3.36)

The sums run on the close-packed layers. \( J_1 \) is the first nearest neighbor, \( J_2 \) is the next nearest neighbor, and so on. Applying this axial interaction model, we can get the energies of some typical close-packed structures, such as:

\[ E_{\text{fcc}} = J_0 + J_1 + J_2 + J_3 + O(J_4) \]

\[ E_{\text{hcp}} = J_0 - J_1 + J_2 - J_3 + O(J_4) \]  

(3.37)

\[ E_{\text{dhcp}} = J_0 - J_2 - O(J_4) \]

In Eq. 3.37 the axial interactions of two layers outside the third nearest neighbor are grouped
into $O(J_4)$. Using the same model, the formation energy of an intrinsic stacking fault, i.e., the stacking fault energy, can be expressed as:

$$\gamma_{SF} = \frac{E_{SF} - E_{fcc}}{A} = \frac{-4J_1 - 4J_2 - 4J_3 - O(J_4)}{A}$$  \hspace{1cm} (3.38)

Combining Eq. 3.37 and Eq. 3.38, we can express the stacking fault energy $\gamma_{SF}$ with the energies of fcc/hcp/dhcp. The derivation is very simple and not given here. If we only consider the first nearest neighbor $J_1$, we get the lowest order approximation:

$$\gamma_{SF}^{1st} = \frac{2(E_{hcp} - E_{fcc})}{A}$$  \hspace{1cm} (3.39)

Eq. 3.39 is a convenient means to estimate the stacking fault energy by calculating the energy difference between the fcc and hcp structures. It is also known at the axial next-nearest-neighbor Ising (ANNNI) model. [65]

If axial interactions up to the third order are included in the derivation, the stacking fault energy becomes a function of the energies of fcc, hcp, and dhcp:

$$\gamma_{SF}^{3rd} = \frac{E_{hcp} + 2E_{dhcp} - 3E_{fcc}}{A}$$  \hspace{1cm} (3.40)
Chapter 4

SQS for HEA Studies

This chapter aims at finding the error scale of SQS calculations in this dissertation. In the practice of DFT studies, there are many factors that may add system errors into the calculated results. In this chapter, we focus on the possible causes of system errors, namely, the energy fluctuation of atomic models and the chemical anisotropy in elastic calculations using atomic models. Contents in this chapter may be partially repeated in the other chapters. However, because these tools are being used in the HEA community, it is very important to establish understandings of limitations of these methods. Based on such consideration, all tests focusing on the accuracy of computational results are gathered in this chapter for easy reference.

4.1 Energetic Scattering of Permutations

The generation of SQS is based on correlation functions between pairs and/or triplets that are calculated as geometric concepts. Chemical elements only play a role as the name of groups for a specific type of atom during the generation of SQS. Their actual chemical definitions are not considered. Exchanging atomic types of two groups may make no difference to a SQS. Of
course, it is not always the case that any two elements can be exchanged. For instance, two elements having different concentrations cannot be exchanged, and two elements at different sub-lattices also cannot be exchanged. The SQS for a quaternary solid solution has $4! = 24$ combinations of the same four elements. These 24 structures have the same correlation functions but different system energies due to changes of local bonding. For any SQS, there are many possible permutations available for calculation.

Four SQS models for the same quaternary NiFeCrCo fcc random solid solution (RSS) are generated. Each differs by number of atoms in the SQS, with the systems having 24 atoms, 64 atoms, and the other two having 120 atoms. They are named SQS-24, SQS-64, SQS-120a, and SQS-120b, respectively. In this quaternary fcc RSS, each atom has 12 nearest neighbors, and each of the four elements should occupy three of the twelve neighbors. The average number of nearest neighbor bondings are calculated and plotted in Fig. 4.1 (b). A model that best represents the RSS should have the $N_{\text{bond}}$ of 3 for all pairs. It is found that all SQS except SQS-120a have three neighbors of each component in the first nearest neighbors.

Energy fluctuation between permutations is also examined. No matter how many atoms in each SQS, they all have 24 permutations and 24 energies. As shown in Fig. 4.1, fluctuation of system energies exist for any SQS. The energy scattering is biggest in SQS-24, gets smaller in SQS-64, and becomes almost equally smallest in SQS-120a and SQS-120b.

In conclusion of this section, it is established that attention must be paid to the following factors when using SQS for HEA studies:

1. Energy scattering/fluctuation exists for SQS within their permutations.

2. The scatter becomes smaller as the number of atoms in the SQS is larger.

3. For big SQS, uneven 1st shell correlation functions mismatch seems not important, overwhelmed by energy scattering due to chemical complexity.
Figure 4.1 (a) Energy of 24 permutations of four SQS models of fcc NiFeCrCo solid solution sorted by magnitude in unit of eV per formula. (b) Number of 1st nearest neighbor (NN) bondings of the four SQS models. The number 3 indicates ideal 1st NN mixing of fcc solid solution (12 NNs) in that $12 \times 25\% = 3$. 

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4.2 Chemical Anisotropy for Elastic Constants

Recall the calculation of elastic constants introduced in Chapter 3. Three types of deformation are applied to an equilibrium structure to collect energy-deformation data, i.e., the uniform hydrostatic pressure for bulk modulus, the orthorhombic deformation $D_0$ (Eq. 3.11) for $(C_{11} - C_{12})$, and the monoclinic deformation $D_m$ (Eq. 3.14) for $C_{44}$. The energy-deformation data can then be used to calculate corresponding elastic properties through fits to relevant equation of state. The latter two types of deformation assume fcc symmetry in the material, which is entirely preserved in the CPA models for EMTO calculations. However, the fcc symmetry is only kept for lattice sites in the SQS models, but not for chemical elements. That is, taking into account the distribution of elements, we should treat a SQS as an anisotropic structure. Orientation of the SQS is important for calculations under the orthorhombic and monoclinic deformation.

![Figure 4.2 There are six rotations for an chemically anisotropic fcc SQS.](image)

Elastic constants of fcc single crystals obtained in experiments are for the [100] directions, e.g., the strain $\varepsilon_{11}$ is along the <100> direction. Other elastic properties, e.g., shear modulus and Young’s modulus, are derived from these [100] elastic constants. So, before calculating the elastic constants of a fcc SQS, we need to find the [100] directions of the SQS. It may be easy to tell the orientation of a regular fcc supercell by the shape, but it becomes difficult in the
case of SQS which usually have irregular shapes, e.g., a triclinic cell. Fortunately, if the SQS is generated by the mcsqs code of the ATAT package, crystalline orientation of the SQS is kept consistent with the input primitive periodic unit. **It is very important to make sure that the elastic constants calculations are based on a SQS whose [100] directions are along the x-, y-, and z-axis.** That is, the primitive unit used to generate the SQS must be properly positioned so that deformation along the three Cartesian axes is applied to the [100] directions of the fcc cell. Otherwise the obtained elastic constants are off-axis.

After we make sure the fcc SQS is correctly oriented, we can start creating parallel SQS with orientations that are unique due to chemical anisotropy. As shown in Fig. 4.2, regardless of the shape of the fcc SQS, there are six possible rotations. These rotations are applied to the SQS cell, while the relative internal atomic coordinates are kept the same.

![Elastic Constants](image)

**Figure 4.3** Elastic constants $C_{11}$, $C_{12}$, and $C_{44}$, shear modulus $G$, and Young’s modulus $E$ calculated from six rotations and the average with standard deviation on three structures. SQS-24-a and SQS-24-b are two permutations from the same 24-atom SQS. SQS-108 is a 108-atom cubic-shaped SQS.

Three structures are tested for the anisotropy test. The first two are two permutations from
the same 24-atom SQS. The third is a specially designed 108-atom SQS with a cubic shape. Six rotations are applied to each structure. Elastic properties, including $C_{11}$, $C_{12}$, $C_{44}$, shear modulus $G$, and Young’s modulus $E$, are calculated for these rotated structures. The average of the six values should be used as the ultimate property for the structure. These results are plotted in Fig. 4.3. It is found that the rotation has a noticeable influence on the elastic properties of a small SQS. The standard deviations of $C_{11}$, $C_{12}$, $C_{44}$, $G$, and $E$ for the SQS-24-a model are 5.1, 2.6, 11.9, 5.2, and 11.6 GPa, respectively. Those for the SQS-24-b model are 10.2, 5.1, 6.5, 7.4, and 16.6 GPa, respectively. These standard deviations describes the potential error in calculations which use the non-rotated SQS without considering rotations. The errors are not likely to cause a disaster to the conclusions, but it is strongly recommended to consider the influence of anisotropy in the SQS models. For the 108-atom SQS, the standard deviations are found to be small. The average values from the bigger SQS agree well with those from the smaller SQS.

In summary, it is recommended to keep in mind for calculations of elastic constants the following conclusions:

1. Chemical anisotropy exists in high entropy alloy SQS.

2. Only SQS models whose [100] are along the x-/y-/z-axis should be used for the calculations of elastic constants.

3. There are six ways to rotate the SQS before the deformation. The average elastic properties of the six rotated structures should be used as the ultimate property.

4. Elastic constants converge as a function of SQS size. For 108-atom SQS, rotation calculations are not necessary, while for 24-atom SQS, the error in modulus can be up to 16.6 GPa.
Chapter 5

Spin-driven Ordering of Cr in Equiatomic NiFeCrCo

This chapter presents a DFT prediction of the ordering of Cr in equiatomic high entropy alloy NiFeCrCo which is driven by the reduction in free energy realized by surrounding antiferromagnetic Cr atoms with other ferromagnetic elements (Ni, Fe, and Co). This study is the first report of partial ordering in NiFeCrCo. The DFT prediction was confirmed by experiments employing magnetization measurements and transmission electronic microscopy techniques.

The full article, titled "Spin-driven ordering of Cr in the equiatomic high entropy alloy NiFeCrCo", was published in Applied Physics Letters, 106, 161906 (2015). I was the leading author of this publication.

I would like to acknowledge the contributions of my experimental collaborators from the Department of Materials Science and Engineering at NC State who provided experimental data to confirm this prediction: Alex Zaddach, Adedapo Oni, Xiahan Sang, James LeBeau, and Carl Koch. I would also like to thank the project PI and my advisor, Douglas L. Irving, and the REU student, James Hurt III, for the collaboration of EMTO calculations.
5.1 Introduction

High entropy alloys (HEAs) are an exciting new class of materials and several systems have exhibited desirable combinations of properties not commonly exhibited by conventional alloys. HEAs are composed of at least four to five principal elements that are present in high concentrations, 5-35 at% [1, 2]. Alloys with equiatomic ratios have the highest configurational entropy contribution to the free energy. Equiatomic NiFeCrCoMn, which is a fcc random solid solution (RSS), has a good combination of mechanical properties in hardness [6, 46], tensile strength [21, 22, 46], ductility [21, 46], and fracture resistance at cryogenic temperatures [22]. Its balanced performance in strength and ductility was attributed to a low stacking fault energy [6]. Non-equiatomic NiFeCrCoMn HEAs were also reported to remain a fcc RSS, which provides promising opportunities in the future for compositional engineering of the mechanical property combinations in this system [6, 47, 48].

Structurally, HEAs form solid-solutions on simple lattices (e.g. fcc, bcc, hcp). This is in contrast to other multicomponent alloys, such as bulk metallic glasses (BMG), that are structurally amorphous, or conventional alloys with high solute concentrations that tend to segregate into secondary or multiple phases. Whether an alloy forms as a BMG vs. HEA has been attributed to a balance between entropy, enthalpy, and relative atomic size [36]. Many HEAs tend to have a near-zero enthalpy and are also composed of atomic species of similar metallic radius. The small enthalpy is believed to allow the entropy to stabilize these as a RSS at relatively low temperatures (i.e. room temperature).

Recent work by Otto et al. further demonstrated the delicate balance between enthalpy and entropy in stabilizing a single phase RSS [17]. Starting with the established single phase HEA, equiatomic NiFeCrCoMn, the authors prepared five alloys that each substituted one host element at a time with a replacement element following the Hume-Rothery criteria. It was found
that all five alloys became multiphase. The authors attributed this to the increased enthalpies between the substitutional and host elements and their results clearly demonstrated that the entropy will not always dominate the free energy when enthalpic contributions become more significant.

What remains unclear is the local or long range atomic distributions in HEAs. NiFeCrCoMn is one of the few systems that remained a single fcc phase during the investigation of Otto et al., but the elements do not share a common bulk crystal or magnetic structure. Ni, Fe, and Co are ferromagnetic (FM) while Cr and Mn are anti-ferromagnetic (A-FM). Klaver et al. investigated the relative energetics of mixing an A-FM solute (Cr) into a FM solvent (Fe) and found that Cr solutes had an energetic preference to spatially separate in the FM host due to a process called magnetic frustration (significant scatter in the local moment of Cr that leads to a rise in total energy) [66]. This was found to be most significant for Cr atoms sitting in their own first nearest-neighbor (1NN) shell and the effect diminished gradually as the distance between Cr atoms increased. Brif et al. recently performed x-ray spectroscopy measurements using scanning electron microscopy and demonstrated that Cr was uniformly distributed throughout the NiFeCrCo alloy [67]. At the resolution of the technique, however, atomic level ordering would not be resolved. Lucas et al. searched for long range order in NiFeCrCo, which contains FM and A-FM elements, using x-ray and neutron diffraction and found none [8]. The authors noted, however, that this did not completely rule out any chance for local ordering.

Here, we implement two complementary first principles approaches to predict the relative energetics of chemical ordering within the NiFeCrCo system. NiFeCrCo is selected because it is the base alloy for many other 5+ element HEAs. Similar findings are anticipated for NiFe-CoMn but they are not explored here. We demonstrate that Cr has a strong energy preference for not sitting within its own 1NN shell. In this equiatomic alloy, Cr can only escape to the second nearest neighbor shell, which creates an alloyed L12 structure. This alloyed L12 is predicted to
have a smaller total magnetic moment as compared to the RSS. To compare with predictions we synthesized equiatomic NiFeCrCo under equilibrium and non-equilibrium approaches. The temperature dependence of the magnetic properties of all samples are measured. Cast alloys have a significantly smaller low temperature magnetic moment than ball milled samples. Cold working cast alloys is found to increase the measured low temperature moment. Finally, we apply advanced electron microscopy to identify ordered nanodomains in this alloy.

There are a number of challenges in the prediction of properties of RSS alloys, so two theoretical approaches using the GGA-PBE exchange-correlation functional [68, 69] were implemented here. The first was the well established Vienna ab initio simulation package (VASP) [70, 71] with atomic centers approximated with PAW pseudo-potentials [72, 73]. A k-point mesh was selected based on the convergence of the enthalpy to 1 meV/atom. Special quasi random structures (SQS), which best represent the targeted alloy within the confines of the periodic unit cell [74], were generated through a Monte Carlo algorithm [53]. For an equiatomic alloy the identity of the atom at each lattice site is not uniquely determined during SQS generation. Therefore, 24 permutations exist for the four component RSS SQS. We tested the convergence of enthalpy for 24, 64, and 120 atom SQSs with all possible permutations. We find that the average enthalpy of formation for these RSSs are $0.309 \pm 0.023$, $0.302 \pm 0.009$, and $0.302 \pm 0.007$ eV per formula unit, respectively. Through averaging the permutations even the small 24-atom SQS leads to a relatively converged enthalpy, albeit with more scatter. The second method implemented was the Exact Muffin-Tin Orbital combined with Coherent Potential Approximation (EMTO-CPA) [54, 75]. The screening parameter for these calculations was set to 0.9 and a k-point mesh was selected based on the convergence of the enthalpy to 1 meV/atom. The CPA technique averages the Green’s function to attain the randomness of atoms in an RSS. This one-site approximation neglects lattice distortions and also loses information on local chemical structure.
5.2 Magnetic Frustration

The local magnetic moments of each element as a function of the average magnetic moment, \( \bar{m}_{NN} \), of 1NN atoms for all permutations in the 24- and 120-atom SQS structures are plotted in Fig. 5.1 (a) and (b), respectively. FM Fe, Ni, and Co generally have positive moments while the A-FM Cr atoms have a distribution of both positive and negative moments. Notably, Cr scatters significantly and is most negative when its neighbors have the largest positive moment, corresponding to when Cr is surrounded by a majority of FM neighbors. The magnetic moment of Cr becomes less negative as the average moment of the neighbors becomes smaller, which is a product, in part, of having more Cr in the 1NN shell. This strong dependence of the local
moment is a result of magnetic frustration of the central Cr atom; similar to the trends identified in Ref. [66] for Fe-Cr alloys.

![Figure 5.2 Atomic structure of (a) fcc random solid solution and (b) L1₂ solid solution with Cr ordered. The (111) plane of the L1₂ phase is illustrated in (c).](image)

In binary Fe-Cr, there is a substantial repulsion when Cr resides in its own 1NN shell. This repulsion weakens as the distance between Cr atoms increases. For the equiatomic NiFeCrCo HEA, each element makes up 25 at% of the system and, assuming no preferential segregation, Cr can only avoid sitting in its own 1NN shell by forming an alloyed L1₂ structure (Fig. 5.2). In the alloyed L1₂ structure, one element occupies the cubic corner (CC) sites while the face centered (FC) sites contain a RSS of the other three elements. Any displacements of the atom occupying the CC site will move it back into its own 1NN shell. Formation of the alloyed L1₂
structure also results in a reduction in configurational entropy as compared to the RSS and this penalty needs to be accounted for when comparing the relative energy of the RSS to the alloyed L\(_{12}\).

### 5.3 Energy Reduction by Ordering

![Graph](image.png)

Figure 5.3 Free energy, defined as enthalpy of formation extracting configurational entropy times 300 K, of equiatomic NiFeCrCo as it transits from the random solid solution (RSS) phase to the L\(_{12}\) phase from EMTO-CPA calculations. Each component is allowed to order, totalling four transition paths. All calculations are spin polarized.

The relative energies of ordering one element (Ni, Fe, Co, or Cr) from the RSS to the CC site of the alloyed L\(_{12}\) are plotted in Fig. 5.3. The EMTO-CPA allows for a continuous
Figure 5.4 Free energy, defined as enthalpy of formation extracting configurational entropy times 300 K (left) and 1000 K (right), of equiatomic NiFeCrCo in the random solid solution (RSS) phase and the L12 phases from EMTO-CPA and VASP+SQS calculations with and without spin polarization, respectively. Each component is allowed to order at a time for the L12 structure, noted as L12-X.

change in composition of each lattice site in the transition between the RSS and L12 (Fig. 5.2), while the SQS structures are only evaluated at the end points (Fig. 5.4). Cr is predicted as non-magnetic by EMTO, which contributes to differences in predicted enthalpies between the two methods. For comparison of trends, we align the enthalpies of the EMTO to those of VASP for the RSS only. No other constraints are applied other than this alignment of the RSS and differences between to the two electronic structure methods is found to be small. In addition to the enthalpy of formation, the plotted values also include configurational entropy as determined for an ideal solution at a temperature of 300 K in Fig. 5.3 and at 300 K and 1000 K in Fig. 5.4. Configurational entropy is given by \( S_{\text{config}} = \sum c_i \ln c_i \), where \( c_i \) is the ratio of the number of atoms of a disordered component over the total number of disordered atoms. In the case of a partially ordered L12 phase, a convenient way of calculating configurational entropy is \( S_{\text{config}} = S_{\text{CC-site}}^{\text{config}} + S_{\text{FC-site}}^{\text{config}} \). Full estimates of the free energy requires contributions from the
vibrational, magnetic, and electronic entropy, which are not included here. From the data presented in Fig. 5.3, the most favorable ordering occurs through moving Cr to the CC site. The non-magnetic results in Fig. 5.4 show that part of the energy reduction is also due to non-spin-related interactions, such as electronic interactions. However, Fig. 5.4 also shows that at 1000 K the non-magnetic Cr ordered phase does not have a lower energy than the random solid solution phase, indicating that it is really the spins that stabilizes the L12 structure over the random solid solution phase.

![Figure 5.5 Atomic magnetic moment, \( m \), vs. average magnetic moment, \( \bar{m}_{NN} \), of twelve nearest neighbors from VASP calculations using a 24-atom SQS in the L12 structure with all Cr ordered.](image)

Fig. 5.5 presents the magnetic moment for each element as a function of the average magnetic moment, \( \bar{m}_{NN} \), of the 12 1NN atoms in the six possible permutations of the alloyed L12 structure. In comparing these results to the similar data in Fig. 5.1 (a) and (b), the magnetic
frustration is avoided as evidenced by the small scatter in the moments of each element. Fe, Co, and Ni all have aligned and positive magnetic moments while Cr has a magnetic moment opposite of all its FM neighbors. This results in a reduction of the bulk magnetic moments when moving from the RSS ($m_{RSS} = 2.59 \pm 0.99 \mu_B$) to the alloyed Cr L1$_2$ ($m_{L1_2} = 0.94 \pm 0.14 \mu_B$). The uniform magnetic alignment also leads to an extremely small scatter on the order of 2 meV per formula unit in the predicted enthalpy of the alloyed L1$_2$ structure.

5.4 Experimental Confirmation

To test the predictions made by first principles methods, samples were prepared in three ways for analysis by SQUID-VSM. One sample was prepared by ball milling pure elemental powders in high-purity argon in a stainless steel vial using a SPEX 8000 mixer mill for 24 hours at room temperature. Two other samples were prepared by melting pure elemental metals in high purity argon atmosphere using an electric arc melter. Each arc melted sample was then cast into a water-cooled copper mold and annealed in Ar-2% H$_2$ at 1273 K for 24 hours. One sample was tested after annealing and the other was cold rolled to 80% rolling reduction before testing. SQUID-VSM measurements were conducted with a Quantum Design MPMS using an applied field of 198.9 kA·m$^{-1}$ from 1.8 to 390 K at a rate of 0.08 K·s$^{-1}$.

As shown in Fig. 5.6, at 1.8 K, the highly disordered sample produced by ball milling exhibits the largest magnetization. Cast samples have low temperature moments are 44% of those measured for ball milled samples. A large difference in moments is expected from the results shown in Figures 5.1 and 5.4, as the contribution from Cr is much more negative in the ordered state, while the contributions from the other elements remain nearly constant. While there are slight compositional differences between the cast and milled samples, none were significant enough to explain the difference in magnetic properties. A smaller, yet still significant increase
in magnetization is seen after cold working, which would disrupt order in the cast/annealed sample.

Local atomic and chemical structure were also explored through scanning transmission electron microscopy (STEM). Samples for electron microscopy were prepared from the cast HEA using a standard twinjet electropolisher. High-angle annular dark field (HAADF) STEM images were acquired using a probe-corrected FEI Titan G2 60-300 kV operated at 200 kV. Further details of the sample preparation and imaging conditions can be found in Ref. [76]. Revolving scanning transmission electron microscopy (RevSTEM) method was employed to remove drift distortion from images [77]. Forty $1024 \times 1024$ pixel frames were acquired with a dwell time of $2\mu s$/pixel. A $90^\circ$ rotation angle step was introduced between each successive frame.

In the TEM images shown in Fig. 5.7, a perfectly ordered structure with alternating inten-
Figure 5.7 (a) A representative HAADF-STEM image acquired along the [110] zone axis of the HEA. Circles are plotted around each atom column with different colors representing (b) intensity ratio and (c) correlation coefficient. The ratio range in (b) is clipped to [0.98,1.02] to better highlight the presence of ordering.

sity would result in a correlation coefficient of unity while a disordered structure would have zero correlation. The correlation coefficient reaches a maximum of approximately 0.67, which, according to a p-value test generated through comparing these correlations to those of a simulated RSS, has a probability of roughly $7.3 \times 10^{-8}$ to occur randomly. Therefore, the result strongly suggest the presence of ordered 2-3 nm domains in the bulk HEA.

5.5 Strengthening Effect by Coherent Ordered Nanoparticles

The formation of a stacking fault in the L1$_2$ phase is the same as in the fcc structure. However, in a L1$_2$ phase in which Cr-Cr interaction has been eliminated, the shift of any (111) layers will regenerate the Cr-Cr bonding, causing a huge energy increase that is much larger than the
energy needed by the formation of a stacking fault in the RSS fcc phase. Therefore, dislocation motion is much more difficult in the L12 phase than in the RSS phase of NiFeCrCo.

In a recent study with even longer annealing time, more homogeneously distributed nanoparticles are observed in equiatomic NiFeCrCo. [5] These nanoparticles are observable under atomic-number-sensitive techniques, and we believe these nanoparticles are in the L12 phase with Cr ordering. Because dislocation motion through these nanoparticles has much higher barrier than in the random solid solution matrix, a strengthening effect arises. Depending on the external driving force, a dislocation may either loop around these nanoparticles or cut through them. Either way, the motion of the dislocation is impeded, thus a higher strength. Such strengthening effect by nanoparticles with a coherent internal boundaries has been reported in Cu and Cu alloys [78] and in AlLi alloys [79]. Further study focusing on the strengthening effect of ordered nanoparticles in equiatomic NiFeCrCo is suggested.

5.6 Conclusions

We have demonstrated that magnetic frustration of Cr exists in random solid-solution NiFe-CrCo, which leads to significant scattering of the local magnetic moment. Ordering of Cr provides a way to eliminate the magnetic frustration and also leads to a reduction of free energy. Temperature dependent SQUID measurements indicate that this alloy has a finite magnetic moment at low temperatures, which is sensitive to synthesis approach. The equilibrium approach leads to a smaller magnetic moment, consistent with theoretical predictions. RevSTEM measurements identified ordered nanodomains present throughout the sample. Although nanodomains were found here, future studies that explore a variety of annealing procedures may be warranted to ultimately achieve long range ordering.
Chapter 6

Exploration of Near-equiatomic NiFeCrCo

This chapter is a first-principles study of composition-dependent properties of non-equiatomic NiFeCrCo HEAs. The full article, titled "First Principles Exploration of Near-equiatomic NiFe-CrCo High Entropy Alloys", is planned for submission. As the first author, I would like to thank the inspirational discussions with Alex Zaddach, Professor Carl C. Koch, and the project PI and my advisor, Professor Douglas L. Irving.

6.1 Introduction

NiFeCrCo and NiFeCrCoMn have exhibited many attractive properties and been extensively studied as one of the most famous system of high entropy alloys. NiFeCrCoMn is one of the earliest HEAs, firstly studied by Cantor et al. [2], and has been investigated by many other researchers for studies of phase stability [17, 18, 20] and mechanical properties [6, 21, 22, 46, 49, 80–82]. These studies show that NiFeCrCoMn remains single phase at any temperature with variant compositions, has good strength and excellent ductility, and has remarkable fracture resistance at cryogenic temperatures. NiFeCrCo, which has the same fcc solid-solution
phase and similar mechanical properties as NiFeCrCoMn does [6, 46], has been the subject of research aiming at theoretical understanding of phase formation [8, 14, 50] due to its less chemical complexity.

The concept of high entropy alloy was proposed by Cantor et al. [2] and Yeh et al. [1] who in 2004 published their mutually independent research on multi-component alloys with equal atomic ratios. Hundreds of HEA systems have been studied up to date, many exhibiting attractive properties. [43, 44, 83] An obvious outcome of the equiatomic setting in multi-component alloys is a very high entropy when they form random solid solutions, so Yeh called them high entropy alloy (HEA) [1]. HEAs differ from conventional alloys consisting of one or two dominant major components with additions. Instead, all components play nearly equally important roles in a HEA, which brings the possibility of great new properties but also the challenge of unpredictability. While some empirical rules have been proposed to predict the phase or crystal structure of HEAs and can be used for preliminary screening [36, 45], theories to accurately predict phase formation and mechanical properties have not been established in this newly discovered field of research.

Given that a good combination of strength and ductility is characterized in equiatomic NiFeCrCo and NiFeCrCoMn, investigation of near-equiaxialomic compositions is of interest in that better performance may be realized in this range. However, systematic study of the near-equiaxialomic range of either NiFeCrCo or NiFeCrCoMn HEAs is not found in literature. Challenges associated with experimental investigation include lack of predictive theories for mechanical properties and the huge number of samples to manufacture for such studies. Computational tools, on the other hand, provide an efficient and economic path towards a systematic understanding of the relation between near-equiaxialomic HEA compositions and properties. In the present work, we report our computational exploration of the near-equiaxialomic range of the four-component NiFeCrCo HEAs in the random solid solution phase. It should be noted though
that a recent study of equiatomic NiFeCrCo showed that ordering of Cr is driven by the reduction in energy realized by surrounding anti-ferromagnetic Cr with ferromagnetic Ni, Fe and Co in an ordered $L1_2$ structure, which exists as nano domains in annealed equiatomic NiFeCrCo samples observed by STEM. [14] The authors also noted that as-milled samples are random solid solution. Taking into account that the ordering is only achieved in nano-domains with long annealing time, we focus on the random-solid-solution phase of Ni-Fe-Cr-Co HEAs such that the conclusions of this study may have broader value for peer experimental researchers.

We have explored the near-equiaatomic range of Ni-Fe-Cr-Co high entropy alloys in terms of enthalpy of mixing, lattice parameters, bulk moduli, elastic constants, shear moduli and B/G ratio. Detailed maps of these properties are obtained. Equations that allow convenient prediction of enthalpy of mixing as well as bulk modulus using only properties of binary alloys are evaluated and found to give accurate approximations. Element-specific trends are summarized for each property, e.g., alloys as $\text{Ni}_{10}\text{Fe}_{40}\text{Cr}_{10}\text{Co}_{40}$ may act more brittle.

6.2 Methods

Two complementary first principles methods were used in the present study. The first was the Exact Muffin-Tin Orbital method combined with Coherent Potential Approximation (EMTO-CPA). Muffin-tin potential spheres with large overlapping were used to accurately describe the exact one-electron potential. The EMTO method calculates total energy using the full charge density (FCD) technique [75]. FCD calculations have similar accuracy to that of full-potential methods but run faster. The CPA technique allows simulation of random solid solutions by blending constituent potentials into one single site. [84] The nature of this one-site approximation by CPA ignores local lattice displacement. However, the EMTO-CPA method turned out to be quite accurate for HEA systems composed of transition metals [6, 85]. The second
method was the Vienna Ab-initio Simulation Package (VASP) [70, 71] with projector augmented wave (PAW) pseudo-potentials [72, 73]. Special quasi-random structures (SQS) [74], which are atomic models that best represent the targeted alloy within the confines of the periodic boundary condition, were generated through a Monte Carlo algorithm [53].

In EMTO-CPA calculations, we used the Perdew-Burke-Ernzerhof version of generalized gradient approximation (GGA-PBE) of exchange-correlation functionals. [68, 69] The Kohn-Sham equations were solved within the so-called soft-core approximation, which let the code recalculate core states after each iteration. The Green’s function was calculated for 16 complex energy points. The basis set of EMTO included s, p, d, and f states. A $13 \times 13 \times 13$ k-point mesh was used; the total energy converged within 1 meV/atom. The Screened Impurity Model (SIM) parameter of 0.902 was applied for electrostatic correction to the single-site CPA. We used the disordered local moment (DLM) to describe the paramagnetic state of Ni-Fe-Cr-Co HEAs. [86] Within the DLM model, each magnetic element was regarded as two separate parts with up and down spins. In this case, all HEAs were simulated as Fe↑Fe↓NiCrCo.

In the VASP calculations, the GGA-PBE approximation was also employed. All k-point mesh settings were tested to meet the 1 meV/atom convergence criterion. The plane-wave cut-off energy was taken as 350 eV. The reciprocal space energy integration was performed by the Methfessel-Paxton technique for atomic relaxations. [87] Spin polarization was considered in all VASP calculations, and VASP predicts ferromagnetic state is the most stable. Simulation of the paramagnetic state in VASP is a non-trivial task and not performed in the present study.

Equilibrium lattice parameters and bulk modulus were obtained by fitting volume-energy data to the Vinet equation of state (EOS) [57]. Compared to the Birch-Murnaghan EOS, our tests showed that the Vinet EOS had a better stability with regard to the volume range when predicting the bulk modulus for Ni-Fe-Cr-Co HEAs. Volumetric deformation in the range of $\sim \pm 9\%$ (i.e., lattice parameter varying $\sim \pm 3\%$) was applied to the unit cell for Vinet EOS.
calculations. A cubic lattice has three independent lattice constants: $C_{11}$, $C_{12}$, and $C_{44}$. The calculation of these elastic constants used a method suggested by Mehl et al. [58], which proved accurate for HEAs [85]. $C_{11}$ and $C_{12}$ were derived from the bulk modulus $B_0$ and the tetragonal shear modulus $C'$, given that $B = (C_{11} + 2C_{12})/3$ and $C' = (C_{11} - C_{12})/2$. The calculation of $C'$ and $C_{44}$ was based on a volume-conserving orthorhombic deformation $\varepsilon_0$ and monoclinic deformation $\varepsilon_m$, respectively, which are given by:

$$\varepsilon_0 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 - \delta & 0 \\ 0 & 0 & \frac{1}{1 - \delta^2} \end{pmatrix} \quad \text{and} \quad \varepsilon_m = \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & \frac{1}{1 - \delta^2} \end{pmatrix} \quad (6.1)$$

where $\delta$ was between 0.00 and 0.05 in increments of 0.01. The values of $C'$ and $C_{44}$ were determined by fitting the energy-deformation data to $E = E_0 + 2VC'\delta^2$ and $E = E_0 + 2VC_{44}\delta^2$, respectively.

Polycrystalline shear modulus was derived via the Voigt-Reuss-Hill averaging method, which defines the shear modulus $G$ as an average of the lower ($G_R$) and upper ($G_V$) bounds given by:

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad \text{and} \quad G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (6.2)$$

### 6.3 Composition-dependent Maps of Properties

The majority of results in this study were produced by EMTO-CPA calculations. In the four-component Ni-Fe-Cr-Co HEA system, the number of possible alloying compositions is a huge number compared to binary or ternary phases: while binary alloys require a 2-D diagram to cover alloying compositions and ternary alloys need a 2-D contour plot, compositions of a quaternary alloy form a 3-D contour space. Here we present our exploration of this big number of
configurations using the CPA technique. Specifically, each components were allowed to vary from 10 at.% to 40 at.% in a step of 2 at.% in the four-component solid solution, totaling 2736 compositions. These compositions occupy the center of the tetrahedron and fulfill the definition of high entropy alloy. In the following discussions, all concentrations are atomic ratios unless noted otherwise. Besides these CPA simulations, VASP+SQS calculations of some special points with interesting properties were also performed for the sake of further verification.

We first present contour maps of selected slices for the properties studied in this work. Although data included in the contour maps only occupy a small portion of all data that are collected (2736 in total), the contour maps are capable of showing the trend of property evolution as the composition varies in the HEA. All slices in the alloying space selected in this section have a fixed element with the other three elements free to vary in composition. The fixed element has a concentration of 10%, 24%, and 40%, respectively, corresponding to low-, medium-, and high-concentration, respectively. All contour plots for each slice of the same property have the same color scale for the sake of comparison between different slices.

6.3.1 Enthalpy of Mixing

In this article, enthalpy of mixing is defined by

\[
\Delta H^{\text{mix}} = E_0 - \sum c_i E^{\text{fcc}}_i
\]  

(6.3)

where \(E^{\text{fcc}}_i\) is the ground state energy of the element in the same fcc lattice as the alloy. Meanwhile, enthalpy of formation is defined by

\[
\Delta H^{\text{f}} = E_0 - \sum c_i E^{\text{stable}}_i
\]  

(6.4)
where \( E_{i}^{\text{stable}} \) is the ground state energy of the element in its stable phase. The difference between enthalpy of formation and enthalpy of mixing is that the former relates to the Gibbs free energy that determines whether a phase is thermodynamically favored while the latter is the energy required to mix constituent atoms to form a solid solution within the same crystal lattice. It is obvious that the relation of enthalpy of formation and enthalpy of mixing is

\[
\Delta H^f = \Delta H^{\text{mix}} + \sum c_i (E_{i}^{\text{fcc}} - E_{i}^{\text{stable}})
\]  

(6.5)

In the present work we focus on the enthalpy of mixing in that it has been used in the prediction of phase formation of high entropy alloys. [36] More discussion about predictive equations will be given in section 6.4.

As shown in Fig. 6.1, twelve slices in the 3-D compositional space are plotted as contour maps, each with one element having a fixed concentration while other three elements form a ternary contour. The slices with fixed Cr concentrations have the most uniform colors, indicating that Cr has a significant influence on the enthalpy of mixing. When the HEA has 10% Cr, it has the highest, or smallest in magnitude, enthalpy of mixing no matter what concentrations the other three elements have. With 24% Cr, the HEA has medium enthalpy of mixing. By finding the dark blue regions in the corners at slices of 10% Ni, 10% Fe, 40% Cr, and 40% Co, it can be concluded that the enthalpy of mixing is the most negative in HEAs near the composition of Ni_{10}Fe_{10}Cr_{40}Co_{40}.

It has been stated that the enthalpy of mixing plays an important role in predicting whether a solid solution phase is energetically preferred. Only enthalpy of mixing close to zero, either positive or negative, favors the solid solution phase, while strongly negative enthalpy of mixing is inclined to lead to intermetallic compound and strongly positive enthalpy of mixing may cause separation or segregation of elements. [36] In our case, low Cr HEAs have enthalpy
Figure 6.1 Enthalpy of mixing, $\Delta H^{\text{mix}}$, as a function of composition in Ni-Fe-Cr-Co HEAs. Each subplot represents a slice in the 3-D compositional tetrahedron with one component fixed at a concentration, all other components ranging from 10-40 at.%.

of mixing closest to zero, and therefore are most likely to form solid solution phases. High concentrations of Cr/Co and low concentrations of Ni/Fe together lead to the most negative enthalpy of mixing, suggesting the possibility of formation of secondary intermetallic phases. This conclusion can be verified in an experimental study of the sigma phase formation in HEAs, in which the authors report that NiFeCr$_2$Co has the intermetallic sigma phase in addition to the fcc solid solution phase after 700°C aging. [88] This composition lies in the center of the 40% Cr map in Fig. 6.1 and has an enthalpy of mixing of $-0.1$ eV. Because of the formation of the secondary phases in certain compositions, we have to put a restriction on predictions made in the present study, that is, these DFT predictions are for single phase solid solution HEAs, not
the ones with multiple phases. While new properties can be introduced during the formation
of multiple phases, a fundamental understanding of the single phase properties are still very
useful for the design of new HEAs.

6.3.2 Lattice Parameter

![Lattice Parameter Diagram]

Figure 6.2 Lattice parameter, $a_0$, as a function of composition in Ni-Fe-Cr-Co HEAs.

We examined the fcc lattice parameter, $a_0$, of these alloys, as shown in Fig. 6.2. It is shown
in Fig. 6.2 that Co has the most significant influence on the lattice parameter $a_0$ of Ni-Fe-
Cr-Co HEAs (see the Co column): when Co is 10/24/40%, $a_0$ is mostly large/medium/small
regardless of concentrations of the other components, and only slight fluctuations of $a_0$ are observed within each Co slice. The significant influence of Co on $a_0$ is also demonstrated in other slices: red regions in Ni-40%, Fe-10% and Cr-40% all locate near the corner where Co is 10%, and dark blue regions in Ni-40%, Fe-10% and Cr-10% all locate where Co is about 40%. The next element that has a large impact on $a_0$ is Cr: the Cr-10% slice has low/medium $a_0$, the Cr-24% slice has medium $a_0$, and the Cr-40% slice has medium/high $a_0$.

Table 6.1 Top 3 alloys with highest/lowest lattice parameter

<table>
<thead>
<tr>
<th>Ni,Fe,Cr,Co%</th>
<th>$a_0$ (Å)</th>
<th>Ni,Fe,Cr,Co%</th>
<th>$a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40, 10, 10, 40</td>
<td>3.509</td>
<td>38, 12, 40, 10</td>
<td>3.545</td>
</tr>
<tr>
<td>38, 10, 12, 40</td>
<td>3.510</td>
<td>40, 10, 40, 10</td>
<td>3.545</td>
</tr>
<tr>
<td>38, 12, 10, 40</td>
<td>3.510</td>
<td>36, 14, 40, 10</td>
<td>3.545</td>
</tr>
</tbody>
</table>

The 12 slices in Fig. 6.2 demonstrate how each component affects $a_0$ by using a small portion of all calculated compositions. We also present the top three compositions with either the smallest or largest $a_0$ among all tested compositions in Table 6.1. The smallest $a_0$ is approximately 3.509 Å, found near Ni$_{40}$Fe$_{10}$Cr$_{10}$Co$_{40}$. The largest $a_0$ is about 3.545 Å, found near Ni$_{40}$Fe$_{10}$Cr$_{40}$Co$_{10}$.

6.3.3 Bulk Modulus

Fig. 6.3 shows the bulk modulus of Ni-Fe-Cr-Co HEAs. It is found that Fe has a significant influence on bulk modulus of these alloys. 10% Fe leads to highest bulk modulus and 40% Fe leads to lowest. The black solid lines in each sub-plot of Fe/Cr/Co are more or less parallel to grid lines of Fe%, indicating a small correlation of bulk modulus to concentrations of Ni/Cr/Co.
Figure 6.3 Bulk modulus, $B_0$, as a function of composition in Ni-Fe-Cr-Co HEAs.

The top 3 alloys with the lowest or highest bulk modulus are listed in Table 6.2. Unsurprisingly, the concentration of Fe is 40% in all three alloys with the lowest bulk modulus and 10% in those with the highest bulk modulus.

6.3.4 Shear Modulus

Shear modulus was derived from elastic constants. The elastic constants of a cubic structure that is mechanically stable must satisfy $C_{11} - C_{12} > 0$ and $C_{44} > 0$. [58] All alloys in the present study were found to fulfill the mechanical stability tests.

Shear modulus $G_0$ depending on the composition of Ni-Fe-Cr-Co HEAs is plotted in Fig. 6.4.
Table 6.2 Top 3 alloys with highest/lowest bulk modulus

<table>
<thead>
<tr>
<th>Ni,Fe,Cr,Co%</th>
<th>$B_0$ (GPa)</th>
<th>Ni,Fe,Cr,Co%</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24, 40, 26, 10</td>
<td>177.2</td>
<td>10, 10, 40, 40</td>
<td>232.3</td>
</tr>
<tr>
<td>10, 40, 16, 34</td>
<td>177.4</td>
<td>12, 10, 40, 38</td>
<td>231.2</td>
</tr>
<tr>
<td>22, 40, 26, 12</td>
<td>177.5</td>
<td>12, 10, 38, 40</td>
<td>230.8</td>
</tr>
</tbody>
</table>

It is shown that Co slices have fewer color scales and clear gaps between each other, which indicates that Co concentration plays a major role for $G_0$. Ni-Fe-Cr-Co HEAs with higher concentration of Co have higher shear moduli. The large dark blue region in Cr-40% indicates that low-Cr compositions are more likely to have a low $G_0$. The large red regions in Fe-10% implies the tendency of low $G_0$ alloys forming with low Fe concentrations. These trends about Co, Cr and Fe agrees with the top 3 compositions for lower and upper bounds of $G_0$ in Table 6.3. All of the three alloys with the lowest $G_0$ consist of 10% Co and 40% Cr while all those with the highest $G_0$ have 40% Co and 10% Fe.

Table 6.3 Top 3 alloys with highest/lowest shear modulus

<table>
<thead>
<tr>
<th>Ni,Fe,Cr,Co%</th>
<th>$G_0$ (GPa)</th>
<th>Ni,Fe,Cr,Co%</th>
<th>$G_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34, 16, 40, 10</td>
<td>84.2</td>
<td>10, 34, 16, 40</td>
<td>116.8</td>
</tr>
<tr>
<td>32, 18, 40, 10</td>
<td>84.3</td>
<td>10, 36, 14, 40</td>
<td>116.7</td>
</tr>
<tr>
<td>36, 14, 40, 10</td>
<td>84.3</td>
<td>10, 32, 18, 40</td>
<td>116.6</td>
</tr>
</tbody>
</table>
Figure 6.4 Shear modulus, $G_0$, as a function of composition in Ni-Fe-Cr-Co HEAs.

6.3.5 $B/G$ Ratio

The ratio of bulk modulus and shear modulus ($B/G$) is often employed to estimate the ductile/brittle property of materials. [89, 90] When $B/G > 1.75$, the material is more ductile; otherwise it is brittle. This ratio for Ni-Fe-Cr-Co HEAs is mapped in Fig. 6.5. As shown in the legend of Fig. 6.5, colors from light blue to red corresponds to $B/G > 1.75$, which covers the majority of all maps. The only dark blue region (most brittle) locates at the low-Ni high-Fe low-Cr high-Co corner, while the red region (most ductile) is at the opposite corner for each
component. By comparing the area of these regions, we found Ni-Fe-Cr-Co HEAs are more likely to have brittle characteristics with maximum Ni and minimum Fe and ductile with maximum Cr. However, it must be pointed out that this conclusion is based on the assumption that the alloy stays single phase. It has been mentioned in the section 6.3.1 that high Cr may lead to secondary intermetallic phases, such as the sigma phase. The sigma phase is extremely hard and brittle, whose formation leads to huge changes to mechanical properties. [88] The conclusion derived from those contour maps needs to be carefully evaluated in such cases where secondary phase forms.
6.4 Prediction of Properties

It was proposed to estimate the enthalpy of mixing of metallic glasses as a function of mixing enthalpy of constituent binary alloys via [91]

\[
\Delta H_{\text{mix}}^{\text{ij}} = \sum_{i=1, i \neq j}^{n} 4c_i c_j \Delta H_{\text{mix}}^{ij}
\]  

(6.6)

Eq. 6.6 was also used to approximate the enthalpy of mixing for solid solution high entropy alloys as to predict phase formation. [36] A parameter \( \Omega \) defined by \( \Omega = T_m \Delta S_{\text{mix}}/|\Delta H_{\text{mix}}| \) is expected to be larger than 1.1 when the high entropy alloy forms solid solution phase. [36] While this \( \Omega \) parameter has been used in many reports as an preliminary screening method for high entropy alloys, its correctness has not been evaluated quantitatively. To verify Eq. 6.6, we then calculated corresponding properties of constituent binary alloys. Besides the enthalpy of mixing, we also proposed a similar equation to predict the bulk modulus of high entropy alloys, which showed good agreement with the DFT results.

6.4.1 Pure Metals and Binary Alloys

We first calculated some bulk properties of the constituent elements, Ni, Fe, Cr, and Co, using both the EMTO method and VASP. No restrictions were applied to these spin polarized calculations such that the structures as well as magnetic moments were fully relaxed to reach the lowest energy. Lattice parameters and bulk moduli of these metals in their naturally stable phases were calculated, namely, Ni in fcc, Fe in bcc, Cr in bcc, and Co in hcp. The calculated results were then compared with experimental measurements from the literature [92] in Table 6.4.

As shown in Table 6.4, EMTO and VASP calculations produce similar lattice parameters
Table 6.4 Lattice parameters and bulk moduli of Ni, Fe, Cr, and Co from FM EMTO calculations

<table>
<thead>
<tr>
<th>Lat.</th>
<th>EMTO</th>
<th>VASP</th>
<th>Expt. [92]</th>
<th>EMTO</th>
<th>VASP</th>
<th>Expt. [92]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>fcc</td>
<td>3.53</td>
<td>3.52</td>
<td>3.52</td>
<td>199</td>
<td>198</td>
</tr>
<tr>
<td>Fe</td>
<td>bcc</td>
<td>2.84</td>
<td>2.83</td>
<td>2.87</td>
<td>185</td>
<td>186</td>
</tr>
<tr>
<td>Cr</td>
<td>bcc</td>
<td>2.85</td>
<td>2.87</td>
<td>2.88</td>
<td>256</td>
<td>178</td>
</tr>
<tr>
<td>Co</td>
<td>hcp</td>
<td>2.50/4.04</td>
<td>2.49/4.02</td>
<td>2.51/4.07</td>
<td>212</td>
<td>211</td>
</tr>
</tbody>
</table>

and bulk moduli as experimental values, except that the predicted bulk modulus of bcc Cr from EMTO (256 GPa) is much larger than the experimental value (190 GPa). This is because EMTO-CPA predicts bcc Cr to be non-magnetic while it is an anti-ferromagnetic metal in experiments. VASP correctly predicts bcc Cr to be anti-ferromagnetic with a bulk modulus (178 GPa) that is much closer to the experimental value. For the sake of comparison of the two methods, non-magnetic bcc Cr is also simulated by VASP. VASP predicts the NM bcc Cr has a bulk modulus of 260 GPa, showing good agreement with the EMTO method.

Table 6.5 Bulk moduli and enthalpy of mixing of fcc binary alloys or pure metals from PM EMTO-CPA calculations

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>202</td>
<td>173</td>
<td>229</td>
</tr>
<tr>
<td>Fe</td>
<td>-47*</td>
<td>100</td>
<td>229</td>
</tr>
<tr>
<td>Cr</td>
<td>-111*</td>
<td>-75*</td>
<td>232</td>
</tr>
<tr>
<td>Co</td>
<td>32*</td>
<td>-25*</td>
<td>-145*</td>
</tr>
</tbody>
</table>

and
Bulk moduli and enthalpy of mixing for 6 fcc binary alloys and 4 fcc pure metals were calculated by the EMTO-CPA method. Because we were interested in seeing the paramagnetic (PM) bulk properties of the quaternary alloys, we assumed these fcc binary alloys and pure metals were also paramagnetic by employing the disordered local moment approximation. As listed in Table 6.5, bulk moduli for the 10 fcc structures are given in the upper right triangle, and enthalpy of mixing for the 6 fcc binary alloys are given in the lower left triangle. Enthalpy of mixing for binary alloys is calculated by

\[
\Delta H_{ij}^{\text{mix}} = E_{ij}^{\text{bcc}} - \frac{1}{2}E_{i}^{\text{bcc}} - \frac{1}{2}E_{j}^{\text{bcc}}
\]  

(6.7)

where \(E\) is the system energy per atom from EMTO calculations. All structures including binary alloys and pure metals in Eq. 6.7 are in fcc lattice with paramagnetic settings.

### 6.4.2 Enthalpy of Mixing

Thanks to the high throughput EMTO calculations obtained in the present study, we were able to evaluate the validity of Eq. 6.6 for high entropy alloys. We compared the enthalpy of mixing results of all 2736 compositions calculated from Eq. 6.3 to those calculated from Eq. 6.6, in which the binary enthalpy of mixing values were taken from Table 6.5. The absolute values of difference between two enthalpy of mixing results were computed. The average of these absolute values is 9 meV/atom with a standard deviation of 6 meV/atom.

We also plot the comparison between DFT values and predicted values in Fig. 6.6. It is shown that the predicted mixing enthalpies all fall near the blue dashed line, which indicates a perfect agreement, for all test alloys. This implies that Eq. 6.6 is rather accurate for high entropy alloys. This conclusion leads to a very convenient means to generate an entire map of enthalpy of formation for a HEA system. Only energies of constituent elements and binary
alloys in the same lattice need to be calculated. Then we can reach a rather accurate estimation of enthalpy of formation of the HEA with any composition by combining Eq. 6.6 and Eq. 6.5.

6.4.3 Bulk Modulus

Bulk modulus describes the resistance of a material against hydrostatic pressure, and can be directly connected to the bonding strength between atoms. Recall that we calculated the bulk moduli of binary random alloys as well as pure metals using the four elements in Table 6.5. These binary alloys and pure metals are in the fcc lattice with the same magnetic settings as in the NiFeCrCo alloys. Note that fcc Fe has the smallest bulk modulus of all four elements while another significantly low bulk modulus is found in fcc FeCo. This indicates weak bondings
between Fe-Fe and Fe-Co atoms. An alloy with higher Fe concentration, therefore, is expected to have a weaker average bonding strength and a lower bulk modulus. If the bulk modulus is mostly controlled by first-nearest-neighbor interactions, it should follow the following relation:

\[
B_0^{predict} = \sum_i c_i^2 B_i + \sum_{i>j} 2c_i c_j B_{ij}
\]

(6.8)

where \(i, j\) indicate elemental types.

Using Equation 6.8, we calculated the predicted bulk moduli of all tested compositions of Ni-Fe-Cr-Co alloys, and found good agreement with the DFT results, as shown in Fig. 6.7.

Figure 6.7 Bulk modulus from DFT calculations vs. predicted values with binary results. The two values are the same on the blue dashed line.
Specifically, the average difference between the predicted bulk moduli and the DFT bulk moduli is 4.9 GPa with a standard deviation of 3.3 GPa. Taking into account systematic errors in DFT calculations of bulk modulus, this prediction is rather accurate. This agreement confirms that the bulk modulus of Ni-Fe-Cr-Co alloys are mainly dependent on the first-nearest-neighbor atomic bondings. Such proportional combination of binary bulk modulus in the forced same lattice structure with the same magnetic settings to predict the bulk modulus of alloys in the near-equiatomic range is anticipated to also work for other high-entropy alloys, although preliminary test of selected compositions is suggested to confirm this method.

6.4.4 Shear Modulus

It is of interest in which way the concentration of Co controls the shear modulus of Ni-Fe-Cr-Co HEAs. First, we plotted the shear modulus $G_0$ as a function of two variables, $C_{11} - C_{12}$ and $C_{44}$, based on the Voigt-Reuss-Hill averaging equations as a contour map in Fig. 6.8(a). We also plotted the $C_{11} - C_{12}$ vs. $C_{44}$ data of all 2736 compositions on top of the contour map. It is found that the $C_{11} - C_{12}$ vs. $C_{44}$ of tested alloys gather as a stripe along the gradient direction of shear modulus. Consequently one can approximate $G_0$ by considering only $C_{44}$. In Fig. 6.8(b), $C_{44}$ was plotted as a function of the concentration of Co. We found a general positive correlation between Co% and $C_{44}$. Therefore, it is concluded that the Co component contributes to $C_{44}$ in the Ni-Fe-Cr-Co HEAs, which in turn controls shear modulus. This contribution from Co is unlikely to be associated with self-interaction between Co atoms in that $C_{44}$ of fcc Co is quite small (only 160 GPa), but rather originates from the complex chemical bonding with other elements. Unlike bulk modulus that can be conveniently predicted through binary bulk moduli in the same lattice and Eq. 6.8, shear modulus, on the other hand, is sensitive to $C_{44}$ of the alloy, which is determined by collective local cluster interactions.
Figure 6.8 (a) $C_{11} - C_{12}$ vs. $C_{44}$ for all 2736 alloys in this study plotted on top of shear modulus contour maps. Shear modulus is a function of $C_{11} - C_{12}$ and $C_{44}$. (b) $C_{44}$ as a function of Co concentration of all alloys.
6.5 Comparison between EMTO and VASP

We have discussed the enthalpy of mixing, lattice parameters, bulk moduli, and shear moduli of Ni-Fe-Cr-Co HEAs that were obtained through the EMTO-CPA method in the paramagnetic state. We also performed VASP+SQS calculations for selected alloys with the highest or lowest lattice parameter, bulk modulus, or shear modulus. SQS models were built by considering the first shell correlation functions of pairs within the restriction of the fcc lattice and 100 atoms. Paramagnetic simulation using VASP is non-trivial, so ferromagnetic (FM) settings were used. FM calculations for the same alloys were also performed by the EMTO-CPA method. Comparisons between the three methods are presented in Table 6.6.

Table 6.6 Comparison of lattice parameters, bulk moduli, and shear moduli from EMTO-CPA (PM), EMTO-CPA (FM), and VASP+SQS (FM) calculations

<table>
<thead>
<tr>
<th>Ni,Fe,Cr,Co%</th>
<th>EMTO,PM</th>
<th>EMTO,FM</th>
<th>VASP,FM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 ) (Å)</td>
<td>40,10,10,40</td>
<td>3.509</td>
<td>3.539</td>
</tr>
<tr>
<td>( B_0 ) (GPa)</td>
<td>24,40,26,10</td>
<td>117.2</td>
<td>168.6</td>
</tr>
<tr>
<td>( G_0 ) (GPa)</td>
<td>34,16,40,10</td>
<td>84.2</td>
<td>81.4</td>
</tr>
</tbody>
</table>

As shown in Table 6.6, the ETMO-CPA calculations in the PM state generate \( a_0, B_0 \) and \( G_0 \) results that differ the FM results from either VASP or EMTO-CPA, while the latter two methods have similar results. Regardless of the difference of properties between the three methods, the high/low comparison of the same property is not changed within each method. That is, the alloy predicted to have a lower \( a_0, B_0 \) or \( G_0 \) by EMTO-CPA in the PM state also has a lower
value in the EMTO-CPA/VASP+SQS calculations in the FM state. Therefore, it is concluded that the deviation of the same property from EMTO-CPA and VASP+SQS is mostly due to the different magnetic states, and that the EMTO-CPA and VASP+SQS method both lead to qualitatively accurate results.

6.6 Conclusions

We have used two complimentary DFT tools, EMTO-CPA and VASP+SQS, to study Ni-Fe-Cr-Co high entropy alloys with each component ranging from 10–40 at.%. Enthalpy of mixing, lattice parameters, bulk moduli, elastic constants, and shear moduli are mapped by EMTO-CPA in the paramagnetic state. It is found that Cr, Co, Fe, Co, and Cr have the most significant influence on enthalpy of mixing, lattice parameter, bulk modulus, shear modulus, and B/G ratio, respectively. The enthalpy of mixing in HEAs with high concentrations of Cr and Co are the most negative and indicate possible formation of secondary intermetallic phases. The majority of Ni-Fe-Cr-Co HEAs studied are ductile as expected. Better ductility is predicted in those with high-Cr high-Ni concentrations. Alloys as Ni_{10}Fe_{40}Cr_{10}Co_{40} may act more brittle. An equation to estimate the enthalpy of mixing of HEAs using binary data, \( \Delta H_{\text{mix}} = \sum 4c_i c_j \Delta H_{ij}^{\text{mix}} \), was evaluated on all tested alloys. This equation was found to be accurate with an average difference of 9 meV/atom. A similar equation to predict bulk modulus with weighted contribution from first shell interaction was proposed and tested on all alloys. This equation, \( B_0 = \sum c_i^2 B_i + \sum 2c_i c_j B_{ij} \), was also found to be accurate with an average difference of 4.9 GPa. These two equations are expected to work for other HEA systems. It is found that shear moduli of all tested alloys are largely dependent on \( C_{44} \), while the concentration of Co has a noticeable control on \( C_{44} \). Alloys predicted to have the lowest or highest \( a_0/B_0/G_0 \) were also simulated by EMTO-CPA and VASP+SQS in the ferromagnetic state. Comparison of the three methods shows the results
have relatively high precision.
Chapter 7

Stacking Fault Energy of NiFeCrCo

Stacking fault energy (SFE) plays a very important role in the determination of deformation mechanism in materials. In this chapter, methods to calculate the stacking fault energy of high entropy alloys are discussed. Two first principles methods are employed, namely, the Vienna ab-initio simulation package (VASP) combined with special quasi-random structure (SQS), and the exact muffin-tin orbital method with coherent potential approximation (EMTO-CPA). Two ways to calculate the SFE are used: the supercell method and the axial interaction model (AIM). The combination of the two computational methods and two SFE simulation methods lead to four ways of SFE calculation, all of which are performed for equiatomic NiFeCrCo in the present study. It is found that results from the supercell models and EMTO-CPA are close to experimental measurement. The supercell models from VASP prove unfeasible for the calculation of SFE. The latter two exhibit a conflict between experimental observation and ground state results. From the present study, it is seen that the independent first principles calculation of SFE is a challenging project. Some preliminary results presented at the end of this chapter show that extra efforts, e.g., vibrational entropy calculations, are necessary for the study of SFE in these high entropy alloys.
In section 7.1 (background), the SFEs of NiFeCrCo and NiFeCrCoMn are studied through a combination of experimental and computational tools. This study was published on JOM, entitled *Mechanical properties and stacking fault energy of NiFeCrCoMn high entropy alloys*. I am the second author of this paper and performed the calculations. [6]

### 7.1 Background

Stacking fault energy (SFE) plays a very important role in the determination of deformation mechanism in materials. On one hand, formation of twins becomes easier in low-SFE crystals. Twinning structures provide extra storage for dislocations, therefore enhance ductility. On the other hand, area of a stacking fault between pair dislocations is larger in low-SFE materials. The larger area makes it more difficult for the dislocations to pass a grain boundary, thus higher strength. The search for low-SFE materials has attracted many researchers’ interest. [6] However, measurement of SFE in high entropy alloys is a non-trivial problem.

Zaddach, Niu, et al. [6] combined experimental measurement of stacking fault probability and computational results of elastic constants to obtain the SFE values of NiFeCrCo and NiFeCrCoMn high entropy alloys. The SFE is calculated as

\[
\gamma = \frac{K_{111} \omega_0 G_{(111)} a_0 A^{-0.37} \cdot \frac{\epsilon^2}{\alpha}}{\pi \sqrt{3}} \cdot \frac{\epsilon^2}{\alpha} \quad \text{comp.}
\]

where the first half is based on computations, and the second half is based on experiments. In Eq. 7.1, \( K_{111} \) is assumed to be a constant 6.6 for all fcc materials, \( G_{(111)} \) is the shear modulus in the (111) plane and can be derived from elastic constants, \( a_0 \) is the lattice parameter, \( A \) is the Zener elastic anisotropy \( A = 2C_{44}/(C_{11} - C_{12}) \), \( \epsilon^2 \) is the mean square microstrain, and \( \alpha \) is the stacking fault probability. All the computational input variables in Eq. 7.1 can be
obtained through the same method as described in Chapter 6. In this study using experimental and computational methods, it is found that as more elements are added into the alloy, the SFE becomes smaller, and that the equiatomic NiFeCrCo and NiFeCrCoMn HEAs have low SFEs.

Huang et al. [93] calculated the stacking fault energy of equiatomic NiFeCrCoMn as a function of temperature using the EMTO-CPA method within the supercell framework. Their calculations were based on the paramagnetic state and included energetic contributions from ground state DFT results, magnetic entropy, and strain. Independent calculation of SFE for HEAs has been a challenging task, and existing studies like the work by Huang et al. [93] are found to be very limited in the literature.

The present study focuses on the quaternary NiFeCrCo high entropy alloy. First, this alloy was found to have a SFE almost as low as equiatomic NiFeCrCoMn does [6], and it has exhibited great mechanical properties comparable to the quinary alloy. Second, chemical complexity in this quaternary alloy is easier to deal with, allowing us to test more computational methods for the study of SFE. A computational study by Niu et al. predicted the formation of a L1_2 type phase with Cr ordering in the equiatomic high entropy alloy NiFeCrCo, which was confirmed by experimental measurement of magnetic moment and transmission electronic microscopy images of NiFeCrCo samples before and after annealing at 1000°C for 24h. [14] In another report [5], dark speckles were seen homogeneously distributed in the matrix of NiFeCrCo after annealing at 1300°C for a week. The matrix and speckles were fully coherent with the same structure. These speckles are likely to be the L1_2 phase proposed by Niu et al. In section 5.5, we have discussed the strengthening effect of the L1_2 nanoparticles by impeding dislocation motion. This L1_2 phase will not be studied here.
7.2 Methods

Two complementary first principles methods were used in the present study. The first was the Exact Muffin-Tin Orbital method combined with Coherent Potential Approximation (EMTO-CPA). Muffin-tin potential spheres with large overlapping were used to accurately describe the exact one-electron potential. The EMTO method calculates total energy using the full charge density (FCD) technique [75]. FCD calculations have similar accuracy to that of full-potential methods but run faster. The CPA technique allows simulation of random solid solutions by blending constituent potentials into one single site. [84] The nature of this one-site approximation by CPA ignores local lattice displacement. However, the EMTO-CPA method turned out to be quite accurate for HEA systems composed of transition metals [6, 85]. The second method was the Vienna Ab-initio Simulation Package (VASP) [70, 71] with projector augmented wave (PAW) pseudo-potentials [72, 73]. Special quasi-random structures (SQS) [74], which are atomic models that best represent the targeted alloy within the confines of the periodic boundary condition, were generated through a Monte Carlo algorithm [53].

In EMTO-CPA calculations, we used the Perdew-Burke-Ernzerhof version of generalized gradient approximation (GGA-PBE) of exchange-correlation functionals. [68, 69] The Kohn-Sham equations were solved within the so-called soft-core approximation, which let the code recalculate core states after each iteration. The Green’s function was calculated for 16 complex energy points. The basis set of EMTO included s, p, d, and f states. A $13 \times 13 \times 13$ k-point mesh was used; the total energy converged within 1 meV/atom. The Screened Impurity Model (SIM) parameter of 0.902 was applied for electrostatic correction to the single-site CPA. We used the disordered local moment (DLM) to describe the paramagnetic state of Ni-Fe-Cr-Co HEAs. [86] Within the DLM model, each magnetic element was regarded as two separate parts with up and down spins. In this case, all HEAs were simulated as Fe↑Fe↓NiCrCo.
In the VASP calculations, the GGA-PBE approximation was also employed. All k-point mesh settings were tested to meet the 1 meV/atom convergence criterion. The plane-wave cut-off energy was taken as 350 eV. The reciprocal space energy integration was performed by the Methfessel-Paxton technique for atomic relaxations. Spin polarization was considered in all VASP calculations, and VASP predicts ferromagnetic state is the most stable. Simulation of the paramagnetic state in VASP is a non-trivial task and not performed in the present study.

Stacking fault energy describes the average energy compensation to form a stacking fault inside the crystal. To simulate a stacking fault in DFT calculations, it is required to build a periodic unit in which some atomic layers are shifted such that an infinite stacking fault forms. This stacking fault in the periodic unit, however, can only represent a single type of stacking faults in the real alloy with similar local chemical environment. The chemical environment is usually uniform within the periodic unit cell of binary alloys, but with more components in the alloy, changes of local chemical environment can be big, and therefore a single stacking fault created in the periodic unit cell cannot capture the average stacking fault energy of the multicomponent alloy. For high entropy alloys with four or more components, this direct calculation of stacking fault energy, or as we call it in this article, the supercell model, requires multiple parallel calculations whose average value may approach the real stacking fault energy. The total number of parallel calculations depends on when they converge and can become an enormous number.

Another method to estimate the stacking fault energy is the axial interaction model. This model assumes that the interaction between atomic layers in a close-packed structure is short-distant. It only takes into account the interaction between first few nearest layers to describe the total energy of the structure. Within the frame of axial interaction model up to the third order, the stacking fault energy is expressed as a function of the energies of fcc, hcp, and dhcp structures: $\gamma = (E_{\text{hcp}} + 2E_{\text{dhcp}} - 3E_{\text{fcc}})/A$, where $A$ is the area of the stacking fault.

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7.3 Supercell Model

A six-layer fcc SQS is generated first, each layer being (111) and having four atoms, with 24 atoms in total. A larger SQS is also built, with six (111) layers and 20 atoms per layer. The 24-atom SQS is illustrated in Fig. 7.1 (a). Assuming the fcc SQS has a stacking sequence \( ABCABC \), a stacking fault changes it to \( ABC|BCA \). If the periodic unit is unchanged and two periodic cells have the same stacking sequence, two A-layers meet at cell boundaries. To avoid
such conflict, the shape of the periodic unit must change according to the shifted layers such that the next periodic unit starts with layer B instead of A. This change in cell shape is shown in Fig. 7.1 (b). Both the shifting of layers to form a stacking fault and the shifting of periodic cell vectors are performed within the (111) layers. According to our analysis of nearest neighbors of each atom, the first-shell environment of all atoms outside the two layers forming a stacking
fault is unchanged. This supercell method therefore allows us to study the energetic difference between two structures that differ only by a stacking fault itself.

The supercell model was first applied to VASP calculations. It has been known that the system energy of this NiFeCrCo system is sensitive to chemical bonding changes, e.g., large energy scattering among permutations of the same SQS. Therefore, the stacking fault energy within a small region of $2 \times 2$ or $5 \times 4$ atoms is expected to have a large random deviation from the real value of the stacking fault energy. As shown in Fig. 7.2, the energies to form an intrinsic stacking fault within such small region by shifting layers towards three directions on five layers are mostly large in magnitude. For the 24-atom SQS, the SFEs range from about -900 to 900 mJ/m$^2$. For the 120-atom SQS, the SFEs are in an even larger range from over -2000 to 1000 mJ/m$^2$. To approach the real stacking fault energy in the alloy, one needs either a much larger layer area or much more individual results from similar structures. The essential idea is to average out the huge impact of chemical bonding on the system energy such that energy compensation due to the structural change emerges. Unfortunately, neither of the two possible solutions is practical for VASP calculations.

The supercell model was also used in EMTO-CPA calculations. Unlike the SQS supercell models which had 24 and 120 atoms, a nine-site structure is enough to capture the $ABCABCABC$ stacking sequence of fcc while maintaining enough space between two stacking faults. This nine-layer model was also used in the study of NiFeCrCoMn stacking fault energy using the same EMTO-CPA method. [93] The stacking fault energy of ferromagnetic NiFeCrCo at 0 K is found to be 37 mJ/m$^2$, while that of paramagnetic NiFeCrCo calculated by the disordered local moment method is 96 mJ/m$^2$ at 0 K. These SFE results from EMTO-CPA calculations are not influenced by the sensitivity of NiFeCrCo to local atomic interactions, therefore they can represent the average energy to be taken up when a stacking fault forms. We also find that the magnetic entropy of the fcc structure is only slightly higher than that of the stacking fault.
structure. The SFE is reduced by 7 mJ/m$^2$ at 300 K and 22 mJ/m$^2$ at 1000 K due to the magnetic entropy difference. The contribution from vibrational entropy cannot be evaluated within the EMTO-CPA method.

### 7.4 Axial Interaction Model

The third-order axial interaction model method uses the energies of fcc, hcp, and dhcp structures to derive the stacking fault energy in a fcc lattice. In the present study, SQS with 24 atoms and 120 atoms are generated for the three lattice structures. Another two SQS with 64 atoms provided by Gao are also available for the fcc and hcp structures. All these SQS models assume ideal random alloying of NiFeCrCo, therefore each allows 24 permutations. The ground state energies of the 24 permutations are calculated. The average ground state energies with a standard deviation are plotted in Fig. 7.3 for all SQS.

While all existing experimental studies report a single fcc crystal in NiFeCrCo samples [5, 6, 8, 14], Fig. 7.3 shows that hcp has the lowest ground state energy of all three phases, fcc having the highest. This means the hcp phase is more stable than fcc or dhcp for equiatomic NiFeCrCo at 0 K. However, the energy difference between the three phases is very small, ranging from less than 0.01 eV per formula unit up to 0.03 eV per formula unit. Such energy gap may be easily overcome by entropic contributions at higher temperatures. The configurational entropy is a function of the concentration of random elements. It is the same for fcc, hcp, and dhcp. Because we are interested in the relative energy difference between the three phases, configurational entropy will be excluded in the present study despite its high value in high entropy alloys.

Vibrational entropy is calculated for the 24-atom SQS models of fcc, hcp, and dhcp. Due to a high demand for computational resource by the calculation of vibrational entropy, we
randomly choose eight fcc permutations, seven hcp permutations, and two dhcp permutations for vibrational entropy calculations. The comparison of vibrational entropy between the fcc and hcp phases is particularly of interest in that fcc must beat hcp to have the lowest energy of all three phases.

The vibrational entropy increases as temperature arises. This increase is so large that the difference between vibrational entropy of SQS permutations is too small to observe in entropy vs. temperature plots. Therefore, we plot the difference between vibrational entropy of the first permutation of the 24-atom fcc SQS and those of the other permutations, as shown in Fig. 7.4 (a). It is found that the variation between permutations of fcc, hcp, and dhcp quickly reaches a plateau above 400 K. At higher temperatures, the variation is almost constant. The vibrational
Figure 7.4 (a) Vibrational entropy and (b) free energy of each permutation of fcc/hcp/dhcp minus that of the first fcc permutation.

entropy of the hcp permutations is generally smaller than that of fcc and dhcp. Free energy, including contributions from zero point energy and vibrational entropy, is also calculated for all permutations. They are plotted in Fig. 7.4 (b) in a similar format as in (a). It clearly shows that the free energy of hcp permutations quickly grows higher than those of fcc and dhcp as temperature raises. The increase in the free energy difference is almost linear above 400 K, which is because of the stable variation of vibrational entropy between those permutations. It can then be concluded that hcp may become less stable than fcc due to the vibrational entropy contribution to free energy. A similar conclusion cannot be made for the dhcp phase because of lack of data points. The equation of the axial interaction model cannot lead to an accurate stacking fault energy due to the scattering of free energies shown in Fig. 7.4 (b).

Ground state enthalpy of formation of fcc, hcp, and dhcp are also studied by the EMTO-CPA method. Both the paramagnetic (PM) state and the ferromagnetic (FM) state are considered, as shown in Fig. 7.5. In both magnetic states, the hcp phase has the lowest energy, consistent with the SQS results. The change in magnetic state is found to have a small impact

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on the dhcp energy while not changing the energy gap between fcc and hcp. The EMTO-CPA results are considered to agree well with the SQS calculations.

### 7.5 Summary

In this chapter, two complimentary DFT tools are employed for a challenging study of stacking fault energy in NiFeCrCo high entropy alloy: the EMTO-CPA method and VASP calculations on special quasi-random structures. The stacking fault energy of equiatomic NiFeCrCo is calculated by two modeling methods. The first method uses supercell models of a fcc structure and a stacking fault structure. The stacking fault energy is the energy difference between the two structures. It is found that when taking into account the complex local chemical interaction
in the VASP+SQS calculations, the stacking fault energy within the small region of $2 \times 2$ or $5 \times 4$ atoms ranges from -2000 mJ/m$^2$ to 1000 mJ/m$^2$. Such huge scattering of SFE indicate the sensitivity of system energy on local bonds in NiFeCrCo. The same supercell models are used in EMTO-CPA calculations, leading to SFE of 37 mJ/m$^2$ and 96 mJ/m$^2$ in ferromagnetic and paramagnetic NiFeCrCo, respectively. Magnetic entropy can reduce the SFE of paramagnetic NiFeCrCo by 7 mJ/m$^2$ at 300 K and 22 mJ/m$^2$ at 1000 K. Vibrational entropy cannot be captured in EMTO-CPA calculations. The second method for SFE calculation is based on the axial interaction model. The SFE is expressed by the energies of fcc, hcp, and dhcp structures of the same alloy. SQS of 24/64/120 atoms for the three lattice structures are used in VASP calculations. It is found that the hcp phase of NiFeCrCo has the lowest energy at 0 K. After adding energetic contribution from vibrational entropy, the hcp energies becomes higher than the fcc energies. EMTO-CPA calculations of the paramagnetic and ferromagnetic NiFeCrCo lead to similar results as the SQS models, confirming the conclusion that hcp is the most stable among the three phases at 0 K. These studies show that phonon vibration must be considered for energetics study of NiFeCrCo phases despite its high demand for computational resource.
Chapter 8

Phase Stability of NiFeCrCoMn

We have discussed the phase stability and chemical ordering in equiatomic NiFeCrCo in Chapter 5, the mixing enthalpy and elastic properties mapped by composition of non-equiatomic NiFeCrCo in Chapter 6, and the stacking fault energy of equiatomic NiFeCrCo in Chapter 7. In this study, it will be demonstrated that, compared to the already complex and challenging quaternary system NiFeCrCo, this quinary NiFeCrCoMn alloy is even more complex due to its chemical compositions and magnetic configurations. This chapter starts with the most fundamental phase stability properties of this alloy, and provides preliminary data of first principles calculations.

8.1 Background

The quinary high entropy alloy NiFeCrCoMn was among the first batch of high entropy alloys ever manufactured and studied. [2] Later people found many extraordinary properties in this HEA, such as outstanding cryogenic temperature fracture resistance [22], and remarkable ductility with good strength [6, 21, 80]. These excellent mechanical properties were characterized
in the single phase random solid solution phase of NiFeCrCoMn. Very recently, reports are found in literature about the multiphase formation in this HEA. One of reports concluded that the NiFeCrCoMn HEA can be described by a schematic phase diagram of the FeCrCo-NiMn system consisting of a liquidus and a solidus, with a partition coefficient of 0.74. [20] The authors found dendrites enriched in Co, Cr and Fe were formed first when the liquid phase was cooled down slowly enough, and afterwards inter-dendrites enriched in Ni and Mn solidified. The solid solution phase was reached by a fast cooling or annealing the dendritic structure at high temperatures, e.g., 1100°C for 1h. Another experimental study of nano-crystalline NiFe-CrCoMn reached similar results. [94] The authors reported the formation of a NiMn phase and Cr-rich phase under annealing for as short as 5 min at 450°C. With increasing annealing time, the volume fractions of the two secondary phases increased and a third phase of FeCo also formed. The authors concluded the surfeit of grain boundaries in the nano-crystalline HEA offer many fast diffusion pathways and nucleation sites to facilitate the phase decomposition.

A recent study of the NiFeCrCo HEA found the tendency of Cr to repel each other due to energy increase realized by magnetic frustration on Cr atoms. The magnetic frustration is caused by two antiferromagnetic Cr atoms sit together among other ferromagnetic atoms. The NiFeCrCoMn HEA has two antiferromagnetic elements, Cr and Mn, together with the ferromagnetic elements of Ni, Fe, and Co. Similar repulsion between Cr/Mn atoms is expected, although the total concentrations of Cr and Mn is larger than the maximum storage (25%) of antiferromagnetic elements in the reported L12 structure of NiFeCrCo. In this study, we will examine the possible phases with ordering of single phase NiFeCrCoMn HEAs. The phase with lowest energy might form under long annealing at higher temperatures. We also investigate the equilibrium multiphase formation of this HEA at 0 K, which may explain the formation of secondary phases in experiments with slow cooling.
8.2 Partial Ordering of Cr/Mn

Table 8.1 Chemical compositions in the L12 structure of NiFeCrCoMn and corresponding configurational entropy.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Corner site (Ni-Fe-Cr-Co-Mn %)</th>
<th>Face-center site (Ni-Fe-Cr-Co-Mn %)</th>
<th>S^{conf} (R)</th>
<th>TS@300 K (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-SS-Mn</td>
<td>0-0-0-0-0</td>
<td>20-20-20-20-20</td>
<td>1.61</td>
<td>166</td>
</tr>
<tr>
<td>02-SS-Cr</td>
<td>0-0-0-0-0</td>
<td>20-20-20-20-20</td>
<td>1.61</td>
<td>166</td>
</tr>
<tr>
<td>03-L12a-Mn</td>
<td>5-5-5-5-80</td>
<td>25-25-25-25-0</td>
<td>1.23</td>
<td>127</td>
</tr>
<tr>
<td>04-L12a-Cr</td>
<td>5-5-80-5-5</td>
<td>25-25-0-25-25</td>
<td>1.23</td>
<td>127</td>
</tr>
<tr>
<td>05-L12b-Mn</td>
<td>0-0-20-0-80</td>
<td>27-27-20-27-0</td>
<td>1.16</td>
<td>119</td>
</tr>
<tr>
<td>06-L12b-Cr</td>
<td>0-0-80-0-20</td>
<td>27-27-0-27-20</td>
<td>1.16</td>
<td>119</td>
</tr>
</tbody>
</table>

Six configurations were designed for the study of ordering of Cr/Mn in NiFeCrCoMn fcc solid solution, as shown in Table 8.1. 01-SS-Mn and 01-SS-Cr are the same structure with different magnetic configurations, the former having antiferromagnetic Mn and the latter having antiferromagnetic Cr. 03-L12a-Mn and 04-L12a-Cr are based on a L12 structure where only one antiferromagnetic element is specially treated to avoid magnetic frustration. After filling entire Mn or Cr in the corner site, we fill the rest of the corner site with all other elements. 05-L12b-Mn and 06-L12b-Cr use another filling strategy. That is, after filling entire Mn/Cr in the corner site, we fill the rest of the corner site with Cr/Mn while keep all ferromagnetic elements in the face-center sites.

The ground state energies as a function of volume per atom for the six configurations are plotted in Fig. 8.1. The energies are relative to the lowest energy of all collected energies. Smooth energy curves are obtained for all structures. The random solid solution phases, i.e.,
Figure 8.1 Ground state energy as a function of volume for NiFeCrCoMn with different phases. All energies are relative to the lowest energy of all six phases.

01-SS-Mn and 02-SS-Cr, have the highest energy regardless of whether Cr or Mn being antiferromagnetic. By placing either Cr or Mn in the corner site to avoid magnetic frustration of that element, we can slightly lower the energy of the NiFeCrCoMn HEA, shown by the energies of 03-L12a-Mn and 04-L12a-Cr. If we maximize the effort to avoid magnetic frustration by filling the corner site entirely with Cr or Mn, the system energy of the HEA becomes the lowest. The energy reduction is about 150 meV, much larger than the energy increase caused by reduction in configurational entropy, about 10 meV. In the last case, the phase with all Cr in the corner...
site has the lowest energy of all. It is concluded that avoiding the magnetic frustration of Cr while minimizing that of Mn leads to the most stable phase of NiFeCrCoMn.

8.3 Multiphase Formation

As studied in Chapter 6, the mixing enthalpy of high entropy alloys can be estimated by

$$\Delta H^{\text{mix}} = \sum_{i=1, i \neq j}^{n} 4c_i c_j \Delta H_{ij}^{\text{mix}}$$  \hspace{1cm} (8.1)$$

where $c_i$ and $c_j$ are the atomic concentrations of two elements, and $\Delta H_{ij}$ is the enthalpy of mixing of the binary alloy with the same crystal structure as the HEA. The binary mixing enthalpy is calculated as the energy of the binary alloy subtracted by energies of pure elements in the same crystal structure as the HEA. In the quinary HEAs of NiFeCrCoMn, mixing enthalpy results of ten binary alloys from EMTO-CPA calculations are given in Table 8.2.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-47.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>-111.5</td>
<td>-75.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>32.5</td>
<td>-25.6</td>
<td>-145.3</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>9.3</td>
<td>-11.2</td>
<td>-21.3</td>
<td>-46.1</td>
</tr>
</tbody>
</table>

Enthalpy of mixing of quinary NiFeCrCoMn HEAs were calculated via Eq. 8.1, each component having an atomic concentration from 10% to 30% in a step of 2%. The total number of compositions is 8801. Of these compositions, the enthalpy of mixing ranges from -39.6
meV/atom to -98.5 meV/atom. It is found that Ni$_{10}$Fe$_{20}$Cr$_{30}$Co$_{30}$Mn$_{10}$ has the lowest mixing enthalpy. A negative mixing enthalpy further away from zero indicates stronger binding force between these atoms in the HEA of this composition. In an equiatomic NiFeCrCoMn HEA, it is likely that Ni and Mn separate from the matrix to form the high-Cr high-Co phase to reach lower system energy, should processing conditions allow thermodynamic equilibrium. This conclusion agrees well with experimental observation of the formation of dendrites enriched in Ni and Mn in NiFeCrCoMn HEA after slow cooling. [20]

8.4 Summary

We have studied the energetics of partial ordering of Cr/Mn in the equiatomic NiFeCrCoMn HEA, and found that this HEA prefers a L$_{12}$ type structure, in which the corner site is occupied by 100% of Cr and 25% of Mn in the alloy while the face-center sites are occupied by the rest with total disorder. The energy reduction from the random solid solution phase to the L$_{12}$ phase with partial ordering is approximately 275 meV/atom, which is much larger than the energy increase caused by reduction of configurational entropy. It is suggested that nano particles of the L$_{12}$ phase may exist in the equiatomic NiFeCrCoMn HEA under long annealing at relatively high temperatures, similar to the L$_{12}$ nano particles found in equiatomic NiFeCrCo HEA. While the partial ordering perhaps can be realized in small ranges via diffusion, the formation of multiple phases may be closer to a thermodynamic equilibrium. Enthalpy of mixing of NiFeCrCoMn HEAs in which each component ranges from 10 to 30 at.% are estimated via an empirical equation that has been confirmed to have a good accuracy for NiFeCrCo HEAs. It is found Ni$_{10}$Fe$_{20}$Cr$_{30}$Co$_{30}$Mn$_{10}$ has the lowest negative enthalpy of mixing. The strongly negative mixing enthalpy suggests strong binding forces between atoms in the alloy of this composition. Therefore, depletion of Ni and Mn occurs in equiatomic NiFeCrCoMn HEA to
achieve such thermodynamic equilibrium. This might be the reason to the observed dendrites enriched in Ni and Mn in NiFeCrCoMn from experiments. However, these calculations are only preliminary results and must be examined through more accurate and, of course, more expansive calculations. The purpose of this chapter is mainly to establish a good understanding of the feasibility of first principles tools in the study of the the highly complex high entropy alloy system NiFeCrCoMn.
Chapter 9

Conclusions and Future Work

9.1 Conclusions

Computational tools have been applied in this dissertation to study NiFeCrCo and NiFeCr-CoMn high entropy alloys. Predictions have been made to reveal better understanding of the phase stability and mechanical properties of the high entropy alloys. Methods established in this work can be borrowed for predictive investigation of similar materials.

It has been found that in equiatomic NiFeCrCo alloy the antiferromagnetic Cr atoms repel each other, described as magnetic frustration effect. By forcing Cr away from each other’s first shell in the fcc lattice, we predicted a L12 phase in which all Cr atoms sit in the corner site of fcc while other three elements randomly occupy the face-center sites. System energy is significantly reduced by the ordering of Cr, make the L12 phase thermodynamically stable. Experiments performed by collaborators and from the literature observed coherent nano particles that support this prediction.

The computational tools have also shined light on the near-equatomic range of NiFeCrCo compositions. Detailed maps of mixing enthalpy, lattice parameter, bulk modulus, shear mod-
ulus, and B/G ratio have been plotted to study how they are dependent on compositions. Con-
clusions obtained from these maps provides unique vision to the design of NiFeCrCo HEAs.
Empirical equations to quickly estimate the mixing enthalpy and bulk modulus have been tested
on the gigantic number of data points. These equations show good accuracy and may be used
for other HEAs.

The stacking fault energy has been studied using different methods for equiatomic NiFe-
CrCo. It is found that for such a chemically complex random alloy whose stacking fault en-
ergy has been reported to be small, calculating its stacking fault energy is non-trivial due to
large noise from chemical permutations of SQS, magnetic entropy, and vibrational entropy.
While a quantitative prediction of the stacking fault energy needs computationally expansive
calculations, this study using a reasonable amount of computing hours provides many useful
information for the HEA. It is concluded that changes within a very small region on chemi-
cal interaction can lead to huge energy fluctuations. Stacking fault energy is a global effect
after averaging out such energy scattering. Free energy calculations show that the hcp phase
of NiFeCrCo is more stable than fcc at 0 K, and that vibrational entropic contribution reverses
this trend. The nano particles with Cr ordering in NiFeCrCo solid solution can greatly impede
dislocation motion, causing a strengthening effect.

Finally, the computational tools that have proved powerful in NiFeCrCo calculations are
applied for the study of the even more chemically complex NiFeCrCoMn. Phase studies of
this quinary HEA focus on the chemical ordering of Cr and Mn and the formation of multiple
phases observed in experiments. It is found that Cr has a stronger preference to repel each
other than Mn does. A similar L12 phase as in NiFeCrCo is also energetically favored by
NiFeCrCoMn. Enthalpy of mixing in the near-equiatomic range are estimated using the same
equation for NiFeCrCo. It is found that Ni_{10}Fe_{20}Cr_{30}Co_{30}Mn_{10} has the most negative mixing
enthalpy, indicating that atoms in a phase of this composition have the strongest binding forces
and that depletion of Ni and Mn is thermodynamically driven.

9.2 Future Work

9.2.1 About NiFeCrCoMn HEAs

First, more calculations about the vibrational entropy difference between NiFeCrCo phases are suggested to quantify the influence of phonon vibration on the stacking fault energy. Then by combining this with EMTO-CPA calculations using the supercell method, it is possible to compute the stacking fault energy of non-equiaxial NiFeCrCo HEAs. The composition-dependent SFE maps will be especially useful for designing of HEAs with better mechanical properties, which may beat the disadvantage of the high computational consumption.

The composition-dependent property maps of the NiFeCrCoMn HEAs are also of interest. As more and more researchers start searching the non-equiaxial range of HEAs, mapping these properties can save much time for experimentalists.

More properties need to be studied in the NiFeCrCoMn HEAs, such as the formation of dislocations. Density functional theory tools are strongly recommended for studies of this HEA system because it has been shown that magnetism plays an important role in the determination of many properties, such as phase formation and entropy.

9.2.2 About Other HEAs

The equation to predict the mixing enthalpy of HEAs may be conveniently applied to the studies of other HEAs. Through combining with the equation to predict the bulk modulus, it is of interest to search for more chemically complex alloys that may form single phase solid solution with desired interatomic binding strength.
The combination of VASP+SQS and EMTO-CPA methods prove powerful in the study of NiFeCrCoMn HEAs and is recommended for other HEAs, too. The two complementary methods have the potential to reach higher accuracy in DFT calculations while reducing computation time.
52. A. van de Walle, Calphad 33, 266–278 (2009).


