

**Computational modelling studies of Fe-Co-M (M=Pd, V, Ti, Cr) magnetic
alloys**

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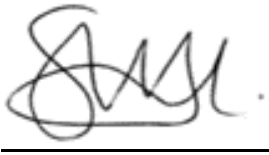
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DECLARATION

I declare that the dissertation hereby submitted to the University of Limpopo, for the degree of Master of Science in Physics has not previously been submitted by me for a degree at this or any other university; that it is my work in design and in execution, and that all material contained herein has been duly acknowledged.



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24/06/2022

Date

DEDICATION

This work is dedicated to **the young women in science and technology.**

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ABSTRACT

FeCo alloys are considered attractive soft materials due to their superior properties, particularly their high saturation magnetization and mechanical strength. These systems are important in applications such as aerospace and automotive industries. However, it was reported that the B2 FeCo binary alloy shows low levels of ductility at room temperature, which makes this alloy difficult to process. Furthermore, the current application of FeCo fails to sustain high-temperature environmental conditions for a long period which poses a limitation for use in the aerospace industry. In this study, multi-scale computational methods were used to investigate the stability and possible phase transformation of binary $\text{Fe}_{50}\text{Co}_{50}$ and the ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) alloys. The ternary alloying with M impurities was conducted to enhance the ductility, workability and the transformation temperature of the binary system.

Firstly, the stability of the binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys were investigated using the density functional theory. A supercell approach has been used to add ternary elements on the Co sub-lattice of $\text{Fe}_{50}\text{Co}_{50}$ system to obtain different atomic percentage compositions. Initially, these structures were fully optimized to obtain better precision of equilibrium lattice parameters, magnetic and thermodynamic properties.

It was found that the lattice constants of the binary $\text{Fe}_{50}\text{Co}_{50}$ are well in agreement with previous experimental data to within 2 %. The heats of formation was found to

decrease with an increase in V, Ti and Cr compositions which suggest that the structures are thermodynamic stable. In the case of Pd addition, it was revealed that the structures are thermodynamically unstable except 6.25 at. % Pd (heats of formation is negative). The magnetic moments decrease slightly with ternary additions. This suggests that these dopants are likely to minimally reduce the magnetism of $\text{Fe}_{50}\text{Co}_{50}$. The elastic constants revealed enhanced mechanical stability for the entire concentrations of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys due to positive C' ($C' > 0$). The ductility and brittleness behavior of the B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys was evaluated through the three quantities: Poisson's ratio, Pugh ratio (B/G), and the Cauchy pressure at different compositions. It was revealed that doping with M effectively enhances the ductility of the binary $\text{Fe}_{50}\text{Co}_{50}$ system.

Secondly, the semi-empirical embedded atom interatomic potentials method incorporated in the LAMMPS code was employed to investigate the temperature dependence on the lattice parameters of the binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys. The lattice parameter increases as the temperature is increased, but no transformation behavior was observed. This was also confirmed from the XRD patterns. Furthermore, the melting temperature of $\text{Fe}_{50}\text{Co}_{50}$ alloy is slightly reduced from 2200 K to 1800 K.

Lastly, cluster expansion (CE) and Monte-Carlo (MC) simulations were employed to determine ground-state structures, phase changes and high temperature properties of binary Fe-Co and ternary Fe-Co-M alloys. Three new ground-state stable structures were generated from Fe-Co and $(\text{FeCo}_2)_2$ is the most stable structure due

to the lowest heats of formation. There are no new stable structures for $\text{FeCo}_{1-x}\text{Pd}_x$ apart from the parent phases. The cluster expansion of $\text{FeCo}_{1-x}\text{V}_x$ generated three new ground-state systems and VFe_2Co is the most thermodynamically stable phase. Furthermore, $\text{FeCo}_{1-x}\text{Ti}_x$ and $\text{FeCo}_{1-x}\text{Cr}_x$ generated one ($\text{Fe}_8\text{Co}_6\text{Ti}_2$) and five ground-state stable structures, respectively. $(\text{CrFe}_2\text{Co})_4$ is the most thermodynamically stable phase with the lowest heats of formation.

Phase diagrams were also constructed to indicate the mixing of the ternary $\text{Fe-Co}_{1-x}\text{M}_x$ systems. The findings revealed that $\text{Fe-Co}_{1-x}\text{Pd}_x$ and $\text{Fe-Co}_{1-x}\text{V}_x$ mix at similar temperatures, whereas $\text{Fe-Co}_{1-x}\text{Ti}_x$ and $\text{Fe-Co}_{1-x}\text{Cr}_x$ mix at higher and lower temperatures, respectively.

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LIST OF SYMBOLS AND ABBREVIATIONS

Fe	Iron
Co	Cobalt
Pd	Palladium
V	Vanadium
Ti	Titanium
Cr	Chromium
Ni	Nickel
Si	Silicon
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
O	Oxygen
C	Carbon
W	Tungsten
Ta	Tantalum
Nb	Niobium
B	Boron
σ	Poisson's ratio
SMM	soft magnetic materials
DFT	Density functional theory
VASP	Vienna Ab initio simulation package
GGA	Generalized gradient approximation
PBE	Perdew-Burke-Ernzerhof
LDA	Local density approximation
LAMMPS	Large-scale atomic/molecular massively parallel simulator
XRD	X-ray diffraction
UNCLE	Universal cluster expansion

BCC	Body-centered cubic
FCC	Face-centered cubic
FLAPW	Fullpotential linearized augmented plane wave
LSDA	Local spin density approximation
DLM	Dynamic linear model
LDA	Local density approximation
DMFT	Dynamical mean-field theory
PMA	Perpendicular magnetic anisotropy
SIESTA	Spanish initiative for electronic simulations with thousands of atoms
SRO	Short-range order
EAM	Embedded atom method
PAW	projector augmented wave
NCP	Norm-conserving pseudopotential
USP	Ultra-soft pseudopotential
BZ	Brillouin zone
ECI	Effective cluster interactions
CVS	Cross-validation Score
RMS	Root mean square
EAM	Embedded atom method

CHAPTER 1

INTRODUCTION

In this chapter, we provide brief background information on soft magnetic materials in particular FeCo alloys from theoretical and experimental studies. Furthermore, the structural aspect, aims, objectives and intention of the study are presented. Finally, the outline of this dissertation is given.

1.1 FeCo soft magnetic alloys

FeCo alloys are widely known as soft magnetic materials (SMM) which represent an important group of engineering materials [1]. Soft magnetic alloys are materials that can be magnetized and demagnetized with ease, even in the existence of very little excitation field [2], resulting in high permeability. These materials have high reliability, low cost, and suitability for mass production, just like other commercial products [3]. Transformers, motors, inductors, and generators all use soft-magnetic materials in their magnetic cores [4]. Other commercially available soft magnetic alloys include FeNi and FeSi [3].

Fe-Co alloys have a very rare mixture of magnetic properties that include high curie temperatures as far as 1250 K [5, 6], good strengths, low coercivity, and large permeability. Compared to most well-known commercial magnetic materials, Fe-Co has the highest saturation magnetization [7, 8, 9] and is preferably a good fit for applications that demand high flux density [10]. The various uses of the alloys

include high conducting transformers, high field magnetic pole tips, actuators that are magnetically powered for impact printers, diaphragms in solenoid valves of telephone handsets, magnetostrictive sensors, flux conducting components in inductive momentum counters, electromagnetically guided ingestion and exhaust nozzles, and interior generator within an aircraft [1, 11, 12]. Fe-Co alloys are also considered attractive soft materials in applications like aerospace and automotive industries owing to their superior properties, particularly their high saturation magnetization. However, the B2 binary Fe-Co suffers poor ductility at room temperature, which makes this alloy difficult to process [11, 13, 14, 15, 16].

Furthermore, the current application of Fe-Co fails to sustain high-temperature environmental conditions for a long period, particularly above the transformation temperature (1073.15 K [17]), which poses a serious concern or limitation for use in the aerospace industry [18, 19]. Attempts were carried out to reduce the brittle nature and refine the ductility of Fe-Co alloys by ternary addition [11], however, it has been reported that alloying elements weaken the magnetic properties of the structure [20]. Studies have shown that some ternary additions like Ni and Pd have the potential to improve the ductility of B2 Fe-Co at room temperature [21, 22]. However, there is no clear information about the precise concentration range of the added elements. In addition, there is limited information regarding the magnetic properties of ternary Fe-Co-M, which is critical for magnetic alloy development.

Currently, the focus is on developing latest alloys that can satisfy the severe performance conditions of an aircraft, i.e., alloys that are able to operate at high

temperatures above 900 K, without compromising their high-inductions and good thermal stability for prolonged periods. The B2 Fe-Co binary alloy at lower temperatures than 1000 K is thermodynamically stable in a long-range ordered structure, which results in poor ductility of the alloy. Attempts were made to enhance the mechanical properties of Fe-Co alloys mainly by using heat treatment and deformation approaches [1, 18, 23, 24].

The study aims to explore ways of enhancing the ductility of B2 Fe-Co at room temperature through ternary alloying other than Ni and Pd, within a concentration range of 0 % to 50 %. Moreover, we will be determining further the impact of the ternary additions on the magnetic, mechanical, thermodynamic, and structural properties of the alloy. We intend to enhance the ductility and workability of B2 Fe-Co alloys by ternary alloying using Pd, V, Ti, and Cr and further by determining the influence of these elements on the magnetic valuables of the alloy. These alloying elements were chosen based on their ability to improve the ductility of the material and because these elements have large atomic radii compared to Co [25]. It was reported that the slip systems are larger in B2 Fe-Co alloys [26, 27], which contribute to the ductility of the material, hence the use of ternary elements with larger atomic radii will help reduce the effect caused by slip systems.

1.2 Structural properties

In this section, we mainly focus on the B2 Fe-Co structure. The B2 phase is a cubic structure with a space group of Pm-3m and the atomic arrangement is as shown in

figure 1. The structure is an ordered body-centered cubic (bcc) incorporating two simple cubic interpenetrating sublattices and it can be stoichiometrically represented by 50:50 atomic distributions ($\text{Fe}_{50}\text{Co}_{50}$). The crystal structure is described by a unit cell (figure 1 (a)) and the $2 \times 2 \times 2$ supercell (figure 1 (b)). The supercell of Fe-Co is a cell that describes the same crystal but has a larger volume than the unit cell.

The supercell will allow us to explore efficiently the different compositions of the structures at different atomic positions (see figure 1 (c)). The atomic substitution of Co by (M = Pd, V, Ti, and Cr) will be done at different atomic positions in the compositions ($0 \leq x \leq 50$). The composition range is limited since the amount of Co should not be lost completely in the system.

Although Co is good at enhancing mechanical properties, Fe has higher magnetic strength and is not expensive, easily accessible and has a slightly higher melting temperature (1 811 K [28]) than Co (1 768 K [28]). Furthermore, considering the application of Fe-Co, the substitution of ternary elements will be done on the Co-site of the alloy to avoid compromising the magnetic properties if Fe is to be reduced.

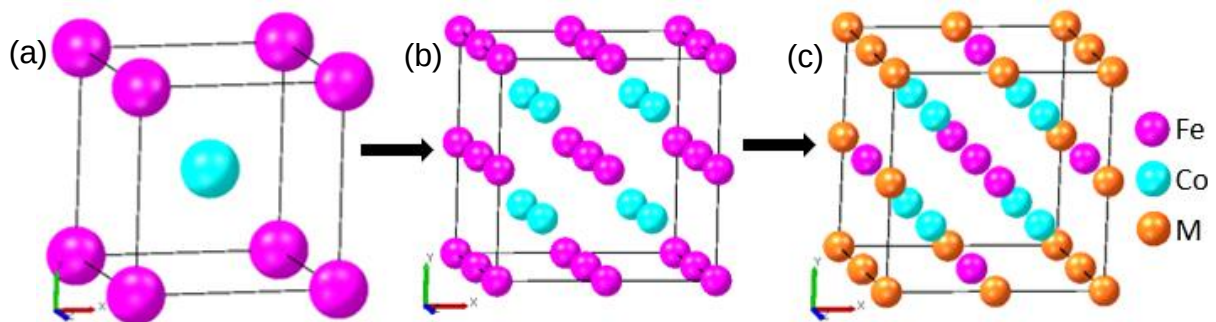


Figure 1. 1 The atomic arrangements of (a) unit cell and (b) $2 \times 2 \times 2$ supercell and (c) substituted structure of B2 Fe-Co with the space group $\text{Pm}\bar{3}\text{m}$.

1.3 Aims and objectives

The study aims to investigate the effect of ternary addition on the magnetic, structural, mechanical, electronic, and thermodynamic stability of Fe-Co alloys for the development of magnetic alloys.

The objectives of the study are to:

- i. Determine the structural, thermodynamic, electronic, and mechanical stability of $\text{Fe}_{50}\text{Co}_{50}$ and $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys,
- ii. Investigate the effect of alloying elements i.e., Pd, V, Ti, and Cr (for $0 \leq x \leq 50$),
- iii. Determine the vibrational properties from phonon dispersion curves,
- iv. Determine the temperature dependence of binary and ternary systems,
- v. Probe the phases of the materials through the X-ray diffractions for binary and ternary systems,
- vi. Predict new stable phases of Fe-Co and Fe-Co-M (M=Pd, V, Ti, Cr),
- vii. Determine the temperature range in which the Fe-Co-M systems mix using Monte Carlo simulations.

1.4 Intentions of the study

Fe-Co alloy is a soft magnetic material that has a potential application in current transformers and the generation of aircraft due to its good magnetic properties. However, this alloy is used rarely because of its low levels of ductility, especially at room temperature. We intend to use computational methods, in particular density

functional theory [29, 30], to understand how ternary alloying can enhance the ductility of Fe-Co alloys without compromising the magnetic properties.

We used DFT employing the VASP code [31] and calculations were performed considering the GGA_PBE functional. A 2X2X2 supercell was constructed on the binary Fe-Co and a substitutional search tool was used to substitute Co with Pd, V, Ti and Cr. A supercell approach will be performed for five different compositions that is 6.25, 18.75, 25, 31.25 and 43.75. Fully geometry optimization will be performed on these compositions to establish the ground-state compositions. The lattice parameters and heats of formation were calculated from the geometry optimization calculations of the binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) systems. The elastic and magnetic properties were determined from the optimized structures to deduce the mechanical stability. To probe the stability, the ductility of the materials was deduced from the Pugh ratio, Poisson's ratio and Cauchy pressure. A PHONON code [32] was used to evaluate the vibrational stability from phonon dispersion curves. Furthermore, the temperature dependence of the lattice parameters and XRDs was studied using LAMMPS code [33] to establish the transformation temperature. Moreover, cluster expansion and Monte Carlo simulations were carried out to predict new stable structures using the UNCLE code [34].

Monte Carlo simulations were also utilized to determine the concentrations and temperature ranges in which systems are likely to mix. This allows prediction of phase diagrams from the critical temperatures, for binary and ternary systems.

1.5 Outline

The dissertation is divided into seven chapters.

Chapter 1: gives out the introduction, structural properties of B2 Fe-Co, aim and objectives, the intention of the study and lastly the outline of the dissertation is specified.

Chapter 2: provides the literature review of the binary Fe-Co, Fe-Pd and ternary Fe-Co-Pd, Fe-Co-V alloys as well as other magnetic alloys.

Chapter 3: presents the methodology followed to perform the calculations in this study. The density functional theory, approximation methods, plane-wave pseudopotentials, k-points, projector augmented wave, VASP and LAMMPS code, cluster expansion and Monte Carlo simulations are summarized. Furthermore, the implementation of the method is given.

Chapter 4: discusses the cut-off energy and k-points of B2 Fe-Co. The structural and thermodynamic properties of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ are also presented.

Chapter 5: provides the discussion of the mechanical properties i.e., elastic constants, anisotropy and elastic moduli. The ductility is also discussed through the Poisson's ratio, Pugh ratio and Cauchy pressure. Moreover, the phonon dispersion curves of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ are given.

Chapter 6: presents the temperature dependence of binary B2 Fe-Co and ternary Fe-Co-M systems.

Chapter 7: deals with the cluster expansion of the binary Fe-Co and ternary Fe-Co-M systems. Monte Carlo simulations for Fe-Co-M are also discussed.

Lastly, the conclusions, recommendations and references are listed.

CHAPTER 2

LITERATURE REVIEW

In this chapter, we give a literature overview of the previous experimental and theoretical work on binary and ternary magnetic alloys.

2.1 Binary alloys

In this section, we show various binary alloys such as Fe-Co and Fe-Pd, these alloys have been investigated previously as possible soft magnetic materials (SMM).

2.1.1 Fe-Co alloys

The B2 phase of Fe-Co is a well-known phase that exists at room temperature within the range 29-75 at. % Co with a limit temperature of 730 °C (1003.15 K), and above this temperature it was illustrated that a disordered structure forms as BCC, which changes again to FCC above 983 °C (1256.15 K). Since in this study we are interested in the B2 phase of the alloy, this informs us on the range we can alloy the phase. Alloying in this ordered range also has possibilities in increasing the limited temperature [35]. The ordered structure is equiatomic, meaning it is made up of an equivalent number of Fe and Co atoms. The phase diagram for binary B2 Fe-Co is shown (see figure 2.1).

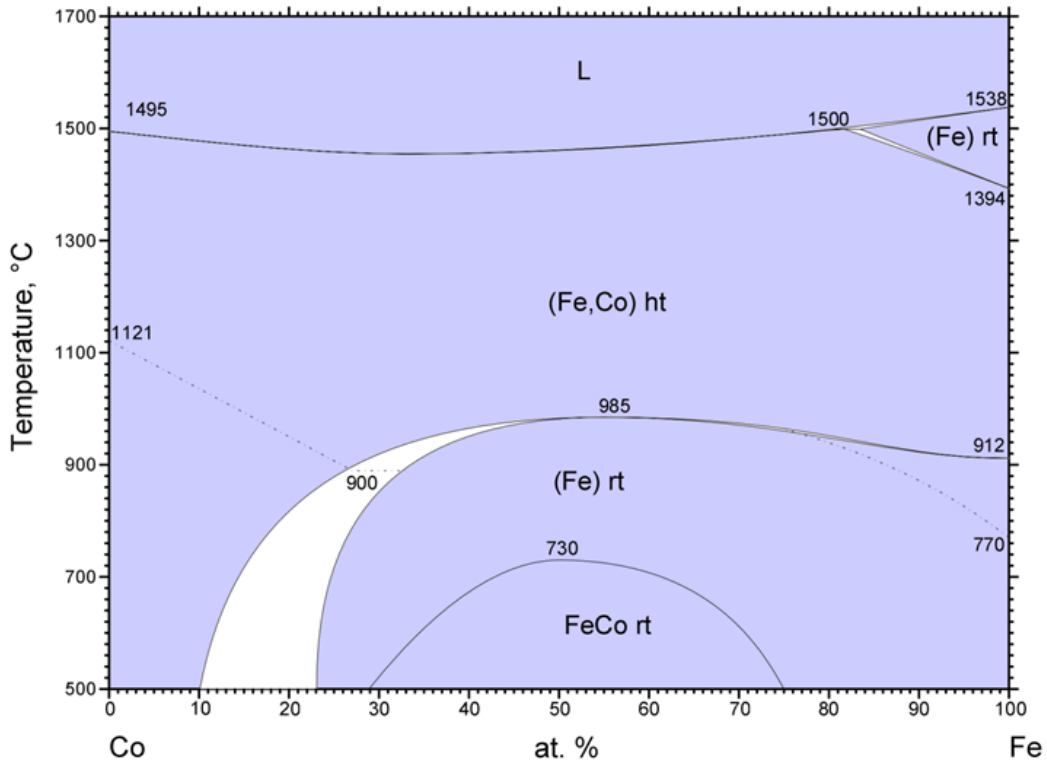


Figure 2. 1 Phase diagram for binary Fe-Co alloy [35].

As we mentioned earlier in the rationale that the B2 Fe-Co alloys suffer poor ductility at room temperature, Sunder and Deevi [36] reported that at room temperature the B2 ordered structure is thermodynamically stable. Moreover, a study by Zhao et al [15] revealed that not only do these alloys have poor ductility, but also have fracture strength with perishing yield strength. Factors such as low density of mobile dislocation and stress were found to be the causes of the undefined yielding of the B2 Fe-Co alloys [37, 38]. In attempts to improve the ductility of the alloys, it has been reported that increasing Co content [15] and assigning wavy slip at grain boundaries by partial ordering [39] enhances ductility. However, no information is given on the effect of this increase on the magnetic properties of Fe-Co alloys.

Wu et al [40], studied the prognosis of improved magnetic anisotropy in Fe-Co alloys using the first-principles approach. All electron FLAPW method was used to determine the magnetocrystalline anisotropy energy and magnetic moments. It was found that $\text{Fe}_{14}\text{Co}_2$ has the highest magnetic moment (2.28μ) and lowest formation energy (-0.107 eV/cell) amongst all the non-equivalent arrangements of compositions for Fe_xCo_y alloys ($x > y$). The findings also revealed that for a good magnetic anisotropy to be achieved, the alloys do not prefer chemically cubic geometries over a wide range of concentrations. The magnetic anisotropy improves the magnetization and causes magnetic interaction.

Previously, Diaz et. al [41] studied the magnetic properties and ordering of the Fe-Co alloys. The distinctive states of ordering in the alloys from perfectly ordered to disordered state and their impact on the formation energies were outlined making use of the cluster expansion method. The findings revealed that the magnetic moment remains the same remarkably alongside ordering. Furthermore, the atomic volume increased with concentration. It was also found that the heats of formation are negative for all the considered structures, showing an intense likelihood for ordering in the Fe-Co alloys.

The essence of the magnetic moment of cobalt (Co) in ordered Fe-Co alloy has been theoretically investigated employing the local spin density approximation based on the density functional theory (DFT) [42]. Non-collinear local density spin approximation (LSDA) calculations revealed that the magnetization value of Co is sensitive to the magnetic configuration of the neighboring ion atoms, as it became

zero only in the artificial orthogonal situation. Nonetheless, this study has not been performed experimentally due to the high cost of energy. Furthermore, the calculations of bare dynamic linear model (DLM) qualitatively also supported the idea and predicted Co as a non-magnetic in the paramagnetic state. It was revealed that the magnetism is much smaller than in LSDA and showed a very strong temperature dependence even at $T > 2000$ K. At the same time, the combination of local density approximation and dynamical mean-field theory (LDA+DMFT) approach demonstrated a robust local magnetic moment of cobalt in the paramagnetic state and a reasonable estimate of the T_c . Thus, the latter approach provided the most complete and physically sound model of the considered system. It was argued that strong local correlations are necessary to properly describe the finite temperature behavior of ordered Fe-Co alloy.

Another study was carried out experimentally and magnetic core loss of ultrahigh strength Fe-Co alloys was investigated [43]. Results showed that the ac core loss of $\text{Fe}_{49}\text{Co}_{49}\text{V}_2$ commercially known as Hiperco ® 50 alloy, annealed at 723.15 K and 923.15 K. Furthermore, it was found that this alloy exhibits exceptionally superior mechanical properties because of the small grain sizes measured up to 4500 Hz. For the as-rolled Hiperco ® 50 alloy, the procedure of annealing was reported to enhance the soft magnetic properties. The total core loss was found to have the frequency dependence of $af+bf^2$, where the linear and the quadratic frequency terms are contributions from hysteresis core loss and eddy-current core loss, respectively.

The eddy-current loss was minor compared to the hysteresis loss (Magnetic core loss of ultrahigh strength) of Fe-Co.

In 2011 [44], a systematic study was conducted on the nanostructure-dependent magnetostriction (the dimensional changes of ferromagnetic materials under an applied field) in Fe-Co alloy using synchrotron X-ray diffraction as well as high-resolution TEM with geometric phase analysis [45] giant magnetostriction was predicted in textured Fe-Co thin films near the (fcc + bcc)/bcc phase boundary. It was reported that the magnetostriction of ferromagnetic alloys was considered an intrinsic homogeneous effect. The study revealed that the enhanced magnetostriction in the Fe-Co was courtesy of its B2 nature and fcc nanoinclusions. Furthermore, it was found that there was a relation between magnetostriction and the nanoheterogeneities when varying the annealing temperature and alloy composition.

2.1.2 Fe-Pd alloys

An experimental study by Mitsuru et al [46] investigated the structure and magnetic properties of Fe-Pd thin films. The films were prepared on MgO (111) substrates and heated at temperatures ranging from 298.15 K and 873.15 K. Fe-Pd epitaxial films were achieved for the probed substrate temperatures. For the Fe-Pd films produced at 873.15 K, an ordered L1₀ phase formation was recognized. The findings also revealed that the type of ordered phase and order degree affected the magnetic properties.

In 2006, Clavero et al [47] studied the perpendicular magnetic anisotropy (PMA) in chemically disordered FePd-FeV (100) alloy thin films. The Fe-Pd films sputter was deposited at various temperatures (298.15 K to 973.15 K) on a monocrystalline V(001) buffer layer. Beyond 673.15 K a strong V inter diffusion into the Fe-Pd layer, and the development of Fe-V alloy was followed by a 2-dimensional to 3-dimensional growth mode transition and an increase of the mosaic spread at these temperatures. Despite the absence of long-range chemical ordering, a PMA phase was established in Fe-V-Fe-Pd films grown at temperatures beyond 673.15 K. The discovered PMA was attributed to the inter diffusion of V in the Fe-Pd layer and the Fe-V alloy being formed. The PMA was established at similar temperatures as in regular Fe-Pd alloys, however, the FePd-FeV blended systems can open other possible ways to acquire high anisotropy systems with lower chemical order and at lower temperatures.

2.2 Ternary alloys

The ternary alloys such as Fe-Co-M where M represents Pd, Ni, V, O, Ti, Cr, Mn, C, Mo, W, Ta and Nb are discussed. The investigations and findings are either experimentally or theoretically.

2.2.1 Fe-Co-Pd alloys

The effect of Pd as the third element on Fe-Co alloys has been investigated. For example, an enhancement of saturation magnetization (B_s) in sputtered Fe-Co-Pd alloy and $(\text{Fe-Co-Pd})_n$ super-lattice films at room temperature was performed [48]. Different $\text{Fe}_{70}\text{Co}_{30}\text{Pd}$ films and $\text{Fe}_{70}\text{Co}_{30}$ sub-layers in $(\text{Fe}_{70}\text{Co}_{30}\text{Pd})_n$ super-lattice

films were probed and the Bs, as well as sub-layer depth, were determined. It was observed that the saturation magnetization of these films was improved by alloying or laminating Fe₇₀Co₃₀ with Pd. (Fe_{0.7}Co_{0.3})_{97.8}Pd_{2.2} film and Fe₇₀Co₃₀ sub-layers in (Fe₇₀Co₃₀)₂₅ super-lattice film revealed high Bs of 2.44 T and 2.57 T, respectively, whereas the Bs of Fe₇₀Co₃₀ film was at most 2.8 T. The improvement of Bs of these films was caused by the magnetic moment (μ/μ_B) in Fe atoms by the neighboring Pd atoms.

In the previous study, an ultrasonic irradiation technique was used to blend the nanocrystals of Co₅Fe₂Pd₁ and an evaluation concerning oxygen reduction reaction (ORR) in an alkaline medium was carried out on their electro-catalytic activities [49]. It was found that when Pd content is decreased, there was an improved reaction process to ORR due to a trimetallic little-alloying outcome. Furthermore, the impact of citric acid content on the physical properties of the parent mixture of Co₅Fe₂Pd₁ nanocrystals was also explored to obtain the best reaction activity nanoparticles. The Co₅Fe₁Pd₁ nanocrystals were highly liberal compared to the poisoning effect of methanol with 20 at. % Pt enzyme and showed notably the subjecting 4e⁻ trace in the ORR activity. The comparable quantity of citric acid on the metal nanoparticle surface can be optimized to achieve excellent ORR electro-catalytic activity on the Co₅Fe₂Pd₁ nanoparticles. As a result, ultrasonic irradiated nanoparticles of Co₅Fe₂Pd₁ can be considered encouraging oxygen limiting catalyst in alkaline fuel cells of direct methanol.

A DFT study was carried out on the $\text{Fe}_x\text{Co}_y\text{Pd}_z$ ($x + y + z \leq 7$) clusters to look at their structural, electronic and magnetic properties [50]. The DFT calculations were implemented in the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [51], in all concentrations conceivable (that is all the x , y and z variables). The source for the achievable homotops were set up using a semi-practical Gupta potential, these and added low correlate structures were then subjected to optimization employing the SIESTA code. It was assured that it was the first time such kinds of calculations are performed for all the possible compositions of up to seven atom ternary nanoclusters. Considering the interatomic distances, the results were as expected larger values were observed for the Pd-rich Nano alloys and smaller ones in the Co-rich region. As far as stability is concerned, the binding energy showed a monotonic dependence; the most stable structure was observed along the binary Fe-Co edge. Binary systems of Fe-Pd and their neighborhood were generally distinguished in their greatest likelihood of mixing with the ternary system. Results for the fragmentation channels indicated that a close correlation with the state of charge of the cluster does exist, also the most likely fragmentation path is through Pd_0 , Pd^+ , Pd^- , for which Pd exists through the cluster. Furthermore, when Pd is absent, the most likely fragmentation channel is through the most abundant element in the cluster. Overall, Fe-Co-Pd nanoclusters seemed to be a good applicant to tailor magnetic properties by tuning the cluster composition.

In other studies, an experimental study was carried out to check the mechanical properties of B2 Fe-Co alloys with additions of Ni or Pd. The study was conducted

to enhance the tensile ductility of these alloys at room temperature [13]. It was found that the addition of Ni and Pd enhances the grain refinement, strength and ductility of Fe-Co alloy at room temperature. Furthermore, a phase change of the Fe-Co with the addition of Ni and Pd was examined by using XRD analysis. The phase changes resulting from partial substitution of Fe or Co by Ni, or Pd in the Fe-Co alloy were investigated by XRD. Figure 2.2 shows the XRD patterns for $\text{Fe}_{50}\text{Co}_{50}$, $\text{Fe}_{50}\text{Co}_{40}\text{Ni}_{10}$, $\text{Co}_{50}\text{Fe}_{40}\text{Ni}_{10}$, $\text{Fe}_{50}\text{Co}_{40}\text{Pd}_{10}$ and $\text{Co}_{50}\text{Fe}_{40}\text{Pd}_{10}$ alloys at room temperature. XRD peaks corresponding to bcc or B2 structures were present in all the alloys. However, there is still a gap in this study as there is no information on the relevant concentration of Ni and Pd to enhance ductility and how the ternary elements affect the structural, elastic and magnetic properties of the Fe-Co based alloys.

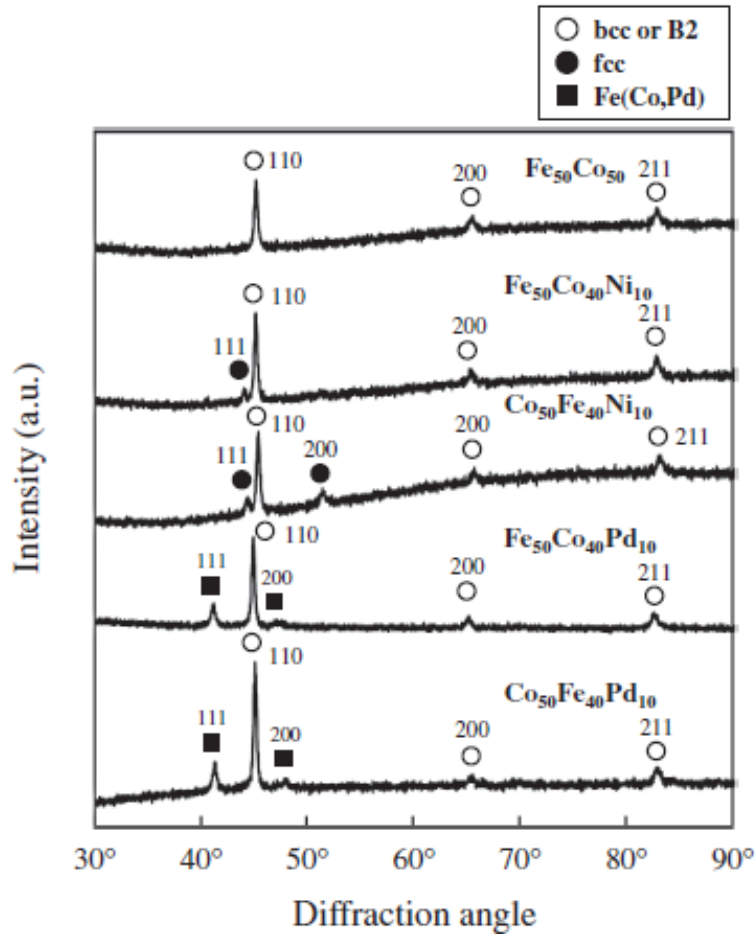


Figure 2. 2 XRD patterns of $\text{Fe}_{50}\text{Co}_{50}$, $\text{Fe}_{50}\text{Co}_{40}\text{Ni}_{10}$, $\text{Co}_{50}\text{Fe}_{40}\text{Ni}_{10}$, $\text{Fe}_{50}\text{Co}_{40}\text{Pd}_{10}$ and $\text{Co}_{50}\text{Fe}_{40}\text{Pd}_{10}$ alloys at room temperature [13].

2.2.2 Fe-Co-V alloys

The impact of V on anti-phase boundary energies and the atomic ordering of B2 Fe-Co alloys was studied in 2010 by Muratahan et al [16]. Interacting effects, such as alloy composition, sub-lattice preference and dissolution mode of V atoms on $\text{B2} \leftrightarrow \text{A2}$ ODT and slip mechanisms of $(\text{Fe-Co})_{100-x}\text{V}_x$ ($x = 0-5$ at%) alloys have been analyzed using the electronic theory of multi-component alloys combined with Monte Carlo simulation method. It was revealed that V atoms are distributed on both Fe

and Co sites equally at $x \approx 3-5$ at. %, while decreasing composition, $x < 2$ at. % exhibits a slight Fe-site occupation tendency of V atoms at low temperatures. Variations of APB energies with attained degree of LRO in binary Fe-Co support the transition from planar to wavy glide with decreasing LRO parameter, in which lower energy simple disordered domain boundaries remain disordered. Characteristic $\langle 111 \rangle$ $\{110\}$ dissolution mode of V and growth/combination of its preferential clustering with decreasing order was found to impose extensive changes in $\{110\}$ and $\{112\}$ APB energies for glide in $\langle 11 \rangle$ direction. Owing to the lowest APB energy of $\{110\}$ planes, $(\text{Fe-Co})_{98}\text{V}_2$ alloy would be predicted to display higher ductility in comparison to binary B2–Fe-Co intermetallic due to more independent movement of $a/2 \langle 111 \rangle$ partials in a temperature range of 300–750 K, i.e., in partially ordered states. It was also found that the recombining effect of V on partials with $\{112\}$ APBs would allow easier cross-slip, the effect becoming more pronounced as the $(\text{Fe-Co})_{100-x}\text{V}_x$ alloy gets more disordered at higher temperatures.

An experimental study was performed to investigate the distillation and the level of the order of the magnetic and mechanical properties of Fe-Co-2V soft alloy [52]. The samples of the Fe-Co-2V alloy were partially recrystallized. It was found that the boundary range is the dominant microstructural variable that is responsible for the near equiatomic Fe-Co-2V alloy and its mechanical and magnetic properties. By determining the ratio between the intensities of the (100) and (111) neutron diffraction peaks, little amounts of the degree of order ($<10\%$) was possible. The findings revealed that the degree of order did not improve coercivity rather the

frictional stress that differs remarkably with the degree of order and as a result, the yield strength. Finally, it was concluded that by improving each property individually, i.e., the magnetic losses by enlarging the boundary spacing and then improving the yield strength by increasing the entropy.

2.3 Other magnetic alloys

Previously, an annealing effect on the soft magnetic properties of the high moment $(\text{Fe}_{0.65}\text{Co}_{0.35})_{100-x}\text{O}_x$ ($0 < x < 5$ at. %) thin films has been investigated [53]. The radio frequency (rf) magnetron sputtering, the thin films were used with a great magnetic induction (B_s) of 24 Kg). At a temperature greater than 350 °C (623.15 K), the soft magnetic properties were found to be remarkably enhanced by the magnetic field annealing process. It was also reported that the enhancement is connected to the formation of CoFe_2O_4 nanoparticles at the time of annealing, followed by excess stress relief. It was assumed that the $(\text{Fe}_{0.65}\text{Co}_{0.35})_{99}\text{O}_1$ film may be considered an excellent candidate for high-density recording head core material.

Experimental studies were conducted on disordered and ordered Fe-Co-M (M=Ti, V, Cr, Mn) alloys where the heat capacity and saturation magnetization of these materials was investigated [10, 54, 55]. Annealing at 780°C (1053.15 K) for four hours and then quenching into the water was used to obtain disordered samples, annealing at 800°C (1073.15 K) for one hour and then cooling (approximately 70°C/h) was used to obtain ordered samples. It was found that the addition of Cr, V or Ti to the disordered Fe-Co leads to a reduction of the mean saturation moment

Fe-Co while the addition of Mn increases the saturation magnetization [55]. It was summarized that the condition for the appearance of a virtual bound state in Fe-Co is a difference of valence of 2 for impurities of the first transition metal series and the virtual bound state is approximately half-empty for Cr and empty for Ti.

The potential for developing high-strength soft magnetic materials in Fe-Co-M alloys was studied by investigating the effects of the combination of cold rolling and heat treatment upon mechanical and magnetic properties [56]. It was revealed that cold rolling improved the yield strength from 100 to 200 kg mm⁻², which goes along with aging or annealing. The findings suggested that these alloys can be used for lessening the weight of parts that are used as soft magnetic materials, although their properties will depend on the combinations of cold rolling and heat treatments, and/or on the added elements and the control of their amount. It was concluded that without reducing the desired soft magnetic properties, high-strength Fe-Co alloys can be developed by combining cold rolling with heat treatments or by adding, singly or complexly, elements like C, Cr, Mo, W, Ta, Nb, Ni and V [56].

A study was conducted to observe how the chemical short-range order (SRO) affects the mechanical and magnetic properties of magnetic materials using Fe-CoNi (AlSi)_x high-entropy alloys [57]. A Warren–Cowley SRO parameter α_{ij} method [58] was used to analyze the extent of the SRO in Fe-CoNi (AlSi)_x high-entropy alloys. It was found that the mixing enthalpies in binary constituent elements contribute to SRO in these alloys. The elements such as Si and Al were found to have highly negative binaries mixing energies with Co, Fe and Ni. Furthermore, it was revealed that pairs of Fe-

Co, Co-Si and Ni-Si have increased energies which rise significantly. The bonding of these atoms was found to affect the potential energy by lowering it. It was reported that some SRO structures are available in Fe-CoNi (AlSi)_x alloys. SRO was found to affect shape memory magnets/ high entropy alloys by decreasing the heats of formation, lowering the magnetic moments by changing the atomic nearest neighbor locations, tempering with the ground-state equilibrium properties of the system, elevating the elastic modulus by destroying isotropy and ductility as well as saturation magnetization.

2.4 Remarks from literature

This study is not the first to investigate ternary alloying on B2 Fe-Co. Using both experimental and computational methods, studies have shown that ternary alloying can improve the ductility of B2 Fe-Co alloys. However, with great progress several fundamental questions are unresolved. For instance, there is limited information about the precise concentration range of the added elements. In addition, since the ferromagnetic properties of Fe-Co alloys are mainly contributed by Fe, previous studies substituted ternary elements on Fe-site without giving information on how it affected the magnetic properties of the alloy. There is moreover limited information regarding the impact of ternary additions on the structural, mechanical and thermodynamic properties of this alloy. This study resolves these issues by looking at Pd, V, Ti and Cr as ternary elements substituted on the Co-site at different concentrations such as 6.25, 18.75, 25, 31.25 and 43.75 at. %.

In Table 2.1, we show various ternary additions on Fe-Co that were previously studied. These are classified according to alloying element, possible phase formation and their possible applications. The alloying elements Pd, V, Ti and Cr have been mostly recommended for enhancing the strength of the Fe-Co alloys. Pd and V increase the ductility and coercivity, respectively [50, 52, 55, 56].

Table 2. 1 The contribution of various alloying elements to the Fe-Co alloy and their applications, from the previous studies.

Structure	Alloying element	Motivation/Reason	Possible alloys	Applications
Fe-Co	O	Improve the soft magnetic properties	$(\text{Fe}_{0.65}\text{Co}_{0.35})_{99}\text{O}_1$	Magnets
	Si and B	enhances glass-forming ability and increase the critical sizes of bulk Fe-Co-based amorphous alloys	Fe-Co-Si-B	High power magnetic devices, catalytic and medical applications
	Mn	Increase the saturation magnetization	Fe-Co-Mn	Magnets
	Cr	Increase the density of states	$\text{Fe}_{50}\text{Co}_{40}\text{Cr}_{10}$, $\text{Fe}_{40}\text{Co}_{50}\text{Cr}_{10}$	Magnets
	Cr, V, Ti	Reduces the mean saturation moment of (disordered) Fe-Co	Fe-Co-2V, Fe-Co-2Cr, Fe-Co-Ti-O	Ferromagnets
	C, V, Cr, Pd	Increase ductility	$\text{Fe}_{50-x}\text{Co}_{50}\text{V}_x$ $\text{Fe}_{50}\text{Co}_{50-x}\text{V}_x$	Magnets, Aircraft motors, generators and transformers More electric aircraft magnets

	N	Minimizes the sensitivity of mechanical properties to the heat treatment temperature	$(\text{Fe}_{0.7}\text{Co}_{0.3})_{1-x}\text{N}_x$	Soft magnetic films
	C	Improve ductility in the (ordered)	Fe-CoC	Potential electromagnetic applications
	V and Nb	Decrease saturation magnetization and increase coercivity	Fe-Co-X (X=Nb, C, Cr, V, Mo, W, Ta, Nb)	Actuators
	C, Cr, Mo, W, Ta, Nb, Ni and V	Develop high strength without reducing the desired soft magnetic properties		High strength soft magnets high-performance permanent magnets capable of reducing the power consumption of motors and data storage devices
Fe-Co-2V	Cr	Improve tensile strength and ductility without deteriorating soft	Fe-Co-2V-Cr	For high-performance applications in fields such as

		magnetic property, Facilitates the formation of the precipitates with bcc structure and increase tensile strength and elongation		rotor or stator laminations in motors for power generation
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CHAPTER 3

METHODOLOGY

In this chapter, we briefly discuss the methods used to study the properties of $\text{Fe}_{50}\text{Co}_{50}$ and $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ magnetic alloys. We have used the density functional theory (DFT) [59, 60], which is a popular computational method, used to probe the electronic structure and determine the ground-state energy of solids and many-body systems. We also used the large-scale atomic/molecular massively parallel simulator (LAMMPS) [61] code which employs the embedded atom method (EAM) [62]. The EAM is structured for large-scale simulations and is used to probe the temperature dependence of the structures. Furthermore, the cluster expansion method and Monte Carlo simulations [34] were used to produce structures and construct phase diagrams, respectively.

3.1 Density functional theory

Density functional theory (DFT) is a quantum mechanical approach used to analyze many-body systems' ground-state energies [60, 59]. The DFT approach is currently the most effective method for calculating the electronic structure of materials [59]. It is one of the most popular and versatile methods in the physics of condensed matter, computational physics, and computational chemistry. The method has made it feasible to calculate the ground-state energy and charge density for real solids with remarkably accurate results. The first Hohenberg-Kohn [63] theorem demonstrates

that an electron density that depends on only three spatial coordinates uniquely describes the ground-state properties of a many-electron system.

$$E = E[\rho(\vec{r})] , \quad (3.1)$$

where E is the total energy and ρ is the density. This enabled Kohn and Sham [60] to derive the effective one-electron Schrödinger equation for solving the many-body problems. Kohn-Sham electrons in an effective potential, V_{eff} for a non-interacting system, is solved as:

$$V_{eff}(\vec{r}) = v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad \text{and} \quad V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} . \quad (3.2)$$

A guide to designing a reasonable DFT calculation has been described by Mattson et al. [64].

3.2 Approximation methods

There are two main types of exchange-correlation functional used in this study which are the local density approximation (LDA) and the generalized gradient approximation (GGA). These exchange-correlations functional will be discussed in sections 3.2.1 and 3.2.2.

3.2.1 Local density approximation

The local density approximation (LDA) is one of the methods of defining an electronic system exchange-correlation energy; it is commonly used in pseudopotential total-energy calculations [64]. The first approximation by Kohn and Sham [60] suggested

that the exchange and correlation energy is considered locally as the same one as in the homogenous electron gas with the same density [65]. Nonetheless, within the local density approximation one assumes that the density function of the n particle system can be described in the following form:

$$E_{XC}^{LDA}[n] = \int d^3r n(r) \epsilon_{XC}(n(r)). \quad (3.3)$$

where $\epsilon_{XC}(n(r))$ is the exchange-correlation energy per particle of a uniform electron gas. The local density approximation, in principle, ignores correction to the exchange-correlation energy at a point r due to nearby inhomogeneities in the electron density.

3.2.2 Generalized gradient approximation

The generalized gradient approximation (GGA) introduces non-locality into the definition of exchange and correlation [63]. The GGA are identified to be semi-local approximations which means that the function does not use the local density $n(r)$ value but its gradient $\nabla n(r)$. Perdew and Wang [66] established GGA which is based on a real-space cut-off of the spurious long-range components for the second-order gradient expansion for the exchange correlation hole. GGA advances total energies, atomization energies, energy barriers, and the difference in structural energies. The development of generalized gradient approximation in the generic form was revealed in the early 1980s as follows:

$$E_{XC}^{GGA}[n] = \int (n(r), \nabla n(r)) dr, \quad (3.4)$$

The spin-independent form is considered in GGA but practically functional are more usually formulated in terms of spin densities ($n\uparrow, n\downarrow$) and their correspondence gradients of ($\nabla n\uparrow, \nabla n\downarrow$).

There other known functionals based on GGA, that is the Perdew-Burke-Ernzerhof (PBE) functional [67], PBE functional revised for solids (PBEsol) [68] and the revised-Perdew-Burke-Ernzerhof (RPBE) [69]. The PBEsol function is a basic revision of the PBE functional that varies with two parameters. The revision is done to enhance the ground state properties of bulk solids and surfaces of the PBE physics and surface science communities. The modified version of PBE like the RPBE functional is mostly utilized in catalysis to enhance the operation of PBE.

This study used the GGA-PBE functional for geometry optimization of the binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ systems since it provided precise results compared to the other functionals.

3.3 Plane-wave pseudopotential method

The plane-wave pseudopotential is an effective and reliable technique for studying the properties of diverse classes of materials, including metals, semiconductors, insulators, minerals, metal alloys, etc. [70]. This method can simulate the total energy and other properties as well as structural studies, which are based on a quantum-mechanical treatment of electronic systems. Using this method, it was possible to simplify DFT problems by considering only the valence electrons. Core

electrons, for instance, are excluded since they are not affected by changes in the chemical environment.

3.3.1. Plane-wave basis

An infinite plane-wave basis set is employed to expand the electronic wave functions [71]. The procedure uses Bloch's theorem, which states that the electronic wave functions at each k -point can be expanded in terms of a discrete plane-wave basis set [71]. Bloch's theorem describes the crystal momentum k as a quantum number and φ_k as a single particle wave function that gives the boundary condition and is written as:

$$\varphi_k(r + R_L) = e^{ik \cdot R_L} \varphi_k(r), \quad (3.5)$$

the equation equals all the Eigen functions φ_{k_i} of a single particle Schrödinger equation with periodic potential written as a periodic function u_{k_i} modulated by a plane-wave vector k [72] and R_L is a direct lattice vector:

$$\varphi_{k_j}(r) = e^{ikr} u_{k_j}(r), \quad (3.6)$$

u_{k_i} can be expanded due to its periodicity as a set of plane-wave basis as follows:

$$u_{k_j}(r) = \sum_G C_{j,G} e^{iG \cdot r}, \quad (3.7)$$

where G represents reciprocal lattice vectors and u_{k_i} can be expanded in a set of plane waves, as it is periodic. Thus, the electronic wave function with the exponential predator can be written as:

$$\varphi_{kj}(\mathbf{r}) = \sum_{\mathbf{G}} C_{j,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (3.8)$$

where $C_{j,\mathbf{k}+\mathbf{G}}$ represent the coefficient of the periodic plane waves. The largest wave vector in the expansion with an infinite number of basis functions, which is required to accurately reproduce the real wave function, determines the number of wave functions used. This is the same as imposing a cut-off on the kinetic energy as the kinetic energy of an electron with wave vector $\mathbf{k}$ as follows:

$$E_{\mathbf{k}} = \frac{\eta^2 |\mathbf{k} + \mathbf{G}|^2}{2m}, \quad (3.9)$$

which obeys only plane-wave in the following:

$$E_{\mathbf{k}} = \frac{\eta^2 |\mathbf{k} + \mathbf{G}|^2}{2m} < E_{cut}, \quad (3.10)$$

and are included in the basis. The energy must be increased until the calculated energy has converged to avoid errors in the computed total energy. It is highly recommended to use much denser $\mathbf{k}$ -points to reduce errors and ensure convergence when calculating the total energy. We write the Kohn-Sham equation of DFT before making use of the plane-wave expansion of the wave function in the following way [73]:

$$\sum_{\mathbf{G}} \left[\frac{\eta^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{eff}(\mathbf{r}) \right] C_{j,\mathbf{k}+\mathbf{G}} = \varepsilon_j C_{j,\mathbf{k}+\mathbf{G}}, \quad (3.11)$$

where

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{XC}[n(\mathbf{r})]. \quad (3.12)$$

$V_{ext}(r)$, $V_H[n(r)]$, and $V_{xc}[n(r)]$ are Fourier transforms of the external potential of the nuclei, Hartree and exchange-correlation potentials, respectively.

3.3.1 Pseudopotential approximation

The pseudopotential approximation [74] describes the complicated quantum mechanical effects of the motion of the core, such that the core electrons and strong Coulomb potential inside the ionic core are replaced by a weaker pseudopotential. A weaker pseudopotential is a valence electron that is undergoing silent effects as it moves through a crystal, as well as relativistic effects [75, 76]. The pseudo-ion cores and pseudo valence electron replaces the original solid. Inside the core region, the two pseudo electrons have a weaker potential than the original electrons, but outside the core region, they have a similar potential to the original electrons.

The ionic potential (Z/r), valence wavefunction (ϕ_v), corresponding potential (V_{pseudo}) and pseudo-wave function (ϕ_{pseudo}) are shown sequentially in figure 3. 1 [77].

The advantages of using the approximation method are that it is computationally favorable [78], makes the calculations run faster and It provides a significant reduction in the size of basis sets, which is especially relevant when researching transition metals, which have a large number of core electrons [79].

There are two kinds of pseudopotentials namely the norm-conserving pseudopotential (NCP) and ultra-soft pseudopotential (USP). In the NCP [80],

different potentials are used for each component of the angular momentum in the wave function, whereas the USP relaxes the norm-conserving constraint to limit the basis-set size [78]. In the USP scheme, the pseudo wave function can be as soft as possible within the core region. Recently, the USP [78] has been implemented in plane-wave calculations.

In this study, we have used the projector augmented wave (PAW) [81] in the VASP code for total energy calculations since they give an accurate result for the systems under investigation. The PAW is described in section 3.5.

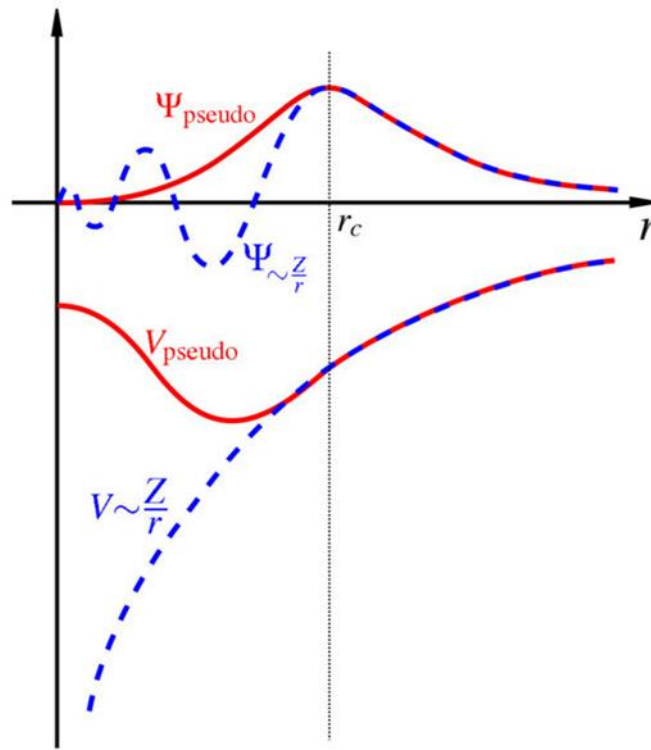


Figure 3. 1 A comparison of the nucleus' Coulomb potential (blue) and the pseudopotential (red) of a wave function. Above a particular cut-off radius r_c , the real and pseudo wavefunctions and potentials are the same [82, 71].

3.4 k-point sampling in metals

The k -points are regarded as sampling points in the first Brillouin zone of the material [83]. The sampling method is perfectly matched to the plane-wave method. This is an important measure in computational simulations because it causes the calculations to be straightforward and precise. The sampling is different for metals, semiconductors and insulators. The metals need denser k -point parameters compared to semiconductors or insulators.

This method was developed by Monkhorst and Pack [84] and it uses symmetry properties when forming the special k -points set. The total energy is calculated using a denser set of k -points, which limits calculation errors. The wave function is nearly the same for all when the k -points are very close. The electronic states are calculated at a finite number of k -points to define the Fermi surface accurately and thus the electronic potential and the total energy for solids. The computational cost increases linearly when performing a very dense sampling of k -space with the number of k -point in the Brillouin zone (BZ).

3.5 Projector augmented wave

The projector augmented wave (PAW) [81] is a method used in ab initio electronic structure calculations that allows DFT calculations to be performed with better computational efficiency. Blöchl [81] developed the method in which a precise and all-electron illustration of the electronic structure corresponds with a treatment like pseudopotential of the outer electrons. The PAW procedure depends on the

transformation between the all-electron Kohn-Sham wave functions, and the smooth pseudo-wave functions with frozen core states of the atoms. PAW is an important upgrade over earlier norm-conserving (NC) and ultra-soft (US) pseudopotential methods because it is derived directly from an all-electron formalism. The PAW formalism is so sensible in theory and computationally efficient, though it's additionally more advanced to implement than an NC or US one.

Implementing this methodology allows DFT to calculate the electronic structure of periodic solids, together with the forces and stresses associated with them. The essential transformation of this methodology happens once all-electron wave functions ψ_{nk} , with the n index resembling a summation over the bands and k indexing the k-points, are obtained ranging from pseudo ones ($\tilde{\psi}_{nk}$) by using linear transformation:

$$|\psi_{nk}\rangle = |\tilde{\psi}_{nk}\rangle + \sum_i \left(|\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\psi}_{nk} \rangle. \quad (3.13)$$

The index i is the atomic position, the angular momentum (l, m) and an additional index n to label differential partial waves for the same site and angular momentum.

Throughout transformation, the all-electron Φ_i and pseudopotential $\tilde{\Phi}_i$ partial waves are equal outside the PAW sphere. Therefore, as within the norm-conserving and ultra-soft pseudopotential scheme, $\psi_n = \tilde{\psi}_n$ outside a core radius (r_c^l).

Therefore, the projector functions ($\tilde{p}_i$) are equal to the pseudopotential partial waves as follows:

$$\langle \tilde{p}_i | \tilde{\Phi}_j \rangle = \delta_{ij}. \quad (3.14)$$

This methodology uses two grids, a radial one inside the PAW sphere and a regular one in the whole simulation cell. In correspondence, partial waves and projector functions are grouped according to angular and radial parts as follows:

$$\Phi_i(\vec{r}) = \frac{\phi_{n_i l_i}(r)}{r} S_{l_i m_i}(\hat{r}); \tilde{\Phi}_i(\vec{r}) = \frac{\tilde{\phi}_{n_i l_i}(r)}{r} S_{l_i m_i}(\hat{r}), \quad (3.15)$$

$$\tilde{p}_i(\vec{r}) = \frac{\tilde{p}_{n_i l_i}(r)}{r} S_{l_i m_i}(\hat{r}), \quad (3.16)$$

with $S_{lm}(\hat{r})$ representing the real spherical harmonics. On the other hand, plane-wave basis sets are used to expand the pseudo wave functions as follows: $\tilde{\psi}_{nk}(\vec{r}) =$

$$\sqrt{\frac{1}{\Omega}} \sum_{\vec{G}} c_{nk}(\vec{G}) e^{i(\vec{K} + \vec{G}) \cdot \vec{R}}, \quad (3.17)$$

with Ω representing the volume of the unit cell.

In this study, the PAW method has been employed as implemented within the VASP code [85].

3.6 VASP code

Vienna Ab initio Simulation Package (VASP) [86] is a computer program for carrying out ab initio quantum mechanical calculations by making use of a plane wave basis along with pseudopotentials or the projector augmented wave (PAW) method [87]. VASP computes an approximate solution to many Schrödinger equations, which is in density functional theory by solving the Kohn-Sham equations. For a particular system, this code is used to generate, the total energy, volume, charge density, optimized geometry, band structure and ground-state properties [88].

For the determination of symmetry of a particular system, VASP includes a fully featured symmetry code and uses either a PAW method or soft pseudopotentials. VASP code uses a variety of exchange-correlation functionals including LDA, GGA and Meta- and hyper-GGA and hybrid functionals. All functionals found in VASP have spin-degenerate and are also spin-polarized versions.

3.7 LAMMPS code

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a classical molecular dynamics code that can model solid-state metals and soft matter [89]. LAMMPS can be used to model atoms as a parallel particle simulator at the atomic, meso, or continuum scale. LAMMPS helps modify or extend new capabilities, such as new force fields, atom types, boundary conditions, or diagnostics. LAMMPS integrates Newton's equations of motion for collections of atoms, molecules, or macroscopic particles that interact via short- or long-range forces with a range of initial and boundary conditions. For computational effectiveness, LAMMPS uses neighbor lists to keep track of nearby particles. The lists are optimized for systems with particles that are repulsive at short distances, so the local density of particles never becomes too large.

The LAMMPS uses the powerful flowchart interface which enables the easy setting up of the complex calculations by connecting the stages. A stage could be a computation, e.g. energy minimization, constant number, volume, and temperature (NVT) and constant number, pressure, and temperature (NPT) dynamics, an action

that determines the density to that computed by the previous stage or modelling a larger simulation box. A summary of the flowchart will be discussed in detail in section 3.10.1.

3.8 Cluster expansion

Cluster expansion [90] is a method to prewise the energy for a well-set-out system concerning its different degrees of freedom. The method has several kinds of excitations like electrons and vibrations. This method confirms the properties of a system based on its concentration and atomic disorder. Crystalline solids, crystal lattices, crystallographic positions, and interstitial positions should be well defined. For solids, due to the relaxation of the ions, atoms do not inhabit correct lattice positions. The configurational disorder is studied to understand how the arrangement of species inside a structure affects the sum amount of energy in the structure. For example, inside a lattice that has m sites and two species possibly occupying those sites, there would be a total of 2^m workable ordering.

We note a cluster function as the product of the occupation variants at the cluster sites for every cluster as:

$$\varphi_{\alpha}(\vec{\sigma}) = \prod_{i \in \alpha} \sigma_i . \quad (3.18)$$

The cluster function equation (3.18) specifies the paired cluster, for which the configuration ϕ_{α} is:

$$\phi_{\alpha} = \delta_{\alpha 1} \times \delta_{\alpha 2} = (-1)(+1) = -1 . \quad (3.19)$$

The functions model a full orthonormal basis in configuration order and any of the structural properties depending on the configuration is a linear compound of the functions, which is expandable [91]. This permits that for a given configuration, the equation of energy is noted as the effective Hamiltonian:

$$E(\vec{\delta}) = V_0 + \sum_{\alpha} V_{\alpha} \varphi_{\alpha}(\vec{\varphi}), \quad (3.20)$$

for which clusters, V_0 and V_{α} are the coefficients that remain the same just like those of the Fourier series. These are named the Effective Cluster Interactions (ECI). The following expression is applicable:

$$E(\vec{\delta}) = V_0 + \sum_i V_i \delta_i + \sum_{i,j} V_{ij} \delta_i \delta_j + \sum_{i,j,k} V_{ijk} \delta_i \delta_j \delta_k, \quad (3.21)$$

for which V represent the ECI and the coefficients i , j , and k represent the independent cluster positions. Notably, the equations 3.20 and 3.21 are the generalized Ising Hamiltonians that embody all many-body collisions in the whole infinite crystal. In the real world, the expression should be shortened at a certain time if and only if it quickly converges. That is to say, if there is a quite small subset of clusters, then only the subset will be evaluated instead of the evaluation by equation 3.21 over the whole infinite set of clusters.

To define the energy of a well-defined structure, equation 3.21 calls for two inputs which are the distinctive arrangement of host and guest atoms upon the lattice as well as the ECI values. In between the guest atoms and host, ECI includes in a certain way some composite interactions and it's hard to link this to any real-world implication. Since equation 3.20 is entirely owing to the broadness of the crystal

basis, the cluster equation can be reduced to involve one or two terms, the ones linking to small clusters in particular. In the light of calculating the ECI, we use a set of heats of formation obtained from the first principles to construct a line of best fit. The parameterization value and where it will be reduced is estimated from the two methods: Cross-Validation Score (CVS) and Root Mean Square (RMS). The former weights the measure of the accuracy of the fit and the latter determines the reproducibility of the heats of formation [92]. The CVS can be determined as:

$$CV^2 = \frac{1}{N} \sum_{i=1}^N \left(E(\vec{\delta}_i) - E'(\vec{\delta}_i) \right)^2, \quad (3.22)$$

for which $E(\vec{\delta}_i)$ represents the i energy determined from first principles, determined from the line of best fit from the $N-1$ arrangements that exclude δ_i^P , the value of $E(\vec{\delta}_i)$ is $E'(\vec{\delta}_i)$. The derived equation is then evaluated at δ_i^P . Upon evolution the values of CVS and RMS can anticipate the arrangements to be stable, meanwhile, the first principle calculations determine if the structure is metastable or unstable.

3.9 Monte Carlo simulations

Monte Carlo (MC) simulation is a method that is used to determine the properties of a material's phase changes because the integration process in calculating the equations of motion will overshoot a transition point due to the discontinuity in energy during a first-order phase transition. We apply in this study, a Monte Carlo method that does not involve lattice vibrations. Although this technique is not as systematic for duties like determining a universal minimum, it is highly appropriate in explaining

a thermodynamical system at defined temperatures given that it can acquire the ordered entropy.

The calculations in Monte Carlo involve two achievable ensembles being the canonical and grand-canonical ensemble. The calculations have a system that contracts with an ideal container (unit cell) of atoms with a specified addition and submits to recurrent constraints. The contrasting fulfilments for the two ensembles are discussed in the following sub-sections.

3.9.1 Canonical ensemble

In canonical Monte Carlo, the defined inputs for a simulation in canonical Monte Carlo are that the volume and number of particles remain constant. With the use of virial relation normalized above an extensive simulation and the defined inputs, the pressure can be determined. We are so much focused on determining the pressure and then the density of a system. The procedure would normally open onto an isothermal-isobaric ensemble. This would then cause a change in the energy of the structure, also the rate of chance is notable as:

$$P_{\delta\delta'}^* = \begin{cases} 1 & \text{if } \epsilon < -\frac{(E(\delta) - E(\delta'))}{kT} \\ 0 & \text{if } \epsilon > -\frac{(E(\delta) - E(\delta'))}{kT} \end{cases} \quad (3.23)$$

The arbitrary periodic area takes place up until the system energy change is less than the limit value.

3.9.2 Grand-canonical ensemble

The grand canonical ensemble is used to illustrate a system's various microstates and determine thermodynamic midpoints at a constant potential, temperature and volume. Through the grand-canonical ensemble the number of particles and energy changes. We implement in particular an algorithm that uses a random configuration and then goes on to fall upon sequential states of the Markov chain [93]. The possibility of change from configuration A to a succeeding configuration B is prescribed by:

$$P(A \rightarrow B) = \begin{cases} 1 & \Omega_B < \Omega_A \\ e^{-\Delta\Omega / k_B T} & \Omega_B \geq \Omega_A \end{cases} \quad (3.24)$$

For which the energy difference between the two configurations is $\Delta\Omega = \Omega_B - \Omega_A$, k_B represents the Boltzmann constant and T represents the temperature. In a different manner, the grand-canonical energy is:

$$\Omega = E(\vec{\delta}) - \mu N \quad (3.25)$$

For which $E(\vec{\delta})$ is the mean energy, μ represents the chemical potential, and N the number of atoms. Should the arbitrarily determined number be less than the probability change $P(A \rightarrow B)$, the succeeding configuration B is then taken on, if not, the system stays in configuration A. During convergence, the algorithm will randomly sample configurations in the simulation as stated by equation 3. 25, this enables simplicity in finding the mean of the configurations arithmetically to determine the thermodynamic mean. At first, the reason for establishing the system's effective

Hamiltonian is to give the right for a quick and accurate approximation of the heats of formation for any given configuration. This mechanism can be employed through Monte Carlo simulations to probe even large systems, to determine a system's thermodynamic properties. Two various Monte Carlo simulations are employed, in particular: cooling and heating performed at a fixed chemical potential and chemical potential performed at a fixed temperature. The two give permission for the establishment of phase diagrams as well as the outline of phase boundaries.

3.10 Implementation of method

The flow charts that deduce the procedures used to carry out this study are shown in figures 3.2, 3.3 and 3.5 for VASP and PHONON codes, LAMMPS code and cluster expansion respectively.

3.10.1 VASP and PHONON codes

Figure 3.2 summarizes the steps carried out within the VASP and PHONON code. Firstly, proper convergence was deduced before any properties could be calculated. This was done to find the appropriate cut-off energy and k-point mesh parameter of the materials, which were 500 eV and 12x12x12, respectively. To determine the ground-state properties, the binary ($\text{Fe}_{50}\text{Co}_{50}$) system was fully optimized. We then calculated the structural, thermodynamic, magnetic, and mechanical properties of the binary system. All calculations were performed considering the GGA-PBE functional. On the B2 $\text{Fe}_{50}\text{Co}_{50}$ alloy, we have constructed a 2x2x2 supercell and used the substitutional search tool to substitute Co with the ternary elements ($M =$

Pd, V, Ti, Cr) at different atomic compositions (with range: $6.25 \leq x \leq 43.75$). The $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ternary systems were fully optimized, followed by determining the structural, thermodynamic, magnetic, and mechanical properties. The structural and thermodynamic properties were observed through the lattice parameters and the heats of formation, respectively. Furthermore, the magnetic moments explained the magnetic properties. To establish the mechanical properties, we looked into the elastic constants, Anisotropy and elastic moduli. Moreover, the PHONON code was used to determine the vibrational stability through the phonon dispersion curves for both binary and ternary systems.

3.10.2 LAMMPS code

Figure 3.3 summarizes the stages carried out during a LAMMPS code-based calculation, which is an Embedded Atom Method (EAM) module. In this study, the code was used to calculate the temperature dependence of binary B2 $\text{Fe}_{50}\text{M}_{50}$ ($\text{M} = \text{Co}, \text{Pd}, \text{Ti}$) and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{Ti}$) alloys. For the simulations, large supercells of $8 \times 8 \times 8$ were constructed for both binary and ternary alloys. This code uses a flowchart as shown in figure 3.3. The NPT ensemble and Nose Hoover thermostat and barostat were employed for 100 ps with a time step of 2 fs. The temperature is varied from 73 to 2500 K.

3.10.3 Universal cluster expansion code

In figure 3.4, the self-consistent working plan as used by UNCLE for finding new input structures is given. The UNCLE code was used to generate ground-state

structures from cluster expansion and phase diagrams from Monte Carlo simulations.

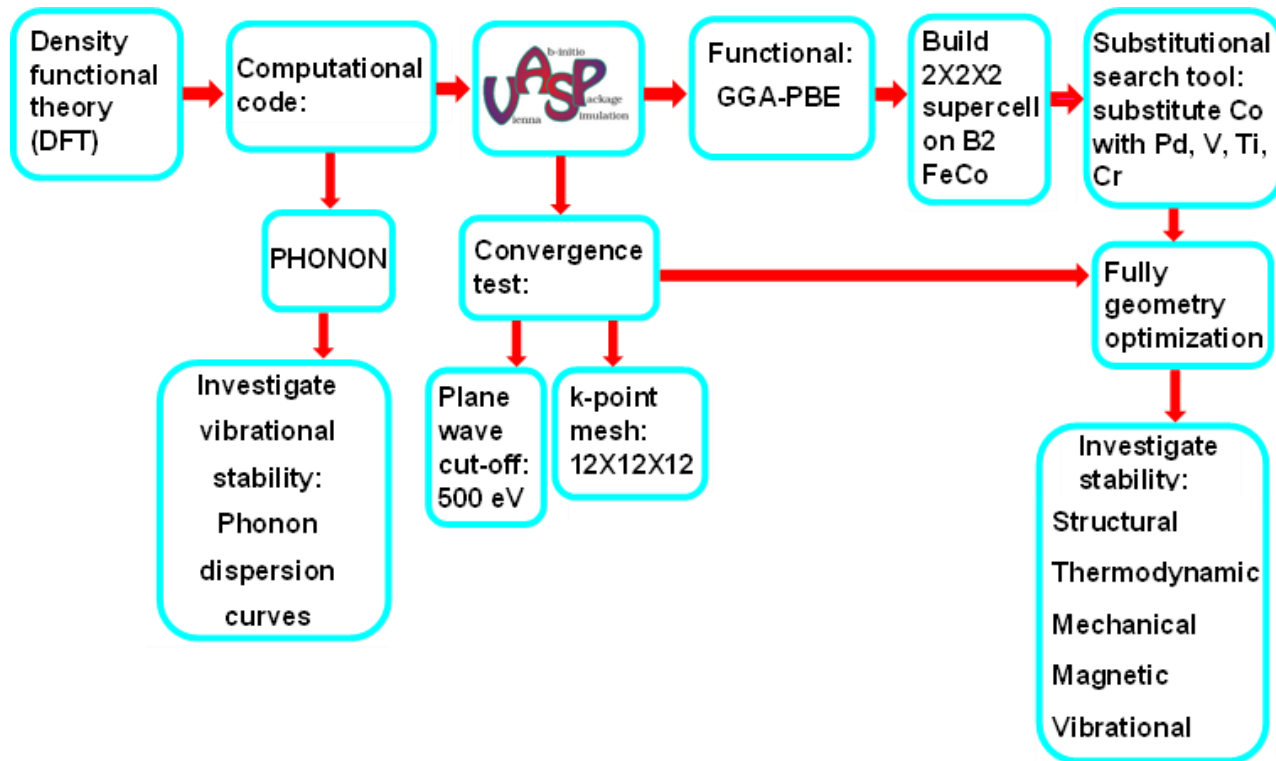


Figure 3. 2 Flowchart of simulation methods in VASP and PHONON codes.

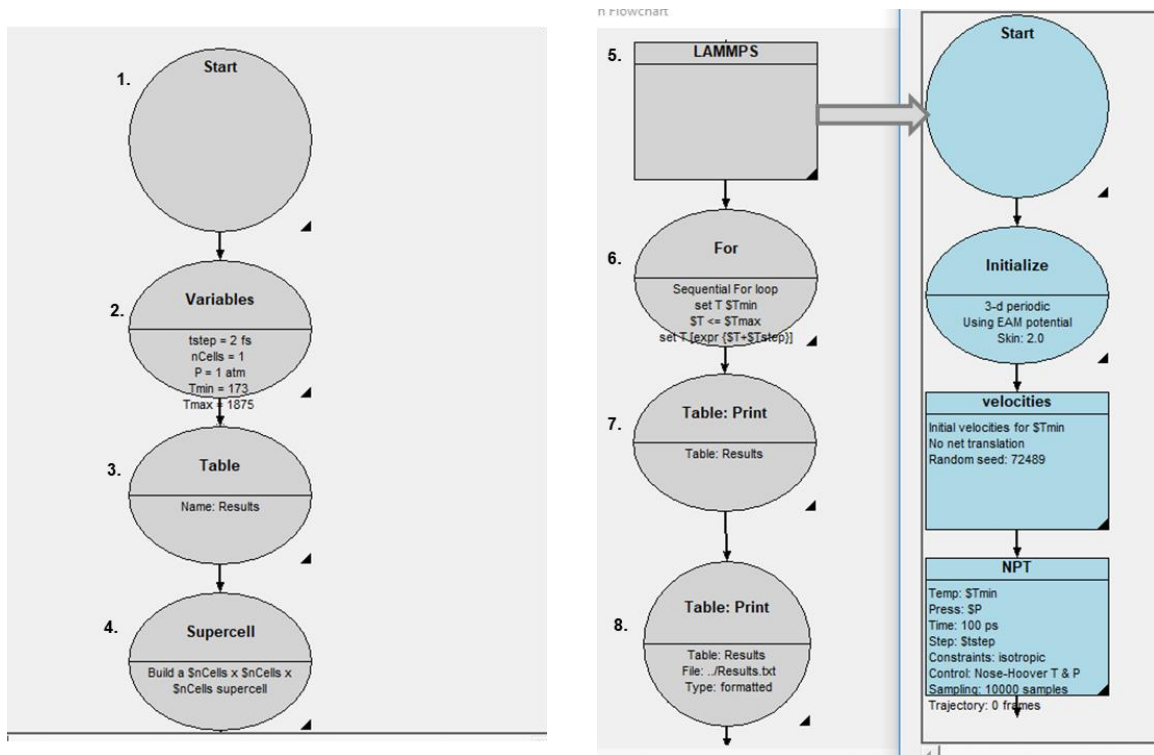


Figure 3. 3 Flowchart of simulation methods in LAMMPS code.

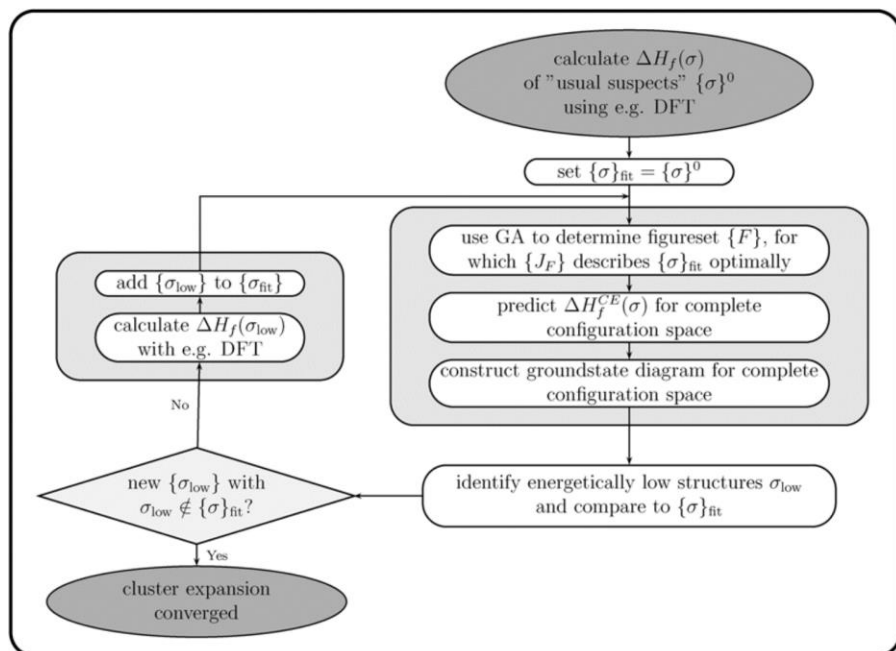


Figure 3. 4 Self-consistent working plan as used by UNCLE for the cluster expansion for finding new input structures [94].

Figure 3.5 provides the steps carried out in the simulation procedures through the UNCLE code. The ground-state structures of binary Fe-Co and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) alloys were performed using the UNCLE code. This code is used as a script interface to VASP which defines a parameter that automatically sets up the k-point mesh for similar systems which we used 0.2 k-spacing. A flowchart is used to determine ground-state structures and is illustrated in figure 3.5. To assess the accurate fit of the cluster expansion, the cross-validation score (CVS) is considered. A cluster expansion is considered accurate if the CVS is <5 meV/atom. The code employs a step-by-step flowchart which consists of 4 steps as in figure 3.5.

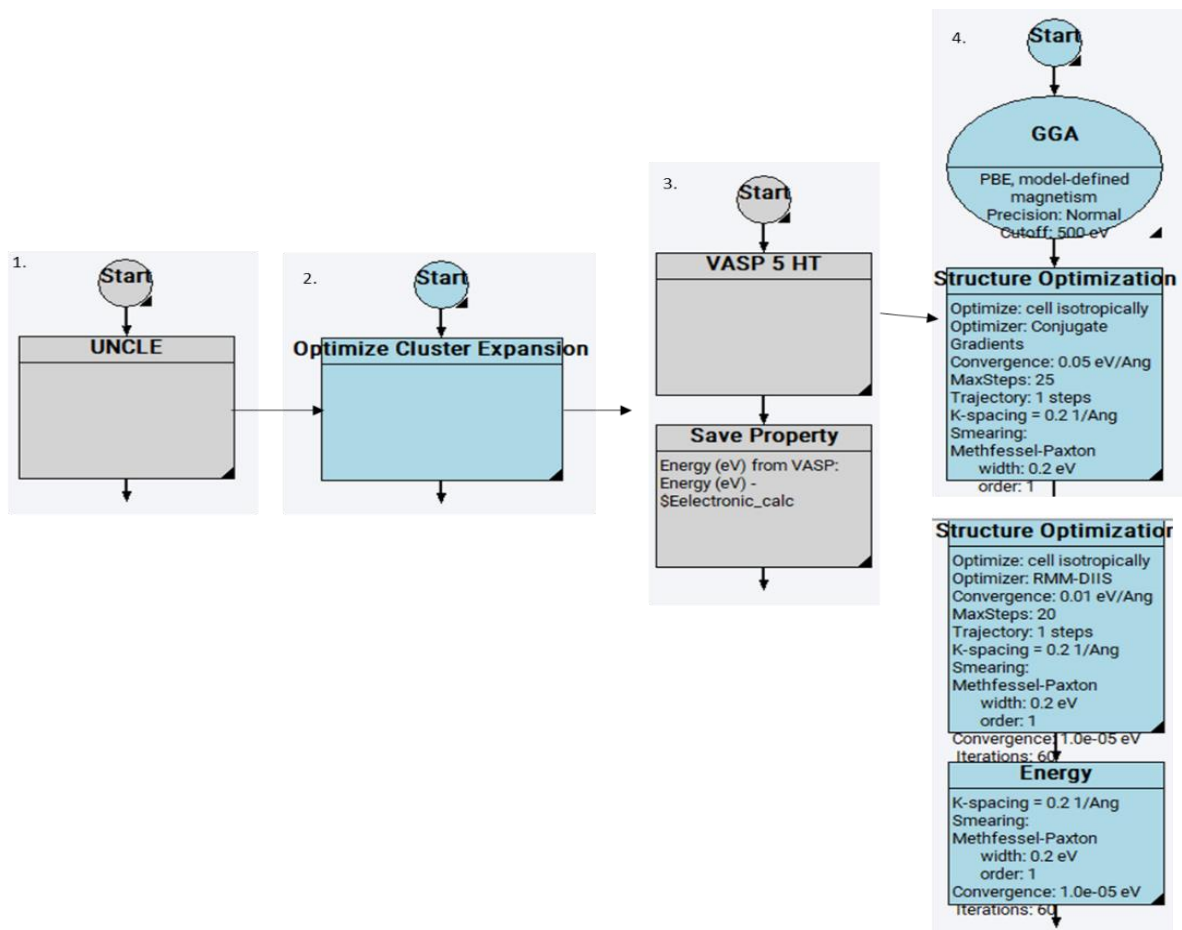


Figure 3. 5 Flowchart of simulation procedures using UNCLE code.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, we present and discuss the DFT results of both binary B2 Fe₅₀Co₅₀ and ternary Fe₅₀Co_{50-x}M_x (M= Pd, V, Ti, Cr). Firstly, we discuss the convergence test concerning the cut-off energy and k-points for the binary Fe₅₀Co₅₀ alloy. From the B2 Fe₅₀Co₅₀ alloy, a 2x2x2 supercell approach was used to create the different compositions (6.25, 18.75, 25, 31.25 and 43.75 at. % M). A substitutional search tool was used to substitute Co with Pd, V, Ti and Cr at the different compositions and the Pm-3m symmetry was used for all the structures. We also discuss the ground-state properties in particular lattice constants and heats of formation and the results are compared with available experimental and theoretical data for the B2 Fe₅₀Co_{50-x}M_x alloys. Secondly, the magnetic properties will also be analyzed and discussed, in particular, the magnetic moments to evaluate the magnetic strength of both binary Fe₅₀Co₅₀ and ternary Fe₅₀Co_{50-x}M_x alloys.

4.1 Cut-off energy and k-point convergence

4.1.1 Cut-off energy

To determine the suitable cut-off energy of the B2 Fe₅₀Co₅₀ structure, we performed single-point energy calculations for various kinetic cut-off energies at a constant number of k-points. The cut-off energy is crucial for discovering the ground-state of the material. This was performed by using the plane-wave pseudopotential (VASP) code within the GGA-PBE functional. The method was employed owing to its

robustness for metallic systems. We used ultra-soft pseudopotentials [74], which require significantly less computational resources than the norm-conserving potentials. In figure 4.1, we show the curves of total energy per atom against cut-off energy for the Fe-Co structure. The cut-off energy was varied from 200 eV to 700 eV at the default k-point and 400 eV was chosen since the energy gave a constant slope at that point and they yielded energy differences of less than 1meV/atom. Thus, cut-off energy of 400 eV was chosen for the system and it will be used throughout the study.

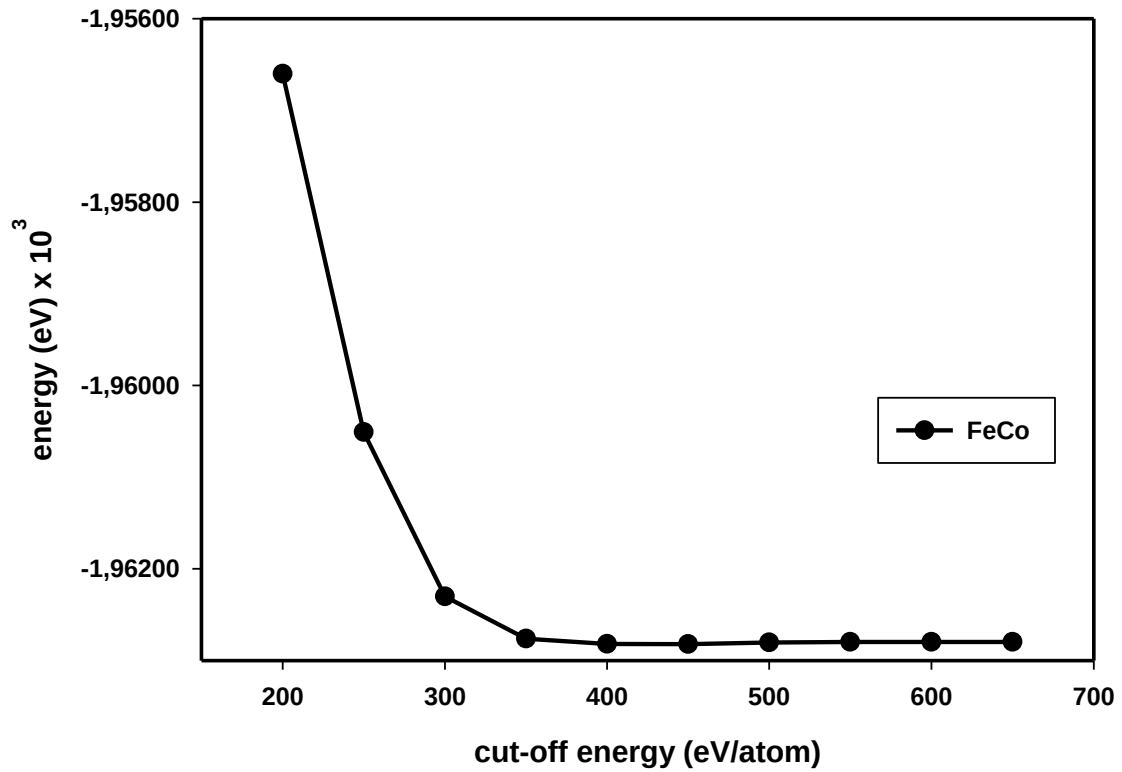


Figure 4. 1 The graph of total energy versus cut-off energy for B2 Fe-Co.

4.1.2 k-point

In this section, we discuss the convergence of the total energies against the k-points sampling size, as shown in figure 4.2. We have carried out a total energy calculation at fixed cut-off energy of 400 eV (as determined in section 4.1.1) for the Fe-Co structure while the number of k-points was varied from 2X2X2 to 16X16X16. The total energy depends on the number of k-points that were reasoned to converge when the change in energy per atom (between two points in succession) was in between 1 meV / atom. The k-point mesh of 12X12X12 was chosen for Fe-Co since the energy difference at this point was found to be less than 1meV as shown in figure 4.2.

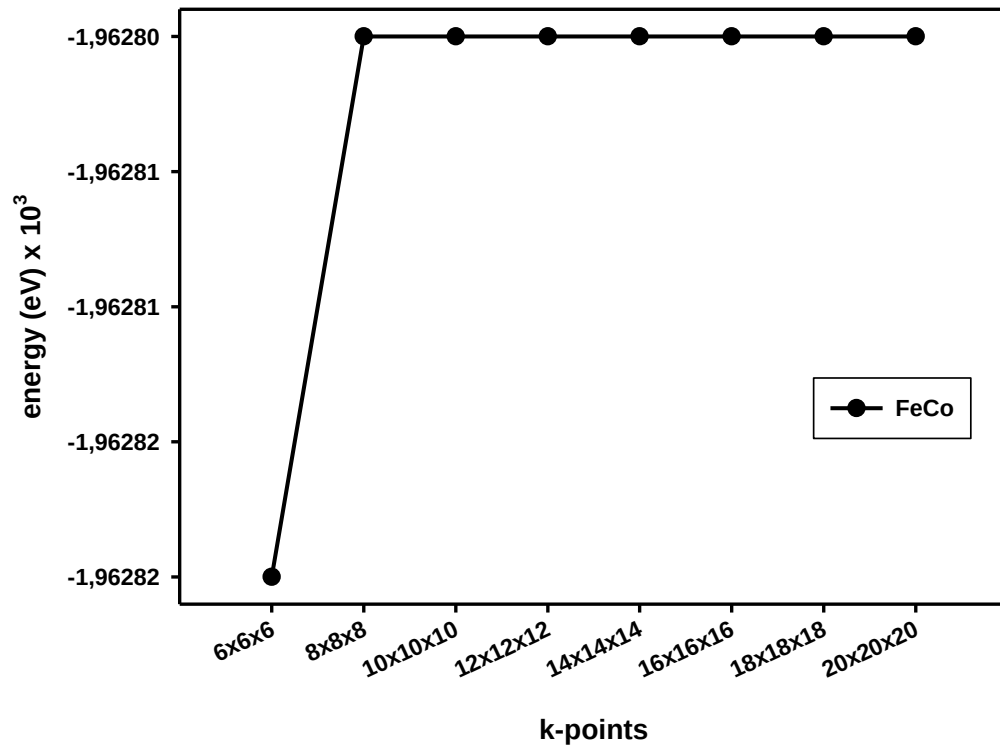


Figure 4. 2 The graph of total energy versus k-points for B2 Fe-Co structure.

4.2 Structural and thermodynamic properties

To determine equilibrium properties, we performed full geometry optimization calculations through the GGA-PBE functional using cut-off energy of 500eV and the chosen k-points as shown in section 4.1. The equilibrium lattice constants were determined from relaxed structures, where the volume and unit cell were allowed to change. This was done for all the B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ structures.

Figure 4.1 demonstrates the equilibrium lattice constants for the binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($0 \leq x \leq 50$) alloys. It was found that the lattice constant of $\text{Fe}_{50}\text{Co}_{50}$ is 2.844 Å (2.843 Å [95]) which compares well with the experimental value in parenthesis to within 0.035%. The lattice constant increases with an increase in Pd content, this is attributed to the large atomic radius of Pd (1.69 Å) compared to Co (1.52 Å), see table 4.2. At 6.25 at. % Pd, the lattice constant was found to be 2.870 Å (2.872 Å [36]) which is in good agreement with the theoretical value in the parenthesis to within 0.070%.

Furthermore, it is seen that the lattice constants increase with an increase in V and Ti, this is understood since the atomic radius of Co is smaller than that of V (1.71 Å) and Ti (1.76 Å). In the case of Cr addition, the lattice parameter decreases slightly, this is because the atomic radius of Cr (1.66 Å) is larger than that of Co (1.52 Å). The atomic radii of the alloying elements (M=Pd, V, Ti, Cr) are summarized in figure 4. 4.

Table 4. 1 The atomic radii for different elements.

Element symbol	Atomic radius [Å]
Fe	1.56
Co	1.52
Pd	1.69
Ti	1.76
V	1.71
Cr	1.66

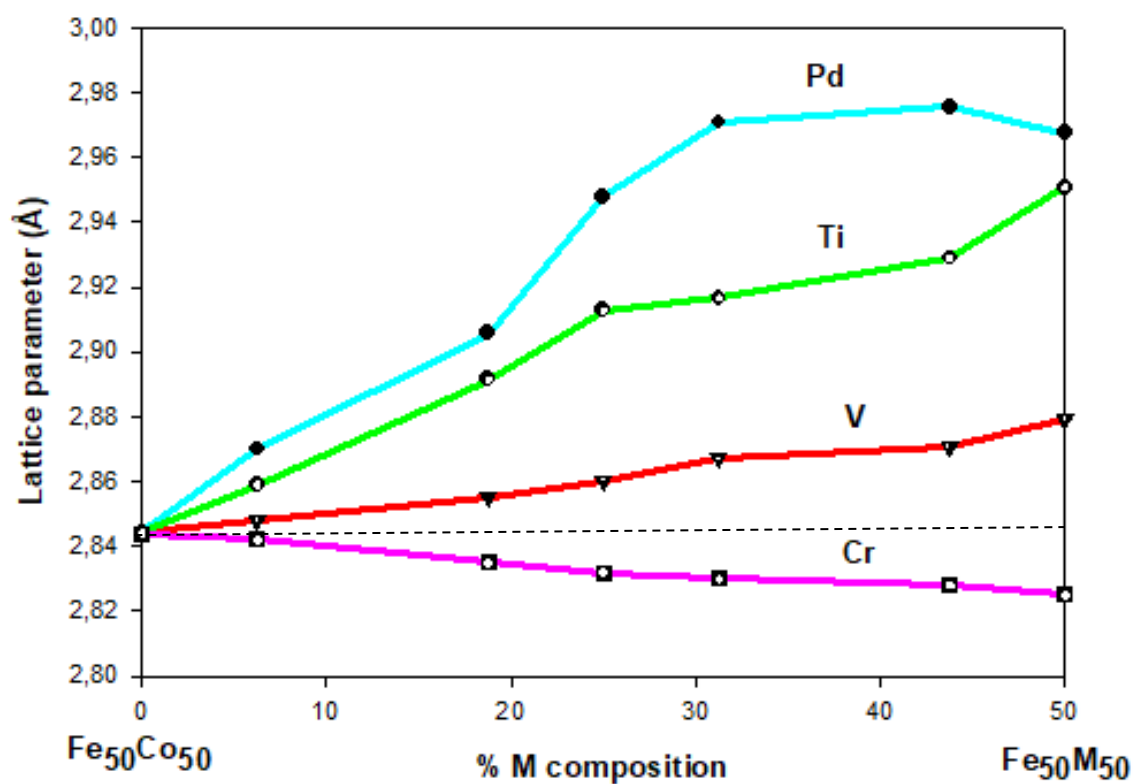


Figure 4. 3 Lattice parameters for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) against atomic % composition, where $0 \leq x \leq 50$.

Now the thermodynamic stability of the binary Fe₅₀Co₅₀ and ternary Fe₅₀Co_{50-x}M_x (0 ≤ x ≤ 50) alloys was determined from heats of formation (ΔH_f). The heats of formation (ΔH_f) can be estimated by the formula:

$$\Delta H_f = E_c - \sum_i x_i E_i \quad (4.1)$$

where E_c is the calculated total energy of the compound and E_i is the calculated total energy of each element in the compound. For a structure to be stable, the heat of formation must have the lowest negative value (ΔH_f < 0) otherwise a positive value implies instability. The results of heats of formation are shown in figure 4.5.

The heats of formations for the binary B2 Fe₅₀Co₅₀ was found to be -0.057 eV/atom (-0.065eV/atom [96]) which is in good agreement with the theoretical value in parenthesis to within 3%. In the case of the B2 Fe₅₀Co_{50-x}M_x, the heats of formation increase with an increase in Pd and Cr content. This suggests that thermodynamic stability is not enhanced with Pd and Cr addition. Furthermore, it is noted that the heats of formation decrease with an increase in V and Ti, condition of stability. The most stable structure was found to be Fe₅₀Co_{6.25}M_{43.75} (M=V, Ti) with the lowest heats of formation (ΔH_f<0). It is seen that Ti addition gave more negative values as compared to V addition.

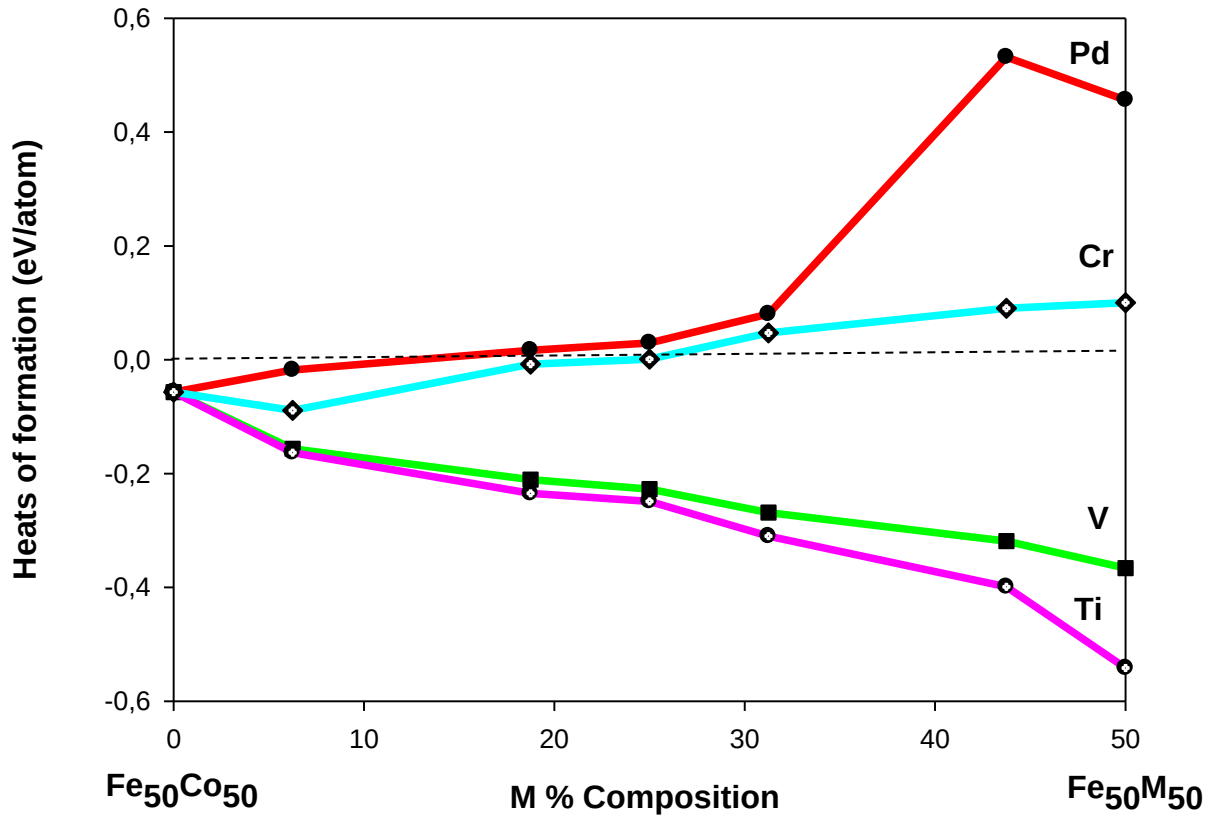


Figure 4. 4 Heats of formation for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) against atomic percent M , where $0 \leq x \leq 50$.

4.3 Magnetic moments

The total magnetic moments were calculated to check the magnetic strength of both binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) systems. A positive value of magnetic moment indicates good magnetic strength. Initially, the magnetic moments were defined for every atom by assigning a chosen value for Fe ($3 \mu\text{B}$) and Co ($2 \mu\text{B}$). Figure 4.6 shows the magnetic moments of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys as a function of M atomic composition. The magnetic moment of the binary B2 Fe-Co alloy was found to be $4.530 \mu\text{B}$ ($4.479 \mu\text{B}$ [95]) which is in good agreement with the

theoretical value in the parenthesis to within 2%. In the case of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$, the magnetic moments decrease with an increase in M addition. This behavior suggests that the magnetic strength is not enhanced. It can be deduced that the correlation trend is the same for all M ternary additions, however, Ti addition has a larger influence on the magnetic moments in $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ alloys compared to other additions. Another element with great influence is V followed by Cr and then Pd, moreover above 43.75 at. % we observe an overtake of V and Cr by Pd meaning that the goodness of Pd ternary addition on Fe-Co magnetic alloys should be less than 43.75 at. %Pd to avoid much effect on the good magnetic properties of Fe-Co alloys. At 43.75 at. % Ti (0 μB), the structure transition from ferromagnetic to diamagnetic, similar observations were discussed elsewhere [97, 98].

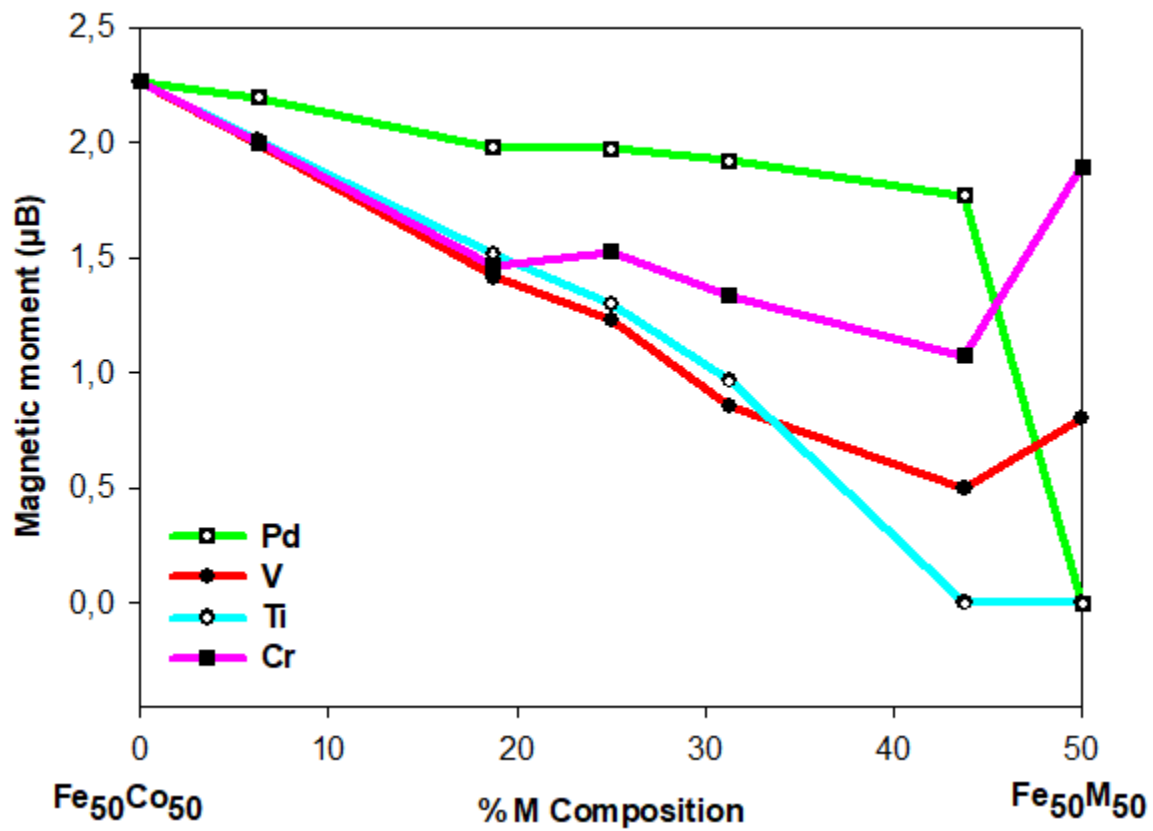


Figure 4. 5 Magnetic moments (μB) against atomic percent M for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ (M = Pd, V, Ti, and Cr), where $0 \leq x \leq 50$.

CHAPTER 5

MECHANICAL AND VIBRATIONAL PROPERTIES

In this chapter, we discuss the mechanical properties in particular the elastic constants, elastic anisotropy, elastic moduli (Bulk, Young ' , Shear) and ductile/brittle behavior of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{Cr}, \text{V}, \text{Ti}$). We used the supercell approach to explore their stability. The elastic properties were performed using the VASP code as discussed in detail in chapter 3. The elastic properties were determined to check the elasticity and strength of the alloys. Furthermore, we discuss the vibrational properties in particular the phonon dispersion curves of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$. The phonon dispersion curves are presented to indicate the vibrational stabilities. The calculated results are compared with the available experimental and theoretical findings.

5.1 Mechanical properties

5.1.1 Elastic constants

Elastic constants are important parameters, which can be used to predict the mechanical stability of materials. For the cubic symmetry B2 crystal structure of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$, there are three independent elastic constants (C_{11} , C_{12} , and C_{44}). The stability criterion for cubic crystal structures [99, 100] is as follows:

$$C_{11} > 0, C_{12} > 0, C_{44} > 0, C_{11} > |C_{12}|, C_{11} + 2C_{12} > 0 \quad (5.1)$$

where the elastic shear modulus (C') can be calculated as:

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad (5.2)$$

In figure 5.1, the calculated elastic constants are shown as a function of atomic composition for the $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys. The stability criterion for the elastic constants must be satisfied for a structure to be considered stable. A positive C' ($(1/2)(C_{11}-C_{12}) > 0$) shows the mechanical stability of a lattice structure, otherwise, it is unstable. The binary B2 $\text{Fe}_{50}\text{Co}_{50}$ alloys have a positive shear modulus ($C' = 63.55$ GPa), indicating mechanical stability. At 6.25 at. % Pd, it is noted that all the independent elastic constants c_{11} , c_{12} and c_{44} are positive (see figure 5.1 (a)). Furthermore, the C' is positive which indicates that the structure is elastically stable. Above 6.25 at. % Pd, it is seen that the c_{11} is less than c_{12} which suggests instability at those compositions.

In the case of $\text{Fe}_{50}\text{Co}_{50-x}\text{V}_x$, it is observed that the independent elastic constants C_{11} , C_{12} , C_{44} and C' are all positive indicating mechanical stability for the entire concentration range of $(0 \leq x \leq 50)$ as shown in figure 5.1 (b). Similar behavior was observed with the addition of Ti and Cr as the C' increase with an increase in the concentration ($C' > 0$) for the entire concentration range (Figure 5.1 (c) and (d)). This suggests that the alloying elements (Ti and Cr) have the potential to improve the C_{ij} of pure $\text{Fe}_{50}\text{Co}_{50}$ structure.

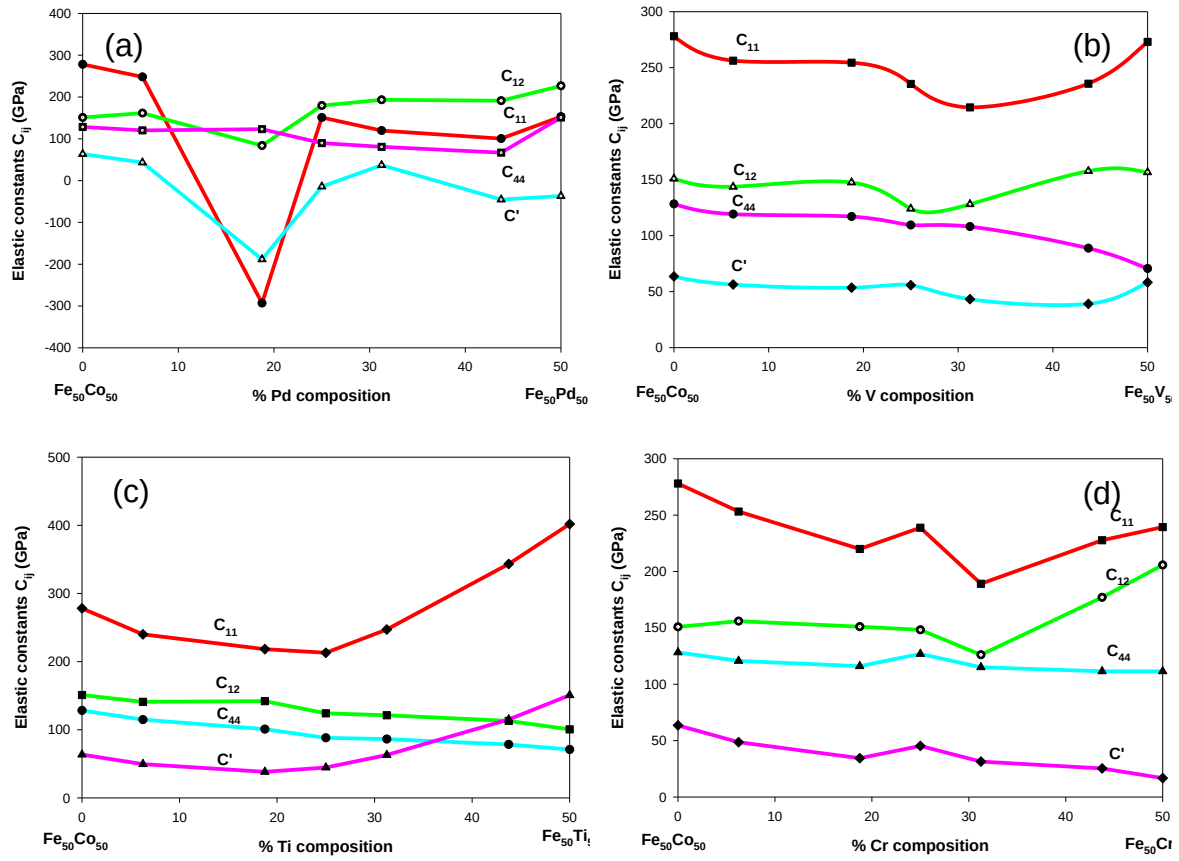


Figure 5.1 Elastic constants (GPa) against atomic percent M for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$), where $0 \leq x \leq 50$.

5.1.2 Anisotropy

The elastic anisotropy is studied to investigate the mechanical durability of materials.

The anisotropy factor can be determined by [101, 102]:

$$A = \frac{C_{44}}{C'} \quad (5.3)$$

The factor $A = 1$ indicates that the material is isotropic and any value greater or smaller than 1 indicates an anisotropic behavior [103, 104]. Figure 5.2 shows anisotropy against compositions of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) alloys. The

calculated A for pure $\text{Fe}_{50}\text{Co}_{50}$ was found to be 2.02 which is not closer to unity ($A \approx 1$) suggesting elastic anisotropy behavior. In the case of Pd addition, it is noted that A is not closer to the unit indicating anisotropic behavior. However, isotropic behavior is observed at 18.75 at. % Pd and anisotropic behavior are retained with further addition of Pd content. In the case of $M=\text{Ti}$, A approaches unity with the increase in composition ($6.25 \leq X \leq 31.25$). The addition of V shows anisotropic behavior for the entire composition range and a similar trend is observed for $M = \text{Cr}$.

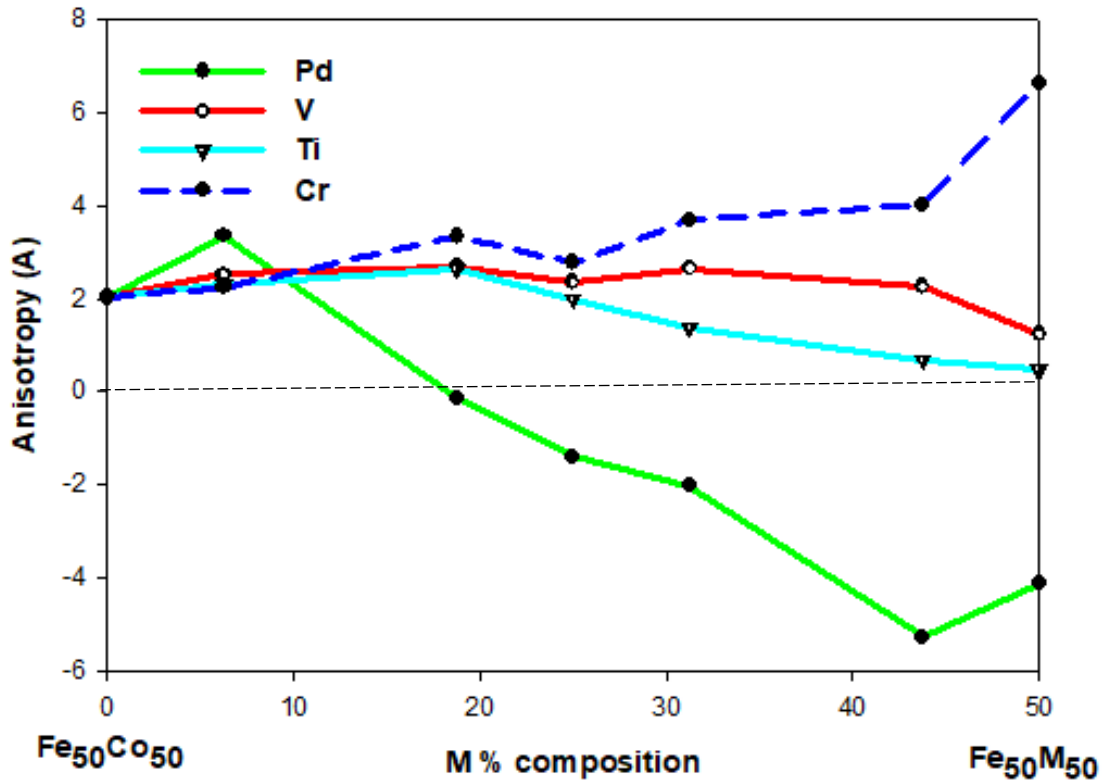


Figure 5. 2 Anisotropy (A) against atomic percent M for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}$, and Cr), where $0 \leq x \leq 50$.

5.1.3 Elastic moduli

To study the strength, compressibility and stiffness of the B2 Fe-Co alloy, we calculated the Bulk modulus, Shear modulus and Young's modulus, respectively. Figure 5.3 shows elastic moduli as functions of atomic percent for the $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) alloys. The Bulk, Shear and Young moduli of the $\text{Fe}_{50}\text{Co}_{50}$ binary alloy were determined and the values were 193.31 GPa (189 GPa [95]), 96.76 GPa (91 GPa [95]) and 248.67 GPa, respectively. The Bulk and Shear moduli agree well with theoretical findings to within 2% and 5%, respectively.

In figure 5.3 (a), It is seen that the Bulk and Shear modulus increases with an increase in Pd content indicating that the hardness is improved and the structure can resist shape deformation, respectively. However, above 6.25 at% Pd, Young 's modulus decreases suggesting weak stiffness of the alloy. In the case of $\text{Fe}_{50}\text{Co}_{50-x}\text{V}_x$, the moduli decrease with an increase in V content showing the ability to resist elastic and shear deformation as shown in figure 5.3 (b). A similar trend is observed in $\text{Fe}_{50}\text{Co}_{50-x}\text{Cr}_x$ alloys (see figure 5.3 (c)). Furthermore, the maximum values of the moduli are observed at 43.75 at.% Ti which suggests the highest strength to battle material deformations for the Fe-Co magnets.

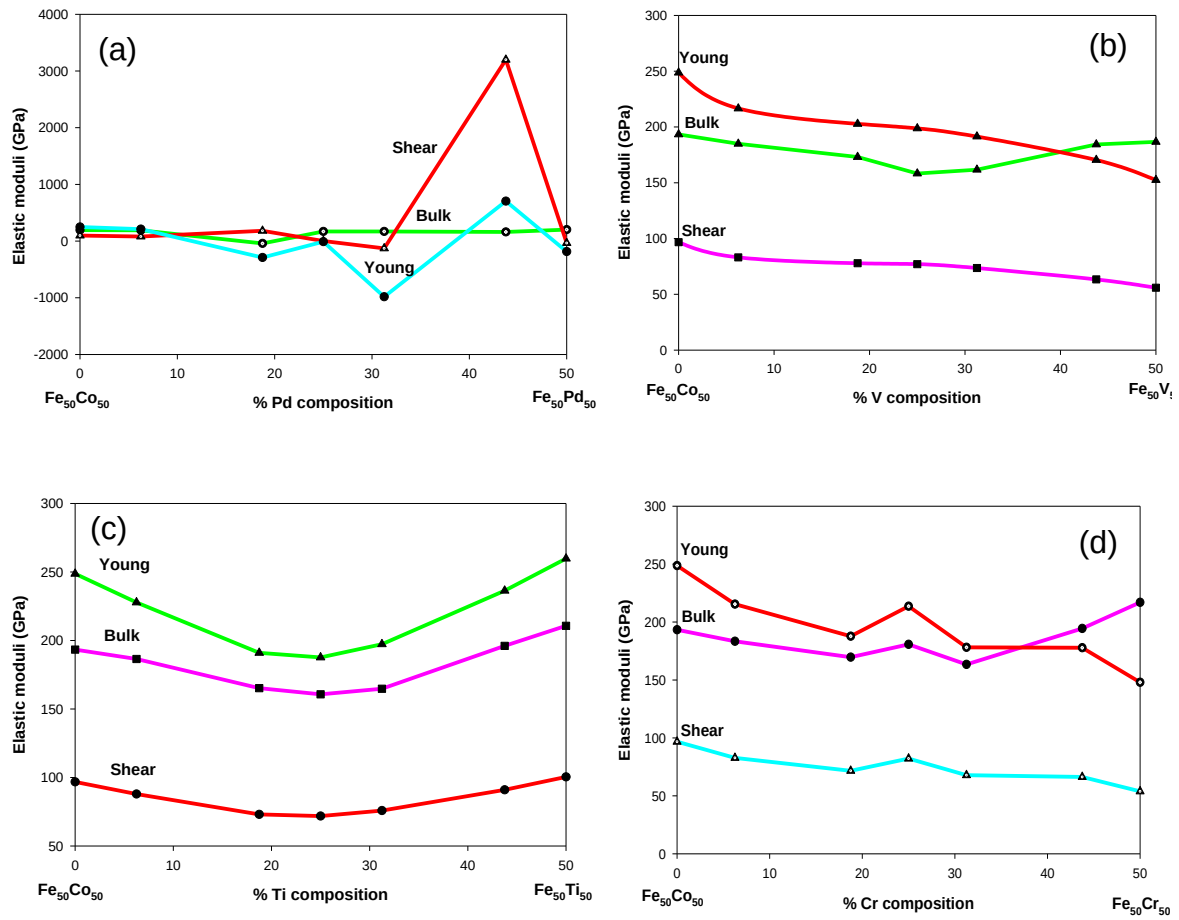


Figure 5.3 Elastic moduli (GPa) against atomic percent M for Fe₅₀Co_{50-x}M_x (M = Pd, V, Ti, and Cr), where $0 \leq x \leq 50$.

5.2 Measurement of ductility

To investigate the ductility and brittleness behaviour of the B2 Fe₅₀Co_{50-x}M_x alloys, we have determined the three quantities: Poisson's ratio, the B/G ratio and the Cauchy pressure at different compositions ($0 \leq x \leq 50$).

5.2.1 Poisson's ratio

Now to measure the ductility of the materials with different atomic compositions we firstly determined the Poisson's ratio. Note that the structure is considered ductile when Poisson's ratio ν is greater than 0.26 and otherwise brittle [105]. The Poisson's ratio for B2 Fe-Co was found to be 0.286 (0.29 [95]) which agrees with the theoretical value to within 1%, implying that the material is ductile. The effect of (M=Pd, V, Ti, Cr) ternary additions on the alloy is shown in figure 5.4. As the content of Pd is increased, the ν values were found to increase and be greater than 0.26 in the entire concentration which is a condition of ductility. Similar was observed with the addition of V, Ti and Cr for the entire concentration range.

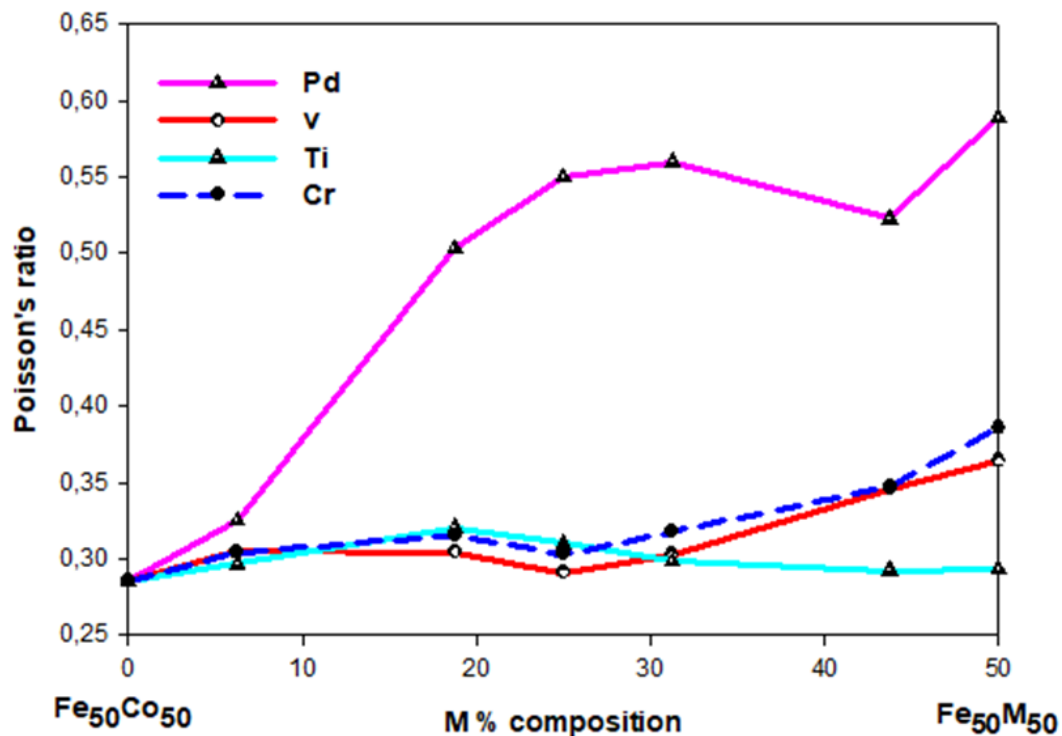


Figure 5. 4 Poisson's ratio against atomic percent M for Fe₅₀Co_{50-x}M_x (M = Pd, V, Ti, and Cr), where $0 \leq x \leq 50$.

5.2.2 Pugh ratio

The B/G ratio was calculated and evaluated to determine the ductility and brittleness of the structures. Pugh [106] indicated that the ductile phase has a higher B/G ratio (> 1.75) while a brittle phase has a smaller B/G ratio (< 1.75). Figure 5.5 shows the behavior of the B/G ratios as functions of M (M = Pd, V, Ti, and Cr) atomic compositions. It is seen that the B/G ratio for the binary $\text{Fe}_{50}\text{Co}_{50}$ was found to be 1.998 ($\text{B/G} > 1.75$) condition of ductility. Furthermore, it was observed that the B/G ratio is greater than the unit at 6.25 at. % Pd indicating the ductility of the structure. At above 18.75, the structure reveals a brittle manner as the ratio is less than the unit as shown in figure 5.5. In the case of $\text{Fe}_{50}\text{Co}_{50-x}\text{V}_x$, the B/G ratio increases gradually with increasing concentrations of V. Similar behavior is observed for the $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ and $\text{Fe}_{50}\text{Co}_{50-x}\text{Cr}_x$. This suggests that the B2 Fe-Co alloy showed good ductility in nature and the ductility became stronger with high concentrations of V, Ti, and Cr and with a small concentration of Pd.

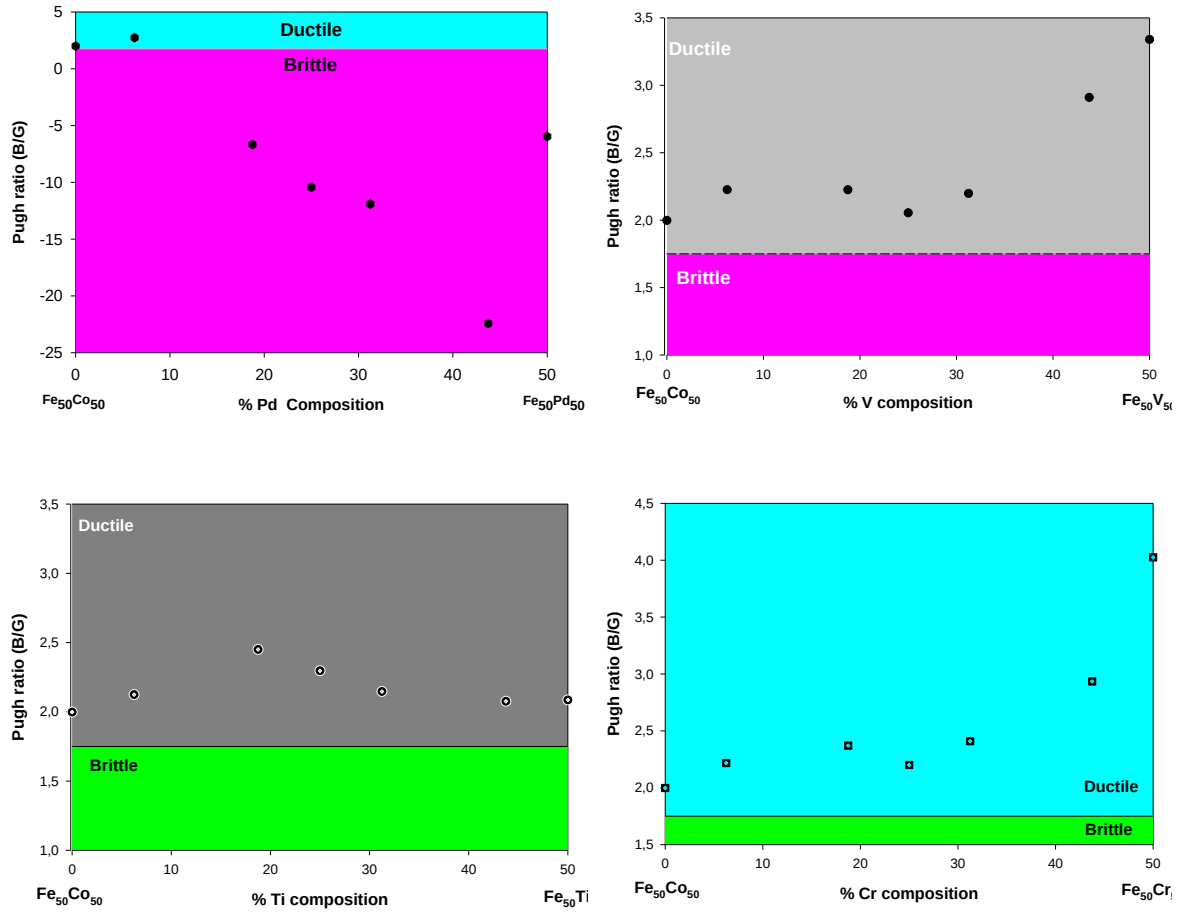


Figure 5. 5 Pugh ratio (B/G) against atomic percent M for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$), where $0 \leq x \leq 50$.

5.2.3 Cauchy pressure

To further investigate the ductility of the B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys, we calculated the Cauchy pressure. The Cauchy pressure of a cubic crystal is determined by finding the difference between the elastic constants C_{12} and C_{44} ($C_{12} - C_{44}$). Studies by Fu et al [102] and Johnson [107] revealed that the negative value of Cauchy pressure shows a weak covalent bond with a brittle behavior while a positive value of Cauchy

pressure indicates metallic properties with ionic character linking atomic bonding with ductile behavior.

Figure 5.6 shows Cauchy pressure for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) materials for different atomic compositions ($0 \leq x \leq 50$). It is observed that the Cauchy pressures for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ remained positive for the entire composition range ($0 \leq x \leq 50$) indicating ductility. It is also visible that with increasing the Pd content, the values of Cauchy pressure significantly increase and begin to drop at 31.25 at. %Pd, but those of V, Ti, and Cr changed a little compared to Pd. This suggests that the ductility and atomic bonding of the $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$) magnetic alloys are identified by the metallic bond and their ductility together with metallic bonds were greatly enhanced under Pd addition as compared to V, Ti, and Cr additions.

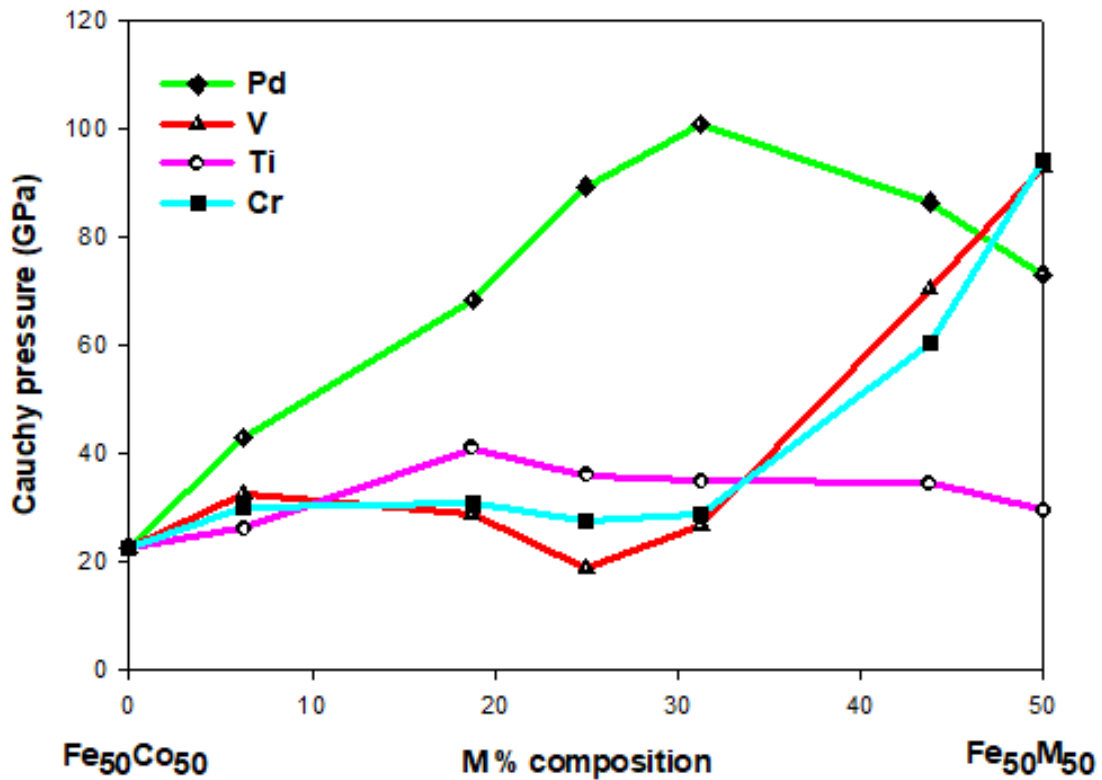


Figure 5. 6 Cauchy pressure (GPa) against atomic percent M for $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{and Cr}$), where $0 \leq x \leq 50$.

5.3 Vibrational properties

To investigate the vibrational stability of the B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) systems, we determined the phonon dispersion curves. The calculations were carried out using the PHONON code [32]. A structure is considered vibrationally stable if there are no soft modes along with negative directions in the Brillouin zone. Figures 5.7 to 5.10 show the determined phonon dispersion curves.

The phonon dispersion curves of B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ are shown in figure 5.7 It is seen that there are no soft modes observed for $\text{Fe}_{50}\text{Co}_{50}$, $\text{Fe}_{50}\text{Co}_{43.75}\text{Pd}_{6.25}$ and $\text{Fe}_{50}\text{Pd}_{50}$ suggesting that the structures are vibrationally stable. It is also noted that at 18.75,

25, 31.25 and 43.75 at. % Pd, the phonon dispersion curves display soft modes along the gamma region showing vibrational instability. These correspond well with their negative shear moduli, C' (see section 5.1.1).

In the case of B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($M = \text{V}, \text{Ti}, \text{and Cr}$), the phonon dispersion curves show vibrational stability due to the absence of soft modes in all directions. This prediction is consistent with their elastic moduli C_{ij} that are given in section 5.1.1. However, the dispersion curves of $\text{Fe}_{50}\text{Co}_{6.25}\text{V}_{43.75}$, $\text{Fe}_{50}\text{V}_{50}$ and $\text{Fe}_{50}\text{Co}_{6.25}\text{Cr}_{43.75}$ display small negative vibrations which do not imply mechanical instability rather it shows imaginary soft modes.

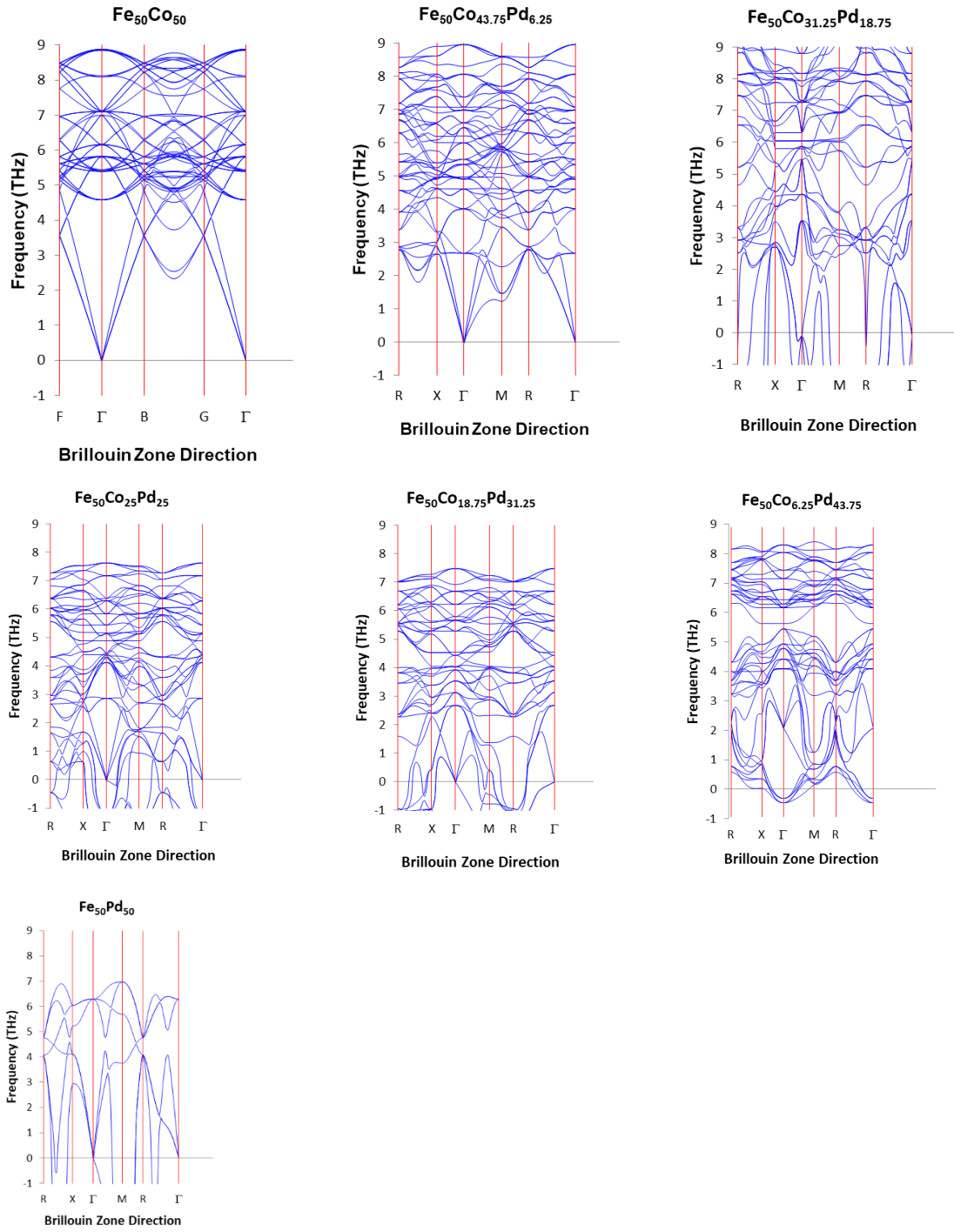


Figure 5. 7 Phonon dispersion curves of the $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ ($0 \leq x \leq 50$) structures.

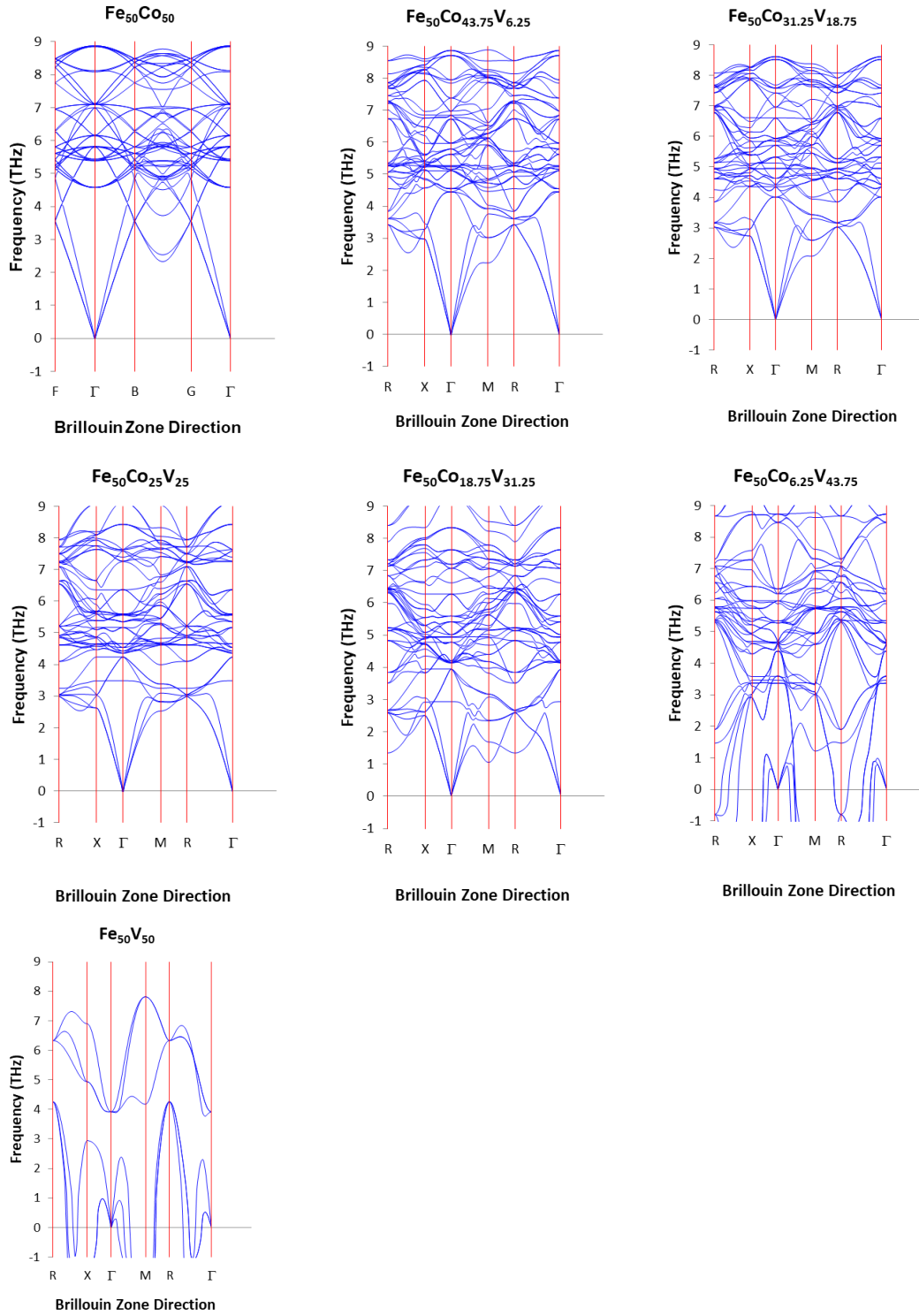


Figure 5. 8 Phonon dispersion curves of the $\text{Fe}_{50}\text{Co}_{50-x}\text{V}_x$ ($0 \leq x \leq 50$) structures.

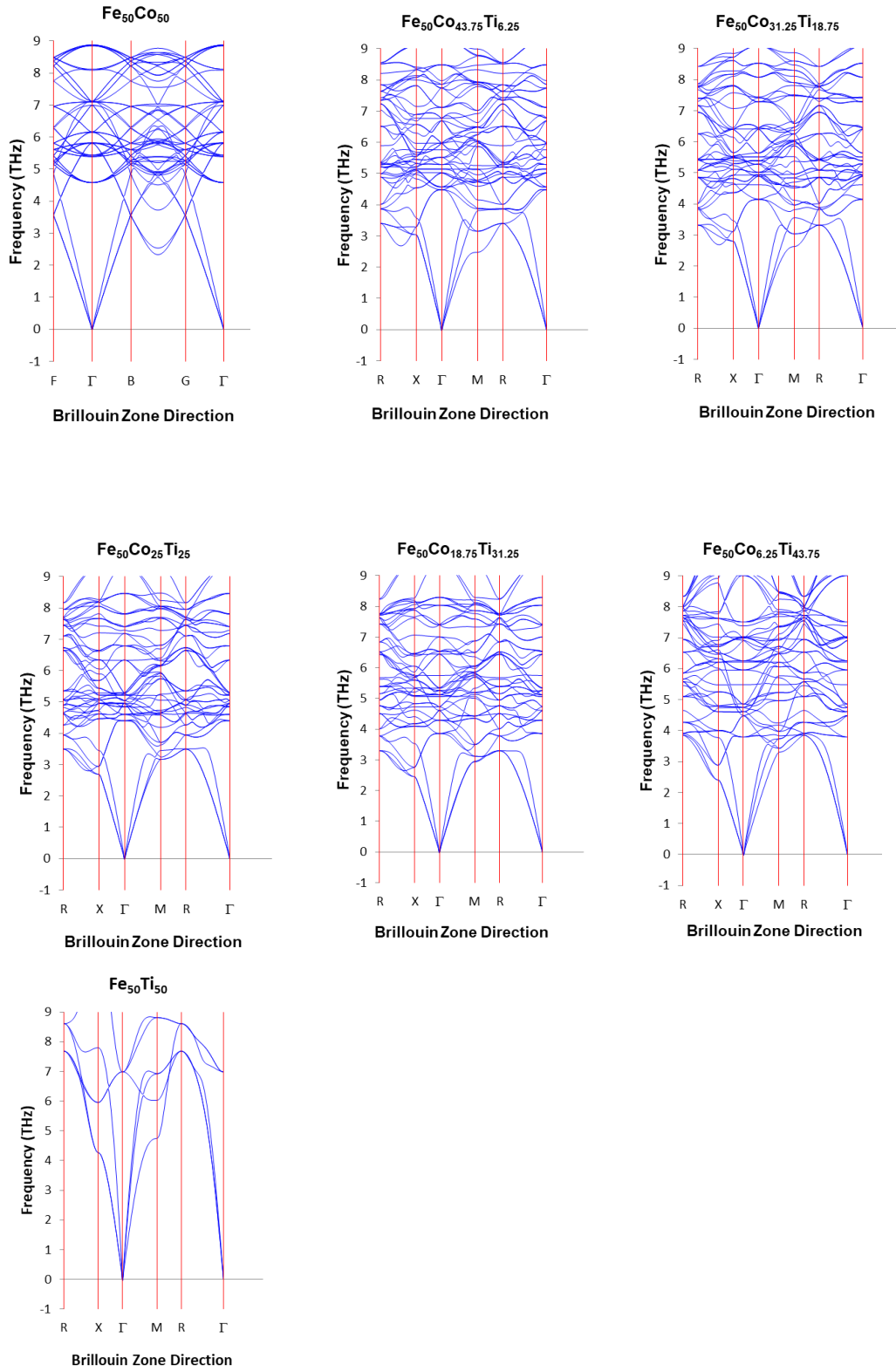


Figure 5. 9 Phonon dispersion curves of the $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ ($0 \leq x \leq 50$) structures.

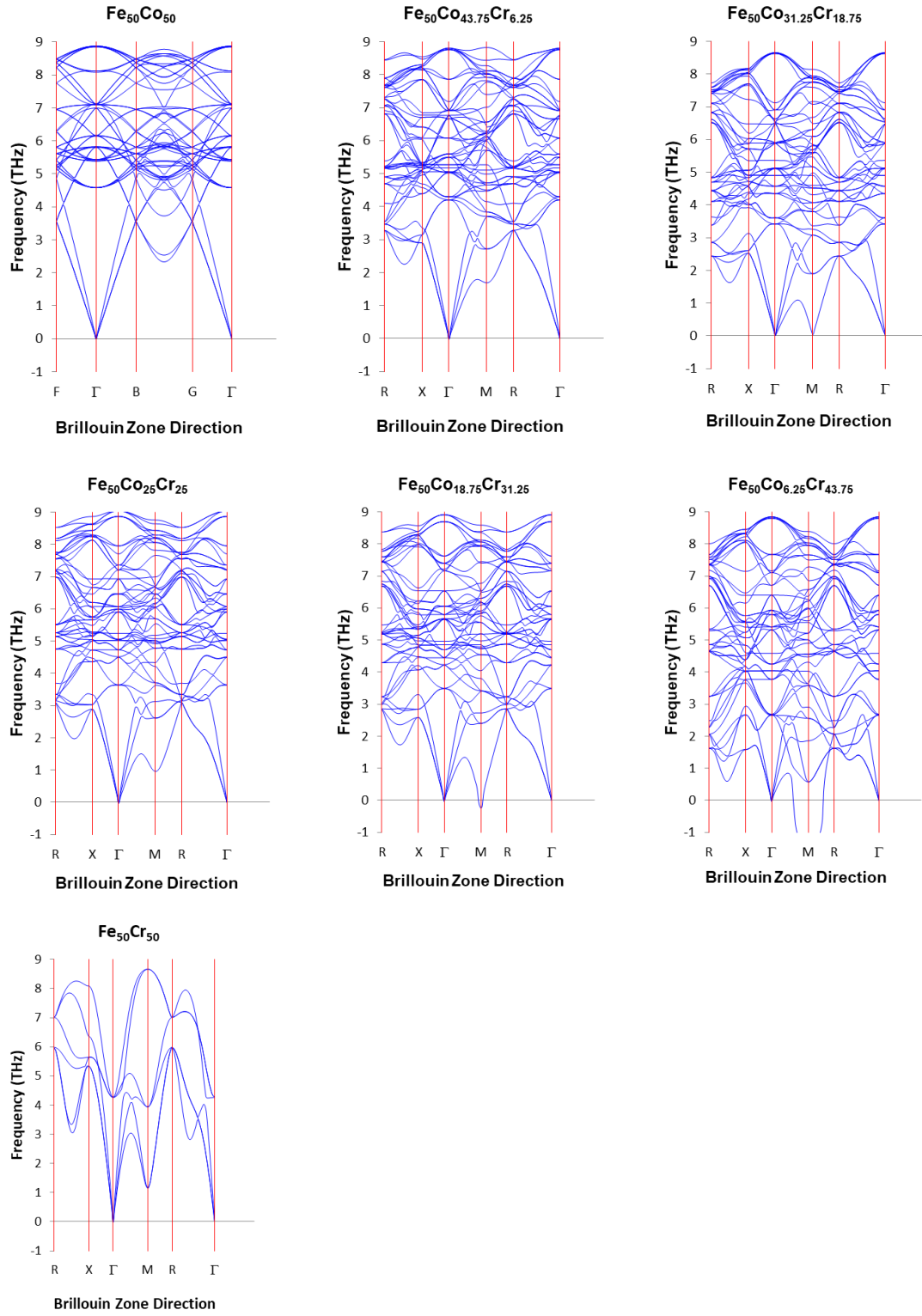


Figure 5. 10 Phonon dispersion curves of the $\text{Fe}_{50}\text{Co}_{50-x}\text{Cr}_x$ ($0 \leq x \leq 50$) structures.

CHAPTER 6

TEMPERATURE DEPENDENCE

In this chapter, we present and discuss the effect of temperature on the volume, density and lattice parameters of B2 Fe-Co $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($x=6.25, 18.75, 25, 31.25$ and 43.75). Although the alloying elements Pd and Ti have a slight increasing effect on the lattice parameter of Fe-Co (section 4.2). Ti is a strong metal with a low density that is quite ductile in an oxygen free environment. On the other hand, Pd belongs to a group of elements referred to as the platinum group metals (PGMs). They have similar chemical properties, but palladium has the lowest melting point and is the least dense of them. Hence the decision to look at these ternary elements in this section. LAMMPS code [61] employing the embedded atom method (EAM) [62] was used where Zhou [108] and inorganic interatomic potentials were chosen. A supercell which consists of 1024 atoms was used for both binary Fe-Co and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys and the structures were treated with NPT ensemble, nose hoover thermostat and barostat. The temperature was varied from 100 to 2500 K to determine the transformation temperature from the lattice parameters and XRDs.

6.1 B2 $\text{Fe}_{50}\text{Co}_{50}$

For the B2 Fe-Co alloy, figure 6.1 and 6.2 shows the graphs of volume and density against temperature, respectively. We note that the volume increases with an increase in temperature while the density decreases with an increase in temperature.

At 2200 K, there is a sudden increase and drop in volume and density, respectively.
This indicates the melting point of this alloy.

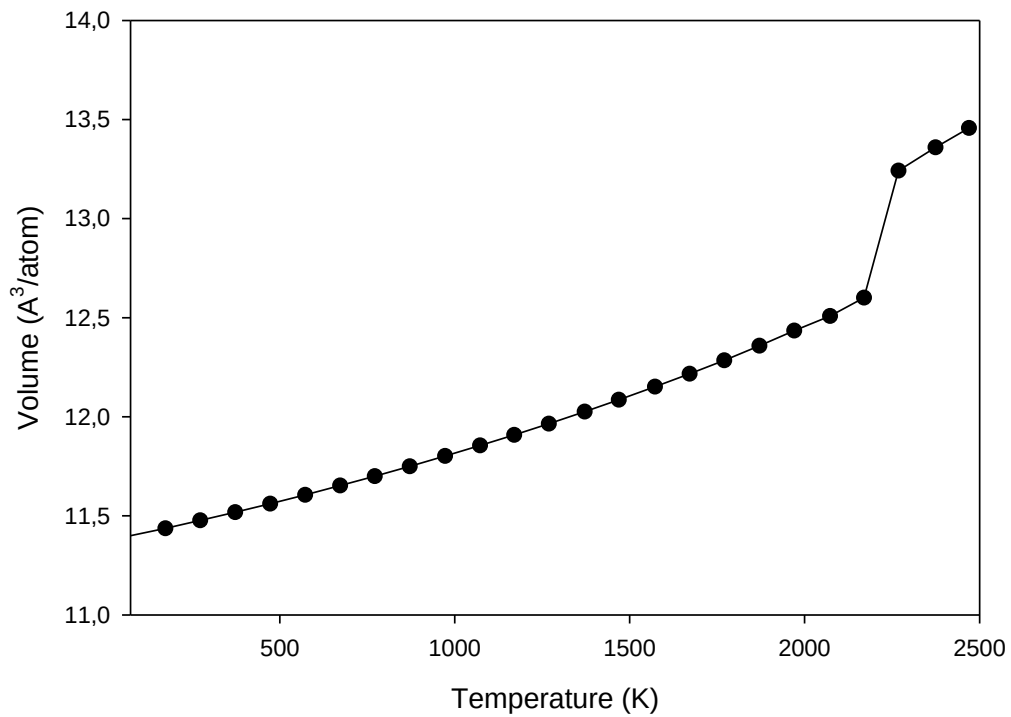


Figure 6. 1 Volume against temperature for B2 Fe₅₀Co₅₀.

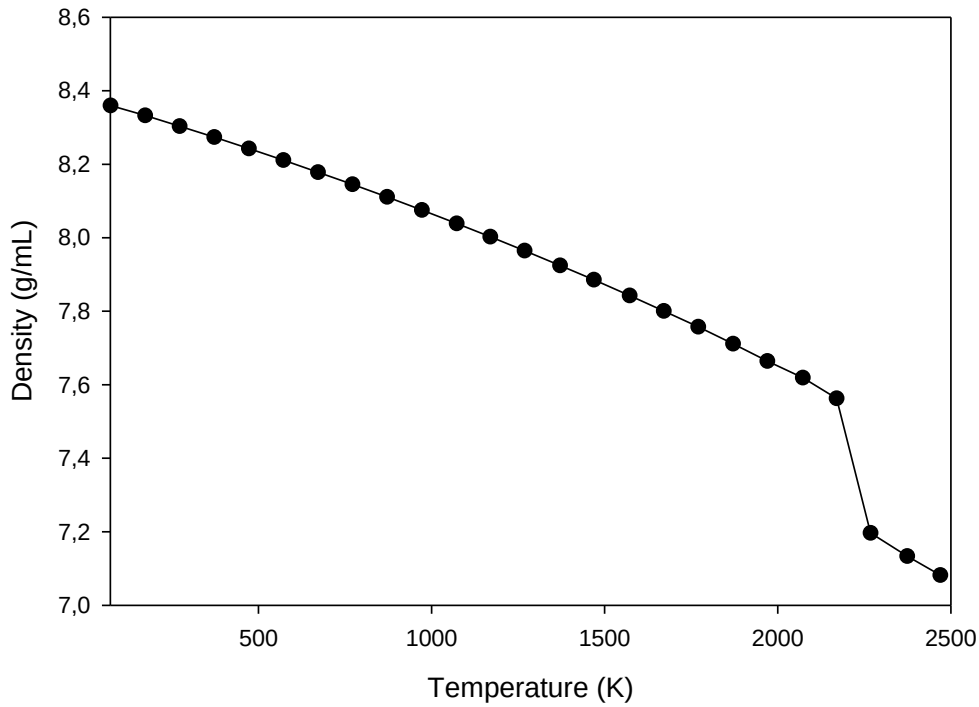


Figure 6. 2 Density against temperature for B2 Fe₅₀Co₅₀.

The lattice expansion is determined to check the transformation temperature and melting of the binary Fe-Co system. Figure 6.3 shows the effect of temperature on the lattice parameters of the system. It is observed that the lattice parameters a , c remains constant with an increase in temperature and the b lattice increase with an increase in temperature until the melting temperature is reached. Furthermore, we note that the c lattice increases monotonically at 2200 K while a and b lattice parameters collapse at this temperature. For the B2 structure to transform to the B19 phase, the a/b and c/b ratios should be close to 1.41 [108]. In figure 6.3 (c), the a/b and c/b ratios are approximately 1 until 2200 K and the c/b ratio approaches 1.41 above this temperature which suggests the melting temperature of the B2 phase.

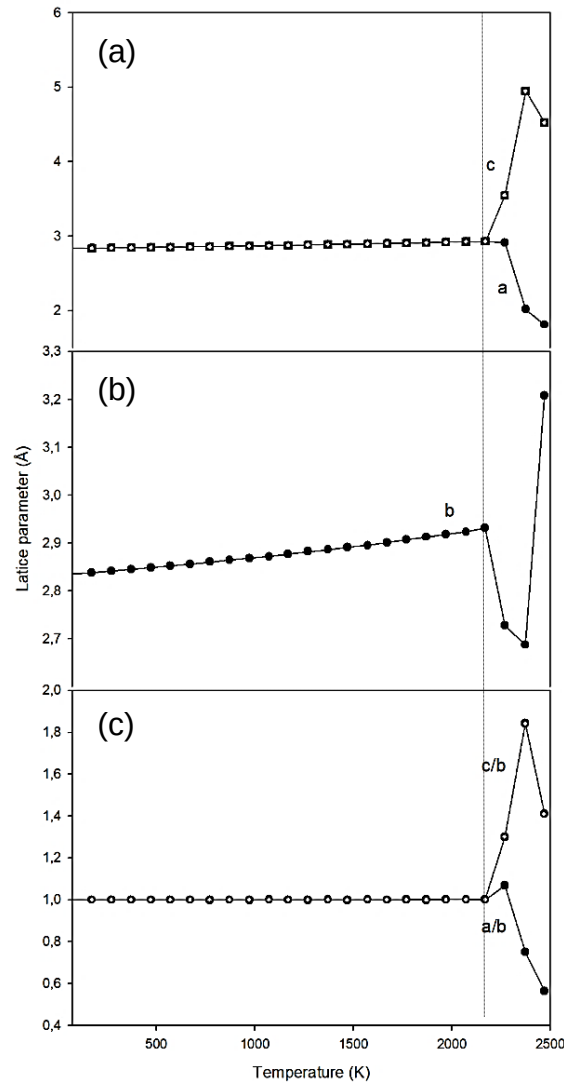


Figure 6. 3 The effect of temperature on the (a) a and c (b) b (c) a/b and c/b lattice parameters of the B2 Fe₅₀Co₅₀.

6.2 B2 Fe₅₀Co_{50-x}Pd_x alloys

The graph of volume against the temperature of the Fe₅₀Co_{50-x}Pd_x ($0 \leq x \leq 43.75$) is shown in figure 6.4. We observe that as the temperature increases, the volume of the structures linearly increases with the same trend for all compositions. When 6.25 at. % Pd is added to the system, the volume is increased and 43.75 at. % Pd has

the highest volume. This means that the volume increase with composition. There is a sudden increase for all compositions at 2000 K, which shows the melting of the structures.

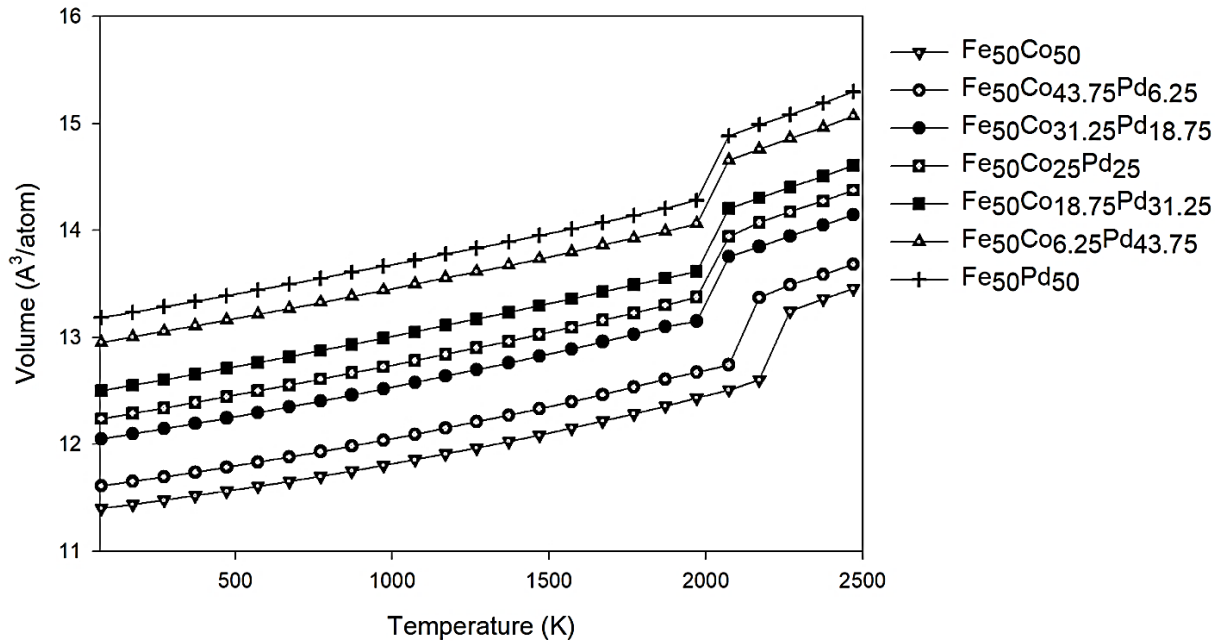


Figure 6. 4 Volume versus temperature for Fe₅₀Co_{50-x}Pd_x alloys.

The density against the temperature of the Fe₅₀Co_{50-x}Pd_x alloys is shown in figure 6.5. For all the compositions ($6.25 \leq x \leq 43.75$) the density decreases with an increase in temperature which could suggest that the system becomes less dense with temperature. We also observe that the density also improves with the addition of Pd, and this is attributed to the fact that Pd (12.02 g/cm³) is denser as compared to Fe (7.874 g/cm³) and Co (8.86 g/cm³).

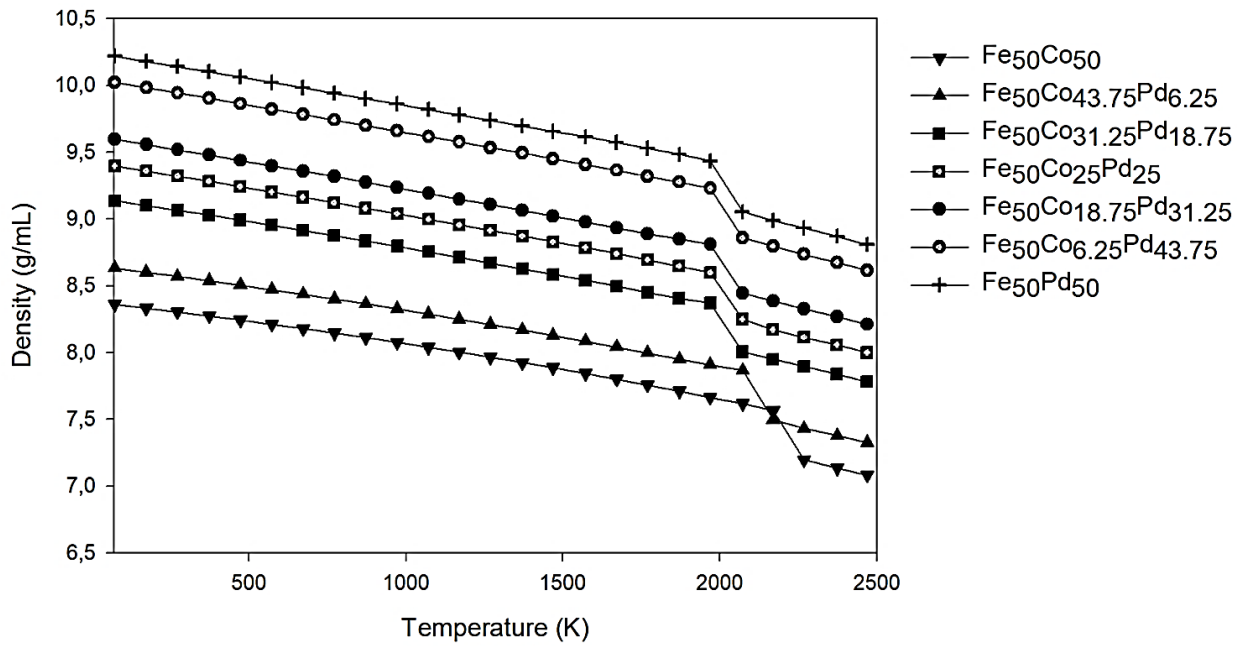


Figure 6. 5 Density versus temperature for $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ alloys.

Figures 6.6, 6.7 and 6.8 show the effect of temperature on the lattice parameters of $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ alloys. At 6.25 at. % Pd, the a, c and b lattice parameters increase linearly with an increase in temperature. Furthermore, we note that a and b lattice increase monotonically at 2000 K and c collapses at this temperature. The a/b and c/b ratios are approximately 1 for the entire temperature range which suggests that there is no possible transformation occurrence. Similar behavior was observed with 18.75, 25, 31.25 and 43.75 at. %Pd as there is no transformation temperature deduced from the graph. Unfortunately, there is no theoretical or experimental work to compare with our findings.

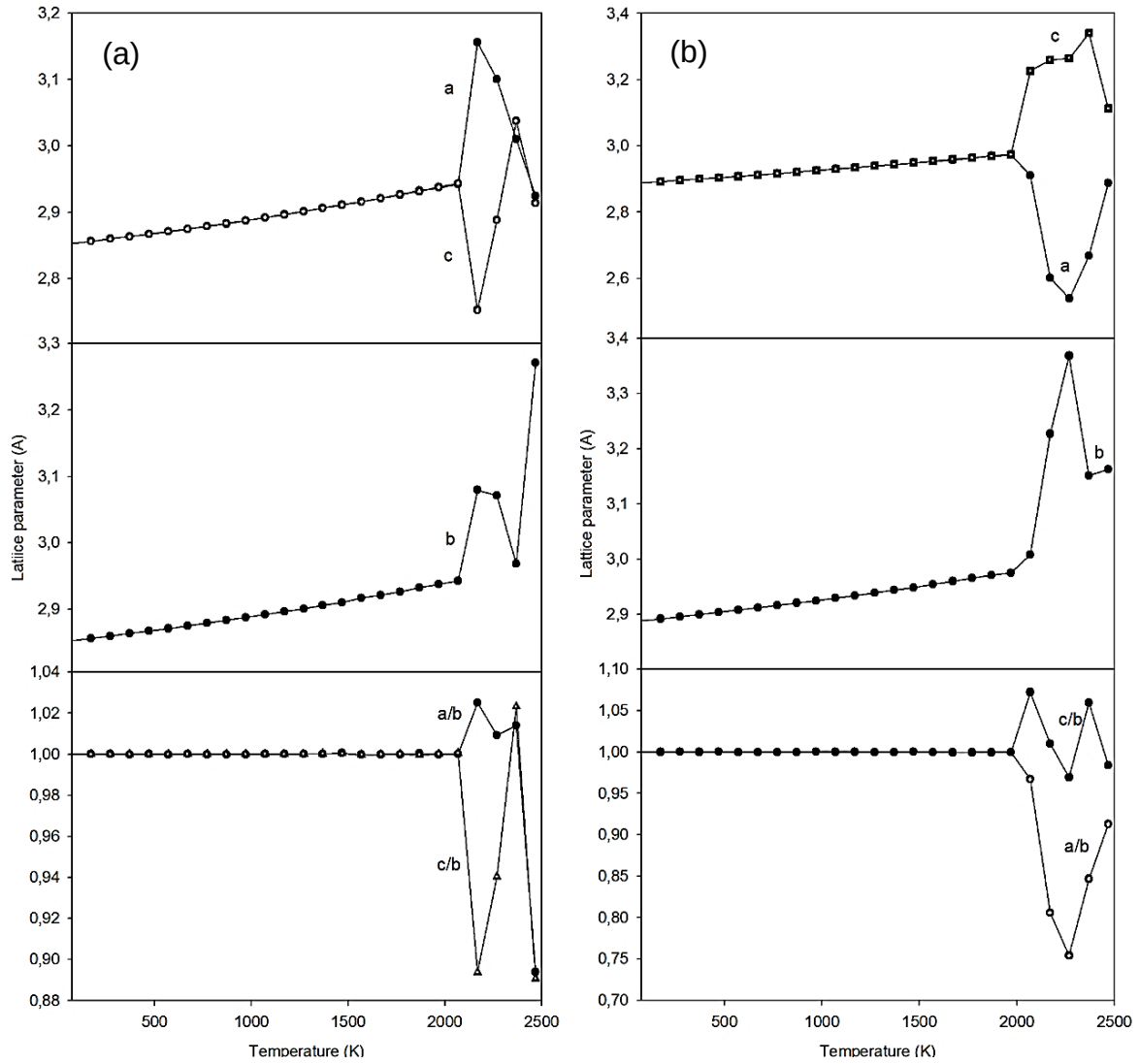


Figure 6. 6 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (a) $\text{Fe}_{50}\text{Co}_{43.75}\text{Pd}_{6.25}$ and (b) $\text{Fe}_{50}\text{Co}_{31.25}\text{Pd}_{18.75}$ alloys.

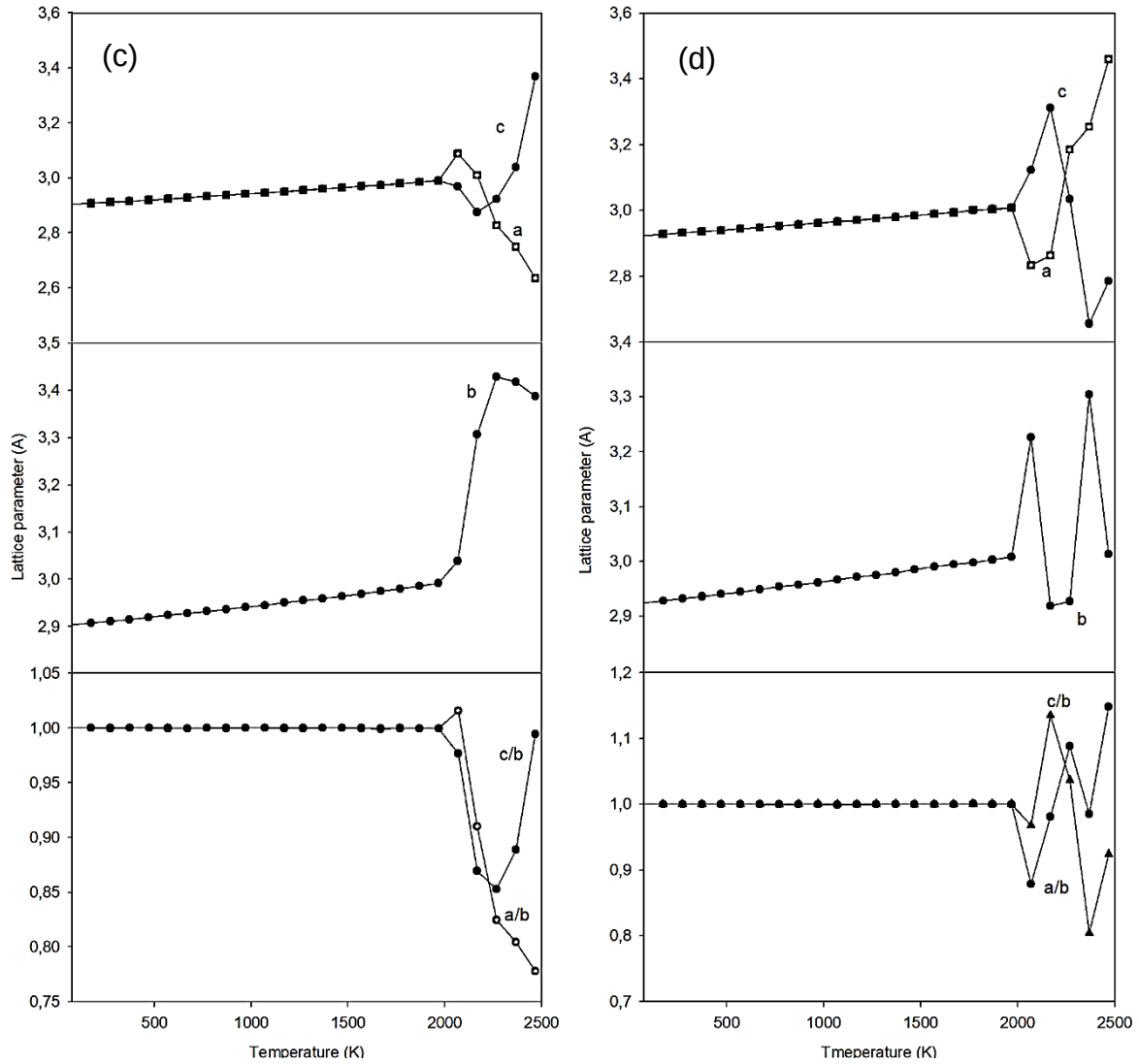


Figure 6. 7 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (c) $\text{Fe}_{50}\text{Co}_{25}\text{Pd}_{25}$ and (d) $\text{Fe}_{50}\text{Co}_{18.75}\text{Pd}_{31.25}$ alloys.

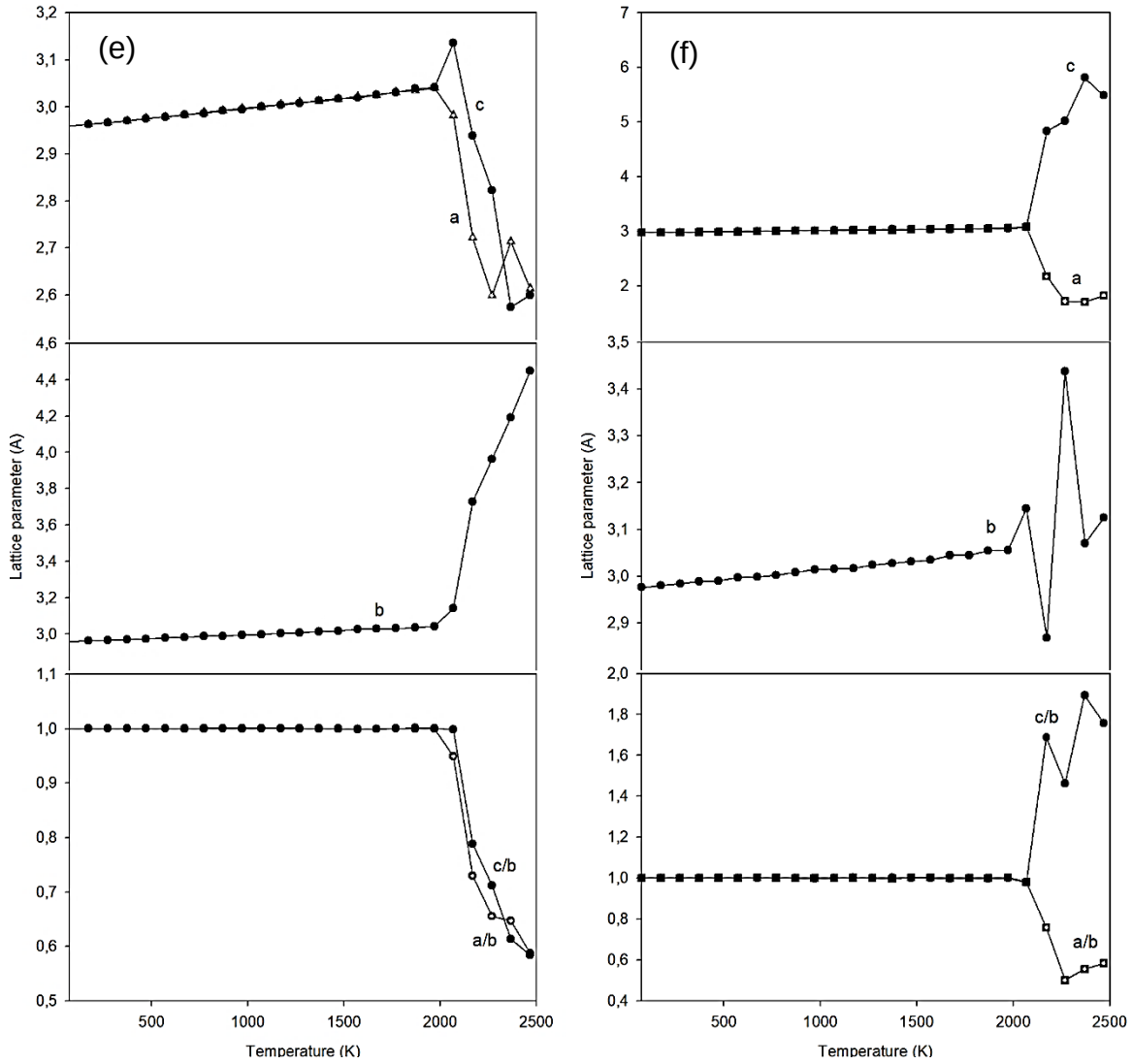


Figure 6. 8 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (e) $\text{Fe}_{50}\text{Co}_{6.25}\text{Pd}_{43.75}$ and (f) $\text{Fe}_{50}\text{Pd}_{50}$ alloys.

6.3 B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ alloys

The figure of volume against temperature for $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ ($0 \leq x \leq 43.75$) is shown in figure 6.9. The volume of the structures increases linearly with an increase in temperature for the entire concentration range. We observe that the volume increases as 6.25 at. % Ti is added to the system and 43.75 at. % Ti has the highest

volume. This indicates that the lattice parameters expand more with an increase in temperature. At 2000 K, we observe a sudden increase for all compositions, which indicates a melting point. The observation also occurs on their temperature dependence.

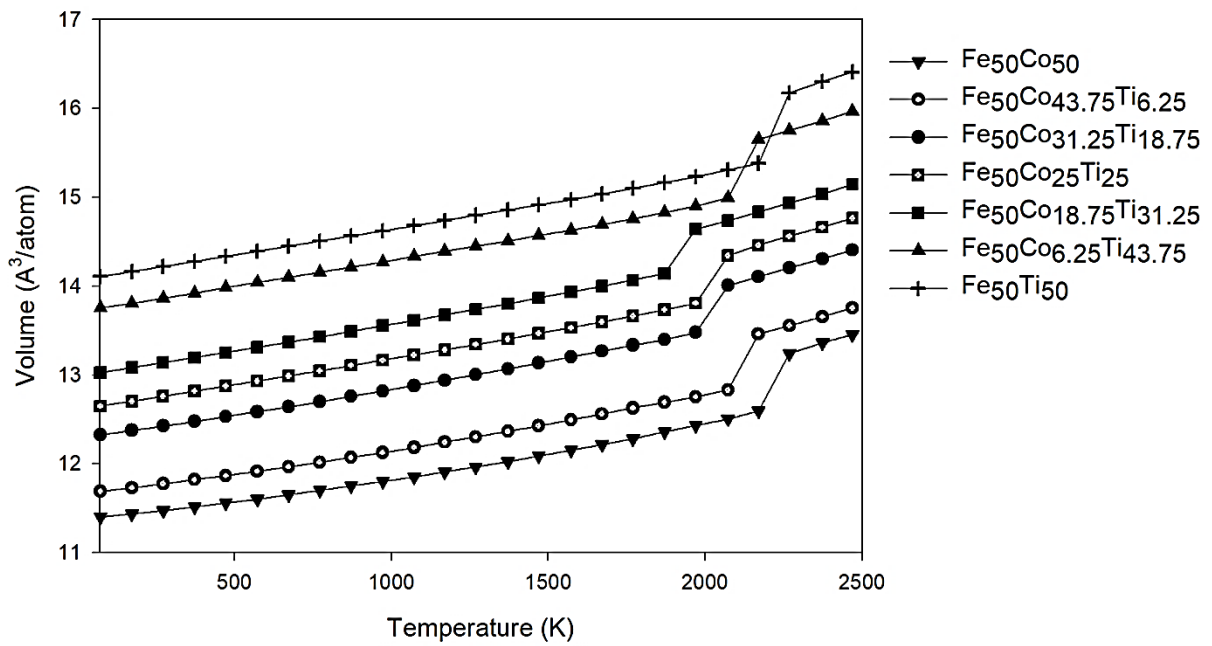


Figure 6. 9 Volume versus temperature for $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ alloys.

Figure 6.10 shows the density against the temperature of the $\text{Fe}_{50}\text{Co}_{50-x}\text{Pd}_x$ alloys. For all the compositions ($6.25 \leq x \leq 43.75$) the density decreased gradually with an increase in temperature which indicates that the system becomes less dense with temperature. We also observe that the density also reduces with the addition of Ti, and this is attributed to the fact that Ti (4.506 g/cm^3) is less dense compared to Fe (7.874 g/cm^3) and Co (8.86 g/cm^3). At 2000 K we observe a drop in density for all

compositions, which indicates melting. This is also observed in their temperature dependence.

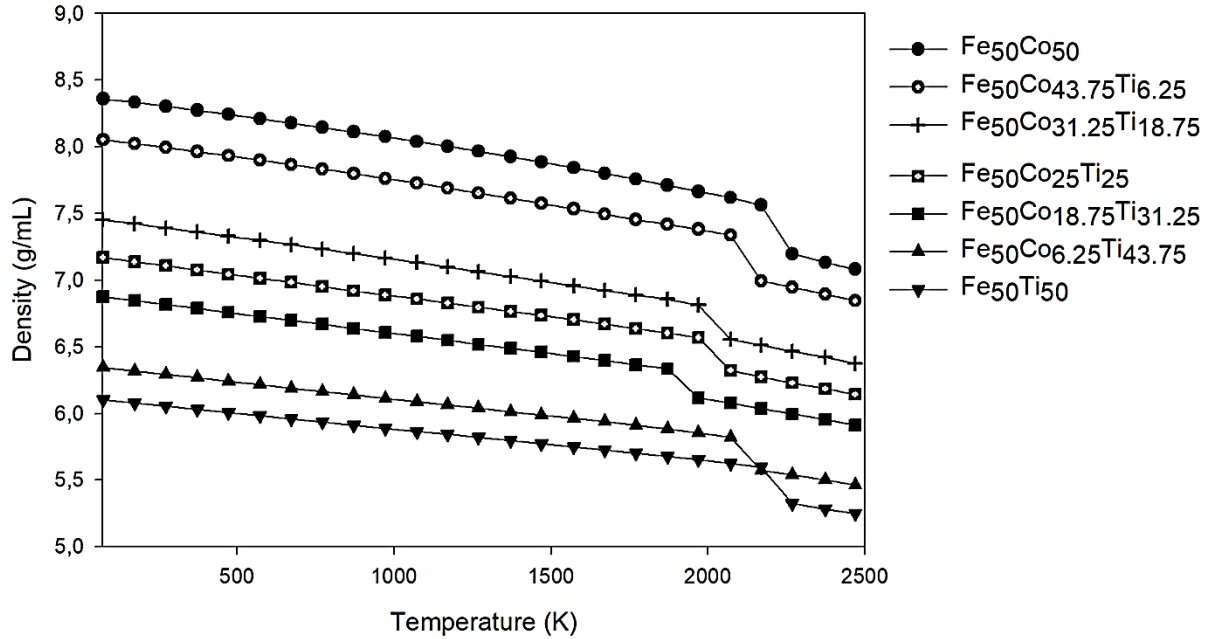


Figure 6. 10 Density versus temperature for Fe₅₀Co_{50-x}Ti_x alloys.

Figures 6.11, 6.12 and 6.13 show the effect of temperature on the lattice parameters of Fe₅₀Co_{50-x}Ti_x. It is noted that the lattice parameters a, c and b of 6.25 at. % Ti increases linearly with temperature until 2000 K. It is at 2000K that the structure starts to melt. It is observed that c and b lattice parameters strictly increase at this temperature. The a/b and c/b ratios are approximately 1 suggesting that there is no transformation temperature. Furthermore, a similar trend was observed with 18.75, 25, 31.25 and 43.75 at. % Ti. Unfortunately, there is no previous work to compare.

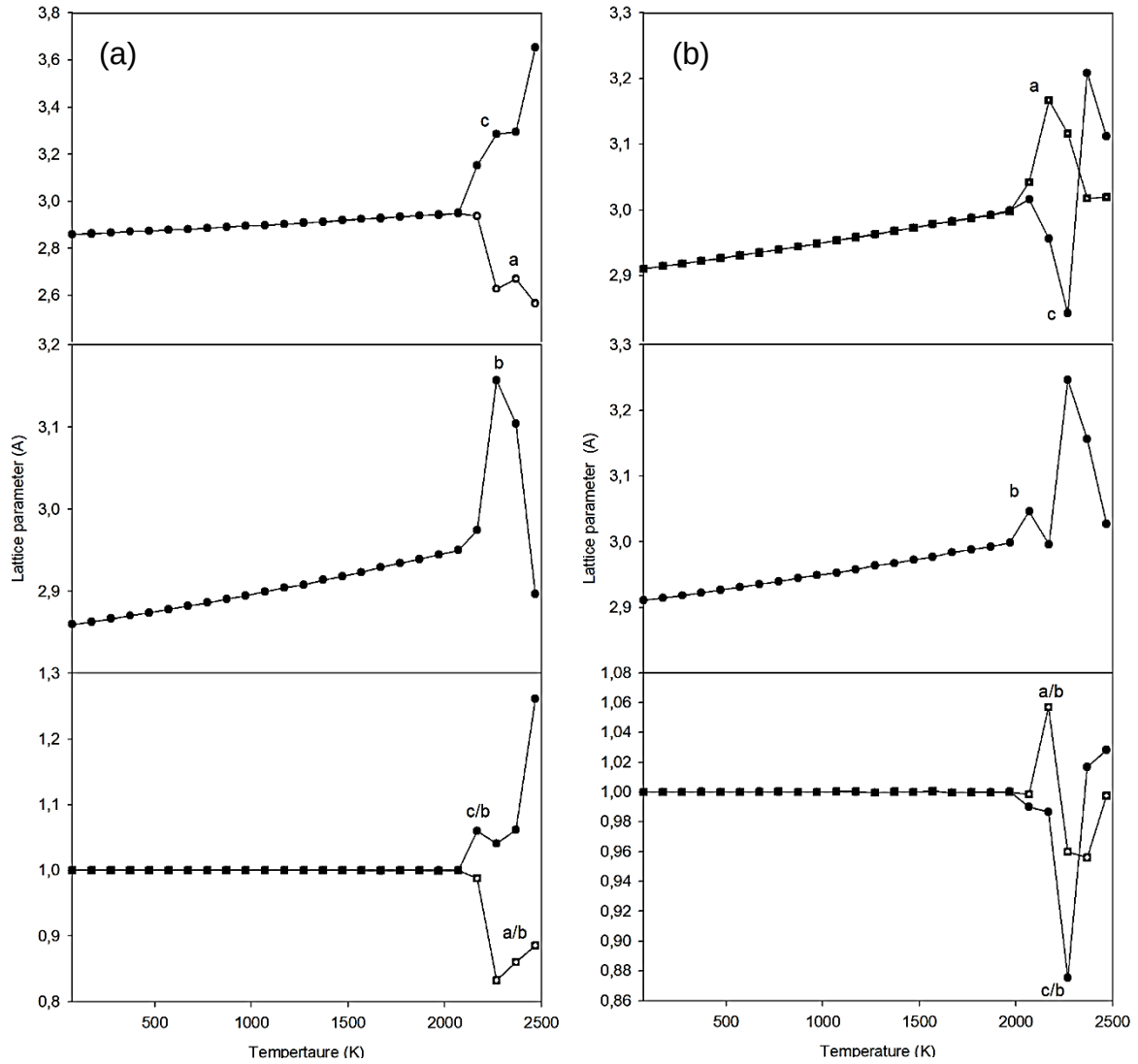


Figure 6. 7 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (a) $\text{Fe}_{50}\text{Co}_{43.75}\text{Ti}_{6.25}$ and (b) $\text{Fe}_{50}\text{Co}_{31.25}\text{Ti}_{18.75}$ alloys.

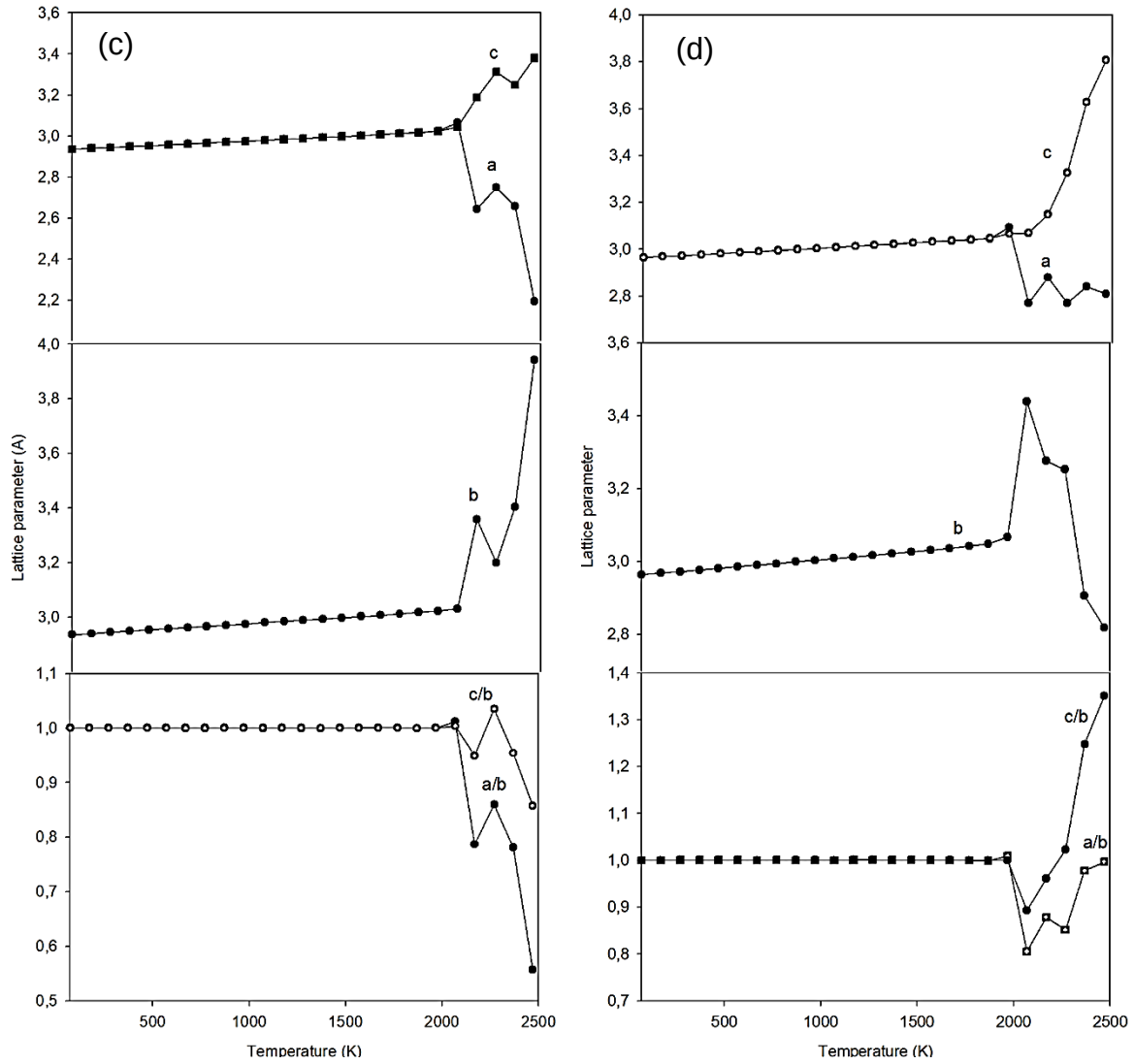


Figure 6. 8 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (c) $\text{Fe}_{50}\text{Co}_{25}\text{Ti}_{25}$ and (d) $\text{Fe}_{50}\text{Co}_{18.75}\text{Ti}_{31.25}$ alloys.

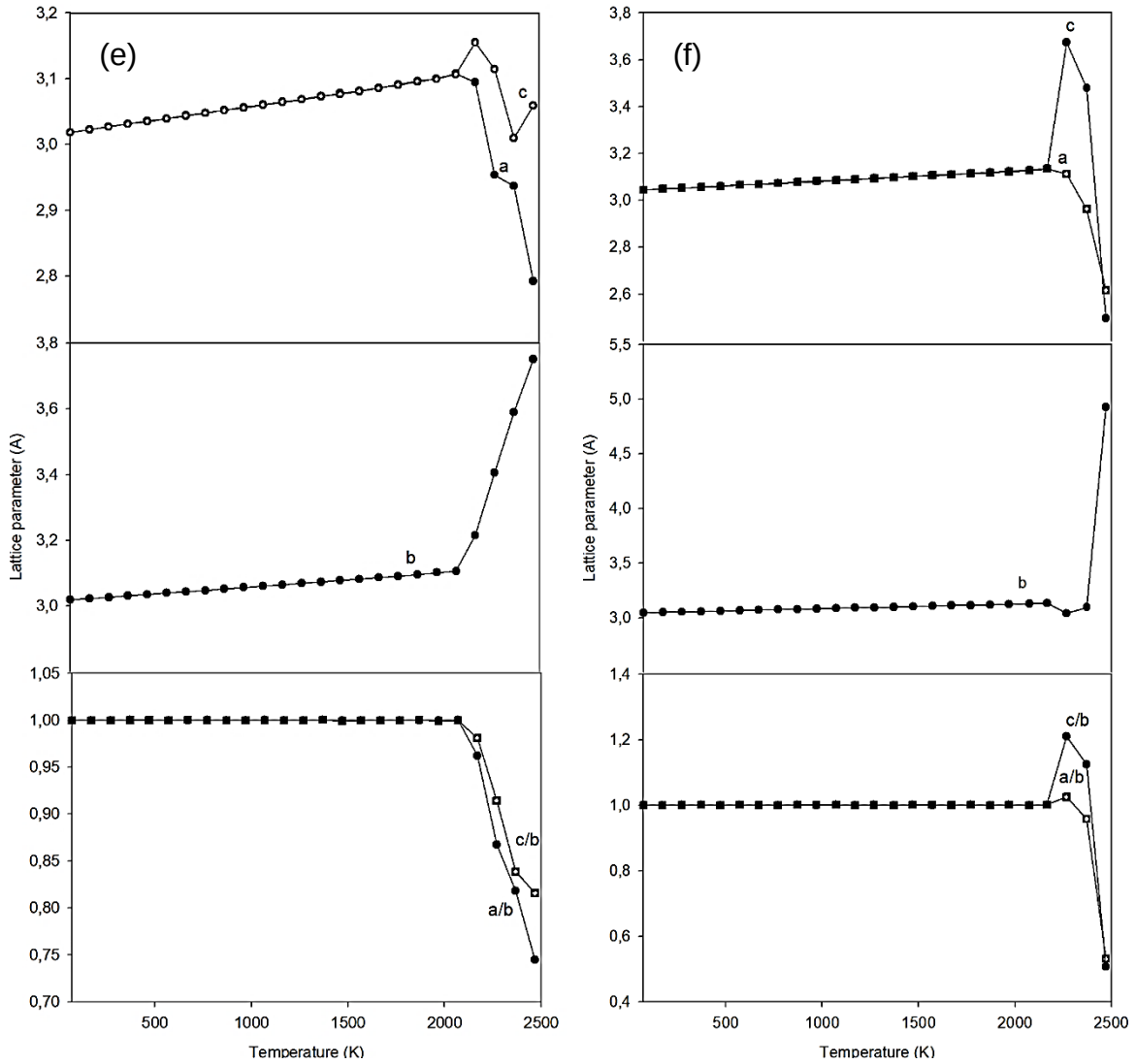


Figure 6. 9 the effect of temperature on the a and c, b and, a/b and c/b lattice parameters of the B2 (e) $\text{Fe}_{50}\text{Co}_{6.25}\text{Ti}_{43.75}$ and (f) $\text{Fe}_{50}\text{Ti}_{50}$ alloys.

6.4 XRD 's for the B2 $\text{Fe}_{50}\text{Co}_{50}$

The XRD patterns were constructed from the temperature dependence of B2 $\text{Fe}_{50}\text{Co}_{50}$. The B2 X-ray indices, 110, 200 and 211 are observed at different temperatures. The same X-ray indices were observed elsewhere [109] (see figure

6.14 (b)). The structure remains B2 phase from 73 K to 2073 K with the same set of peaks observed. At a temperature of 2268 K and above, the peaks are broad and suggesting that the structure has melted at this temperature and thus the structure is lost. Interestingly, the melting temperature of the B2 phase correlates well with the a/b and c/b ratios change, which is at approximately 2200 K (section 6.1).

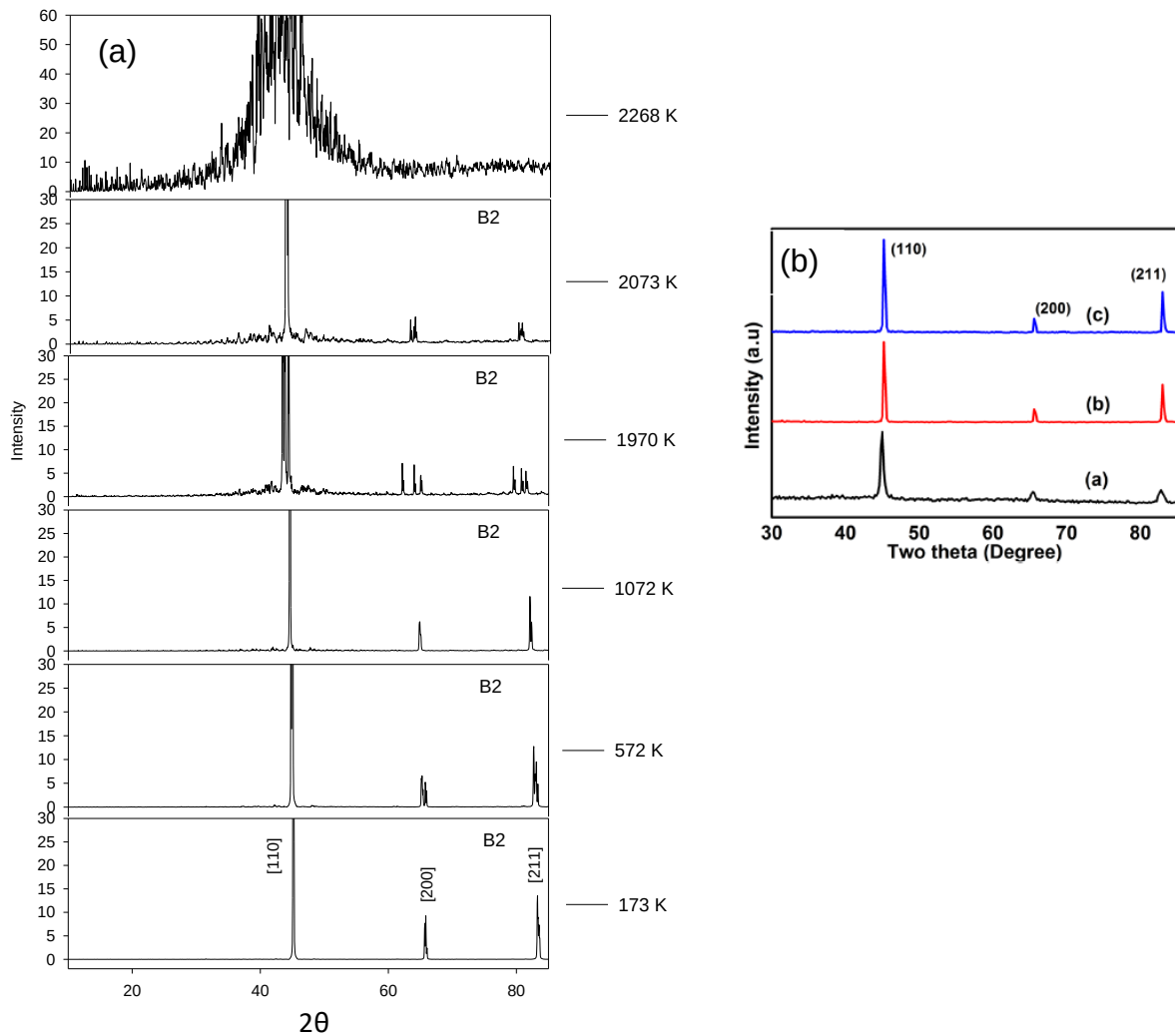


Figure 6. 10 Diffraction patterns at a various temperature from 73-2500 K for B2 $\text{Fe}_{50}\text{Co}_{50}$.

6.5 XRD 's for B2 Fe₅₀Co_{50-x}Pd_x alloys

Figures 6.15, 6.16 and 6.17 show the calculated X-ray diffraction patterns (XRD) of B2 Fe₅₀Co_{50-x}Pd_x alloys from 73-2500 K. The XRD patterns of B2 Fe₅₀Co_{50-x}Pd_x alloys were constructed from their temperature dependence. For Fe₅₀Co_{43.75}Pd_{6.25}, the B2 X-ray indices, 110, 200 and 211 are observed at different temperatures. The structure remains B2 phase from 73 K to 2069 K with the same set of peaks observed. At a temperature of 2168 K and above, the peaks are broad and suggesting that the structure has melted at this temperature and thus the structure is lost. A similar trend is observed for the B2 Fe₅₀Co_{31.25}Pd_{18.75} with the addition of three peaks 010, 001 and 10-1. The X-ray indices of Fe₅₀Co₂₅Pd₂₅ are 010, 01-1, 100, 110, 200 and 211. The peaks for Fe₅₀Co_{18.75}Pd_{31.25} are 100, 001, 110, 200 and 211 and 010, 110, 100, 200 and 211 for Fe₅₀Co_{6.25}Pd_{43.75} alloy. The XRD results of the alloys correspond well with their temperature dependence.

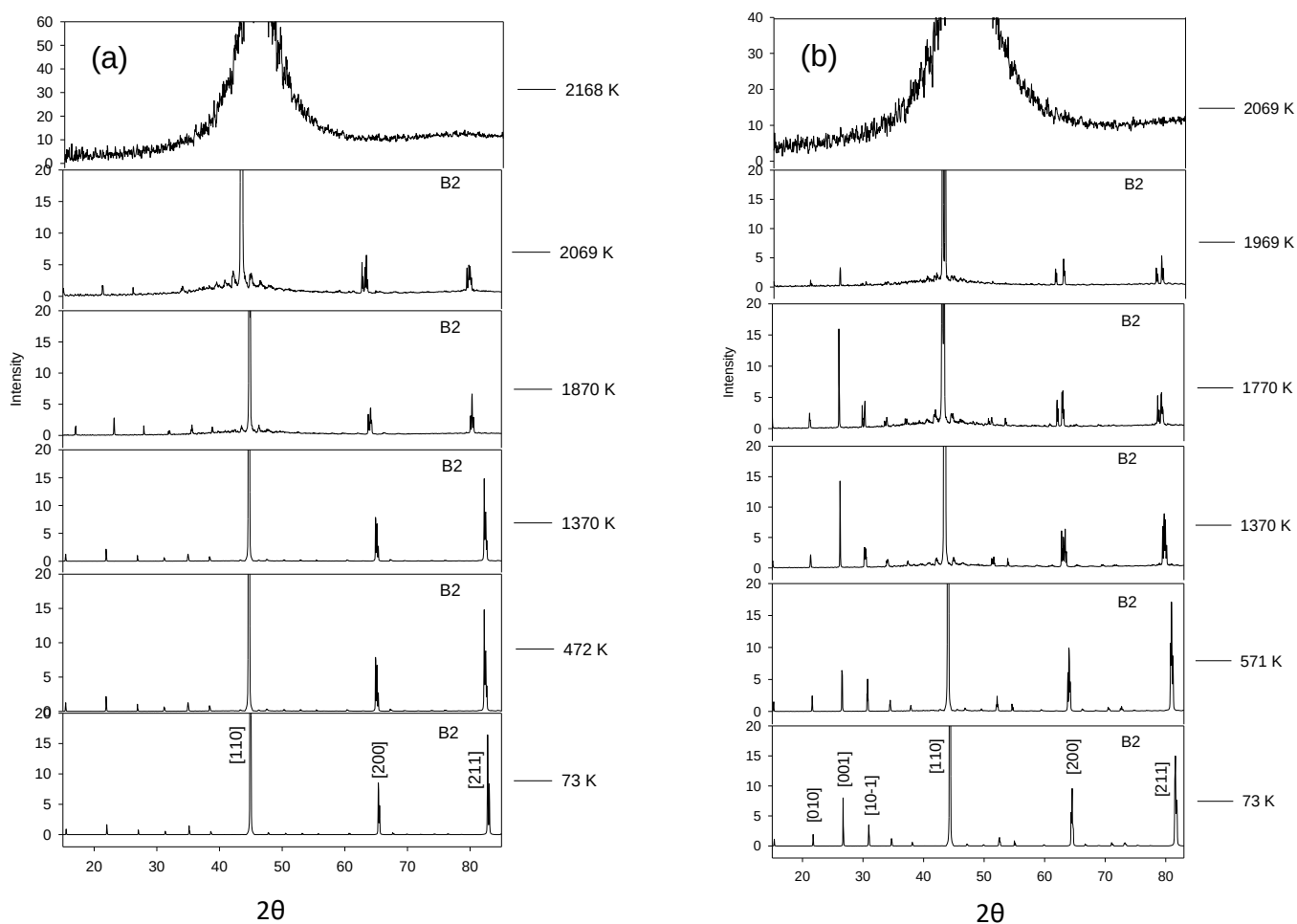


Figure 6. 11 The simulated B2 (a) $\text{Fe}_{50}\text{Co}_{43.75}\text{Pd}_{6.25}$ and (b) $\text{Fe}_{50}\text{Co}_{31.25}\text{Pd}_{18.75}$ diffraction patterns from 73 to 2500 K.

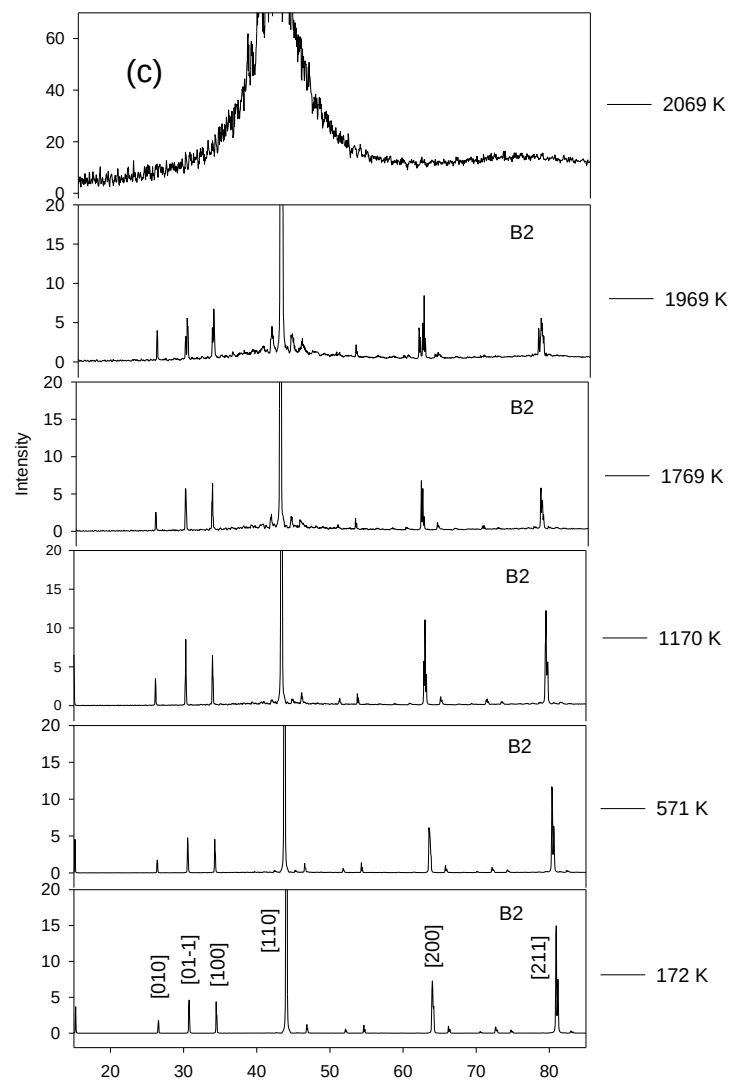


Figure 6. 12 The simulated B2 (c) $\text{Fe}_{50}\text{Co}_{25}\text{Pd}_{25}$ diffraction patterns from 73 to 2500 K.

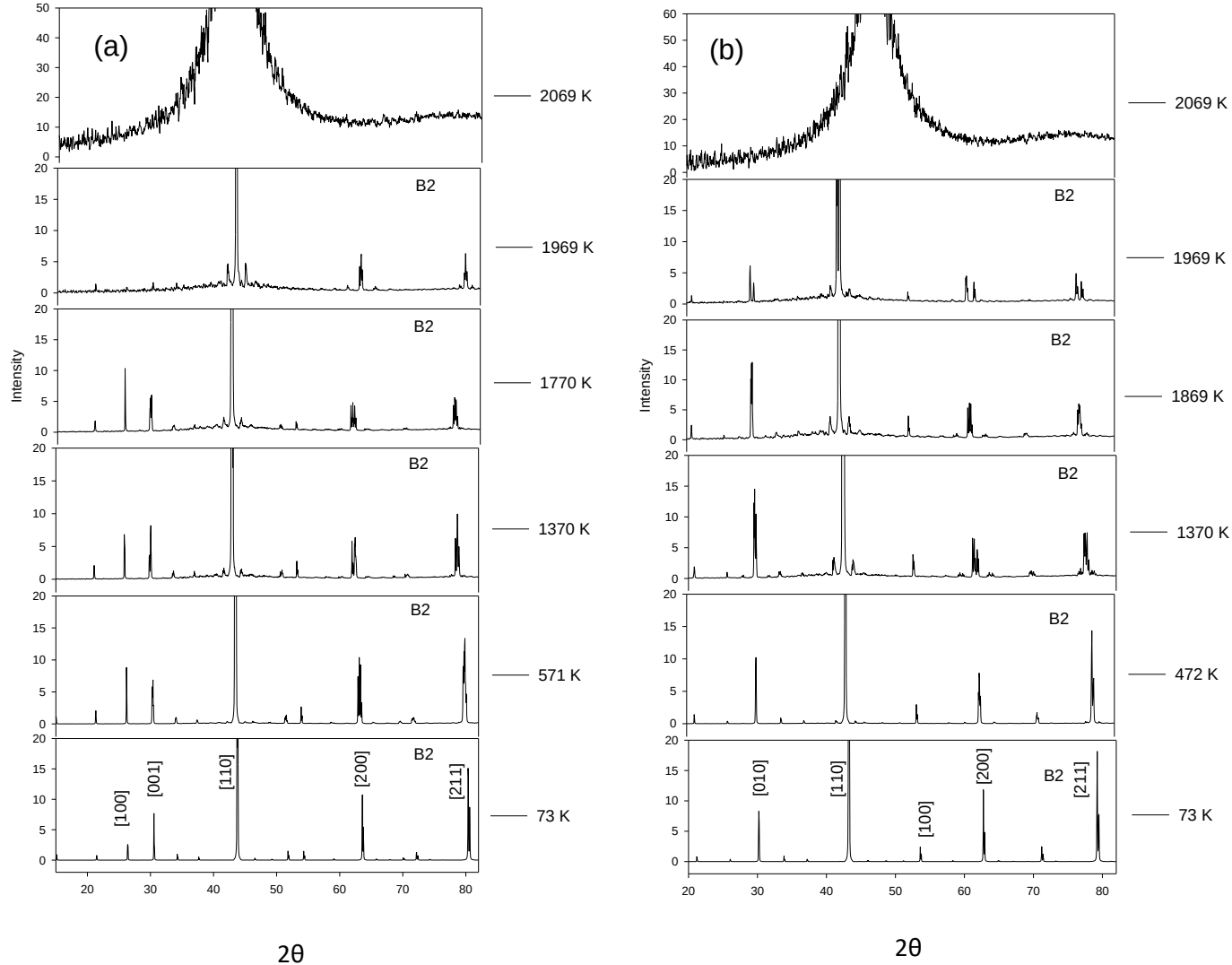


Figure 6. 13 The simulated B2 (a) $\text{Fe}_{50}\text{Co}_{18.75}\text{Pd}_{31.25}$ and (b) $\text{Fe}_{50}\text{Co}_{6.25}\text{Pd}_{43.75}$ diffraction patterns from 73 to 2500 K.

6.6 XRD 's for B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ alloys

Figures 6.18, 6.19 and 6.20 show the calculated X-ray diffraction patterns (XRD) of B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ alloys from 73-2500 K. The XRD patterns of B2 $\text{Fe}_{50}\text{Co}_{50-x}\text{Ti}_x$ alloys were constructed from their temperature dependence. For $\text{Fe}_{50}\text{Co}_{43.75}\text{Ti}_{6.25}$, the B2 X-ray indices, 020, 110, 200 and 211 are observed at different temperatures. The structure remains B2 phase from 73 K to 2069 K with the same set of peaks

observed. At a temperature of 2168 K and above, the peaks are broad and suggesting that the structure has melted at this temperature and thus the structure is lost. For $\text{Fe}_{50}\text{Co}_{31.25}\text{Ti}_{18.75}$, the peaks are 110, 200 and 211 and a similar trend is observed for $\text{Fe}_{50}\text{Co}_{25}\text{Ti}_{25}$ and $\text{Fe}_{50}\text{Co}_{6.25}\text{Ti}_{43.75}$ alloys. The peaks for $\text{Fe}_{50}\text{Co}_{18.75}\text{Ti}_{31.25}$ are 200, 110, 1-1-1, 200 and 211. The XRD melting temperature correspond well with their temperature dependence.

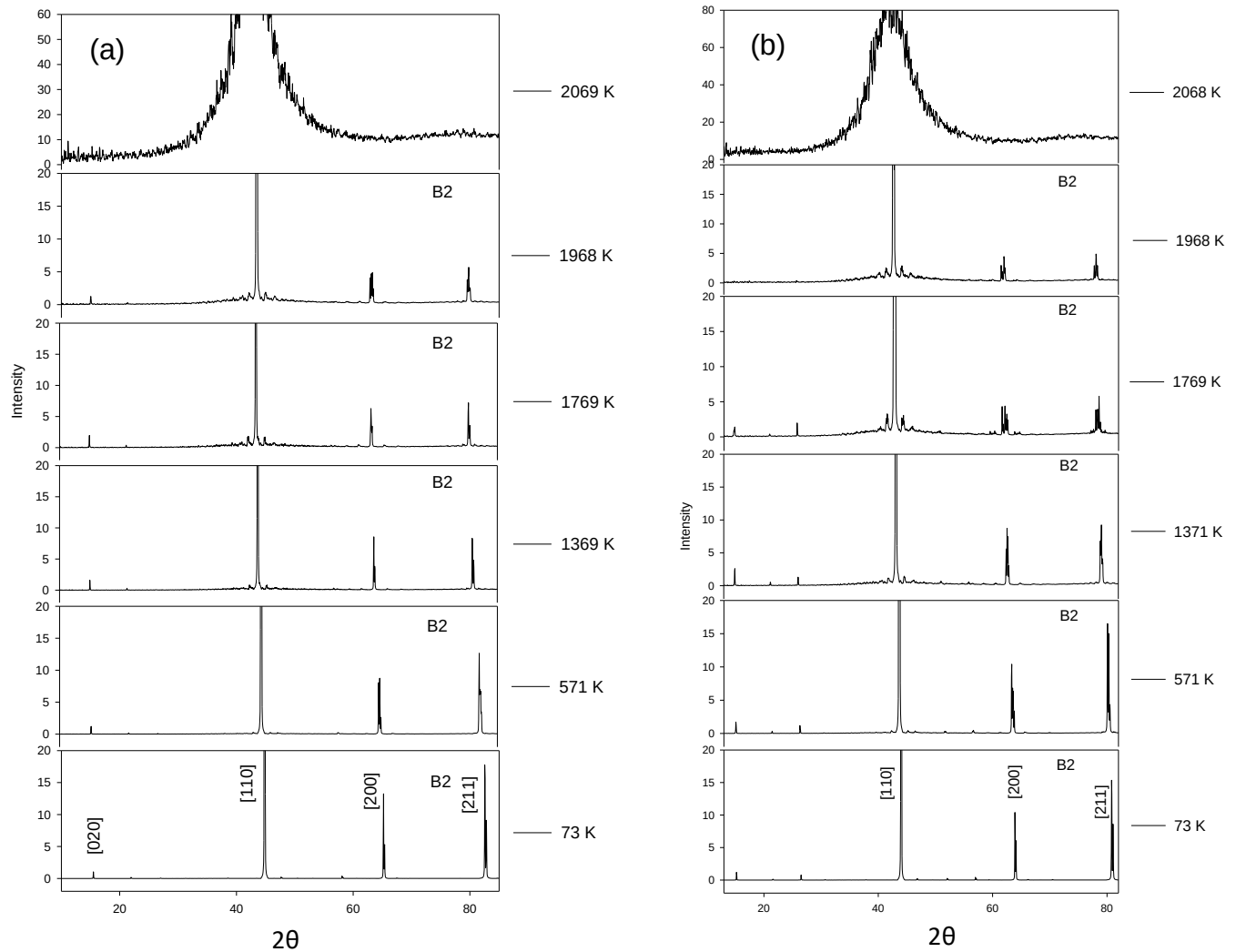


Figure 6. 14 The simulated B2 (a) $\text{Fe}_{50}\text{Co}_{43.75}\text{Ti}_{6.25}$, (b) $\text{Fe}_{50}\text{Co}_{31.25}\text{Ti}_{18.75}$ diffraction patterns from 73 to 2500 K.

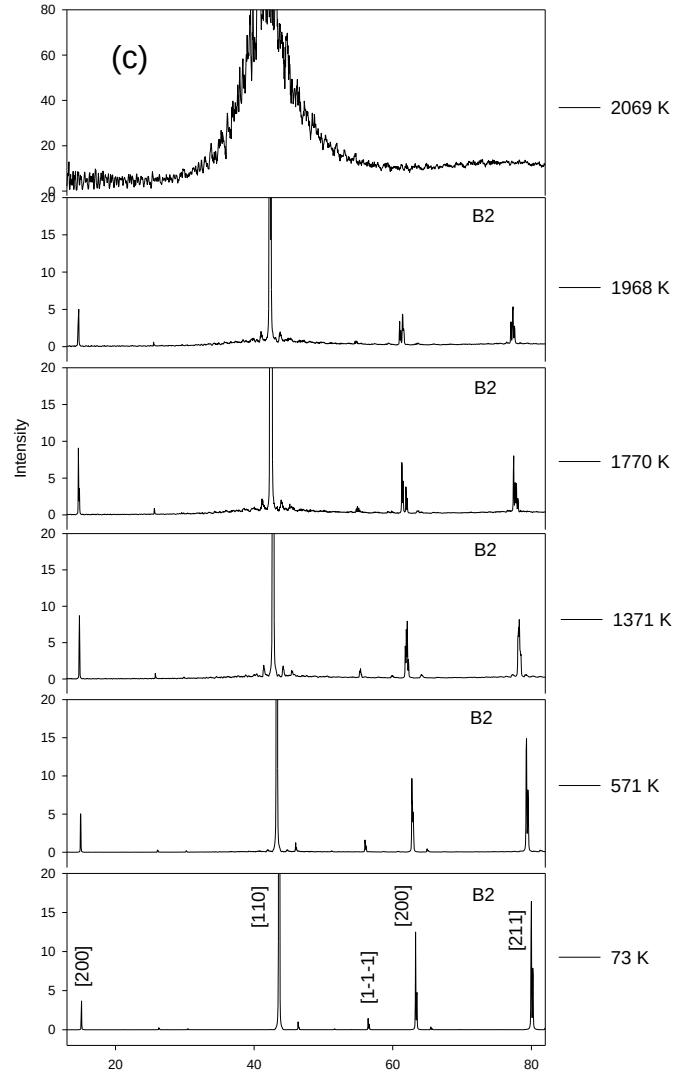


Figure 6. 15 The simulated B2 (c) $\text{Fe}_{50}\text{Co}_{25}\text{Ti}_{25}$ diffraction patterns from 73 to 2500 K.

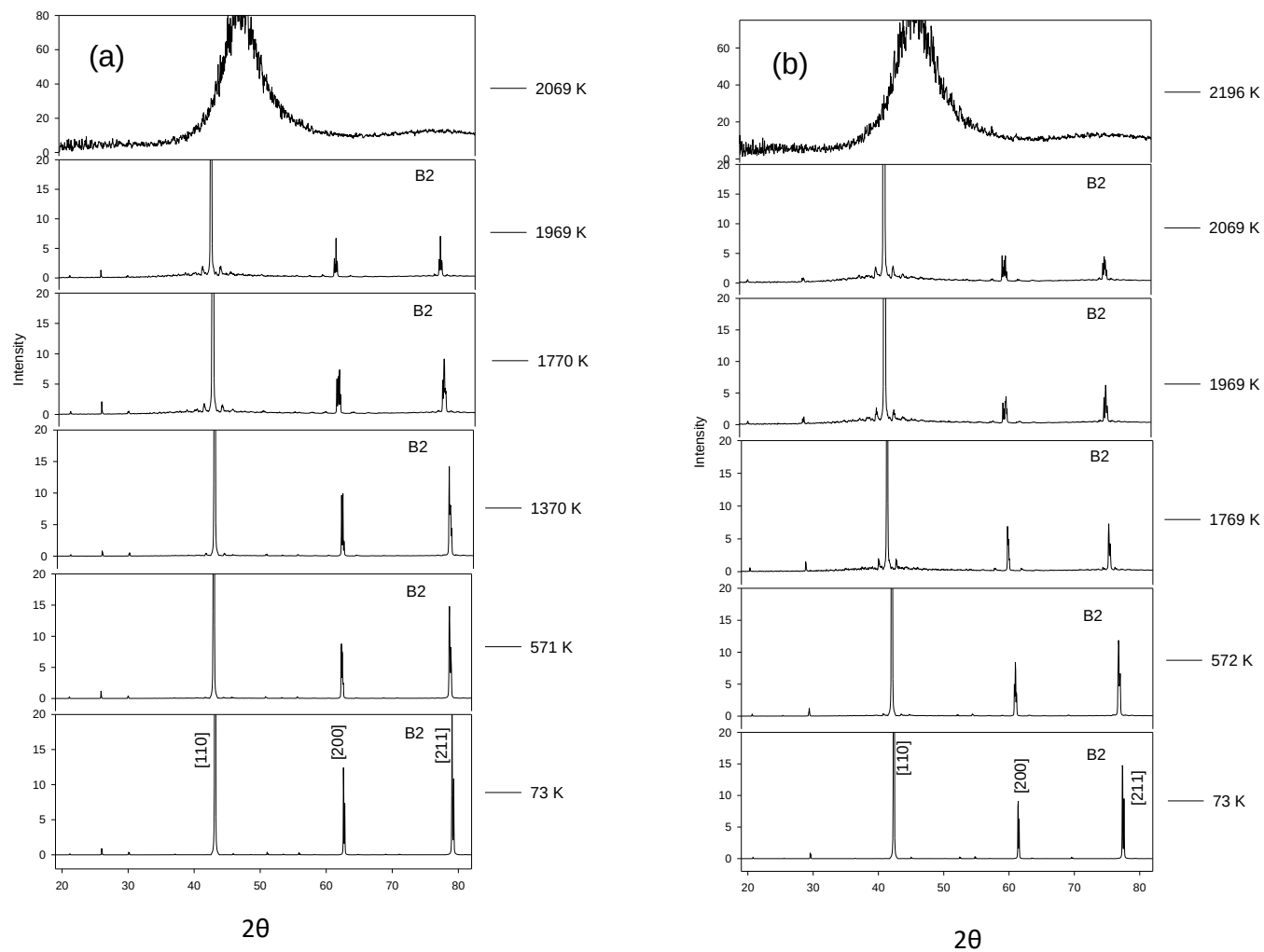


Figure 6. 20 The simulated B2 (a) $\text{Fe}_{50}\text{Co}_{18.75}\text{Ti}_{31.25}$ and (b) $\text{Fe}_{50}\text{Co}_{6.25}\text{Ti}_{43.75}$ diffraction patterns from 73 to 2500 K.

CHAPTER 7

CLUSTER EXPANSIONS AND MONTE CARLO SIMULATIONS

In this chapter, we present and discuss generated ground-state structures for both binary Fe-Co and ternary Fe-Co-M (M= Pd, V, Ti, Cr) alloys from the Universal Cluster Expansion (UNCLE) code [34]. We also discuss lattice parameters and formation energies of optimized ground-state structures for both binary and ternary systems. Furthermore, we present the temperature profile and constructed phase diagram of Fe-Co_{1-x}M_x alloys using Monte Carlo simulations [91].

7.1 Cluster expansion

The ground-state structures for both binary Fe-Co and ternary Fe-Co-M (M = Pd, V, Ti, Cr) systems were determined using UNCLE code. Note that the calculation runs until the maximum iteration is reached while adding more structures on each alteration. The procedure generates available structures with different concentrations together with their energies. To assess the predictive power of the CE, the cross-validation score (CVS) is used. The lowest CVS value (CVS<5 meV) shows a good predictive power of the CE calculation.

7.1.1 Binary cluster expansion of Fe-Co

Table 7.1 shows the number of structures and cross-validation score (CVS) for each iteration of the Fe-Co system. During full geometry optimization in the minimization stages, a VASP flowchart was used to calculate DFT total energy values with a plane

wave cut-off of 500 eV in the GGA stage and a k-spacing of 0.2 in the second minimization stage. A total of 15 new structures were generated for the binary Fe-Co system from the cluster expansion. The cluster expansion was completed at iteration 4, for which the corresponding zero (0) number of new structures, indicating that the system has converged. The CVS for the last iteration is 0.0056 meV/pos < 5 meV, this validates the precision of the cluster expansion.

The ground-state structures, and their corresponding formation energies are shown in table 7.2. The structures are all thermodynamically stable due to their negative formation energies.

Table 7. 1 The number of structures and CVS determined in the cluster expansion for the binary Fe-Co.

Iteration	No. of structures	No. of new structures	CVS (meV/pos.)
0	0	2	-
0	0	6	-
1	6	4	1.400
2	10	3	0.030
3	13	2	0.013
4	15	0	0.006

Table 7. 2 Ground-state formation energies (ΔE_f) as derived by CE for the binary Fe-Co.

Compositions	Cell formula	Space group	ΔE_f (eV/atom)
0.00	Co	Fm-3m	0.000
25.00	Fe-Co ₃	I4/mmm	-0.004
25.00	Fe-Co ₃	P4/mmm	-0.009
33.33	Fe-Co ₂	P-3m1	-0.008
33.33	Fe-Co ₂	I4/mmm	-0.014
50.00	Fe ₂ Co ₂	I4_1/amd	-0.004
50.00	Fe ₂ Co ₂	R-3m	-0.010
50.00	Fe ₂ Co ₂	P4/nmm	-0.013
66.67	Fe ₂ Co	P-3m1	-0.008
66.67	Fe ₂ Co	I4/mmm	-0.012
75.00	Fe ₃ Co	I4/mmm	-0.004
75.00	Fe ₃ Co	C2/m	-0.006
75.00	Fe ₃ Co	Pm-3m	-0.006
75.00	Fe ₃ Co	P4/mmm	-0.006
100.00	Fe	Fm-3m	0.000

The structures constituting the DFT ground-state line of the cluster expansion with their compositions and formation energies are shown in table 7.3. It is noted that the cluster expansion predicted three (3) ground-state structures i.e., Fe-Co₂, Fe₂Co₂ and Fe₂Co with negative formation energy showing thermodynamic stability. Furthermore, Fe-Co₂ (I4/mmm) is the most thermodynamically stable structure as compared to other compositions due to its lowest heats of formation ($\Delta E_f = -0.014$ eV/atom).

Table 7. 3 Lists the ground-state stable structures contained in the Fe-Co system.

Composition	Structure	ΔE_f (eV/atom)	Space group
0.00	Co	0.000	Fm-3m
33.33	Fe-Co ₂	-0.014	I4/mmm
50.00	Fe ₂ Co ₂	-0.013	P4/nmm
66.66	Fe ₂ Co	-0.012	I4/mmm
100.00	Fe	0.000	Fm-3m

Figure 7.1 shows the ground-state structures of Fe-Co. The ground-state structures are located on the red line and are considered thermodynamically stable. The five (5) structures on the DFT ground-state line are considered stable due to their negative heats of formation.

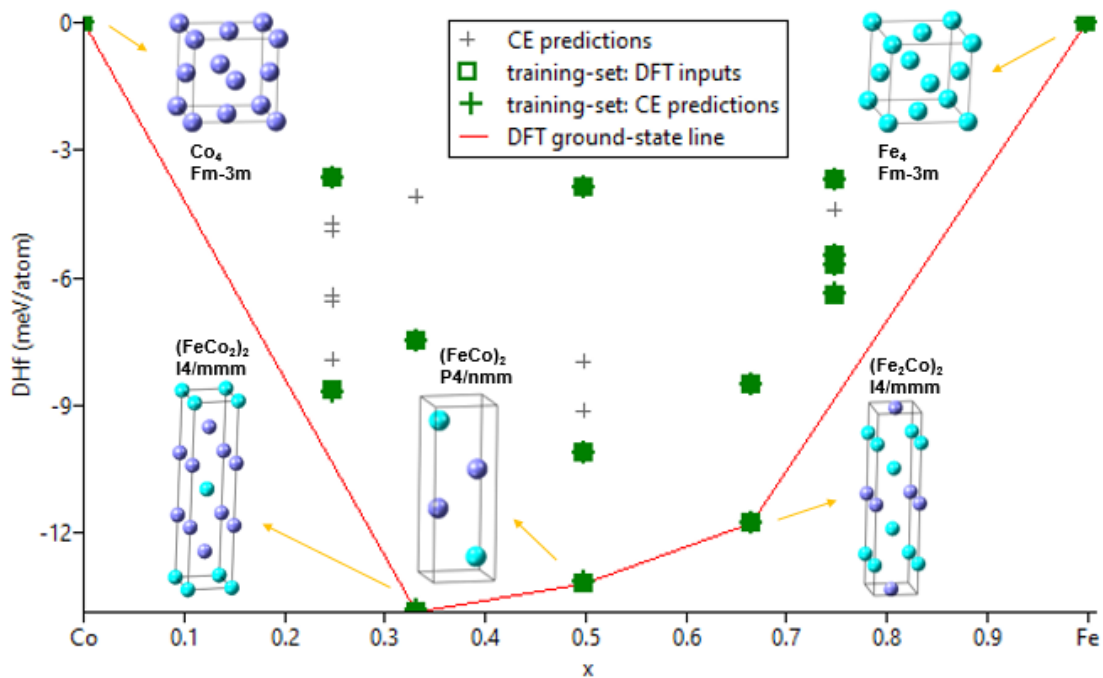


Figure 7. 1 Ground-state line of the binary B2 Fe-Co systems enthalpy of formation against concentration.

7.1.2 Ternary cluster expansion

To discover the ground-state structures for the B2 Fe-Co-M (M = Pd, V, Ti, Cr) alloys, the CE was used. In this study, to probe the effect of M addition on the Co sub-lattice of Fe-Co, ternary cluster expansion on Fe-Co_{1-x}M_x alloys is performed.

7.1.2.1 Ternary B2 Fe-Co_{1-x}Pd_x alloys

Table 7.4 shows the iterations, corresponding CVS values and the number of structures of Fe-Co_{1-x}Pd_x. Full geometry optimization was deduced in the minimization stage with the same plane wave cut-off energy and k-spacing (section 1.2). 35 new structures were produced for Fe-Co_{1-x}Pd_x. The CVS value was found to be 0.34 meV (<5) indicating a good CE prediction.

Tables 7.5 show the results of formation energies $\Delta E_f(\sigma)$ that have been used in the fitting of cluster expansion Hamiltonians Fe-Co_{1-x}Pd_x. It was found that the formation energies of the structures are positive, which implies that the generated structures are thermodynamically unstable ($\Delta E_f > 0$). It is also clear that overall, the predicted structures, only the parent phases B2 Fe-Co and B2 Fe-Pd are stable.

Table 7. 4 Show the number of structures and CVS determined in the cluster expansion for the ternary Fe-Co_{1-x}Pd_x.

Iteration	No. of structures	No. of new structures	CVS (meV/pos.)
0	0	2	-
0	0	7	-
1	7	5	3.200
2	12	3	7.700
3	15	4	3.700
4	19	3	5.100
5	22	5	4.700
6	27	3	4.100
7	30	5	0.160
8	35	0	0.340

Table 7. 5 Ground-state formation energies (ΔE_f) as derived by CE for the ternary Fe Co_{1-x}Pd_x.

Compositions	Cell formula	Space group	ΔE_f (eV/atom)
0.00	Fe-Pd	Pm-3m	0.000
25.00	Fe ₄ CoPd ₃	P4/mmm	0.131
25.00	Fe ₄ CoPd ₃	Cmmm	0.126
25.00	Fe ₄ CoPd ₃	P4/mmm	0.126
25.00	Fe ₄ CoPd ₃	Pmmm	0.125
25.00	Fe ₄ CoPd ₃	Im-3m	0.120
25.00	Fe ₄ CoPd ₃	P4/mmm	0.120
25.00	Fe ₄ CoPd ₃	I4/mmm	0.120
25.00	Fe ₄ CoPd ₃	R-3m	0.119
25.00	Fe ₄ CoPd ₃	Cmmm	0.118
33.33	Fe ₃ CoPd ₂	P4/mmm	0.160
33.33	Fe ₃ CoPd ₂	Cmmm	0.151
33.33	Fe ₃ CoPd ₂	P-3m1	0.141
50.00	Fe ₄ Co ₂ Pd ₂	P4/mmm	0.000
50.00	Fe ₂ CoPd	P4/mmm	0.188
50.00	Fe ₄ Co ₂ Pd ₂	Pmma	0.186
50.00	Fe ₄ Co ₂ Pd ₂	Cmmm	0.181
50.00	Fe ₄ Co ₂ Pd ₂	R-3m	0.180
50.00	Fe ₂ CoPd	P4/mmm	0.172
50.00	Fe ₄ Co ₂ Pd ₂	Cmcm	0.172
50.00	Fe ₄ Co ₂ Pd ₂	I4/mmm	0.167
50.00	Fe ₂ CoPd	Fm-3m	0.161
66.67	Fe ₃ Co ₂ Pd	P4/mmm	0.000
66.67	Fe ₃ Co ₂ Pd	Cmmm	0.170
66.67	Fe ₃ Co ₂ Pd	P-3m1	0.159
75.00	Fe ₄ Co ₃ Pd	P4/mmm	0.159

75.00	Fe ₄ Co ₃ Pd	P4/mmm	0.151
75.00	Fe ₄ Co ₃ Pd	Cmmm	0.151
75.00	Fe ₄ Co ₃ Pd	Pmmm	0.151
75.00	Fe ₄ Co ₃ Pd	P4/mmm	0.143
75.00	Fe ₄ Co ₃ Pd	I4/mmm	0.142
75.00	Fe ₄ Co ₃ Pd	R-3m	0.142
75.00	Fe ₄ Co ₃ Pd	Cmmm	0.141
75.00	Fe ₄ Co ₃ Pd	Im-3m	0.140
100	Fe-Co	Pm-3m	0.000

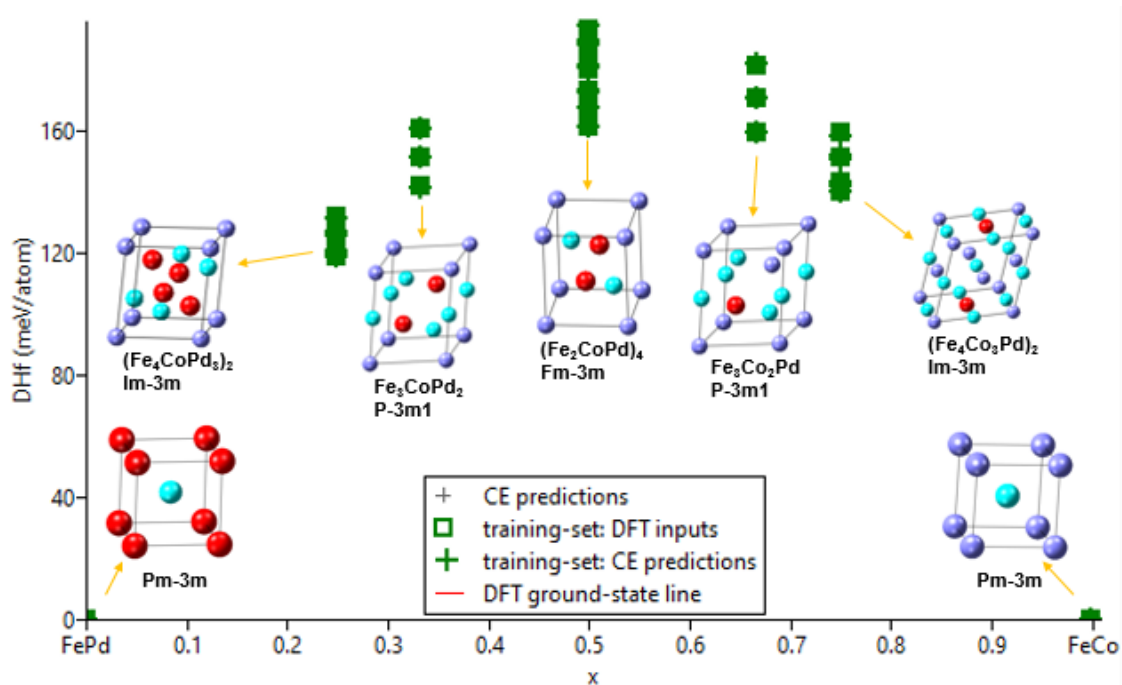


Figure 7. 2 Ground-state line of the ternary B2 Fe-Co_{1-x}Pd_x systems enthalpy of formation against Pd concentration.

7.1.2.2 Ternary B2 Fe-Co_{1-x}V_x alloys

Table 7.6 shows the iterations, number of structures and their corresponding CVS.

It is noted that the CE converged at iteration 4 with 16 structures. The CVS was found to be 0.1 meV (<5), suggesting a good fit.

Table 7. 6 Show the number of structures and CVS determined in the cluster expansion for the ternary Fe-Co_{1-x}V_x.

Iteration	No. of structures	No. of new structures	CVS (meV/pos.)
0	0	2	-
0	0	7	-
1	7	4	0.590
2	11	4	0.044
3	15	1	0.015
4	16	0	0.100

Tables 7.7 show the predicted 16 structures with their space group and formation energies of ternary Fe-Co_{1-x}V_x. The formation energies predicted by CE are all negative showing thermodynamically stability for every composition that exists in tables 7.7. It is seen that the lowest formation energies are observed for 50 at. % V VFe₂Co (P4/mmm) suggesting that the structure is the most stable as compared to other compositions.

Table 7. 7 Ground-state formation energies (ΔE_f) as derived by CE for the ternary Fe-Co_{1-x}V_x.

Compositions	Cell formula	Space group	ΔE_f (eV/atom)
0.00	VFe	Pm-3m	0.000
25.00	V ₃ Fe ₄ Co	Pmmm	-0.074
25.00	V ₃ Fe ₄ Co	R-3m	-0.085
25.00	V ₃ Fe ₄ Co	Cmmm	-0.091
25.00	V ₃ Fe ₄ Co	Im-3m	-0.161
33.33	V ₂ Fe ₃ Co	Cmmm	-0.116
33.33	V ₂ Fe ₃ Co	P-3m1	-0.124
50.00	V ₂ Fe ₄ Co ₂	Pmma	-0.056
50.00	VFe ₂ Co	Fm-3m	-0.078
50.00	VFe ₂ Co	P4/mmm	-0.167
66.67	VFe ₃ Co ₂	P4/mmm	-0.032
66.67	VFe ₃ Co ₂	Cmmm	-0.092
66.67	VFe ₃ Co ₂	P-3m1	-0.102
75.00	VFe ₄ Co ₃	I4/mmm	-0.072
75.00	VFe ₄ Co ₃	Im-3m	-0.098
100	Fe-Co	Pm-3m	0.000

Table 7.8 shows the structures constituting the DFT ground-state line, their compositions and heats of formation for Fe-Co_{1-x}V_x. The ground-state structures predicted from the ternary cluster expansions have different space groups. Due to the lowest heats of formation, the most thermodynamically stable structure is VFe₂Co.

Table 7. 8 The predicted structure constituting the DFT ground-state line with their compositions and the formation energies of Fe-Co_{1-x}V_x.

Composition	Structure	ΔE_f (eV/atom)	Space group
0.00	VFe	0.000	Pm-3m
25.00	V ₃ Fe ₄ Co	-0.161	Im-3m
50.00	VFe ₂ Co	-0.167	P4/mmm
75.00	VFe ₄ Co ₃	-0.098	Im-3m
100	Fe-Co	0.000	Pm-3m

Figure 7.3 shows the ground-state structures of Fe-Co_{1-x}V_x system. From the predicted structures five stable DFT ground-state structures are located on the ternary line. Among the stable structures, VFe₂Co was found to be the most thermodynamically stable structure due to the lowest ΔE_f value compared to other structures. The predicted structures that are not on the ground-state line are meta-stable.

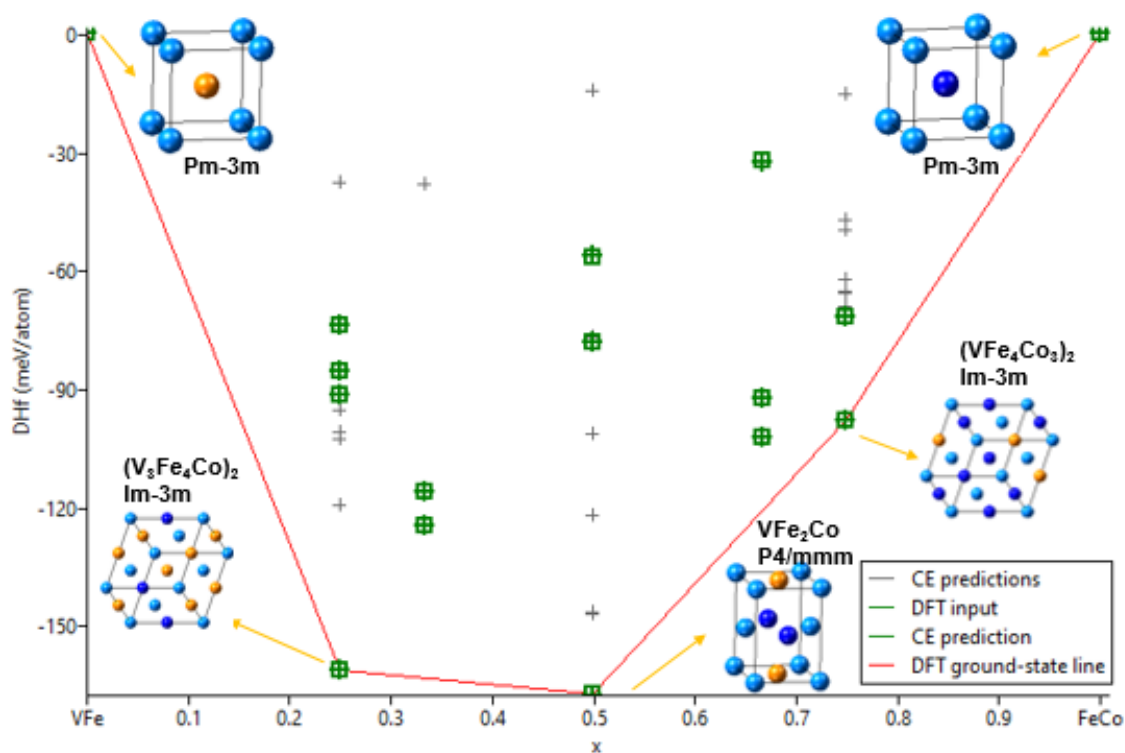


Figure 7.3 Ground-state line of the ternary B2 Fe-Co_{1-x}V_x systems enthalpy of formation against V concentration.

7.1.2.3 Ternary B2 Fe-Co_{1-x}Ti_x alloys

Table 7.9 shows the iterations, CVS and their number of structures. At iteration 8, the cluster expansion has converged with 27 structures produced for Fe-Co_{1-x}Ti_x. The CVS was found to be 4.8 meV (<5) indicating a precise fit.

Table 7. 9 Show the number of structures and CVS determined in the cluster expansion for the ternary Fe-Co_{1-x}Ti_x.

Iteration	No. of structures	No. of new structures	CVS (meV/pos.)
0	0	2	-
0	0	6	-
1	6	5	24.000
2	11	5	1.100
3	16	3	4.100
4	19	4	4.000
5	23	2	1.300
6	25	1	4.000
7	26	1	5.600
8	27	0	4.800

The predicted 27 structures with their space groups and formation energies for ternary Fe-Co_{1-x}Ti_x are shown in table 7.10. Apart from the parent phases Fe-Co and TiFe, TiFe₄Co₃ is the thermodynamically stable structure due to the negative formation energy ($\Delta E_f < 0$).

Table 7. 10 Ground-state formation energies (ΔE_f) as derived by CE for the ternary Fe-Co_{1-x}Ti_x.

Compositions	Cell formula	Space group	ΔE_f (eV/atom)
0.00	TiFe	Pm-3m	0.000
25.00	Ti ₃ Fe ₄ Co	P4/mmm	0.148
25.00	Ti ₃ Fe ₄ Co	P4/mmm	0.104
25.00	Ti ₃ Fe ₄ Co	Cmmm	0.103
25.00	Ti ₃ Fe ₄ Co	Im-3m	0.029
33.33	Ti ₂ Fe ₃ Co	Cmmm	0.223
33.33	Ti ₂ Fe ₃ Co	P4/mmm	0.192
33.33	Ti ₂ Fe ₃ Co	P-3m1	0.105
50.00	TiFe ₂ Co	P4/mmm	0.215
50.00	Ti ₂ Fe ₄ Co ₂	P4/mmm	0.167
50.00	TiFe ₂ Co	Fm-3m	0.136
50.00	Ti ₂ Fe ₄ Co ₂	Pmma	0.135
50.00	Ti ₂ Fe ₄ Co ₂	Cmmm	0.086
50.00	Ti ₂ Fe ₄ Co ₂	Cmcm	0.072
50.00	Ti ₂ Fe ₄ Co ₂	I4/mmm	0.075
50.00	TiFe ₂ Co	P4/mmm	0.016
66.67	TiFe ₃ Co ₂	P4/mmm	0.168
66.67	TiFe ₃ Co ₂	P-3m1	0.050
75.00	TiFe ₄ Co ₃	P4/mmm	0.118
75.00	TiFe ₄ Co ₃	P4/mmm	0.105
75.00	TiFe ₄ Co ₃	Cmmm	0.098
75.00	TiFe ₄ Co ₃	P4/mmm	0.073
75.00	TiFe ₄ Co ₃	I4/mmm	0.060
75.00	TiFe ₄ Co ₃	R-3m	0.059
75.00	TiFe ₄ Co ₃	Cmmm	0.027
75.00	TiFe ₄ Co ₃	Im-3m	-0.006

100	Fe-Co	Pm-3m	0.000
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Tables 7.11 show the structures constituting the DFT ground-state line, their compositions and heats of formation for Fe-Co_{1-x}Ti_x. The ground-state structures predicted from the ternary cluster expansions have independent space groups. It was found that TiFe₄Co₃ is the most thermodynamically stable structure due to the lowest energy of formation.

Table 7. 11 The predicted structure constituting the DFT ground-state line with their compositions and the formation energies of Fe-Co_{1-x}Ti_x.

Composition	Structure	ΔE_f (eV/atom)	Space group
0.00	TiFe	0.000	Pm-3m
75.00	TiFe ₄ Co ₃	-0.008	Im-3m
100	Fe-Co	0.000	Pm-3m

The ground-state structures of Fe-Co_{1-x}Ti_x are shown in figure 7.4. Three (3) structures are located on the ground-state line and (TiFe₄Co₂)₂ is the most stable structure.

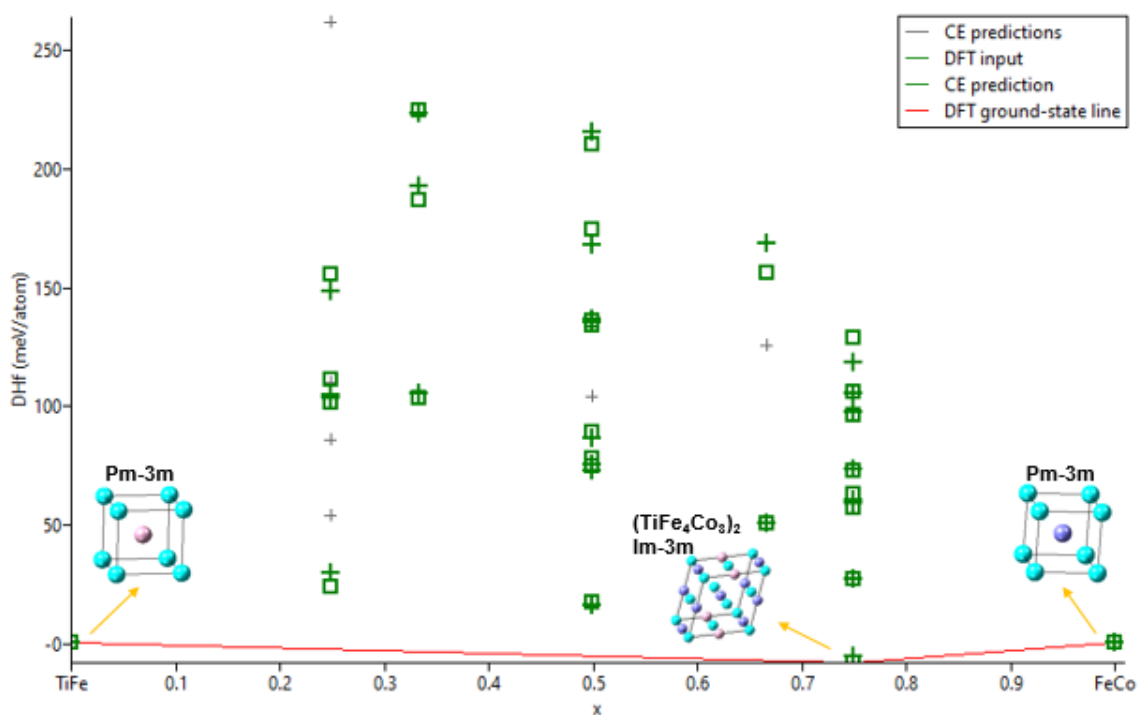


Figure 7. 4 Ground-state line of the ternary B2 Fe-Co_{1-x}Ti_x systems enthalpy of formation against Ti concentration.

7.1.2.4 Ternary B2 Fe-Co_{1-x}Cr_x alloys

The iterations, number of structures and their corresponding CVS are shown in table 7.12. The cluster expansions converged at iteration 3 as there are no new structures. There are 13 structures produced by CE for Fe-Co_{1-x}Cr_x. Furthermore, the CVS was found to be 0.041 meV (<5) showing a good fit.

Table 7. 12 Shows the number of structures and CVS determined in the cluster expansion for the ternary Fe-Co_{1-x}Cr_x.

Iteration	No. of structures	No. of new structures	CVS (meV/pos.)
0	0	2	-
0	0	6	-
1	6	5	12.000
2	11	2	0.220
3	13	0	0.041

Table 7.13 shows the predicted 13 structures with their space groups and formation energies for ternary Fe-Co_{1-x}Cr_x. The formation energies predicted by CE are negative showing thermodynamically stability for every composition that exists. It is seen that the lowest formation energy is observed for 50 at. % Cr (Cr₂Fe₄Co₂) with a space group of I4/mmm suggesting that the structure is the most stable as compared to other compositions.

Table 7. 13 Ground-state formation energies (ΔE_f) as derived by CE for the ternary Fe-Co_{1-x}Cr_x.

Compositions	Cell formula	Space group	ΔE_f (eV/atom)
0.00	CrFe	Pm-3m	0.000
25.00	Cr ₃ Fe ₄ Co	Pmmm	-0.079
25.00	Cr ₃ Fe ₄ Co	I4/mmm	-0.123
25.00	Cr ₃ Fe ₄ Co	Im-3m	-0.136
33.33	Cr ₂ Fe ₃ Co	P-3m1	-0.157
50.00	Cr ₂ Fe ₄ Co ₂	Pmma	-0.080
50.00	Cr ₂ Fe ₄ Co ₂	Cmmm	-0.129
50.00	CrFe ₂ Co	Fm-3m	-0.169
50.00	Cr ₂ Fe ₄ Co ₂	I4/mmm	-0.172
66.67	CrFe ₃ Co ₂	P-3m1	-0.128
75.00	CrFe ₄ Co ₃	Im-3m	-0.098
75.00	CrFe ₄ Co ₃	I4/mmm	-0.101
100	Fe-Co	Pm-3m	0.000

The structures constituting the DFT ground-state line, compositions and formation energies for Fe-Co_{1-x}Cr_x are shown in table 7.14. It is seen that the ground-state structures predicted from the ternary cluster expansions have different space groups. Similarly, to table 7.13, the most thermodynamically stable structure is Cr₂Fe₄Co₂ for Fe-Co_{1-x}Cr_x.

Table 7. 14 The predicted structure constituting the DFT ground-state line with their compositions and the formation energies of Fe-Co_{1-x}Cr_x.

Composition	Structure	ΔE_f (eV/atom)	Space group
0.00	CrFe	0.000	Pm-3m
25.00	Cr ₃ Fe ₄ Co	-0.136	Im-3m
33.33	Cr ₂ Fe ₃ Co	-0.157	P-3m1
50.00	Cr ₂ Fe ₄ Co ₂	-0.172	I4/mmm
66.67	CrFe ₃ Co ₂	-0.128	P-3m1
75.00	CrFe ₄ Co ₃	-0.102	I4/mmm
100	Fe-Co	0.000	Pm-3m

Figure 7.5 summarizes the ground-state structures of Fe-Co_{1-x}Cr_x. These results give the available structures of ternary B2 Fe-Co-Cr with Cr being substituted on the Co side of the alloy. There are seven structures on the ground-state line with negative formation energies indicating thermodynamic stability. Amongst the structures (CrFe₂Co)₂ is the most thermodynamically stable structure for Fe-Co_{1-x}Cr_x, with the lowest formation energy (-0.172 eV/atom).

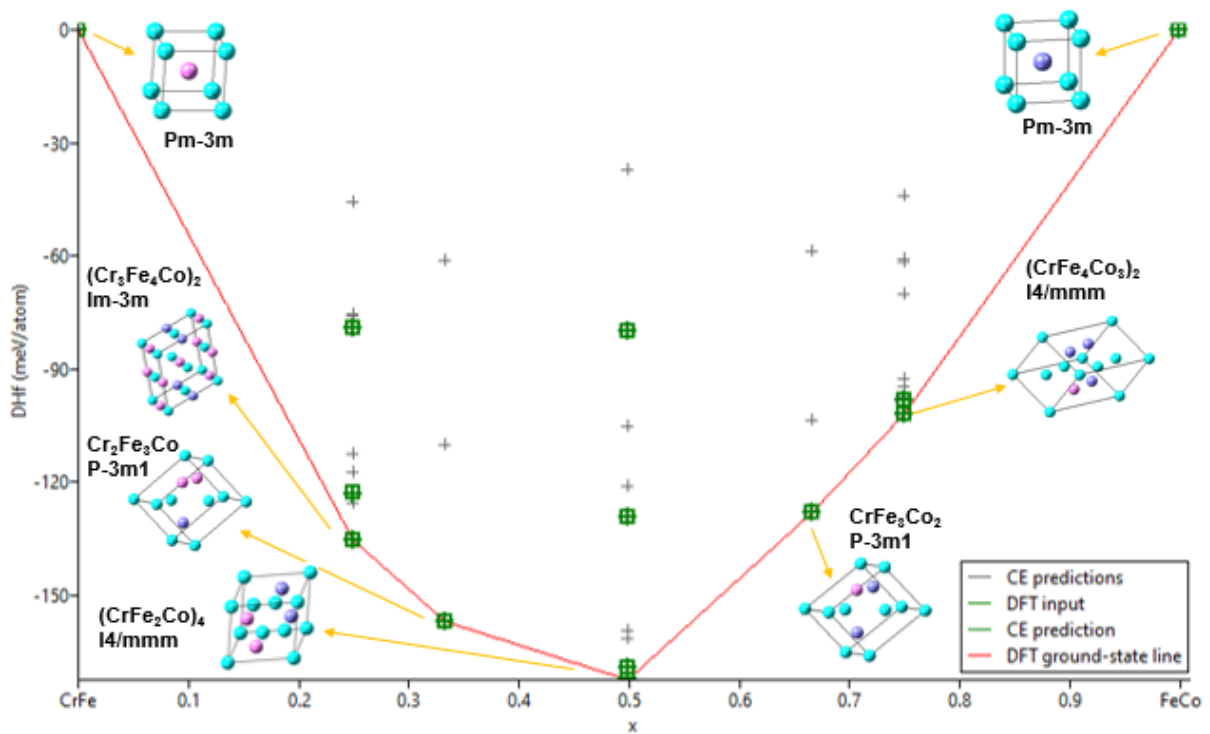


Figure 7. 5 Ground-state line of the ternary B2 Fe-Co_{1-x}Cr_x systems enthalpy of formation against V concentration.

7.1.3 Summary of optimized ground-state structures from cluster expansion

The structural, thermodynamic and magnetic properties of Fe-Co_{1-x}Pd_x are shown in table 7.15. Full geometry optimization was performed on the ground-state structures which are the parent phases Fe-Pd and Fe-Co. It is observed that the heats of formation for the structures are negative indicating thermodynamic stability and Fe-Pd is more stable than Fe-Co. It was found that the structures have positive magnetic moments indicating good magnetic strength. The Fe-Co structure is more magnetic with the highest magnetic moment (4.530 μ_B) and the values compare well with previous work to within 1%.

Table 7. 15 The predicted lattice parameters, heats of formation and magnetic moments of B2 Fe-Co_{1-x}Pd_x alloys.

Structure	Space group	a(Å)	b(Å)	c(Å)	ΔH_f (eV/atom)	Magnetic moment (μ_B)
Fe-Pd	Pm-3m	2.966	2.966	2.966	-0.064	0.001
Fe-Co	Pm-3m	2.841	2.841	2.841 (2.84 [87], 2.86 [90])	-0.057	4.530 (4.479 [88])

For the Fe-Co_{1-x}V_x system, we assess the structural and thermodynamic ground-state properties. This is to further study the effect of V addition on the Co sub-lattice. Full geometry optimization was performed on the structures by allowing both the shape and lattice constant to change. We only focus on the ground-state structures namely; VFe, V₃Fe₄Co, VFe₂Co, VFe₄Co₃ and Fe-Co since they are the stable structures from the ground-state line.

The space groups, equilibrium lattice parameters, heats of formation and magnetic moments for Fe-Co_{1-x}V_x are given in table 7. 16. The binary systems Fe-Co gave the equilibrium lattice parameter 2.841 Å (2.843 Å [91]). It can be noted that the result obtained compares well with the experimental value to within 0.07 %.

The heats of formation were determined to confirm the thermodynamic stability of the structures. For a structure to be stable, the heat of formation value should be negative otherwise a positive value implies instability. It is observed that the heats of formation for the structures are negative indicating thermodynamic stability. The

most stable structure is predicted to be the VFe₂Co with the lowest heat of formation (-0.222 eV/atom). Moreover, the predicted stability trend according to the calculated ΔH_f deduced from the cluster expansions is as follows:

$$\text{VFe} > \text{VFe}_2\text{Co} > \text{V}_3\text{Fe}_4\text{Co} > \text{VFe}_4\text{Co}_3 > \text{Fe-Co}.$$

To further investigate the stability of the optimized ground-state structures from cluster expansion, we calculated the magnetic moments. Magnetic moments were calculated to check the magnetic strength of the structures. It was found that the structures have positive magnetic moments showing good magnetic strength. The VFe₂Co structure is more magnetic with the highest magnetic moment (3.898 μB).

Table 7. 16 The predicted lattice parameters, heats of formation and magnetic moments of B2 Fe-Co_{1-x}V_x alloys.

Structure	Space group	a(Å)	b(Å)	c(Å)	ΔH_f (eV/atom)	Magnetic moment (μB)
VFe	Pm-3m	2.870	2.870	2.870	-0.330	0.807
(V ₃ Fe ₄ Co) ₂	Im-3m	2.822	2.822	2.822	-0.201	0.001
VFe ₂ Co	P4/mmm	3.882	3.882	3.052	-0.222	3.898
(VFe ₄ Co ₃) ₂	Im-3m	2.850	2.850	2.850	-0.164	0,832
Fe-Co	Pm-3m	2.841	2.841	2.841	-0.057	4.530

Table 7. 17 shows the space groups, equilibrium lattice parameters, heats of formation and magnetic moments for Fe-Co_{1-x}Ti_x. From the results, a good magnetic strength was observed on the structures due to positive magnetic moments. However, TiFe has a poor magnetic moment (0.000 μB) indicating poor magnetic

strength. The Fe-Co structure is more magnetic with the highest magnetic moment (4.530 μB).

Table 7. 17 The predicted lattice parameters, heats of formation and magnetic moments of B2 Fe-Co_{1-x}Ti_x alloys.

Structure	Space group	a(Å)	b(Å)	c(Å)	ΔH_f (eV/atom)	Magnetic moment (μB)
TiFe	Pm-3m	2.946	2.946	2.946	-0.000	0.000
(TiFe ₄ Co ₃) ₂	Im-3m	2.870	2.870	2.870	-0.008	0.850
Fe-Co	Pm-3m	2.841	2.841	2.841	-0.000	4.530

The space groups, equilibrium lattice parameters, heats of formation and magnetic moments for Fe-Co_{1-x}Cr_x are shown in table 7. 18. This is to further study the effect of Cr addition on the Co sub-lattice of Fe-Co. The magnetic moments of the structures are positive showing good magnetic strength. Higher magnetic strength is observed on the CrFe₃Co₂ structure with the highest magnetic moment (1,645 μB).

Table 7. 18 The predicted lattice parameters, heats of formation and magnetic moments of B2 Fe-Co_{1-x}Cr_x alloys.

Structure	Space group	a(Å)	b(Å)	c(Å)	ΔH_f (eV/atom)	Magnetic moment (μ_B)
CrFe	Pm-3m	2.820	2.820	2.820	0.000	1.899
(Cr ₃ Fe ₄ Co) ₂	Im-3m	2.827	2.827	2.827	-0.136	0,585
Cr ₂ Fe ₃ Co	P-3m1	2.002	2.002	2.456	-0.157	1,233
(CrFe ₂ Co) ₄	I4/mmm	2.005	2.005	5.647	-0.172	0,677
CrFe ₃ Co ₂	P-3m1	2.006	2.006	2.460	-0.129	1,645
(CrFe ₄ Co ₃) ₂	I4/mmm	2.001	2.001	5.673	-0.102	0,846
Fe-Co	Pm-3m	2.841	2.841	2.841	0.000	4.530

7.2 Monte Carlo simulations for ternary alloys

Monte Carlo simulations were carried out to study the mixing of the Fe-Co_{1-x}M_x (M = Pd, V, Ti, Cr) ternary alloys. Monte Carlo simulations were carried out employing the UNCLE code. In these simulations, the canonical ensemble was used to determine the critical temperatures. Unit cells of 25x25x25 atoms were used to avoid boundary effects. The alloying elements stabilize the Fe-Co system at small composition (6.25 at. %) (as discussed in Chapter 4), we ranged the concentration for Monte Carlo simulations at $0.02 \leq x \leq 0.1$. This was done to cover the supercell composition i.e., 6.25 at. % as the magnetic strength is compromised above.

7.2.1 MC for B2 Fe-Co_{1-x}Pd_x

Figure 7. 6 shows temperature profiles of Fe-Co_{1-x}Pd_x alloys at various concentrations ($0.02 \leq x \leq 0.1$). For the entire concentration range, we observe that with increasing temperature the energy differences between atoms also increase but become constant from a certain temperature. The phase separations occur at lower temperatures for all concentrations and with increasing energy differences the systems start to mix at higher critical temperatures.

At $x = 0.02$, the system mix well at 600 K and as Pd content increases to $x = 0.04$ it mixes 800 K. Moreover, with further increasing of Pd concentration to $x = 0.06$ and $x = 0.0625$, we observe that the temperatures for which systems mix well are the same temperature (1000 K). This is because the concentrations do not differ much. Lastly, on $x = 0.1$, the alloy mixes at a higher temperature (1200 K) compared to other concentrations.

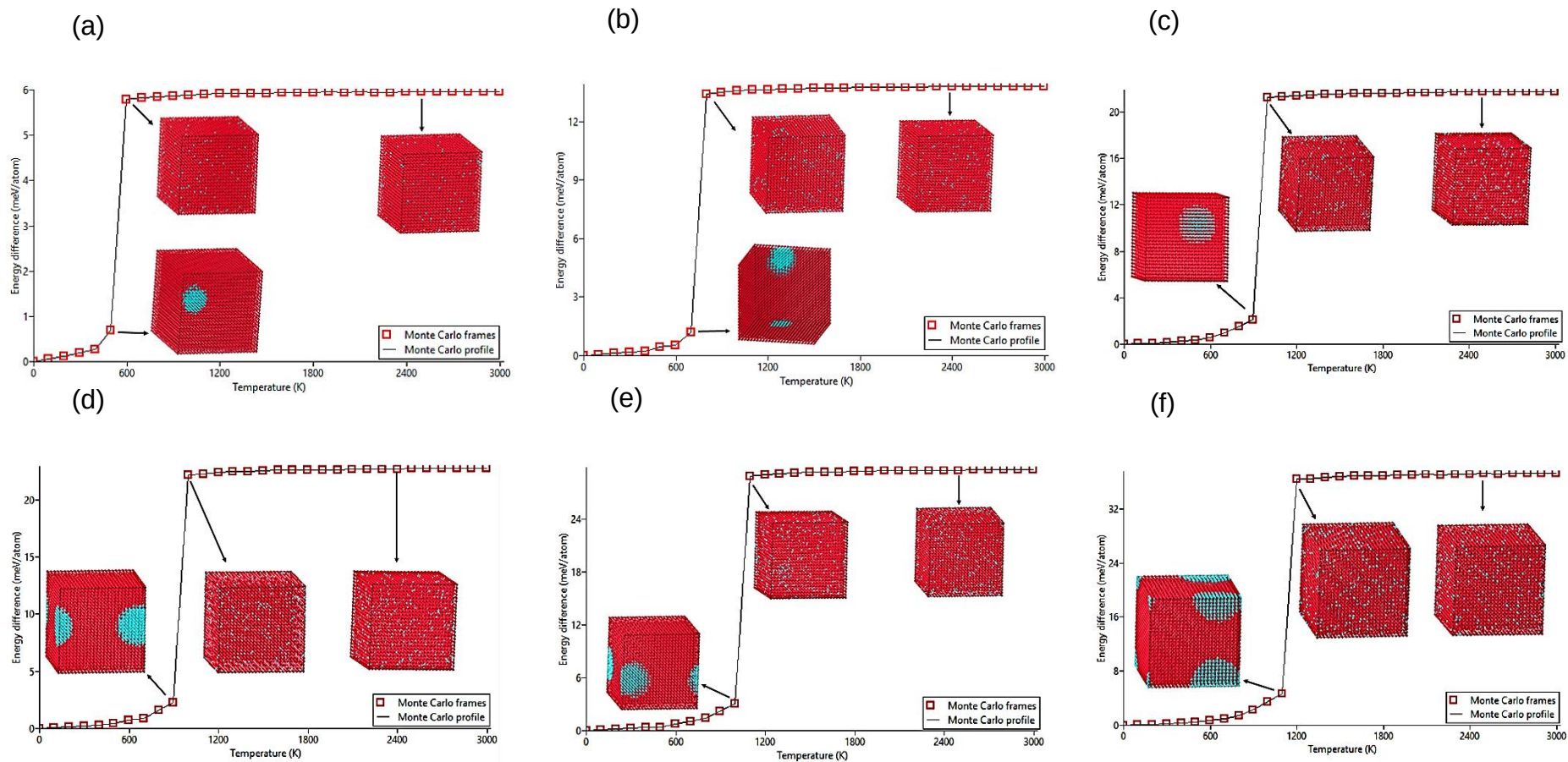


Figure 7. 6 Temperatures Monte Carlo profiles of B2 Fe-Co-Pd at different concentrations (a) Fe-Co_{0.98}Pd_{0.02}, (b) Fe-Co_{0.96}Pd_{0.04}, (c) Fe-Co_{0.94}Pd_{0.06}, (d) Fe-Co_{0.92}Pd_{0.08} (e) Fe-Co_{0.9375}Pd_{0.0625}, (f) Fe-Co_{0.9}Pd_{0.1}.

7.2.2 MC for B2 Fe-Co_{1-x}V_x

Figure 7. 7 shows temperature profiles of Fe-Co_{1-x}V_x alloys at various concentrations ($0.02 \leq x \leq 0.1$). The phase separations occur at lower temperatures and with increasing energy differences the systems start to mix at higher critical temperatures.

It was found that at $x = 0.02$, the atoms in the system separate at 0 K to 600 K and mix well at 650 K. In the case of $x = 0.04$ and $x = 0.06$ the systems start to mix at 800 K and 900 K, respectively. Similar to Fe-Co_{0.9375}Pd_{0.0625}, the Fe-Co_{0.9375}V_{0.0625} system mix well at 1000 K. The Fe-Co_{0.9}V_{0.1} alloy mix at a higher temperature (1200 K) compared to other concentrations.

7.2.3 MC for B2 Fe-Co_{1-x}Ti_x

Figure 7. 8 represent temperature profiles of Fe-Co_{1-x}Ti_x alloys at various concentrations ($0.02 \leq x \leq 0.1$). Compared to the systems of Fe-Co_{1-x}Pd_x and Fe-Co_{1-x}V_x discussed earlier. It was found that at $x = 0.02$ concentration of Ti, the system mixes well at a high temperature above 1600 K. At $x = 0.04$ and 0.1, the mixing occurs at 3000 K and 4000 K, respectively. It was found that mixing occurs at higher temperatures for Fe-Co_{1-x}Ti_x compared to other elements. This is because Ti melts at a higher temperature (1941 K).

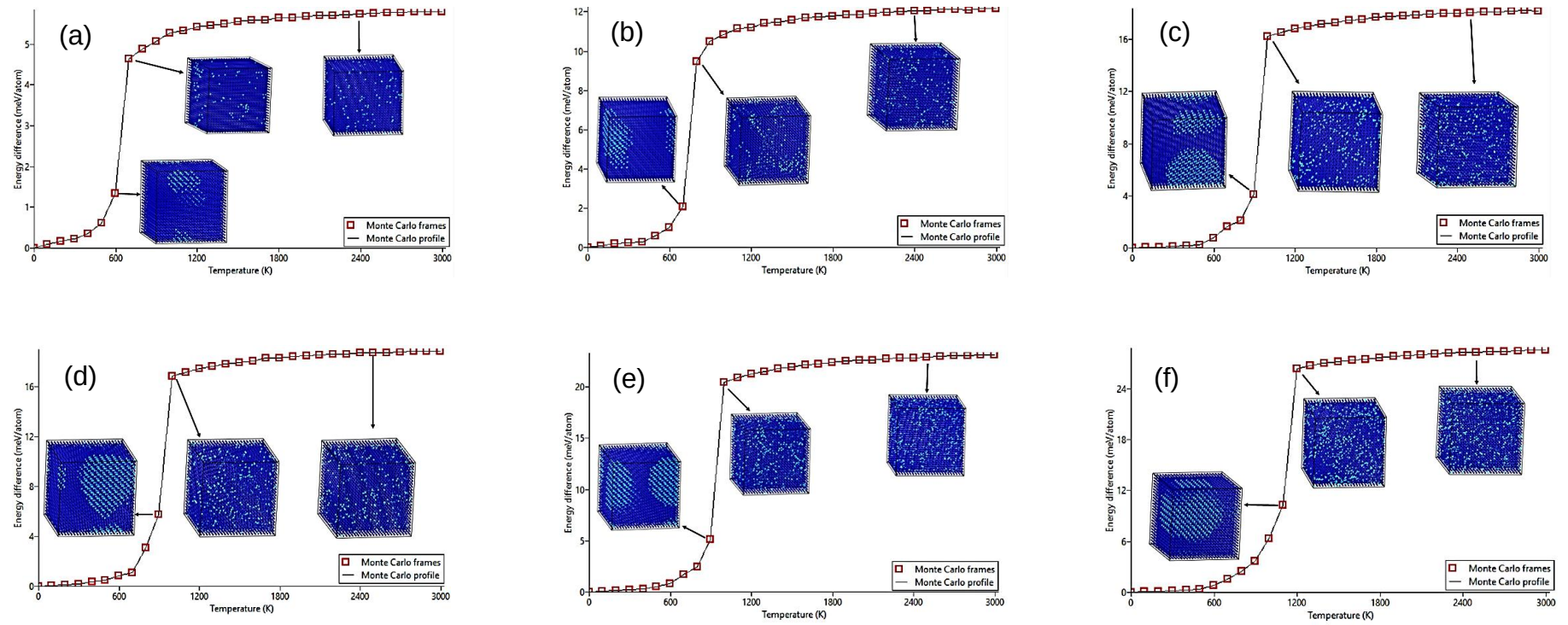


Figure 7. 7 Temperatures Monte Carlo profiles of B2 Fe-Co-V at different concentrations (a) Fe-Co_{0.98}V_{0.02}, (b) Fe-Co_{0.96}V_{0.04}, (c) Fe-Co_{0.94}V_{0.06}, (d) Fe-Co_{0.92}V_{0.08} (e) Fe-Co_{0.9375}V_{0.0625}, (f) Fe-Co_{0.9}V_{0.1}.

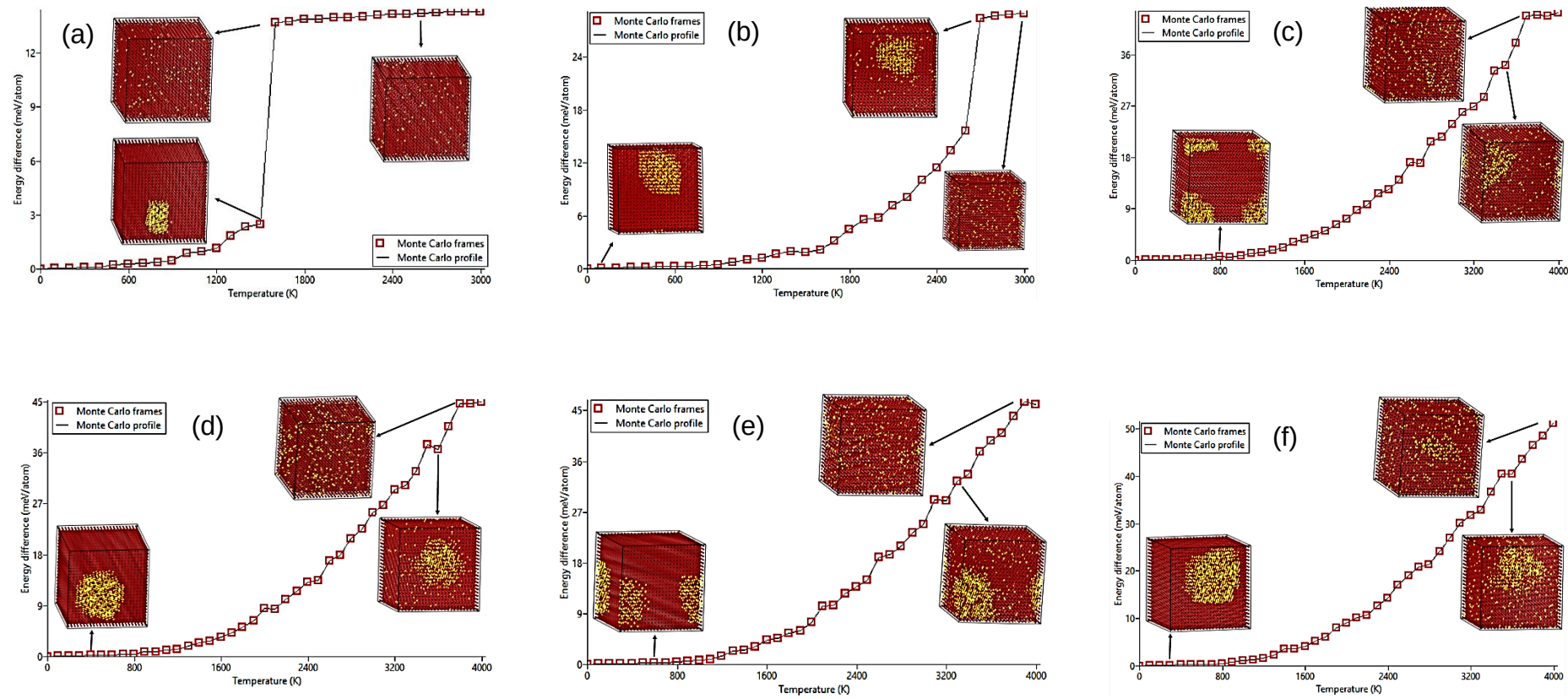


Figure 7. 8 Temperatures Monte Carlo profiles of B2 Fe-Co-Ti at different concentrations (a) Fe-Co_{0.98}Ti_{0.02}, (b) Fe-Co_{0.96}Ti_{0.04}, (c) Fe-Co_{0.94}Ti_{0.06}, (d) Fe-Co_{0.92}Ti_{0.08} (e) Fe-Co_{0.9375}Ti_{0.0625}, (f) Fe-Co_{0.9}Ti_{0.1}.

7.2.4 MC for B2 Fe-Co_{1-x}Cr_x

Figure 7. 9 shows temperature profiles of Fe-Co_{1-x}Cr_x alloys at various concentrations ($0.02 \leq x \leq 0.1$). At $x = 0.02$ the system mixes well at a very low temperature (100 K). As the concentration is increased to $x = 0.04$, the mixing occurs at 200 K. The mixing at $x = 0.06$ occurs at 250 K and at $x = 0.0625$ the mixing occurs at 200 K. At $x = 0.08$ and 0.1 the systems mix at 200 K and 300K, respectively. This observation reveals that the working temperatures of these alloys are low. Unfortunately, there is no previous work to compare.

7.2.5 Phase diagram of Fe-Co_{1-x}M_x ternary alloys

Figure 7.10 shows a generated phase diagram of ternary Fe-Co_{1-x}M_x alloys (M = Pd, V, Ti, Cr). The phase diagram was constructed using the critical temperatures deduced from temperature profiles. Critical temperature can be observed where there is a zero slope on the graph. Ternary alloys of Fe-Co_{1-x}Pd_x and Fe-Co_{1-x}V_x have similar mixing temperatures and this may be attributed to the closeness of their atomic radii which is 1.69 Å and 1.71 Å for Pd and V, respectively. Fe-Co_{1-x}Ti_x systems mix at higher temperatures compared to other elements.

Moreover, Fe-Co_{1-x}Cr_x systems demonstrated lower mixing temperatures compared to other alloys and for this reason, we deduce that Cr is a better element in terms of mixing. Similar to the magnetic moments results discussed in Chapter 4, the 0.0625 concentration is the best, the composition does not take time or high temperatures to mix well.

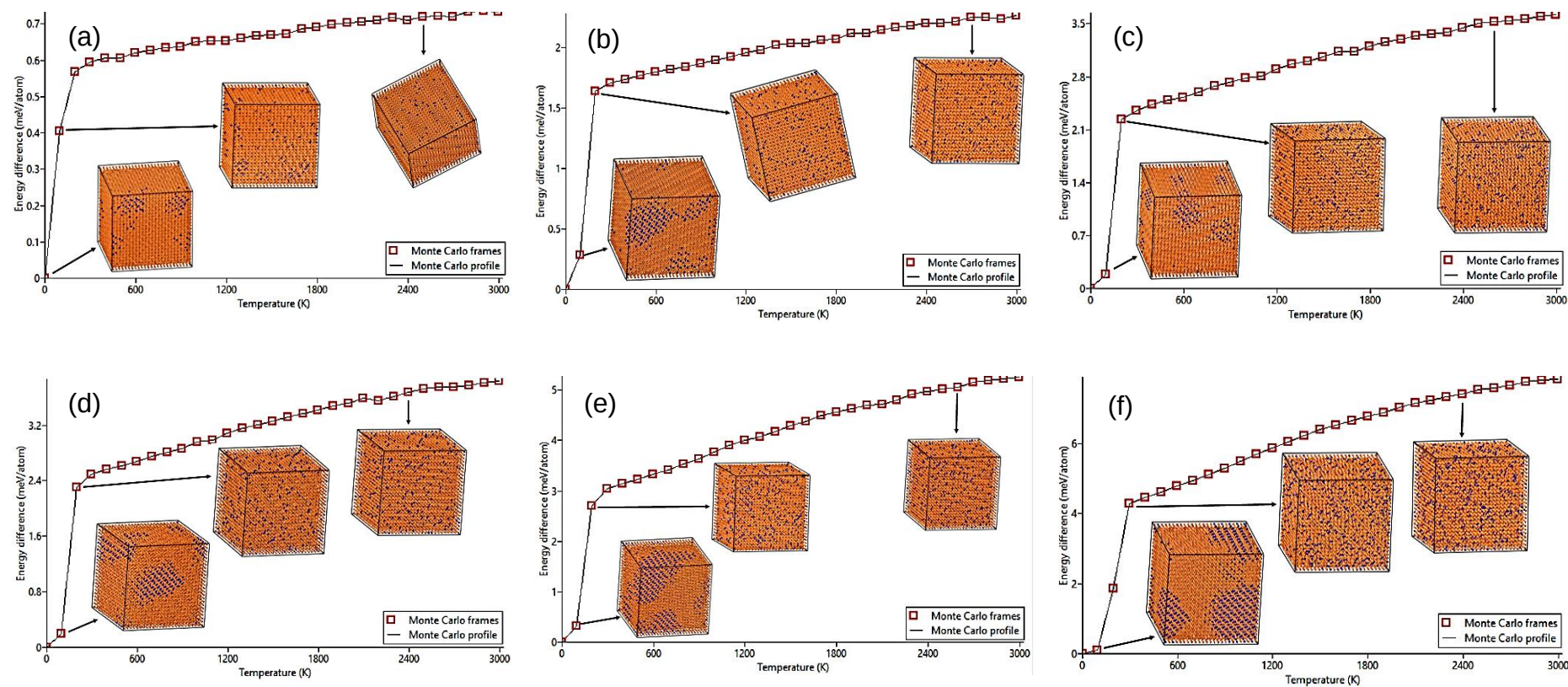


Figure 7. 9 Temperatures Monte Carlo profiles of B2 Fe-Co-Cr at different concentrations (a) Fe-Co_{0.98}Cr_{0.02}, (b) Fe-Co_{0.96}Cr_{0.04}, (c) Fe-Co_{0.94}Cr_{0.06}, (d) Fe-Co_{0.92}Cr_{0.08} (e) Fe-Co_{0.9375}Cr_{0.0625}, (f) Fe-Co_{0.9}Cr_{0.1}.

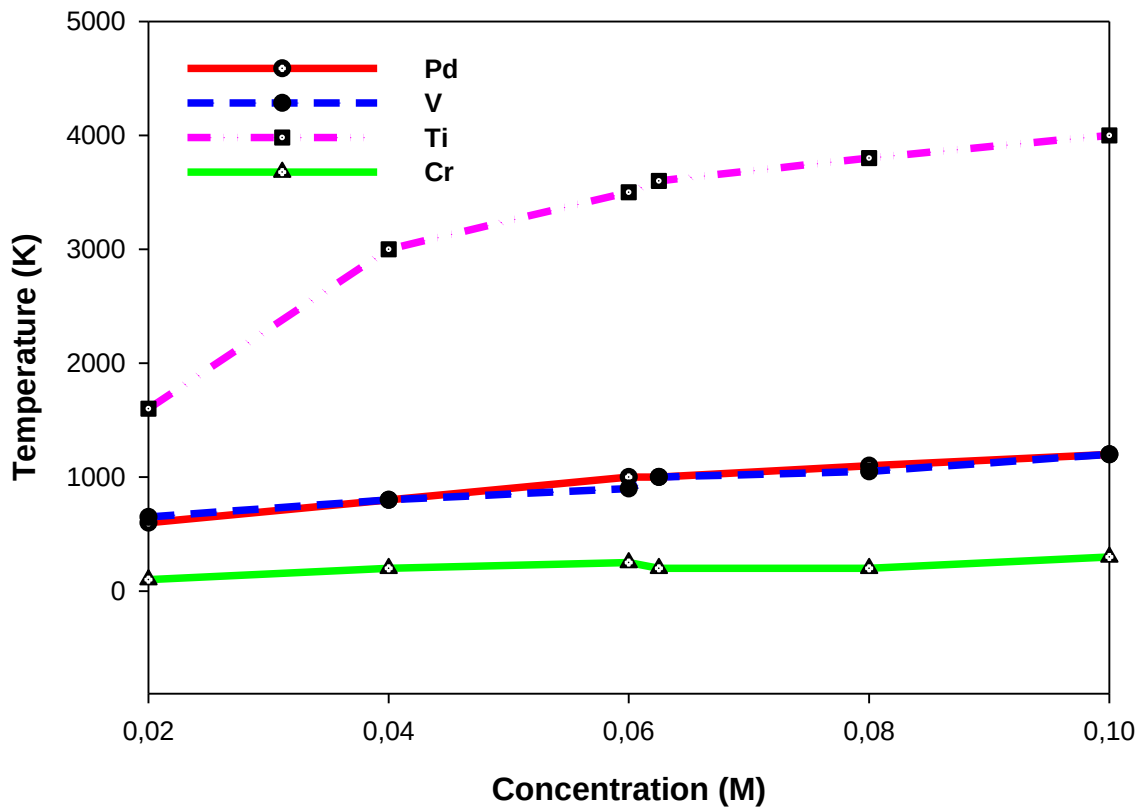


Figure 7. 10 Constructed phase diagram of Fe-Co_{1-x}M_x (M = Pd, V, Ti, Cr) alloys using phase transition temperature at different concentrations.

CHAPTER 8

SUMMARY AND CONCLUSIONS

In this chapter, we present a summary of the study and give a conclusion on the results obtained. In addition, recommendations for future work are specified.

FeCo alloys constitute an important class of soft magnetic materials with a wide range of technological applications. This class of materials offers exceptional magnetic properties due to their rare combination of good properties like high mechanical strength, high permeability and high saturation magnetization. Fortunately, this alloy has good magnetic properties, but they show low levels of ductility at room temperature. This study intends to use computational methods, to understand how ternary alloying with Pd, V, Ti and Cr can improve the ductility and stability of B2 FeCo system. Furthermore, the study will also investigate how ternary alloying may affect the structural, magnetic, mechanical and thermodynamic properties of the B2 FeCo alloy.

The study employed the ab initio density functional theory (DFT) to explore the stability of binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ ($\text{M} = \text{Pd}, \text{V}, \text{Ti}, \text{Cr}$) alloys. The additions of the dopants on $\text{Fe}_{50}\text{Co}_{50}$ alloy were performed using the supercell approach and different compositions (6.25, 18.75, 25, 31.25, 43.75 and 50) were evaluated. A LAMMPS code was utilized to determine the effect of temperature on the lattice parameters and XRDs of both binary B2 $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys. Furthermore, the Cluster expansion and Monte Carlo simulations were

used to generate new stable phases and prediction of ternary phase diagrams, respectively.

In chapter 4, the lattice parameters, heats of formation and magnetic moments were studied to investigate the ground-state properties and magnetic properties of the structures. The lattice parameter of the B2 Fe₅₀Co₅₀ was found to fairly agree with previous experimental and theoretical data to within 2%. The lattice parameters of B2 Fe₅₀Co_{50-x}M_x (M = Pd, V, Ti) increase with an increase in M compositions, this is due to the large atomic radii of M compared to that of Co. Heats of formation were used to deduce the thermodynamic stability of the binary and ternary systems. The calculated heats of formation for the binary B2 Fe₅₀Co₅₀ was found to be in good agreement with previous theoretical and experimental results to within 1%. Thermodynamically, the results suggested that the addition of the V, Ti, and Cr stabilizes the FeCo alloy due to a decrease in heats of formation with an increase in composition. It was revealed that a smaller concentration of Pd (<10 at. %) is required to improve the thermodynamic stability of B2 FeCo, otherwise, the thermodynamic stability reduces at higher compositions. Furthermore, It was found that the calculated magnetic moment of the binary Fe₅₀Co₅₀ alloy agrees very well with that of previous theoretical work to within 2%. In the case of ternary alloying, it was noted that the dopants V, Ti and Cr compromise the magnetism of B2 FeCo. However, the reduction is minimal with Pd addition, this suggest that Pd does not temper with the magnetic strength of the B2 FeCo alloy that much and it is worth for further experimental investigations.

The mechanical properties were evaluated from the elastic constants, anisotropy and elastic moduli as presented in chapter 5. It was found that the mechanical stability conditions ($C' > 0$) are satisfied for the entire concentrations of $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys, in good agreement with the phonon dispersion curves. From the bulk and young moduli, it was observed that high concentrations of Pd enhances the ability to resist deformation for the B2 FeCo magnetic alloy. It was also revealed that higher concentrations (>25 at. %) of V and Cr as ternary elements can affect the ability to resist elastic and shear deformation in the B2 FeCo alloy. To measure the ductility of both binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ systems, Poisson's ratio, Pugh ratio (B/G) and Cauchy pressure were determined. The ductility is enhanced with an increase in Pd, V, Ti and Cr compositions for the entire concentration range. The phonon dispersion curves were studied to examine the vibrational properties of the systems. It was revealed that the addition of Pd (>10 at. %) causes vibrational instability.

In chapter 6, the LAMMPS code was used to determine the phase transformation temperature of binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys. It was found that Pd and Ti addition resulted in no transformation since there were no changes in lattice parameters. The XRD patterns for the binary $\text{Fe}_{50}\text{Co}_{50}$ were comparable with those in the literature. In the case of ternary, the XRD patterns confirmed the melting temperature of 2200 K which was also confirmed by their lattice expansions.

The cluster expansion method was used to generate new stable structures as detailed in chapter 7. All the structures displayed negative heats of formation,

showing no tendency of phase separations for both systems. Three new ground-state structures were generated from Fe-Co, where $(\text{FeCo}_2)_2$ p4/nmm was found to be the most stable structure due to the lowest heats of formation. There are no new stable structures for $\text{FeCo}_{1-x}\text{Pd}_x$ apart from the parent phases FeCo, FePd and PdCo (Pm-3m). The cluster expansion of $\text{FeCo}_{1-x}\text{V}_x$ generated three new ground-state systems ($\text{V}_3\text{Fe}_4\text{Co}$, VFe_2Co and VFe_4Co_3). The VFe_2Co (p4/mmm) structure is the most thermodynamically stable phase. Furthermore, $\text{FeCo}_{1-x}\text{Ti}_x$ and $\text{FeCo}_{1-x}\text{Cr}_x$ generated one structure ($\text{Fe}_8\text{Co}_6\text{Ti}_2$, Im-3m) and five ground-state structures (figure 7.5), respectively. The $(\text{CrFe}_2\text{Co})_4$ I4/mmm structure was found to be the most thermodynamically stable phase with the lowest heats of formation (-0.172 eV/atom). Lastly, Monte Carlo simulations was utilized to construct ternary phase diagrams of Fe- $\text{Co}_{1-x}\text{M}_x$ (M = Pd, V, Ti, Cr). The structures were predicted to mix at 1000K for Fe- $\text{Co}_{1-x}\text{M}_x$ (M= Pd and V). While Fe- $\text{Co}_{1-x}\text{Ti}_x$ and Fe- $\text{Co}_{1-x}\text{Cr}_x$ structures mix at 3800 K and 200 K, respectively.

The multi-scale methods were successfully used to study the stability and transformation behavior of binary $\text{Fe}_{50}\text{Co}_{50}$ and ternary $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ systems. This study revealed that Pd, V, Ti and Cr have the potential to improve the ductility of the B2 FeCo alloy. The findings suggest that $\text{Fe}_{50}\text{Co}_{50-x}\text{M}_x$ alloys can be used for the future development of magnetic components with good strength.

APPENDIX A

Publications, Awards and Presentations at the Conferences

A. Presentations at conferences

1. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke, “The effects of Ti addition on the stability of B2 Fe-Co: a computational study”, South African Institute of Physics Conference (SAIP-2021), 22-30 July 2021, Interactive Virtual Conference.
2. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke, “Mechanical and magnetic properties of B2 Fe₅₀Co_{50-x}Cr_x alloys”, 11th Faculty of Science and Agriculture Research Day, 06-08 October 2021, Bolivia Lodge, Polokwane, South Africa.
3. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke, “Structural and stability of B2 Fe_{1-x}CoV_x and Fe-Co_{1-x}V_x systems: Cluster expansion approach” Conference of the South African Advanced Materials Initiative (CoSAaMi-2021), 18-22 October 2021, Interactive Virtual Conference.
4. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke, “The effect of V content on the magnetic and mechanical properties of B2 Fe-Co alloy: a DFT approach”, 15th Centre for High Performance Computing National (CHPC) Conference, 1-3 December 2021, Interactive Virtual Conference.
5. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke “Magnetic and Mechanical properties in Mn-doped B2 FeCo soft magnetic material” 12th

Faculty of Science and Agriculture Research Day, 21-23 September 2022,
Bolivia Lodge, Polokwane, South Africa.

B. Awards

- Award for Poster Presentation, Second Place Masters Category. The 2021 CHPC National Conference.
- Best oral presenter, 3rd place master's category. The 12th Faculty of Science and Agriculture Research Day, 2022.

C. Publications

- i. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke, "Effect of Ti content on the magnetic and mechanical properties of B2 Fe-Co alloy: a DFT study," *SAIP2021 Proceedings*, pp. 636-643, 2021.
- ii. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke "Structural and stability of B2 Fe-Co_{1-x}V_x and Fe_{1-x}CoV_x systems: Cluster expansion approach", *South African Journal of Science and Technology*, vol. 40, pp. 98-101, 2021.
- iii. T. M. Ledwaba, R. G. Diale, P. E. Ngoepe and H. R. Chauke "Computational studies of structural, mechanical and magnetic properties of the B2-phase Fe₅₀Co_{50-x}Cr_x soft magnetic alloys" (to be published).

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