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DESIGN OF NI-BASE SUPERALLOYS AND MCrAlY COATINGS FROM FIRST-PRINCIPLES AND COMPUTATIONAL THERMODYNAMICS

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Abstract

This thesis explores the thermodynamics of Ni-base superalloys and metallic coatings used in the protection of these alloys. Due to the large design space in composition and temperature for many new superalloys and coatings, trial-and-error methodologies of the past prove ineffective and costly. All mechanical or corrosion properties for superalloys depend heavily on the processing and the resulting phases. Multi-component alloys often contain a gamut of phases, many of which are actually detrimental to the alloy. This problem is exacerbated with the addition of refractory transition metals such as Nb, Re, and W to improve mechanical properties. However, computational phase diagram studies for the constituent systems have proven successful for the prediction of detrimental phases in superalloys. Unfortunately, some of the constituent systems have not been examined in detail, one of which is the Nb-Re binary system.

First, a thermodynamic description of the Nb–Re binary system is developed by means of the CALculation of PHAse Diagrams (CALPHAD) method supplemented by first-principles calculations based on density functional theory (DFT) and experimental data in the literature. In addition to terminal solution phases in the Nb-Re system, there are two intermetallic phases, sigma (σ) and chi (χ), all modeled with sublattice models. Special quasi-random structures (SQS) are employed to mimic the random mixing of the bcc, hcp, and fcc solid solution phases from first-principles. Finite temperature thermodynamic properties of end-members and dilute mixing in each sublattice of the complex σ and χ phases are predicted from first-principles calculations and the Debye-Grüneisen model. The calculated phase diagram agrees well with selected experimental phase equilibrium data in the literature.
The utility of the Debye-Grüneisen model is then investigated with respect to its fitting parameter known as the scaling factor, and it is found that the prediction of finite-temperature properties can be improved by modification of this factor. This scaling factor is studied using bcc, fcc, hcp systems and the Mg-Zn binary system due to the abundance of thermodynamic data. Predicted Debye temperatures ($\theta_D$), using a calculated scaling factor, show good agreement with experiments and improvements over the scaling factor derived by Moruzzi et al. Finite-temperature thermodynamic properties of intermetallics are investigated to show the efficiency and improved accuracy of the calculated scaling factor. However, for the intermetallic Mg$_2$Zn$_{11}$, the Debye-Grüneisen model cannot account for anomalous lattice dynamics at low temperatures. The calculated scaling factor is then used throughout the present work for finite-temperature predictions.

Another missing piece of the literature includes the thermodynamics of Al-Co-Cr-Ni bond coat system used in the protection of superalloys. First, it is found that there is an incomplete description of the crucial ternary Al-Co-Cr subsystem. As a result, the phase relations and thermodynamic properties of this system are investigated using first-principles calculations based on DFT and phase-equilibria experiments that led to X-ray diffraction (XRD) and electron probe microanalysis (EPMA) measurements. A thermodynamic description is developed by means of the CALPHAD method using experimental and computational data from the present work and the literature. Emphasis is placed on modeling the bcc-A2, B2, fcc-$\gamma$, and $\sigma$ phases in the temperature range of 1173 to 1623 K. Liquid, bcc-A2 and fcc-$\gamma$ phases are modeled using substitutional solution descriptions. First-principles SQS calculations predict a large bcc-A2 (disordered)/B2 (ordered) miscibility gap, in agreement with experiments. A partitioning model is then used for the A2/B2 phase to effectively describe the order-disorder transitions. The critically assessed
thermodynamic description describes all phase equilibria data well. A2/B2 transitions are also shown to agree well with previous experimental findings.

In order to build a correct quaternary description of the Al-Co-Cr-Ni system, additional ternaries must also be modeled to combine with the Al-Co-Cr system. The phase relations and thermodynamic properties of the Al-Co-Ni and Co-Cr-Ni ternary alloys are investigated using first-principles calculations based on DFT. Thermodynamic descriptions are developed by means of the CALPHAD method using experimental and computational data from the present work and the literature. In addition to the phases found in the Al-Co-Cr system, the ordered fcc-γ phase, L\textsubscript{12}-γ’, is taken into account. A partitioning model is used again for the A2/B2 phase to effectively describe the order-disorder transitions when coupled with the Al-Co-Cr system. The thermodynamic description describes all phase equilibria data well. The Al-Co-Cr, Al-Co-Ni, and Co-Cr-Ni systems are combined with the Al-Cr-Ni system from Dupin et al. [1] to produce a complete Al-Co-Cr-Ni thermodynamic model. Predictions are shown to agree well with experimental alloys from collaborators. It is shown that by critically assessing each of the ternary subsystems, a full quaternary description can be developed successfully with minimal use of excess thermodynamic parameters.

This thesis also studies the stability of interfaces that form in Ni-base superalloys during microstructure evolution processes. Understanding the coarsening of superalloy microstructures during processing or service requires the knowledge of the stabilities of solid-solid interfaces. As a result, the technologically important \{100\} coherent γ/γ’ interface is investigated using first-principles calculations. The change in the interfacial energy of the Ni-Al γ/γ’ coherent interface when a ternary element is segregated near the interface is studied. Binary calculations are performed to validate previous results; it is predicted that the Ni-Al γ/γ’ interfacial energy is 19
mJ/m² at 0 K which is in agreement with the literature. When a ternary element is added into the system and partitions to the γ phase, the interfacial energy can vary between 4-28 mJ/m². It is found that the additions of the Mo, Re, and W elements can decrease the interfacial energy significantly to 4-5 mJ/m² while the additions of the Ru and Pt elements can increase it to 25-28 mJ/m². When elements reside in γ, magnetic ordering contributions at the interface are shown to have the greatest effect on the change in the interfacial energy. Ferromagnetic elements Co and Fe are shown to have little effect on the interfacial energy as they do not disrupt magnetic spin across the interface. All ternary additions to γ’ are shown to increase the interfacial energy except for Pt, which decreases it to 16 mJ/m². Otherwise, ternary additions in γ’ can vary the interfacial energies between 20-37 mJ/m².

Overall, a fundamental understanding of the thermodynamics relevant to Ni-base superalloys and coatings is developed using first-principles and CALPHAD approaches.
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1 Introduction

1.1 Motivation of work

*Nickel-base superalloys:*

In 1929, Beford, Pilling, and Merica patented small additions of Al and Ti to an austenitic nickel-chromium (“80/20”) alloy, which gave this corrosion-resistant alloy high-temperature creep strengthening; thus the superalloy was born. Interestingly, it was not until decades later that the strengthening precipitate in this alloy was found [2]. In the broad definition, nickel-base superalloys are Ni-rich alloys often containing more than 10 alloying elements tailored for use in high temperature, mechanically demanding and corrosive environments. Their resistance to deformation and corrosion at 60-70 % of their melting temperatures (600-900 °C) enable use in various propulsion and power generation applications [3]. These highly desirable properties result from the complex microstructures formed during processing: coherent γ (gamma) and γ’ (gamma prime) in most superalloys and γ” (gamma double prime) in a small group of alloys [3]. The γ phase consists of the face-centered cubic (fcc) solid solution comprising mainly of 3d transition metals (Ni, Co, Cr, Fe) and 4d/5d refractory elements (Nb, Mo, W, Re, Ru). In lattice coherency (discussed later) with γ is the ordered cubic phase γ’ comprising mainly of intermetallic forming metals (Al, Ti, Ta) [3], [4]. Deviations from the ideal microstructure of small coherent γ’ (up to a few hundred nm in size) dispersed evenly in the γ becomes detrimental in the performance of the alloy. Expectedly, during service at high temperatures, coarsening/growth of γ’ occurs in single-crystal type superalloys and degrades performance [5].
Protection of Ni-base superalloys

The oxidation and corrosion resistance of superalloys rely heavily on the presence of Al and Cr in the alloy to form adherent oxide layers on the surface [6]. However, the push for higher operating conditions in gas turbines requires the design of extremely high-melting single-crystal superalloys that often have low Al and Cr contents [3], contradicting the first statement. Low-melting Al decreases the overall solidus temperature of the alloy and Cr forms detrimental phases such as σ (sigma) [7]. Solutions to this problem include metallic and ceramic coatings designed specifically for weathering oxidation and corrosion conditions [3], [8]. Overlay MCrAlY (M=Ni, Co or NiCo) coatings (bond coats) are widely used for this purpose, either solely or in conjunction with a thermally insulating ceramic topcoat, most commonly yttria-stabilized zirconia (YSZ), then forming a thermal barrier coating (TBC) system [9]–[12]. As seen in Figure 1.1, the metallic bond coat sits atop the superalloy substrate with a thermally grown oxide (TGO) residing below the YSZ topcoat.

M-Cr-Al-Y overlay coatings

CoCrAlY alloys containing 20-40 wt. % Cr, 12-20 wt. % Al and minor Y were proven successful as corrosion resistance coatings in the 1970s [13]. Since then, various new additions have come along, including NiCrAlY, CoNiCrAlY, and NiCoCrAlY types that all vary widely in composition, as seen in Figure 1.2. High Cr contents give exceptional corrosion resistance while NiCrAlY (low/no Co) alloys are great for oxidation. More recently, minor constituents such as Si, Ta, and Hf have also proven to aid in oxidation and corrosion resistance [13]. Overlay coatings differ from diffusion coatings as they do not strictly depend on the substrate compositions for
performance, and thus can be tailored for a balance of oxidation and corrosion resistance. As a result, many compositions include both Co and Ni, giving rise to CoNiCrAlY and NiCoCrAlY alloys. The oxidation, corrosion, and mechanical properties of MCrAlY coatings depend heavily on the thermodynamic stabilities of favorable phases present in the alloy at service temperatures, and are affected by reactions with the environment, as selective oxidation removes Al in the subsurface, and also by interdiffusion with the substrate material, which is driven by differences in chemical potentials between the two components. Maintenance of an Al-rich β (B2) and a soft matrix γ (Ni,Co,Cr) proves key in the performance of MCrAlY coatings. Degradation can also arise from the formation of TCPs such as σ when depletion of other elements occur. Currently, most MCrAlY thermal stability studies have been approached from experiments coupled with thermodynamic models designed for Ni-base superalloys with low Co contents [13], [14]. Hence, there lacks, in the literature, a systematic computational and experimental study of many MCrAlY compositions. Additionally, given the wide composition ranges seen in Figure 1.2 and the service temperatures present (600-950 °C), it would time and cost prohibitive to examine every type of coating alloy experimentally.

This work will focus on investigating the overall phase stability of the important phases in overlay MCrAlY coatings. Computational materials science approaches will be taken for each section. Prediction of thermodynamic properties rely on fundamental first-principles calculations based on Density Functional Theory (DFT). Parameterization of these fundamental properties and validation to experimental measurements depend on the CALculation of PHAse Diagrams (CALPHAD) method. The effectiveness of combining DFT and CALPHAD methods will be proven for the systems shown in the present work. Overall, the current work will produce a fundamental understanding of the thermodynamics of MCrAlY alloys.
1.2 Objectives

*Phase stabilities:*

Information about phase stabilities is especially important for superalloys and their bond coat systems due to huge gradients in operating temperatures. Phases present in the alloys must be stable from sub-zero up to engine temperatures exceeding over 1000°C. Of the many phases present in superalloys, γ and γ’ are the most important. For coatings, B2-β is desired over γ’ due to the higher Al content. However, these alloy systems also contain a gamut of detrimental topologically close-packed phases (TCPs) [15]. The suppression of such phases has been approached from both empirical and theoretical points of view. One method that implements both theoretical and experimental data is CALculation of PHAse Diagram (CALPHAD). This method has been employed by both industry and academia as a replacement for traditional expensive trial-and-error metallurgy [16]. The CALPHAD method allows metallurgists to investigate a wealth of information about a particular alloy or phase before processing. One can predict the formation of unwanted phases, such as TCPs, based on thermodynamic assessments of the constitutional systems. Elements found in superalloys and coatings, such as Ni, Al, Co, Cr, etc. are evaluated for their binary, ternary and even quaternary interactions with each other based on thermodynamic data. It is then imperative to construct the databases necessary for accurate predictions. The construction of the databases starts at the binary level where interactions between two elements are assessed in great detail to produce a computational phase diagram. Thermochemical data such as the enthalpy of formation or heat capacity as well as phase equilibria data such as phase boundaries are taken from either experiments or computational predictions. Such inputs are critically assessed via the CALPHAD method to produce the final model of the system.
For both superalloys and their coatings, some critical binary and ternary systems for phase predictions remain un-modeled. Modeling of these systems, such as Nb-Re, require thermochemical data that is often unavailable. This is also true for the Al-Co-Cr-Ni coating system, as the Al-Co-Cr system has not previously been assessed thermodynamically. An accurate thermodynamic description of Al-Co-Cr will enable more reliable predictions of phase formation in bond coat systems. Finite temperature data, such as the heat capacity of different Nb-Re and Al-Co-Cr alloys, are not available experimentally, but can be predicted using quantum mechanics-based methods coupled with the Debye-Grueneisen model for use in CALPHAD modeling.

Interfaces:

Before discussing the importance of studying crystallographic interfaces in Ni-base superalloys, coarsening must be introduced. Coarsening can both beneficially and detrimentally change the microstructural features of an alloy. During processing and heat treatment, fine γ’ precipitates out of the γ matrix and can coarsen to form larger γ’; this is beneficial in strengthening the alloy. Under operating conditions, the strengthening γ’ precipitates coalesce to form even larger precipitates that are raft-like in structure. Ultimately, the rafts compromise the mechanical stability of the alloy [5]. The coarsening process is controlled kinetically by the diffusion of elemental species near the matrix (γ) – precipitate (γ’) interface (γ/γ’) and thermodynamically by the energetics of the interface and the bulk. This current research, coupled with previous work done on diffusivities of elemental species in γ and γ’, will attempt to shed light on ternary element effects on coarsening in the Al-Ni system.
This completed thesis will consist of the following main tasks:

1. Using first-principles and the CALPHAD methods to investigate the thermodynamics of the following systems, as they lack critical experimental thermochemical data and require first-principle predictions:
   a. Nb-Re pertaining to TCP formation in superalloys
   b. Al-Co-Cr-Ni pertaining to bond coats with the following subsystems:
      i. Al-Co-Cr
      ii. Al-Co-Ni
      iii. Co-Cr-Ni

2. Improved predictions of finite-temperature thermodynamic properties of condensed phases by assessment of the average speeds of sound used in the current Debye-Grüneisen model. First-principles calculations is used to calculate elastic compliance matrices that are then used to predict the average speeds of sound. This technique is used to predict important thermodynamic properties for the Nb-Re and Ni-Co-Cr-Al systems.

3. Using first-principles to study the coherent interface between the two most important phases of Ni-base superalloys, γ and γ’. This study is then extended to a ternary system Ni-Al-X where X is a dilute addition to the Ni-Al binary (X = 3d-Ti, Cr, Fe, Co; 4d-Y, Zr, Nb, Mo, Ru, Pd; 5d-Hf, Ta, W, Re, Pt).
Figure 1.1: Adapted from Clarke & Levi (page 385) [11]. Shown is a schematic of a superalloy-bond coat-TGO-thermal barrier coating (TBC) system as is integrated in many aerospace applications.
Figure 1.2: Adapted from Nicholls (page 32, originally from Novak) [13]. Map of relative oxidation and corrosion resistance for high temperature coatings, including MCrAlY alloys.
2 Methodology

2.1 First-principles calculations based on density functional theory

A solution to a quantum mechanical many-body problem for a crystalline system can be described with the Schrödinger equation. The time-independent, non-relativistic Schrödinger equation, within the Born-Oppenheimer approximation can be written as:

Eq. 2.1:  \[ \hat{H}\Psi(r_1,r_2,...,r_N) = E\Psi(r_1,r_2,...,r_N) \]

With \( E \) denoting the energy of the system, \( \Psi(r_1,r_2,...,r_N) \) representing the wavefunction of particles (1 to \( N \)) and \( \hat{H} \) expressed as the Hamiltonian operator consisting of three terms:

Eq. 2.2:  \[ \hat{H} = \sum_i^N (-\frac{\hbar^2}{2m} \nabla_i^2 + \hat{V}_{\text{ext}}) + \frac{1}{2} \sum_{i<j}^N \frac{1}{|r_i-r_j|} \]

Here, the first term represents the kinetic energy, the second term \( \hat{V}_{\text{ext}} \) gives the interaction with some external potential, and the last term is the electron-electron interaction potential \( \hat{V}_{e-e} \). In atomistic simulations, the \( \hat{V}_{\text{ext}} \) term is expressed as the electron interactions with the nuclei:

Eq. 2.3:  \[ \hat{V}_{\text{ext}} = -\sum_{\alpha}^{N_{\text{at}}} \frac{Z_\alpha}{|r_i-R_\alpha|} \]

Where \( r_i \) is the electron \( i \) coordinate, \( R_\alpha \) is the coordinate of nuclei \( \alpha \) with a charge \( Z_\alpha \). Eq. 2.1 can then be solved for \( \Psi \) subject to antisymmetric constraints with the lowest energy eigenvalue \( E_0 \) being the ground state energy. Even within approximations, solutions to Eq. 2.1 are completely intractable if a particular set coordinates \( (r_1, r_2, ..., r_N) \) must be determined [17], [18].

Fortunately, Hohenberg and Kohn proved in 1964 [19] that given an electron density, it uniquely determines the Hamiltonian operator acting upon it, making the electron density the
variable of interest. Therefore, with an electron density, or more importantly a functional of the electron density, it is possible to obtain the wave functions of all states and the energy; E can be expressed as $E[\rho(r)]$ where $\rho(r)$ is the electron density [18]. Additionally, an $\rho(r)$ that minimizes the overall functional is indeed the $\rho(r)$ that corresponds to the full solution to the Schrödinger equation [19]. It is useful to express the functional described by the Hohenberg-Kohn theorem as individual single-electron wave functions, $\psi_i(r)$:

$$E[(\psi_i)] = E_{\text{Known}}[(\psi_i)] + E_{\text{Exchange-Correlation}}[(\psi_i)]$$

with the known analytical parts separated from “everything else” that is unknown (quantum effects unaccounted for). The term $E_{\text{Known}}[(\psi_i)]$ can be expressed in a similar form to Eq. 2.2 with the addition of an $E_{\text{Ion}}$ term describing Columbic interactions between pairs of atomic nuclei. Given the difficulty even in the previously shown equations, Kohn and Sham in 1965 provides an insight into solving for the right electron density. The equations arrived upon, known as the Kohn-Sham equations, have the form:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right] \psi_i(r) = \epsilon_i(r) \psi_i(r)$$

The solutions to the Kohn-Sham equations are single-electron wave functions and differ from the full Schrödinger equation (summation over each other electron) as it only depends on three spatial variables, $\psi_i(r)$. In the equation, the potential $V(r)$ has a form similar to Eq. 2.3, representing the electron-ion interactions. The potential $V_H(r)$ defines the electron-electron (total density) interactions that include a self-interaction contribution, or account for the fact that the electron of interest is already defined in the electron density, and can be shown as:

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r'$$
Accounting for the unphysical self-interaction error, alongside with other effects, is the derivative (functional) $V_{XC}(\mathbf{r})$ relating to the exchange-correlation energy:

Eq. 2.7: \[ V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})} \]

It is important to deal with the elephant in the room, that is $E_{XC}(\mathbf{r})$, which has no explicit analytical form that can be used to solve the Kohn-Sham equations. However, by using an uniform electron gas (UEG), $n(\mathbf{r})$, which has a constant density everywhere in space, it is possible to determine the exact exchange-correlation for that uniform gas by setting $V_{XC}(\mathbf{r}) = V_{XC}^{UEG}[n(\mathbf{r})]$. This approximation is dependently solely on the value of $\rho(\mathbf{r})$ at a coordinate in space and is effectively the local density approximation (LDA); the most famous implementation demonstrated by Ceperley & Alder [20]. The expansion to include the gradient of $\rho(\mathbf{r})$ results in the generalized gradient approximation (GGA). Implementations of the GGA include those by Perdew & Zunger (PZ) [21] as well as by Perdew, Burke, and Ernzerhof (PBE) [22]. Then, with an iterative method [18], it is possible to solve the Kohn-Sham equations to obtain a self-consistent solution. This thesis does not detail the complex way that these iterative methods need to implemented in order to obtain a true solution. DFT calculations in the present work are performed using the well-established The Vienna ab-initio Simulation Package (VASP) [23].

2.1.1 Density functional theory at 0 K

The formation energy, $\Delta_fH$, of a compound $A_xB_yC_zD$ ... at 0 K can be defined as a difference between the reference states and the compound of interest (ternary in this case):

Eq. 2.8: \[ \Delta_fH(A_xB_yC_z) = E(A_xB_yC_z) - x_AE(A) - x_BE(B) - x_CE(C) \]
In the previous equation, the formation energy of $A_xB_yC_z$ is taken with respect to the energies of the elements A, B and C in some reference state, not necessarily the standard elemental reference state (SER). Given that the formation enthalpy varies little with temperature, the formation enthalpy can be used directly in CALPHAD modeling [24]. Finite temperature contributions will be discussed later in the chapter.

Additional indirect methods are required to obtain the finite-temperature properties of materials, often using an equation of state (EOS) to describe the change of energy over a variation. $E_{0K}(V)$ is obtained using a four parameter Birch-Murnaghan (BM4) equation of state fitting shown below [25], [26]:

Eq. 2.9:  
$$E_{0K}(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}.$$  

Shang et al. [25] recommended the BM4 equation over the original Birch-Murnaghan equation because the second derivative of the bulk modulus with respect to pressure, $B''_0$, an important fitting factor for metal systems, does not go to 0 as in the original equation. Calculations for at least six volumes are used in fitting the EOS using the following procedure. The supercell is initially relaxed with respect to ion positions, cell shape and cell size to obtain a volume close to the equilibrium volume. After this relaxation, 6 additional volumes with up to 6\% difference in lattice parameter in expansion and compression are constructed. These additional supercells with fixed volumes are relaxed with respect to ion positions and cell shape. The $E_{0K}(V)$ data, energies and pressures, are extracted from each volume. By fitting the extracted data to the BM4 equation, an energy (E-V) and pressure (P-V) vs. volume relationships are found. Important materials properties can be derived, such as the bulk modulus ($B$) and its derivative ($B'$) from the EOS fitting:

Eq. 2.10:  
$$B = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E}{\partial V^2} \quad \text{where} \quad P = -\frac{\partial E}{\partial V} \quad \text{and} \quad B' = \frac{\partial B}{\partial P}$$
The EOS and its derived parameters are important in finite-temperature thermodynamics and will be described in the following sections.

2.1.2 Elastic stiffness calculations

Another necessary component to predicting the finite temperature properties of condensed matter systems is understanding its elastic properties, more specifically the variations in the speeds of sound in the longitudinal and transverse directions relating to the Poisson’s ratio. Prediction of the Poisson’s ratio can be accomplished with *ab initio* methods. In the present work, Poisson’s ratios are calculated from elastic stiffness constant calculations at 0K via first-principles calculations. These calculations follow the accurate stress-strain method and codes developed by Shang et al. [27]. After validation of methodology, some values of elastic constants for pure elements are taken with permission from Shang et al. [28] to reduce calculation redundancy. To determine, from *ab initio* and Hooke’s law, elastic constants for a crystal, a set of strains (expressed in Voigt notation) $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$ is placed on a crystal with lattice vectors $R$ (Cartesian):

\[
\text{Eq. 2.11: } R = \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix}
\]

After a deformation, the resulting lattice vectors $R'$ can be expressed as

\[
\text{Eq. 2.12: } R' = R \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix}
\]

Corresponding stresses $\sigma = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$ generated via the deformation will be calculated using *ab initio* methods to determine the elastic compliance coefficients 6x6 matrix, $C_{ij}$:
Eq. 2.13: \[ \sigma_i = C_{ij} \varepsilon_j \]

The Poisson’s ratio can then be evaluated with the Voigt, Reuss, and Voigt-Reuss-Hill (VRH) approximations for a polycrystalline aggregate (expressed in \( C_{ijkl} \) instead of Voigt notation) [29].

2.1.3 Special quasirandom structures (SQS)

Disordered solutions become a crucial part of the modeling work as mixing in solution phases dominate many parts of the models in the current work. However, given the possible structural configurations of \( N \) sites in even a simple binary system, there are \( 2^N \) possible configurations for atoms that must be calculated and averaged. Sample sizes become large for Monte Carlo simulations (~\( 10^6 \)) and cell sizes become large (~\( 10^3 \) atoms) for first-principles studies. Zunger et al. shows that constructing a small periodic supercell with special occupation of \( N \) sites for an A-B binary system can mimic the correlation functions of a disordered substitutional random alloy [30] better than random occupation of those \( N \) sites. In the limit \( N \rightarrow \infty \), both cases would be true but the method proposed by Zunger et al. holds true for even a small \( N = O(10) \). These structures are so called “special quasirandom structures” or SQS. Previous authors have demonstrated the effectiveness of the SQS methods in calculating the mixing solution enthalpies for binary-fcc [31], bcc [32], hcp [33] and ternary-fcc [34], bcc [35], B2 [36], and L12 [37] alloys. More specific discussions for each system in the current work will be found in their respective chapters.

These structures can be generated using a stochastic Monte Carlo method proposed by van de Walle et al. [38]. This method, as is implemented in the Alloy Theoretic Automated Toolkit
written by van de Walle et al. [39], is used in the current work to generate crystal structures that have not been previously investigated.

2.2 Finite-temperature thermodynamics

The Helmholtz energy, \( F(V, T) \), of a condensed phase as a function of volume \((V)\) and temperature \((T)\) can be obtained from first-principles calculations based on DFT and is expressed as follows [25], [40]:

\[
F(V, T) = E_{0K}(V) + F_{Vib}(V, T) + F_{T-el}(T)
\]

where \( E_{0K}(V) \) is the static contribution at 0 K without zero-point vibrational energy, and \( F_{Vib}(V, T) \) and \( F_{T-el}(T) \) represent the temperature-dependent vibrational and thermal-electronic contributions, respectively. \( F_{Vib}(V, T) \) contributions result from phonon vibrations within the solid that can be calculated with the Debye, harmonic, or quasiharmonic model in increasing complexity. At ambient pressure, the Helmholtz energy is equivalent to the Gibbs energy. It is important to include the thermal electronic contribution for the systems in this work due to their metallic nature with finite electronic density at the Fermi level. The thermal electronic contribution is based on the electronic density of states and calculated using Fermi-Dirac statistics. Contributions from other effects such as anharmonicity or van der Waals interactions can also be accounted for in other cases. Due to the metallic nature of all systems calculated in the current work, van der Waals forces are negligible.
All finite-temperature vibrational and electronic contributions are calculated using methods proposed and written by Shang et al. [41] in the computational software Matlab. Some aspects of the calculations require the use of the Alloy Theoretic Automated Toolkit (ATAT) written by van de Walle et al. [39].

2.2.1 Debye-Grünseisen model

Vibrational contributions to the free energy come from the degrees of freedom allowed to atomic movements in the crystal. Normal frequencies in crystals are concerted harmonic movement of atoms rather than contributions from single atoms. These frequencies can vary between nearly 0 to on the order of \(10^{13}\) cycles/sec (Hz). Peter Debye proposed a model that emphasizes the normal modes, which are much longer than the atomic spacings, which can be calculated using a continuous elastic medium. This model, or the Debye model, is a simple effective way to describe the normal vibration modes of an isotropic medium to estimate specific heat contributions. By assuming that the speed of sound through the medium, \(v\), is the same for all vibrational modes, the longitudinal (in the direction of wave propagation) and transverse (perpendicular to the direction) speeds of sounds are taken as an average. Therefore, for a given \(k\)-vector, the phonon dispersion relation for a vibrational frequency \(\omega\) can be expressed as:

\[
\omega = vk
\]

where \(v\) can be written in terms of the bulk modulus (coefficient of stiffness in classical mechanics) and density of the system:

\[
v = \sqrt{\frac{B}{\rho}}
\]
Debye proposed that all lattice vibrations can occur at all frequencies until some cut-off frequency, or the Debye frequency, 

Eq. 2.17: \[ \omega_D = \frac{2\pi k_B \theta_D}{\hbar} \]

where \( \theta_D \) is the related Debye "temperature", \( k_B \) the Boltzmann constant. It will be shown later in Chapter 4 that the modifications to the speed of sound is important in producing correct \( \theta_D \) for real crystal systems, with \( \theta_D \) itself a function of temperature. This function is often tabulated (McQuarrie, Appendix C [42]) or can be assessed numerically and can be used to calculate the specific heat, shown below:

Eq. 2.18: \[ C_V = 3Nk_BD \left( \frac{T}{\theta_D} \right) \]

In the above equation, \( 3N \) is the total number of normal frequencies, \( D \left( \frac{T}{\theta_D} \right) \) is the Debye function, and \( k_B \) the Boltzmann constant. It can be shown that the Debye model recovers to the classic Dulong-Petit limit of \( C_V = 3R \) at high \( T \) and is proportional to \( T^3 \) at low \( T \). This is the essential characteristic of the Debye model that triumphs over Einstein’s heat capacity model which does not exhibit the low temperature behavior [42], [43].

In order to account for anharmonic behavior that is not accounted for in the harmonic Debye model, the Grünseisen parameter is introduced. It can be defined on a microscale as:

Eq. 2.19: \[ \gamma = -\frac{\partial \ln \theta_D}{\partial \ln \nu} \]

Morruzzi et al. shows that this can be expressed as the bulk modulus, given its relations to \( \theta_D \),

Eq. 2.20: \[ \gamma = -\frac{1}{6} - \frac{1}{2} \frac{\partial \ln \nu}{\partial \ln \nu} \]
This relationship and some of the consequences will be discussed in more detail in Chapter 4 relating to anharmonic effects at higher temperatures. Some limits will be discussed based on case studies.

### 2.2.2 Thermal electronic free energy contributions

Unlike semi-conductors and insulators, metallic systems have finite electronic densities of state at the Fermi level and with contributions to the specific heat. However, these contributions are un-classical (not on the order of \(3/2Nk_B\) in contribution) in nature and must follow the Pauli exclusion principle and more specifically the Fermi-Dirac distribution. Fermi-Dirac statistics are applied in this case as the electrons have \(1/2\) integer spin (fermions), which is shown below:

\[
f_{\mu,T}(\varepsilon_i) = \frac{1}{e^{[\varepsilon_i - \mu(T)]/k_BT} + 1}
\]

where \(\varepsilon_i\) is the energy of a single particle state \(i\) and \(\mu(T)\) is the solution to \(\int n(\varepsilon)f_{\mu,T}(\varepsilon)d\varepsilon = n_e\) where \(n_e\) is the number of electrons. This is very different from bosons following Bose-Einstein statistics which can occupy any number of states at some energy level. The result above can be shown with the derivation from the grand canonical ensemble, \(\Xi(\mu,V,T)\), with volume, temperature and chemical potential as natural variables. McQuarrie [42] shows first that the partition function of an \(N\)-body energy system \(E_{ijkl\ldots} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \cdots\) can be written as (canonical ensemble),

\[
Q(N,V,T) = \sum_{i,j,k,l\ldots} e^{-(\varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \cdots)/k_BT}
\]
where the sum over i,j,k,… is not trivial as the molecules are indistinguishable. McQuarrie [42] then demonstrates the expression for the statistics using the previous consideration, and a quantum mechanical system with energy $E_j(N,V)$ and the grand canonical ensemble:

Eq. 2.23: $$\Xi(\mu, V, T) = \prod_k \sum_{n_k=0}^{n_k_{max}} (\lambda e^{-\beta \epsilon_k})^{n_k}$$

In the above equation, $\epsilon_k$ defines the molecular states, $n_k(E_j)$ gives the number of molecules in the kth state when the system is in the energy state $E_j$, $\lambda$ is the absolute activity $e^{\beta \mu}$, and $\beta = 1/k_B T$. Then, for fermions, $n_k$ can only take on states 0 or 1 as no two particles can be in the same quantum state. This yields the result $n_k_{max} = 1$, producing the Fermi-Dirac grand canonical ensemble:

Eq. 2.24: $$\Xi_{FD}(\mu, V, T) = \prod_k (1 + \lambda e^{-\beta \epsilon_k})$$

The distribution $f(\epsilon_i, V, T)$ cannot take on a value greater than 1, or there can never be more than one fermion in a single-particle given state. Expectedly, this is in accordance with the Pauli exclusion principle which states that identical fermions cannot simultaneously occupy the same quantum mechanically state.

Given the Fermi-Dirac distribution, it is possible to then calculate the contributions of electrons to the free energy as a function of $T$ by allowing partial occupations of electronic states [25], [44].

Eq. 2.25: $$F_{T-el}(T) = E_{T-el}(T) - T S_{T-el}(T)$$

where $E_{T-el}(T)$ and $S_{T-el}(T)$ are the internal energy and entropic electronic contributions. The internal energy change, $E_{T-el}(T)$, can be calculated by,
Eq. 2.26:  \[ E_{T-\text{el}}(T) = \int n(\epsilon)f_{\mu,T}(\epsilon)\epsilon d\epsilon - \int^{\epsilon_f} n(\epsilon)\epsilon d\epsilon \]

where \( n(\epsilon) \) is the electronic DOS, \( \epsilon_f \) is the Fermi level energy and \( f(\epsilon) \) is the Fermi-Dirac distribution shown above. In the same sense, the entropy contributions due to electronic excitations can be calculated as,

Eq. 2.27:  \[ S_{T-\text{el}}(T) = -k_B \int n(\epsilon)\{f_{\mu,T}(\epsilon) \ln f_{\mu,T}(\epsilon) + [1 - f_{\mu,T}(\epsilon)] \ln[1 - f_{\mu,T}(\epsilon)]\} d\epsilon \]

DFT methods can then be used to predict the electronic DOS and the Fermi-energy in order to calculate the total thermal-electronic contributions to the free energy.

## 2.3 CALPHAD method

The CALPHAD method, or the CALculation of PHAse Diagrams, tackles the problem of modeling solution phases, especially in multicomponent systems, head on. Most phases, whether in an alloy or a ceramic, are not stoichiometric in nature and have finite solubility for different species. The 4 types of solution phases often dealt with in the CALPHAD method include (1) random substitutional, (2) sublattice, (3) ionic, and (4) aqueous. This work focuses on random substitutional and sublattice solid solutions and they will be discussed in detail. Given that temperature, pressure and composition controls most alloy processes, a solution phase can be represented by its Gibbs energy function, \( G(T,P,n) \), with this standard form:

Eq. 2.28:  \[ G(T,P,n) = G^o + G^\text{ideal}_{\text{mix}} + G^\text{excess}_{\text{mix}} \]
where $G^o$ is the pure component Gibbs contribution, $G_{mix}^{ideal}$ is the contribution from ideal mixing, and $G_{mix}^{excess}$ is the excess non-ideal interactions (Gibbs excess energy of mixing). Note that the magnetic contribution to the pure species or to the solution can be wrapped into the Gibbs excess term, and denoted as $G_m^{Magnetic}$. The important integral Gibbs energy of a pure species or stoichiometric compound, before mixing, can be shown as:

Eq. 2.29: \[ G = H - TS \]

which can be parameterized to a set of polynomials and set relative to the standard element reference state (SER) per mole for database convenience:

Eq. 2.30: \[ G_m - H_m^{SER} = a + b T + c T \ln T + \sum d_n T^n \]

In the previous equation, $H_m^{SER}$ is the elemental enthalpy in its SER state at 298 K with a, b, c, and $d_n$ as coefficients (expansion also includes integer values of $n$). Other thermodynamic quantities can be derived from this form, including:

Eq. 2.31: \[ H = G + TS = a - cT - \sum (n - 1)d_n T^n \]

Eq. 2.32: \[ S = - \left( \frac{dG}{dT} \right)_p = -b - c \ln T - \sum n d_n T^{n-1} \]

Eq. 2.33: \[ C_P = \left( \frac{dH}{dT} \right)_p = -c - \sum n(n - 1)d_n T^{n-1} \]

Calculations from first-principles are used to fit the coefficients of $H$, $S$, and $C_P$, more specifically their formation or excess values. The formation values are fit for a stoichiometric phase or "end-member" (described later) using a thermodynamic assessment program such as the PARROT [45] module of Thermo-Calc [46], [47].
Additionally, due to the ferromagnetic nature of elements such as Co, Fe, Ni and the antiferromagnetic nature of Cr, \( G_m^{\text{Magnetic}} \) is included to capture magnetic contributions to the Gibbs energy [48], [49]. Hillert and Jarl [48] expressed the magnetic contribution as:

\[
G_m^{\text{Magnetic}} = RT \ln(\beta + 1) f(\tau)
\]

where \( \beta \) represents the average magnetic moment and the function \( f(\tau) \) is related to the Curie temperature \( (T_c) \):

\[
f(\tau) = 1 - \frac{1}{A} \left\{ \frac{79 \tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right\}, \text{if } \tau = \frac{T}{T_c} \leq 1
\]

\[
f(\tau) = -\frac{1}{A} \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right), \text{if } \tau = \frac{T}{T_c} \geq 1
\]

\[A = \frac{518}{1125} + \frac{11,692}{15,975} (\frac{1}{p} - 1)\]

The constant \( p \) takes on values of 0.28 for fcc and hcp metals and 0.4 for bcc metals.

2.3.1 Compound energy formalism (CEF)

The compound energy formalism is a way to expand on the idea of mixing in a solution phase using sublattice models that can include mixing on many sublattices (internal degrees of freedom). For a solution phase with one sublattice this can be shown as:

\[
G_m^\Phi = \sum x_i^\Phi G_i^\Phi + RT \sum x_i \ln x_i + xs G_m^s + RT G_m^{\text{Magnetic}}
\]

where \( G_i^\Phi \) represents the molar Gibbs energy of the pure elements \( i \) with structure \( \Phi \) taken from a database, usually SGTE Unary PURE4 [50]. In the above equation, the first term represents the
mechanical mixing of the elements and the second term is the contribution from ideal entropy of mixing. The excess term, $^{\chi S}G_m^\Phi$, is modeled using the Redlich-Kister polynomial [51] to represent the non-ideal interactions between species i and j in the solution phases, as shown below:

Eq. 2.37:

$$^{\chi S}G_m^\Phi = \sum_i \sum_{j>i} x_i x_j \sum_{\nu=0}^\infty v L_{i,j}^\Phi (x_i - x_j)\nu$$

In the multi-component extension to species i, j, and k by Muggianu, it is represented as:

Eq. 2.38:

$$^{\chi S}G_m^\Phi = \sum_i \sum_{j>i} x_i x_j \sum_{\nu=0}^\infty v L_{i,j}^\Phi (x_i - x_j)\nu$$

$$+ \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \left\{ L_{i,j,k}^\Phi (x_i + \delta_{i,j,k}) + L_{i,j,k}^\Phi (x_j + \delta_{i,j,k}) + L_{i,j,k}^\Phi (x_k + \delta_{i,j,k}) \right\}$$

where $\delta_{i,j,k} = (1 - x_i - x_j - x_k)/3$. The binary and ternary interaction terms, $\nu L_{i,j}^\Phi$ and $\nu L_{i,j,k}^\Phi$ are expressed in the form $A + B \cdot T$ with $A$ and $B$ as model parameters to be evaluated. This formalism allows composition dependent adjustments of the energy surface in the ternary mixtures.

Phases with more than one sublattice introduce the idea of sites and their respective site fractions. Sites are often representative of the crystallographic Wyckoff positions within a crystal lattice with components taking on various compositions on said sites. More about how Wyckoff positions are related to CALPHAD models can be found in ref. [52], [53]. This occupation parameter for a component, including vacancies (Va), can be expressed as:
Eq. 2.39:

\[ y_i^s = \frac{n_i^s}{n_{Va}^s + \sum_i n_i^s} \]

where \( n_i^s \) is the number of atoms of component i or vacancies on sublattice s and \( N^s = n_{Va}^s + \sum_i n_i^s \). As a result of the sites mixing, the ideal entropy of mixing for all sites is taken into account with the following contributions:

Eq. 2.40:

\[ G_{mix}^{ideal} = -T S_{mix}^{ideal} = RT \sum_s N^s \sum_i y_i^s \ln y_i^s \]

In the multi-sublattice construct, the idea of "end-member(s)" must also be introduced. These are permutations that generate the pure component ends of each sublattice, and set the important reference states. This can be represented by the following equation for the "surface" reference states:

Eq. 2.41:

\[ G_m^{ref} = \sum^0 G_{end} \prod y_i^s \]

where \( ^0 G_{end} \) are the end-member energies.

The Gibbs excess energy of mixing for the sites can also be defined. This is best demonstrated using a model for a 2 sublattice system (A,B)(C,D). In this case, the permutations of sites generate the following excess energy [54]:

Eq. 2.42:

\[ G_{mixing}^{xs} = y_A^1 y_B^1 y_C^2 L_{A:B:C} + y_A^1 y_B^1 y_D^2 L_{A:B:D} + y_C^2 y_D^2 y_A^1 L_{A:C,D} + y_C^2 y_D^2 y_B^1 L_{B:C,D} \]
where $L_0$ parameters can be modeled using the Redlich-Kister polynomial [51]. In the following chapters, specific sublattice models will be described for each of the systems of interest. The following section will discuss the implication of ordering and disordering that can occur in some phases, especially within the confines of the CEF.

Phases that implement the CEF with multi-component solubility modeled in the current work include B2, $\gamma'$, and TCP phases $\sigma$ and $\chi$. The next section will describe the modeling B2 and $\gamma'$ using the order-disorder model. Additional information on the modeling of the TCP phases exist in Nb-Re.

### 2.3.2 Order-disorder models

In some phases, strict site occupation for certain components does not always hold, especially at higher temperatures; ordering and site preferences at low temperatures is substituted with random mixing on all sublattices at higher temperatures [54]. A classic case is the Al-Fe system where the addition of more Al in the Fe bcc-A2 lattice leads to ordering to simple cubic B2 (CsCl-type) with no intermediate two-phase region; i.e. a second-order phase transition [55]. In the Al-Ni system, however, the disordered $\gamma$-fcc phase is often modeled with ordering to cubic $\gamma'$-L$_{12}$ where two-phase regions do exist; i.e. a first-order transition [1]. Therefore, this type of model can be applied to first- and second-order transitions where the coordination of crystallographic sites do not change but the occupation does. In the current work, the A2/B2 and $\gamma'/\gamma'$ phases are modeled using the two-sublattice order-disorder model (2SLOD) which uses the same Gibbs energy function for the disordered and its complementary ordered phase(s) [54].
The 2SLOD model describes the ordered and disordered phase with one single Gibbs energy function and the same sublattice model construct. One example can be shown with the Al-Ni system where the A2 phase is described with \((\text{Al}, \text{Ni}, \text{Va})\) and the B2 with \((\text{Al}, \text{Ni}, \text{Va})\) \((\text{Al}, \text{Ni}, \text{Va})\); one can see the extension of the disordered phase single sublattice model to the same components occupying two sublattices in the ordered phase. As a result, the Gibbs energy of combined phases is described as:

\[
G_m^{\text{disorder/order}} = G_m^{\text{disorder}}(x_i) + \Delta G_m^{\text{order}}(y_i^{(s)})
\]

where the Gibbs energy of the combined order-disorder phase include contributions from the disordered solution, \(G_m^{\text{disorder}}(x_i)\), in the disordered phase as well as the ordered phase itself, \(\Delta G_m^{\text{order}}(y_i^{(s)})\). Here, \(\Delta G_m^{\text{order}}(y_i^{(s)})\) is the ordering energy extracted from the CEF and can be separated into two terms and the total Gibbs energy becomes:

\[
G_m^{\text{disorder/order}} = G_m^{\text{disorder}}(x_i) + G_m^{\text{order}}(y_i^{(s)}) - G_m^{\text{order}}(y_i^{(s)} = x_i)
\]

where \(y_i^{(s)}\) denotes the site fraction of element \(i\) on the \(s\) sublattice. It can be seen that the ordering independent term, \(G_m^{\text{disorder}}(x_i)\), and the ordering dependent terms \(G_m^{\text{order}}(y_i^{(s)})\) and \(G_m^{\text{order}}(y_i^{(s)} = x_i)\) are separated in a way to allow each to be modeled independently. When the phase becomes disordered, i.e. \(y_i' = y_i'' = x_i\), \(G_m^{\text{order}}(y_i^{(s)}) - G_m^{\text{order}}(y_i^{(s)} = x_i)\) equals zero and eliminates the ordering energy contribution to allow full disorder. The term \(G_m^{\text{order}}(y_i^{(s)})\) takes on the partitioned form, as described by Dupin & Ansara [1], [56],

\[
G_m^{\text{disorder/order}} = G_m^{\text{disorder}}(x_i) + G_m^{\text{order}}(y_i^{(s)}) - G_m^{\text{order}}(y_i^{(s)} = x_i)
\]
\[ G_{m}\text{order}(y_i^{(s)}) = \sum_{i} \sum_{j} y_i' y_j'' oG_{i,j}^{\text{order}} + RT \left[ a \sum_{i} y_i' \ln(y_i') + b \sum_{j} y_j'' \ln(y_j'') \right] \]

\[ + \sum_{i} \sum_{j>i} \sum_{k} \left( y_i' y_j'' y_k' \left[ \sum_{k} L_{i,j,k}^{\text{order}} (y_i' - y_j') \right] \right) \]

\[ + \sum_{i} \sum_{j>i} \sum_{k} \left( y_k' y_l'' y_i' \left[ \sum_{l} L_{k,i,j}^{\text{order}} (y_k'' - y_i') \right] \right) \]

\[ + \sum_{l} \sum_{k>l} \sum_{j>i} \left( y_l' y_k'' y_j' \left[ \sum_{l} L_{l,j,k}^{\text{order}} \right] \right) = x_i \]

where \( oG_{i,j}^{\text{order}} \) represent the ordering end-members and \( L^{\text{order}} \) are the order-dependent interaction parameters in the form of \( A + B \cdot T \) with \( A \) and \( B \) as model parameters to be evaluated in modeling process. In the following sections, restrictions on the \( L^{\text{order}} \) are demonstrated. Coefficients \( a \) and \( b \) relate to the mole fraction of the sublattices. As is shown by Dupin et al. [56], due to the internal degree of freedom in determining the ordering parameters, only the difference \( G_{m}\text{order}(y_i^{(s)}) - G_{m}\text{order}(y_i^{(s)}) = x_i \) becomes meaningful in Eq. 2.44 and not just \( G_{m}\text{order}(y_i^{(s)}) \) [56]. In the next sections, the 2SLOD is described in detail for the A2/B2 and \( \gamma/\gamma' \) phases.

### 2.3.2.1 Fcc-\( \gamma \)/L12-\( \gamma' \) phase modeling

The \( \gamma' \)-L12 phase orders from \( \gamma \) with a reduction in symmetry where the corner (0,0,0) and the 3 face-centered (0,0.5,0.5),(0.5,0,0.5),(0.5,0.5,0) equivalent sites take on different compositions in the \( \gamma' \) and the same compositions in the \( \gamma \) cases. As is demonstrated by Ansara et al. [57] in the Al-
Ni system, the $\gamma$ can be modeled as (Al,Ni) while $\gamma'$-L12 can be expressed as (Al,Ni)$_{0.75}$ (Al,Ni)$_{0.25}$.

By using coefficients $a=3/4$ and $b=1/4$, Eq. 2.44 and Eq. 2.45 fully describes the Gibbs energy, $G_m^{\gamma/\gamma'}$, of the $\gamma/\gamma'$ phase. Site fraction to mole fraction relationships can then be shown as:

Eq. 2.46: \[ x_{Al} = 0.75y_{Al}^1 + 0.25y_{Al}^2 \quad \text{and} \quad x_{Ni} = 0.75y_{Ni}^1 + 0.25y_{Ni}^2 \]

Given the site to mole fraction relationships, it is possible to construct a composition square for $\gamma/\gamma'$ with representation for both the ordered and disordered states, as seen Figure 2.2. This figure demonstrates a composition square where $\gamma'$ ordering occurs everywhere except on the $\gamma$ disorder line from A$_3$A to B$_3$B (Ni is B) as site fractions are equivalent to mole fractions on this line. Also shown are some $x_B$ compositions with the related site fraction internal degrees of freedom plotted.

It is therefore possible to derive constraints that allow the phase to disorder when the site fractions are equal, or when $y_B^1 = y_B^2 = x_B$. If the disordered state is always possible, then the Gibbs energy should have an extremum with respect to site fractions $y_i^1 = y_i^2 = x_i$, corresponding to the disorder line in Figure 2.2. This can be expressed as the derivative [1], [57],

Eq. 2.47: \[ (dG_m^{\gamma/\gamma'})_{x_i} = \sum_i \sum_s \left( \frac{\partial G_m^{\gamma/\gamma'}}{\partial y_i^{(s)}} \right)_{x_i} dy_i^{(s)} = 0. \]

The binary constraints derived by Ansara et al. [57] are shown below:

Eq. 2.48: \[ G_{A:B} = u_1 \]

Eq. 2.49: \[ G_{B:A} = u_2 \]

Eq. 2.50: \[ 0L_{A,B:A} = 3u_1 + \frac{u_2}{2} + 3u_3 \]

Eq. 2.51: \[ 1L_{A,B:A} = 3u_4 \]
Eq. 2.52: \[ L_{A,B:B}^0 = \frac{u_1}{2} + 3u_2 + 3u_3 \]

Eq. 2.53: \[ L_{A,B:B}^1 = 3u_5 \]

Eq. 2.54: \[ L_{A:A,B}^0 = \frac{u_2}{2} + u_3 \]

Eq. 2.55: \[ L_{A:A,B}^1 = u_4 \]

Eq. 2.56: \[ L_{B:A,B}^0 = \frac{u_1}{2} + u_3 \]

Eq. 2.57: \[ L_{B:A,B}^1 = u_5 \]

Eq. 2.58: \[ L_{A,B:A,B}^0 = 4u_4 - 4u_5 \]

where the U’s are the independent parameters to be evaluated. Additional constraints, such as \( G_{A:B} = G_{B:A} \), can be applied if the A\textsubscript{3}B and B\textsubscript{3}A bonding energies are similar to reduce parameters.

Li et al. have derived binary constraints for arbitrary 2SL order-disorder models with various sublattice coefficients \([58]\) \((A,B)_m(A,B)_n\).

As is used in the important Al-Cr-Ni ternary system by Dupin et al. [1], Ansara et al. [59] proposes an alternative way of representing the constraints in Eq. 2.48 to Eq. 2.58 with the 4-sublattice order-disorder model (4SLOD). This is shown with the mathematically equivalent four sublattice model \((A,B,\ldots)_{0.25}(A,B,\ldots)_{0.25}(A,B,\ldots)_{0.25}(A,B,\ldots)_{0.25}\) where all sublattices are equivalent. While not true for the 2SL, the 4SL model has all sites equivalent where two species can be interchanged on sublattices without changing the energy of the system, and can be represented in the following equation.

Eq. 2.59: \[ G_{A:A:A:B}^{4SL} = G_{A:A:B:A}^{4SL} = \cdots = G_{A_3B}^{4SL} \]
In the same way, interaction parameters \( L^{4SL}_{A,B:C:D:E} = L^{4SL}_{A:B:D:E:C} = \cdots \) are also modeled to be independent of the constituents of the other sublattices. As described by Dupin et al. [1], the mathematical equivalence of the 4SL and 2SL models allows 2SL parameters to be represented in terms of 4SL parameters for the binaries, ternaries, and the quaternary. However, \( L_{10} \) ordering is lost in the conversion of the 4SL to the 2SL fcc model because the 4SL end-member \( G^{4SL}_{A:A:B:B} \) has no 2 SL equivalent. End-members with \( L_{12} \) ordering, \( G^{4SL}_{A:A:B:B} \) and \( G^{4SL}_{A:B:B} \), can be expressed as \( G_{A:B} \) and \( G_{AB} \), respectively. The constraints for the 2SL model using 4SL derivation, as shown by Dupin et al. [1], [16] are for the binary,

Eq. 2.60: \[ G^{y'}_{A:B} = G_{AB} \]

Eq. 2.61: \[ G^{y'}_{B:A} = G_{A:B} \]

Eq. 2.62: \[ 0 \, L^{y'}_{A:B:A} = -\frac{3}{2} G_{AB} + \frac{3}{2} G_{A:B} + \frac{3}{2} G_{A:B} \]

Eq. 2.63: \[ 0 \, L^{y'}_{A:B:B} = +\frac{3}{2} G_{AB} + \frac{3}{2} G_{A:B} - \frac{3}{2} G_{A:B} \]

Eq. 2.64: \[ 1 \, L^{y'}_{A:B:A} = +\frac{1}{2} G_{AB} - \frac{3}{2} G_{A:B} + \frac{3}{2} G_{A:B} \]

Eq. 2.65: \[ 1 \, L^{y'}_{A:B:B} = +\frac{3}{2} G_{AB} + \frac{3}{2} G_{A:B} - \frac{1}{2} G_{A:B} \]

Eq. 2.66: \[ 0 \, L^{y'}_{*:A:B} = 0 \, L^{y'}_{A:B} \]

Eq. 2.67: \[ 1 \, L^{y'}_{*:A:B} = 1 \, L^{y'}_{A:B} \]

Eq. 2.68: \[ 0 \, L^{y'}_{A:B:*} = 3 \, 0 \, L^{y'}_{A:B} \]

Eq. 2.69: \[ 1 \, L^{y'}_{A:B:*} = 3 \, 1 \, L^{y'}_{A:B} \]
For the ternary,

\[
0 L_{A,B:C}^{\gamma'} = -\frac{3}{2}G_{A_3C} - \frac{3}{2}G_{B_3C} + \frac{3}{2}G_{A_2B_2C} + \frac{3}{2}G_{A_2BC}
\]

\[
0 L_{A,C:B}^{\gamma'} = -\frac{3}{2}G_{A_3B} - \frac{3}{2}G_{B_3C} + \frac{3}{2}G_{ABC} + \frac{3}{2}G_{A_2BC}
\]

\[
0 L_{B,C:A}^{\gamma'} = -\frac{3}{2}G_{A_3B} - \frac{3}{2}G_{AC_3} + \frac{3}{2}G_{ABC} + \frac{3}{2}G_{A_2BC}
\]

\[
1 L_{A,B:C}^{\gamma'} = -\frac{1}{2}G_{A_3C} + \frac{3}{2}G_{B_3C} - \frac{3}{2}G_{A_2B_2C} + \frac{3}{2}G_{A_2BC}
\]

\[
1 L_{A,C:B}^{\gamma'} = -\frac{1}{2}G_{A_3B} + \frac{3}{2}G_{B_3C} - \frac{3}{2}G_{ABC} + \frac{3}{2}G_{A_2BC}
\]

\[
1 L_{B,C:A}^{\gamma'} = -\frac{1}{2}G_{AB_3} + \frac{3}{2}G_{AC_3} - \frac{3}{2}G_{ABC} + \frac{3}{2}G_{A_2BC}
\]

\[
0 L_{A,B,C:A}^{\gamma'} = +G_{AB_3} - \frac{3}{2}G_{A_2B_2C} - \frac{3}{2}G_{A_3B} + G_{AC_3} + \frac{3}{2}G_{A_2C_2} - \frac{3}{2}G_{A_3C} -
\]

\[
\frac{3}{2}G_{ABC} - \frac{3}{2}G_{A_2BC} + 6G_{A_2BC}
\]

\[
0 L_{A,B,C:B}^{\gamma'} = -\frac{3}{2}G_{AB_3} - \frac{3}{2}G_{A_2B_2} + G_{A_3B} + G_{BC_3} - \frac{3}{2}G_{B_2C_2} - \frac{3}{2}G_{B_3C} -
\]

\[
\frac{3}{2}G_{ABC} + 6G_{A_2BC} - \frac{3}{2}G_{A_2BC}
\]

\[
0 L_{A,B,C:C}^{\gamma'} = -\frac{3}{2}G_{AC_3} - \frac{3}{2}G_{A_2C_2} + G_{A_3C} - \frac{3}{2}G_{BC_3} - \frac{3}{2}G_{B_2C_2} + G_{B_3C} +
\]

\[
6G_{ABC} - \frac{3}{2}G_{A_2BC} - \frac{3}{2}G_{A_2BC}.
\]

And for the quaternary:

\[
0 L_{A,B,C:D}^{\gamma'} = +G_{A_3D} + G_{B_3D} + G_{C_3D} - \frac{3}{2}G_{A_2B_2D} - \frac{3}{2}G_{A_2BD} - \frac{3}{2}G_{AC_2D} -
\]

\[
\frac{3}{2}G_{BC_2D} - \frac{3}{2}G_{A_2CD} - \frac{3}{2}G_{B_2CD} + 6G_{ABCD}
\]

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The Gibbs energy of each stoichiometric compound can be expressed as the sum of the bond energies:

Eq. 2.83: \[ G_{A:B:C:D} = U_{AB} + U_{AC} + U_{AD} + U_{BC} + U_{BD} + U_{CD} + \alpha_{ABCD} \]

For binary and ternary compounds, the Gibbs energies are:

Eq. 2.84: \[ G_{AB_3} = 3U_{AB} + 3\alpha_{AB_3} \]

Eq. 2.85: \[ G_{A_2B_2} = 3U_{AB} \]

Eq. 2.86: \[ G_{A_3B} = 3U_{AB} + 3\alpha_{A_3B} \]

Eq. 2.87: \[ G_{A_2BC} = 2U_{AB} + 2U_{AC} + U_{BC} + \alpha_{A_2BC} \]

The correction terms are applied for the Gibbs energies when the results \( \alpha_{ABCD} = 0 \) are not satisfactory, as is shown by Kusoffsky et al. [60]. However, this introduces additional parameters and is preferably not implemented unless first-principles results show strong dissimilarity between
\( G_{AB} \) and \( G_{A_2B} \). This formalism is adopted in the current work as it is used in the important subsystem Al-Cr-Ni by Dupin et al. [1].

### 2.3.2.2 Bcc-A2/β-B2 phase modeling

The B2 phase orders from the A2 phase with a reduction in symmetry where the \( \alpha \)-site (0,0,0) and \( \beta \)-site (0.5,0.5,0.5) sites take on different compositions in the B2 and the same compositions in the A2 [61]. It is important to discuss the triple-defect mechanisms that dominate the B2 phase at off-stoichiometry compositions. This type of defect is typically found in B2 phases consisting of a Group VIIIB (Co, Fe, Ni) and a Group IIIA (Al, Ga, In) atom. In the ideal structure, the A atom (Co, Fe, Ni,...) sits on the \( \alpha \)-site and the B atom (Al, Ga, In,...) on the \( \beta \). However, A atoms can occupy \( \beta \)-sites and vacancies can occupy \( \alpha \)-sites when the phase is off-stoichiometry [61]. In the current work, B2-CoAl [62] and NiAl [57] adopt the triple-defect model from the work by Dupin et al. [1]. When \( x_{Al} > 0.5 \), Al fully occupies the \( \beta \)-site and atom A (Co,Ni) mixes with Va on the \( \alpha \)-sites. On the contrary, when \( x_{Al} < 0.5 \), Al can mix with atom A on its site with the \( \alpha \)-site fully occupied by atom A. In these systems, the B2 phase for B2-CoAl [62] and NiAl [57] is often modeled separately from the A2 using the model \((A,...,Va)(A,B,...)\) [57], [62]. This quickly becomes a problem in systems where a second-order A2/B2 transformation exists, such as Al-Fe [55]. Ansara et al. [59] and Dupin & Ansara [56] later shows the equivalency of the asymmetric \((A,B,...)(B,...,Va)\) model to a symmetric one where the same species exist on both sublattices. Doing so, allows one to model the important A2/B2 transformation, as is shown in the previous section for \( \gamma/\gamma' \). This work will treat the modeling of the A2 and B2 phases in the sublattice formalism where equivalent species exist in both sublattices \((A,B,C,...,Va)_{0.5}(A,B,C,...,Va)_{0.5}\). By using coefficients \( a=1/2 \) and \( b=1/2 \), Eq. 2.44 and Eq. 2.45 fully describes the Gibbs energy, \( G_{m}^{A2/B2} \).
of the A2/B2 phase. Site fraction to mole fraction relationships can then be shown as, using Al-Ni as an example:

\[ x_{Al} = \frac{y_{Al}^1 + y_{Al}^2}{(1-y_{Va}^1)+(1-y_{Va}^2)} \quad \text{and} \quad x_{Al} = \frac{y_{Ni}^1 + y_{Ni}^2}{(1-y_{Va}^1)+(1-y_{Va}^2)} \]

Due to the symmetry of the α- and β-sites in the current model, the following relations must be enforced, much like in the case of γ/γ' [56]:

\[ oG_{i:j}^{B2} = oG_{j:i}^{B2} \]

\[ vL_{i,j:k}^{B2} = vL_{k:i,j}^{B2} \]

\[ vL_{i,j:k,l}^{B2} = vL_{k,l:i,j}^{B2} \]

\[ vL_{i,j:k,l}^{B2} = vL_{l,k:i,j}^{B2} \]

Otherwise, site-preference becomes inherent and produces unphysical results; e.g. the energy of Al:Ni should not differ from Ni:Al.

Dupin & Ansara derived a set of parameters and constraints that can be used to convert the B2 sublattice model with the asymmetrical construct \((A,B,\ldots)_{0.5} (B,\ldots,Va)_{0.5}\) into the 2SLOD symmetrical formalism \((A,B,\ldots,Va)_{0.5}(A,B,\ldots,Va)_{0.5}\). Please note that the exact conversion formulations are too cumbersome to list in this thesis but can be found in ref. [56]. Doing so allows for easier integration of binary models with high-order multi-component systems and it has been demonstrated for the Al-Ni [59] and Al-Cr-Ni [1] systems.
2.3.3 Optimization of thermodynamic parameters using data

Thermodynamic parameters derived in the current work are parameterized using data points from experiments of first-principles calculations. These data points, which can be at stable or metastable equilibrium conditions, are input into the PARROT [45] module of the Thermo-Calc thermodynamic software for assessment. Data points are then weighted according a set of criteria by the user in order to model the thermodynamic parameters by a minimized squares method.

2.3.4 Note about Al-Co adopted in the current work

Direct conversion of the B2 to the MSL formalism for the Al-Co model by Dupin and Ansara [62] produces a correct stable phase diagram but an incorrect metastable phase diagram when plotted to 6000 K, shown in Figure 2.3. This is also the case with the asymmetrical B2 model from the original publication [62] before conversion. B2 becomes more stable than liquid at very high temperatures. There are two reasons for this occurrence, the stability of vacancies in the B2 at high temperatures as well as the stability of B2 itself due to some of the interaction parameter choices by Dupin and Ansara [62]. These are the parameters,

Eq. 2.93:

\[ ^0L_{Al,Co:Co}^{B2} = +45590 - 32.39T, \]

\[ ^0L_{Al,Co:Va}^{B2} = +45590 - 32.39T, \]

\[ ^0L_{Al,Co, Va}^{B2} = +45030 - 34.47T, \]
\[ 0L^{B2}_{Co:Co,Ja} = +45030 - 34.47T, \]

which make the B2 stable as they all have large negative temperature dependence. This is in direct contrast to the similar Al-Ni system assessed by the same authors [59] where similar interactions have positive temperature dependent terms where this problem is not found. It is expected, intuitively, that B2 in Al-Co and Al-Ni should have similar interactions given their similarities. Additionally, plotting the B2 formation energy at 298 K shows that pure Al in B2 is not higher in energy than Al in A2 such as in Al-Ni. In a recent publication by Franke [63], it is additionally suggested that a value of 0 for the term \( G^{A2}_{Va:Va} \) when substitutional vacancies are modeled is both unphysical and can introduce no global minimum if starting compositions are close to vacancies. This is the case in the adopted Al-Cr-Ni model by Dupin et al. [1] which is crucial to the current thesis. However, changing the value of \( G^{A2}_{Va:Va} \) will change the stable phase diagrams for Al-Co and Al-Ni adopted in the current work. Furthermore, there is a large liquid miscibility gap that persists in the Al-Co system at high temperatures (over 3500 K).

Nevertheless, some solutions to these problems in Al-Co can be introduced. \( G^{A2}_{Va:Va} \) can be set to a positive value multiplied by RT to remove the stability of vacancies at high temperatures [63]. Modifications to the interaction \( 0L^{B2}_{Al:Co,Ja} \) should also be made to reduce vacancy stabilities at high temperatures. As a result, the phase stability of B2 will change in the stable phase diagram which will require the re-assessment of some phases and B2 itself if differences are large enough. The least elegant solution can be the removal of substitutional vacancies from all A2/B2 phases, which will effect stable phase equilibria. A compromise includes the modification of \( G^{A2}_{Va:Va}, \)

\[ 0L^{B2}_{Al:Co,Ja} \] and liquid interaction parameters from Dupin et al. [62]. Modifying Al-Co with the
following parameters produces a model with no B2 at high temperatures and no liquid miscibility
gaps:

Eq. 2.94:

\[ 0 L^{B2}_{\text{Al,Co}} = -15000 + 30T, \ G^A_{\text{Co,Co}} = 2RT, \]
\[ 0 L^{\text{Liq}}_{\text{Al,Co}} = -130954 + 30.50T, \ G_{\text{Al,Co}}^{\text{Al,Co}} = -19501 + 4.832T, \]
\[ 1 L^{\text{Liq}}_{\text{Al,Co}} = -130954 + 30.50T, \ G_{\text{Al,Co}}^{\text{Al,Co}} = +1117 - 1.080T, \]
\[ G_{\text{Al,Co}}^{\text{Al,Co}} = -174490 + 43.457T, \]
\[ G_{\text{Al,Co}}^{\text{Al,Co}} = -335100 + 86.325T, \]
\[ G_{\text{Al,Co}}^{\text{Al,Co}} = -391800 + 106.599T, \]
\[ G_{\text{Al,Co}}^{\text{Al,Co}} = -711760 + 176.814T. \]

This modified model is shown in Figure 2.4 and shows the change of the liquidus and solidus as a
result. A better fit could not be achieved without heavy modification of all phases in the system.
In this case, pure Al in B2 recovers to above the zero point much like in Al-Ni [59].

While the shortcomings with the original Al-Co model can be detrimental to higher order
extrapolations, especially at very high temperatures, they are not expected to produce erroneous
results at the temperatures of interest in the current work at temperatures below 2500 K; especially
since Al and Co are in their gaseous states at these temperatures. Additionally, it is hard to define
a true physical meaning for an interaction parameter far from its region of stability (>2500 K for
B2). Therefore, the original Al-Co model is adopted with a conversion to MSL without
modifications to the vacancies in B2.
Tables and Figures

Figure 2.1: Crystal structures of bcc-A2 (a), β-B2 (b), fcc-γ (c), and L_{12}-γ’ (d). Different colors denote different types of atoms.

Figure 2.2: Composition square for the fcc-γ/γ'-L_{12} phase plotted for $y_B^1$ vs. $y_B^2$ showing various $x_B$ in its ordered states (e.g. dotted lines). The dashed line represents the disordered state site fractions.
Figure 2.3: Stable B2 rich in vacancies (Va) produced with the parameters shown in [62] before conversion to the MSL formalism. The presence of a liquid miscibility gap at high temperature is not shown here.
Figure 2.4: Revised model of Al-Co originally by Dupin and Ansara [62] after parameters shown in Eq. 2.94 are used instead of the parameters by Dupin and Ansara [62] after MSL conversion. The liquidus in the original model is shown in (- - -).
3 First-principles aided thermodynamic modeling of the Nb–Re system

Ni-base superalloys have allowed the aerospace industry to design more efficient engines that run at higher temperatures with increased service lifetimes. These superalloys require up to ten or more alloying elements in order to achieve the required mechanical properties at elevated temperatures. However, some of these alloying elements, especially rhenium and other precious metals, are prohibitively expensive even when added in small quantities. To combat this challenge, researchers are seeking alternative, less expensive alloying elements while retaining the same high-temperature mechanical properties[64]. To reduce the expensive experimental work needed in developing the next generation of superalloys, the development of a Ni-base superalloys database in the CALculation of PHAse Diagram (CALPHAD) community aids in the search[65]. The CALPHAD technique parameterizes the Gibbs energy function of each phase present in the system by using phase equilibrium data between phases and thermochemical data of individual phases. The technique is unique because it can be used to extrapolate binary and ternary thermodynamic descriptions to multi-component systems where less experimental data is available with good accuracy[2]. Nb-Re is one of the constituent binary systems of this database and is studied in the present work.

In addition to bcc and hcp solution phases as well as the liquid phase in the Nb-Re system, there are two intermetallic phases, sigma (σ, $P4_2/nmm$, Re$_{0.3}$Nb$_{0.7}$)[52] and chi ($\chi$, $\overline{I}43m$, Re$_{0.83}$Nb$_{0.17}$)[53]. σ exists approximately from 53 to 55 at. % Re, while χ exists from 61 to 87 at. % Re (all compositions are in at. % unless otherwise specified). Multiple sets of phase equilibrium data are available in the literature[52], [53], [66]–[69]. However, there are no published data on
thermodynamic properties for either intermetallic phase. In the present work, thermodynamic data of σ and χ are predicted from first-principles calculations based on density functional theory (DFT) and then used in the CALPHAD modeling to create a consistent thermodynamic description of the Nb-Re system. Furthermore, thermochemical data of the bcc, fcc, and hcp solution phases are also predicted by the first-principles calculations using supercells based on special quasirandom structures (SQS) which mimic random mixing in solution phases with a small number of atoms [30]. It should be mentioned that even though the fcc phase does not exist in the Nb-Re binary system, its thermodynamic description is needed for extrapolation to multi-component Ni-base superalloys because of the existence of the fcc phase in the multi-component alloys.

3.1 Literature Review

Several experimental studies have been performed on the system, notably those by Knapton[67], Giessen et al.[68], Savitskii et al.[69], Greenfield and Beck[66], and Joubert and Phejar[52], [53]. Based on the experimental investigations reported in the literature, both σ and the hcp phases show narrow solubility ranges while χ and the bcc phases display wide solubility ranges, extending to 44 % Re in bcc Nb and from 63 to 87 % Re in χ, respectively. The experimental observations are described in more detail in the remainder of this section.

Knapton[67] prepared alloy samples via arc melting in an argon atmosphere and collected X-ray powder diffractions for the determination of invariant reactions and the congruent melting of χ. He evaluated one eutectic point at 2673 K and 53 % Re (L → bcc + σ) and a second one at
3003 K and 88 % Re \((L \rightarrow \chi + \text{hcp})\). A peritectic point was found at 2723 K and 57 % Re \((L + \chi \rightarrow \sigma)\). Knapton also noted the congruent melting of \(\chi\) at 3073 K [67].

Giessen et al.[68] annealed samples with times varying from 1 hour to 35 days. Solidus measurements yielded a Re-rich eutectic point at 2988 ± 15 K and 88 ± 0.5 % Re \((L \rightarrow \chi + \text{hcp})\), a peritectic at 2838 ± 15 K and 53 ± 1 % Re \((L + \chi \rightarrow \sigma)\), and a second eutectic at 2708 ± 10 K and 48 ± 1 % Re \((L \rightarrow \text{bcc} + \sigma)\). X-ray techniques were used to find the eutectoid at 2435 ± 10 K and 56 ± 1 % Re \((\sigma \rightarrow \text{bcc} + \chi)\). They also reported the bcc, \(\sigma\), \(\chi\), and hcp one- and two-phase boundaries with an X-ray parametric technique[68]. Phase boundary experiments were performed at 1473 ± 10 K and 1773 ± 10 K. The phase boundary for bcc and bcc + \(\chi\) was found at approximately 45 % Re. For bcc + \(\chi\) and \(\chi\), the phase boundary was detected at about 63 % Re. The phase boundary for \(\chi\) and \(\chi + \text{hcp}\) is located roughly 86 % Re.

Savitskii et al.[69] investigated samples with the annealing time ranging from 1 to 600 hours and used X-ray diffractions to conduct phase analysis. A peritectic reaction forming \(\chi\), existing from 69.5 to 86.5 % Re, was found at 2793 K \((L + \text{hcp} \rightarrow \chi)\). At 2613 K, a eutectic reaction exists with the composition of 50-51 % Re \((L \rightarrow \text{bcc} + \chi)\). Savitskii et al. did not report the high-temperature \(\sigma\) phase that Knapton identified [69].

Greenfield and Beck[66] were able to identify the existence of \(\chi\), and Steadman and Nuttall [70] determined the site occupancies in the phase using X-ray diffractions with samples annealed in an argon arc furnace at 25 and 75 % Re, respectively. Steadman and Nuttall found four groups of lattice sites for \(\chi\) based on the \(\alpha\)-Mn structure [70]. In the work by Joubert and Phejar [52], [53], a composition of \(\text{Nb}_{45}\text{Re}_{55}\) was cast and annealed at 1950°C for 1 hour as well as at 1000°C for 1
month. They concluded that σ should exist at high temperatures but could not confirm the σ decomposition temperature of 2160°C reported by Giessen et al. [52], [68].

Data from Giessen et al.[68] is chosen as the data set for the evaluation of the Gibbs energy functions because it is the most complete set of self-consistent data that includes phase boundaries, one- and two-phase regions, and all invariant reaction temperatures.

3.2 Modeling and Calculations

3.2.1 CALPHAD

In this work, the Gibbs energies of bcc, fcc, hcp, and liquid solution phases are modeled using the following equation,

\[ G_m^\Phi = x_{Re}^0 G_{Re}^{\Phi} + x_{Nb}^0 G_{Nb}^{\Phi} + RT[x_{Re} \ln(x_{Re}) + x_{Nb} \ln(x_{Nb})] + ^{XS}G_m^{\Phi} \]

where \( G_i^{\Phi} \) expresses the molar Gibbs energy of the pure element \( i \) with structure \( \Phi \) taken from the SGTE Unary PURE4 databases[50]. The first two terms represent the mechanical mixing of the alloying elements and the third term represents the ideal mixing between Re and Nb. The excess term, \(^{XS}G_m^{\Phi}\), is modeled using the Redlich-Kister polynomial[51] to represent the non-ideal interactions between Re and Nb as shown below

\[ ^{XS}G_m^{\Phi} = x_{Re} x_{Nb} \sum_{j=0}^{j} c_j \left(x_{Re} - x_{Nb}\right)^j \]

\[ ^{j}L_{Re,Nb}^{\Phi} = a_j + b_j T \]
The binary interaction term $L_{Re,Nb}^\Phi$ has $^j a$ and $^j b$ as model parameters to be evaluated.

The solubility ranges of $\sigma$ and $\chi$ covers 53 to 54 % Re and 44 to 63 % Re, respectively. Three-sublattice models based on the compound energy formalism[71], as used in the nearly identical Re-Ta system by Liu et. al[72], are adopted in the presented work, i.e. $\sigma$-(Re)$_{10}$(Nb)$_4$(Re,Nb)$_{16}$ with mixing on the third sublattice, and $\chi$-(Re)$_{24}$(Re,Nb)$_{10}$(Re,Nb)$_{24}$ with mixing on the second and third sublattices. The two end-members of $\sigma$-(Re)$_{10}$(Nb)$_4$(Re,Nb)$_{16}$ and $\sigma$-(Re)$_{10}$(Nb)$_4$(Re)$_{16}$, cover the atomic percent ranges of 33 to 87 % Re, while the end-members for $\chi$ include $\chi$-(Re)$_{24}$(Nb)$_{10}$(Nb)$_{24}$, $\chi$-(Re)$_{24}$(Re)$_{10}$(Nb)$_{24}$, $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$, and $\chi$-(Re)$_{24}$(Re)$_{10}$(Re)$_{24}$ covering the atomic percent ranges of 41 to 100 % Re. The described end-members are modeled as follows,

Eq. 3.4: 

$$G_m^{Re,Nb_y} = x^oG_{Re}^{hcp} + y^oG_{Nb}^{bcc} + \Delta_fG^{Re_xNb_y}$$

where, $\Delta_fG^{Re_xNb_y} = \Delta_fH^{Re_xNb_y} + T\Delta_fS^{Re_xNb_y}$ represents the Gibbs energy of formation of a particular $\sigma$ or $\chi$ end-member with the composition Re$_x$Nb$_y$. The Debye-Grüneisen model is used to calculate the enthalpy and entropy of the compounds as a function of temperature, and the details for these calculations are presented in the following section. These calculated values are used to evaluate $\Delta_fH^{Re_xNb_y}$ and $\Delta_fS^{Re_xNb_y}$[73] for each end-member as a function of temperature.

The Gibbs energy of $\sigma$ in per mole of formula units has the form,

Eq. 3.5:

$$G_m^\sigma = y_{Nb}^''oG_{Re: Nb:Nb} + y_{Re}^''oG_{Re: Nb:Re} + 16RT[y_{Nb}'''ln(y_{Nb}'') + y_{Re}'''ln(y_{Re}'')]
+ y_{Nb}''y_{Re}''L_{Re: Nb:Nb, Re}$$

45
where \( y'''' \) denotes the mole fraction in the third sublattice, \( ^oG_{Re: Nb: X} \) represents the Gibbs energy of particular \( \sigma \) end-members as shown by Eq. 3.4, and \( L_{Re: Nb: Re} \) is the interaction term between end-members that takes the form of Eq. 3.3 with the \( a \) and \( b \) being the interaction parameters to be evaluated in the modeling process.

The Gibbs energy of \( \chi \) in per mole of formula units takes the following form,

Eq. 3.6:

\[
G_m^\chi = y''_R e y'''_R e ^oG_{Re:Re:Re} + y''_R e y''_N b ^oG_{Re:Nb:Re} + y''_N b y'''_N b ^oG_{Re:Nb:Nb} \\
+ 10RT[y''_R e ln(y''_R e) + y''''_N b ln(y''''_N b)] + 24RT[y''''_R e ln(y''''_R e) + y''''_N b ln(y''''_N b)] \\
+ y''_R e y'''_R e y''''_N b L_{Re:Re:Re,Nb} + y''''_N b y''''_N b L_{Re:Re:Nb,Re,Nb} + y''''_R e y''''_N b y''''_N b L_{Re:Nb:Re,Nb} \\
+ y''_R e y''_N b y''''_N b L_{Re:Nb:Nb}
\]

where \( y''_x \) and \( y''''_x \) represent the mole fractions in the second and third sublattices, respectively, and \( ^oG_{Re:X,Y} \) the Gibbs energy of an end-member expressed by Eq. 3.4. There are four interaction parameters with the form of Eq. 3.3 utilizing \( a \) and \( b \) values that will be evaluated during modeling.

The PARROT module within Thermo-Calc [45]–[47] is used to evaluate all model parameters for each phase in the system using the phase equilibrium data from Giessen et al.[68] and first-principles thermochemical data calculated in the present work.
3.2.2 First-principles

While the phonon supercell method is generally accepted as the more accurate approach for finite temperature thermodynamics[25], [40], it is computationally expensive and cannot be directly used to calculate thermochemical properties of the dynamically unstable end-members needed for thermodynamic modeling[74]. The Debye model is thus used in the present work with the benefit of simplicity and efficiency[75]. Moruzzi et al. determined that a scaling factor of $s=0.617$, based on a survey of 14 nonmagnetic cubic metals, can be used to accurately reproduce the bulk modulus of those 14 metals[25], [76]. Niobium is one of the bcc nonmagnetic metals tested. Zacherl et al. also showed that this scaling factor produced accurate results for hcp Re[75]. To account for anharmonicity in the system, the Grüneisen parameter can be expressed as $\gamma = (1 + B'_0)/2 - x$ [76], where $B'_0$ is the first derivative of the Bulk modulus with respect to pressure. The temperature-dependent term, $x$, is 1 when the temperature is below the Debye temperature and $x = 2/3$ at temperatures above the Debye temperature. The value $x = 2/3$ is used in the present work because the phase diagram will be calculated at temperatures above the Debye temperature of the particular element or end-member[76].

The Vienna ab-initio Simulation Package (VASP)[23] is used for DFT calculations in the present work. Electron-ion interactions are described by the projector augmented-wave (PAW) method [77], [78]. The generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE)[22] is used as the exchange and correlation functional. A plane wave cutoff energy of 300 eV is used, a value that is more than 1.3 times greater than the highest plane wave energy cutoff of the elements in the system, as recommended by the VASP manual[79]. $k$-meshes for hcp-Re, bcc-Nb, $\sigma$ and $\chi$ are $19 \times 19 \times 10$, $19 \times 19 \times 19$, $5 \times 5 \times 9$, and $6 \times 6 \times 6$, respectively. The structures are relaxed by implementing the Methfessel-Paxton method [28] in
order to calculate the forces acting on the atoms. After relaxations, a final calculation using the
tetrahedron with Blöchl corrections[81] is applied to ensure an accurate total energy calculation.

Calculations of the enthalpy of mixing of the bcc, fcc and hcp solution phases based on
SQS are performed using the 16-atom hcp model developed by Shin et al.[33], the 16-atom bcc
model developed by Jiang et al. [32] and the 16-atom fcc model developed by Wolverton[31] for
25, 50 and 75 % Re, respectively. SQS calculation procedures for the present work are performed
with the method implemented by Lieser et al.[82]. The SQS supercells are relaxed with respect to
cell volume only first, cell volume and shape only second, and finally cell volume, shape as well
as ion positions simultaneously. Radial distribution functions (RDF) of relaxed supercells are
compared with those of ideal bcc, fcc or hcp structures after each relaxation step. The structure
with the lowest energy that retains the structural symmetry is used in the present work, and results
will be discussed in the following section. The 16-atom bcc and fcc SQS cells implemented 6x6x6
Monkhorst-Pack k-point meshes, and the 16-atom hcp SQS cell used 9x8x5 Monkhorst-Pack
meshes. Finally, the Debye model is applied to the bcc and hcp models at 50% Re to predict finite
temperature vibrational entropies of formation.

While the SQS model is used to predict interactions of the bcc, fcc, and hcp solid solutions,
a simpler approach is taken to predict the mixing energetics of σ and χ end-members with one Re
or Nb atom in the mixing sublattice replaced with the opposite atom. These generate two data
points for mixing in each sublattice. The same relaxation scheme used for SQS is employed for
these structures, and RDFs for each structure is compared against those of the ideal end-members.
The structures with the lowest energies that still retain the end-member symmetries are used in the
modeling.
3.3 Results and Discussion

3.3.1 First-principles

To provide a benchmark for the first-principles methodology used in the present work, the lattice parameters are compared with experimental values from Kittel[43]. Table 3.1 shows the space group and lattice parameter comparisons for the pure elements and the most stable end-members of σ and χ. For the pure elements, comparisons are also made to DFT results using the original generalized gradient approximation (PW91-GGA) exchange-correlations[21] calculated by Wang et al.[83]. Agreement within 0.5% is observed when compared to the experimental data[43], which is typical for such DFT calculations.

Results from this work on pure Re and Nb as well as previous studies by Zacherl et al.[75], [84] indicate that the Debye-Grüneisen model approach is a valid method to predict thermodynamic properties of pure element phases in comparison with the more computationally demanding phonon supercell approach. Table 3.2 shows that the pure element properties derived from the EOS fitting to be used in the Debye model match experiments and the DFT values from Zacherl et al.[75]. Therefore, the Debye approach is used to estimate the thermodynamic properties for all end-members of σ and χ. Figure 3.1 presents the finite temperature entropies, enthalpies and heat capacities of the most stable end-members of σ and χ, i.e. σ-(Re)_{10}(Nb)_{16} and χ-(Re)_{24}(Nb)_{10}(Re)_{24}, respectively. No experimental data on these structures are available in the literature for comparison. The results from Figure 3.1 are used as inputs for the CALPHAD modeling.
Predicted enthalpies of formation ($\Delta fH$) for each end-member of $\sigma$ and $\chi$ are calculated at 298 K and shown in Table 3.3, indicating that at 298 K, the structures $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$ and $\sigma$-(Re)$_{10}$(Nb)$_{4}$(Nb)$_{16}$ are the end-members with the lowest enthalpies of formation. Levy et al.[85] performed first-principles calculations on ordered compounds of rhenium binary alloys and found an enthalpy of formation of -14.376 kJ/mol-atom for the ordered $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$ structure at 0 K. In the present work, the calculated formation energy for the same structure at 0 K is -13.448 kJ/mol-atom. Zacherl et al.[75] also found the formation energy of $\chi$-(Re)$_{24}$(Ti)$_{10}$(Re)$_{24}$, another $\chi$ compound, to be less negative than the value calculated by Levy et al. [85].

Table 3.3 depicts that the $\Delta fH$ for $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$ calculated with the Debye-Grüneisen model at 298 K in this work is -13.542 kJ/mol-atom. It shows that the end-members of $\chi$, $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$ and $\chi$-(Re)$_{24}$(Nb)$_{10}$(Nb)$_{24}$, have lower formation enthalpies, -13.542 kJ/mol-atom and -10.519 kJ/mol-atom, respectively, of the four end-members of the $\chi$ phase. Joubert and Phejar[53] also found, for $\chi$ in binary systems, there is a tendency to order at the $B_{24}A_{5}$ [$\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$] and $B_{12}A_{17}$ [$\chi$-(Re)$_{24}$(Nb)$_{10}$(Nb)$_{24}$] end-members[53]. This ordering is consistent with our findings of greater stability of $\chi$ at these two compositions. For $\sigma$, the $\sigma$-(Re)$_{10}$(Nb)$_{4}$(Nb)$_{16}$ structure is shown to be the most stable one, with a formation enthalpy of -13.59 kJ/mol-atom, when compared to the $\sigma$-(Re)$_{10}$(Nb)$_{4}$(Re)$_{16}$ structure. Joubert[52] concluded that for binary systems with $\sigma$, there is a tendency for ordering at $B_{10}A_{20}$ [$\sigma$-(Re)$_{10}$(Nb)$_{4}$(Nb)$_{16}$] and no tendency for order at [$\sigma$-(Re)$_{10}$(Nb)$_{4}$(Re)$_{16}$], which is supported by data in Table 3.1 and Table 3.3.

For the bcc SQS calculations, RDFs showed that symmetry is kept during the full relaxation of all degrees of freedom including cell volume, cell shape and ion positions. However, for the fcc and hcp structures, the RDFs indicated that symmetry is lost when cell shape or ion positions are allowed to relax. Consequently, the data from the cell volume, cell shape and ion position
relaxation scheme is used for the bcc structure, and the data from the cell volume only relaxation is used for the fcc and hcp SQS calculations. Figure 3.2 shows volume per atom of each SQS cell as a function of Re mole fraction, and it is observed that as more rhenium atoms are placed into SQS for the hcp, fcc, and bcc cases, the volume per atom decreases. This is expected as rhenium has a smaller atomic radius than Nb[43] and is in accordance with previous SQS studies[75], [82], [84]. For the bcc volume vs. mole fraction plot, a minor deviation is seen at 75 % Re, and calculations showed that the structure was properly relaxed without a loss of symmetry. Figure 3.3 shows the predicted finite-temperature vibrational entropies for the bcc-SQS and hcp-SQS with 50 % Re, respectively. It can be seen that greater entropic contributions are seen in bcc-SQS compared to hcp-SQS. These predicted finite-temperature results improve the calculation of the model parameters of the bcc and hcp solid solution phases as no experimental data on these structures are available in the literature.

Table 3.4 shows the predicted interaction parameters of σ and χ end-members at 0 K. All σ and χ interaction parameters are predicted to be negative with those between χ-(Re)24(Nb)24, χ-(Re)24(Nb)10(Nb)24 and χ-(Re)24(Re)10(Re)24, χ-(Re)24(Re)10(Nb)24 being the more negative ones and favorable when mixing occurs. Results from Table 3.4 are used for modeling the interaction parameters between σ and χ end-members.

3.3.2 CALPHAD

The model parameters are evaluated using the PARROT module in Thermo-Calc [45]–[47] and shown in Table 3.5. Figure 3.4 plots the enthalpy of mixing results from first-principles
calculations with the curves from CALPHAD modeling at 298 K. This figure shows a positive enthalpy of mixing for the hcp solid solution, indicating instability at lower temperatures. This is in the accordance with the experimental phase diagrams of Giessen et al.[68] and Knapton[67] where there is only a few atomic % (less than 5%) solubility of Nb in hcp-Re until approximately 2500 K. For the bcc solid solution, a negative enthalpy of mixing is calculated and shown in Figure 3.4, indicating that the bcc solid solution is energetically favored. Giessen et al. [68] and Knapton’s [67] results show that Re is very soluble in bcc-Nb, up to 44 % Re, so the calculations agree with the experimental work. Figure 3.4 shows that the magnitude of the bcc mixing curve is optimized to the data predicted by first-principles using both the 0L regular and 1L sub-regular solution terms. The curve, however, does not capture exactly the asymmetrical nature of the data predicted by first-principles. When the bcc mixing curve is fit exactly to data predicted by first-principles calculations, congruent melting is seen in the liquidus on the Nb-rich side of the phase diagram, which is not reported in the literature and must be suppressed. Therefore, the modeling is performed to prevent the existence of a bcc congruent melting. Figure 3.4 also indicates that the fcc solid solution phase has a slightly positive enthalpy of mixing while the liquid has a negative enthalpy of mixing similar to the bcc.

Modeling of σ and χ utilizes the predicted finite temperature properties shown in Figure 3.1 as well as properties for the less stable end-members from Table 3.3. Figure 3.5 and Figure 3.6 show the enthalpies of formation calculated from the Debye model for the end-members of σ and χ at 298K compared with the CALPHAD modeling at 298 K and first-principles predictions at 0K. The entropy of formation at 298 K plotted in Figure 3.7 include both vibrational entropy from the Debye model, \( \Delta_f S_{Re_xNb_y} \), and the ideal entropy of mixing in sublattices as shown by Eq. 3.5 and Eq. 3.6. Plotted in Figure 3.8 are the heat capacities of the most stable end-members of σ, σ-
(Re)_{10}(Nb)_{4}(Nb)_{16}, and χ, \chi-(Re)_{24}(Nb)_{10}(Re)_{24}; included are the predicted Debye model results for comparison. Good agreement is seen for not only the most stable end-members, but also the less stable end-members (not shown).

The large negative value of $^{0}L_{Re:Nb:Re,Nb}$ in $\sigma$ shown in Table 3.5 is indicative of preferential mixing in the 3rd sublattice. A similar trend is seen in the interaction parameters of $\chi$ with all 4 interaction parameters being negative, indicating favorable mixing on those sublattices. It is evident that the interaction parameters involving the most stable end-member, $\chi-(Re)_{24}(Nb)_{10}(Re)_{24}$ ($^{0}L_{Re:Nb:Re,Nb}$ and $^{0}L_{Re:Re,Nb:Re}$), have the greatest effect on the solubility range of $\chi$ and its stability, while the interaction parameters $^{0}L_{Re:Re:Re,Nb}$ and $^{0}L_{Re:Re,Nb:Nb}$ have a much smaller effect on the solubility range of $\chi$. The difference between the evaluated and predicted values for the interaction terms, shown in Table 3.4, Table 3.5, and Figure 3.5 can be attributed to the simple first-principles methodology utilized. Replacing only one atom in the mixing sublattice for each of the $\sigma$ and $\chi$ end-members represent a few atomic percent change in composition of the two constructed mixing structures. Such a calculation is very useful for predicting the sign and relative magnitude of the interaction parameter, while SQS calculations are desirable to predict more accurate interaction parameter values, which requires the creation of complex SQS for the two phases and will be carried out in future works. It is noted that the extreme stability of bcc solid solution, at more than -25 kJ/mol at 50 % Re shown in Figure 3.4 demands for very negative interaction parameters in $\sigma$ and $\chi$ for them to be in equilibrium with bcc. The stability of the bcc solid solution is also shown by Giessen et al.[68] as its phase boundary is determined to extend all the way to approximately 45 % Re. Interaction parameters $^{0}L_{Re:Nb:Re,Nb}$, $^{0}L_{Re:Nb:Re,Nb}$ and $^{0}L_{Re:Re,Nb:Re}$ all have temperature dependent terms to fit phase boundary data at higher temperatures as they are the most dominate interaction terms. Figure 3.9 shows the composition square for $\chi$ with the
temperature and composition dependence of site fractions on the second and third sublattices of $\chi$ depicted. As temperature decreases, the equilibrium site fractions shows increased ordering with Nb favoring the second sublattice. The equilibrium site fractions at 500 K are farther away from the completely random mixture in the second and third sublattices, represented by the diagonal, in comparison to the site fractions at 3000 K.

For $\sigma$, another sublattice model, $\sigma$-(Re)$_8$(Nb)$_4$(Re,Nb)$_{18}$, or $\sigma_1$, developed by Andersson & Sundman[86] is also investigated in the present work. When this model is used, the narrow solubility range of $\sigma$ cannot be captured without severely pushing the phase boundary of $\chi$ towards the Re-rich side of the phase diagram. Joubert[52] noted that there is no experimental evidence to support this model, and it was made by convenience to extend the composition of the Cr atom in the Cr-Fe system. Joubert[52] also states that the recommended $\sigma$ model $\sigma$-(Re)$_{10}$(Nb)$_4$(Re,Nb)$_{16}$ is more appropriate in terms of site occupation, atomic coordination, and thermodynamics.

Once the solid solution, $\sigma$ and $\chi$ phases are modeled preliminarily, the model parameters of the liquid phase are evaluated from the invariant reactions and melting points by Giessen et al.[68]. The $^0L$ regular and $^1L$ sub-regular solution terms are used, with special attention being paid to the bcc solid solution to ensure that congruent melting did not appear on the Nb-rich side of the phase diagram. Figure 3.10 and Figure 3.11 show the final phase diagram of the Nb-Re system from the present work compared to experimental data from Giessen et al.[68]. Table 3.6 compares the calculated invariant reactions in the system with the corresponding experimental values. When all of the parameters predicted via the Debye model are input into the CALPHAD model for $\chi$, its melting is seen at much higher temperatures than observed by experiments. The $\chi$ solidus varies from the observed melting temperature by several hundred degrees. This discrepancy can be traced back to the prediction by the Debye model. The predicted enthalpy of formation for the most stable
end-member of $\chi$, $\chi$-(Re)$_{24}$(Nb)$_{10}$(Re)$_{24}$, is probably too stable at high temperatures. Therefore, its
enthalpy of formation is refined with a greater weight placed on high temperature melting data
observed by Giessen et al [68] in order to produce a more accurate solidus.

Starting on the Nb-rich side of the phase diagram, the present work shows a eutectic at 46
% Re at a temperature of 2724 K ($L \rightarrow bcc + \sigma$) in close agreement with the reported 48 ± 1 % Re
and 2740 ± 10 K. Moving towards the Re-rich side, the peritectic ($L + \chi \rightarrow \sigma$) reaction is also
reproduced well. However, the eutectoid ($\sigma \rightarrow bcc + \chi$) reaction shows slightly less agreement.
The larger discrepancy in Re content and temperature for the eutectoid reaction may be due to the
large uncertainty in experimental data. Giessen et al.[68], even with the most detailed description
of the region around $\sigma$, reported that the peritectic and eutectoid transformation temperatures were
inaccurate in temperature and composition due to difficulties interpreting X-ray patterns [68].
Further experiments in this region of the phase diagram are desirable. Excellent agreement is seen
in the Re-rich eutectic at 86 % Re and 2982 K ($L \rightarrow \chi + hcp$) when compared to the experimental
values of 88 ± 0.5 % Re and 3004 ± 15 K [68]. Figure 3.10 also shows an excellent agreement
between the calculated phase boundaries and those found by Giessen et al. [68]. While not used
in the modeling, Figure 3.12 shows the calculated phase diagram appended with data from
Knapton[67].

3.4 Conclusions

The present work couples the thermodynamic data predicted from first-principles calculations
and experimental phase equilibrium data in the CALPHAD modeling of the Gibbs energy function
of all phases in the Nb-Re binary system. The Debye model is used to predict finite-temperature data of $\sigma$ and $\chi$ such as entropies, enthalpies and heat capacities. In addition, special quasirandom structures (SQS) are used to calculate solid solution enthalpies of mixing to aid the thermodynamic modeling. The calculated phase diagram shows good agreement with the reported phase boundaries and invariant reactions. Some differences between the modeling and experiments are seen around the $\sigma$ region of the phase diagram due to a lack of accurate data pertaining to $\sigma$. 
Tables and Figures

Table 3.1: Lattice parameters of Re, Nb, and the most stable end-members of σ and χ, σ-(Re)_{10}(Nb)_{4}(Nb)_{16} χ-(Re)_{24}(Nb)_{10}(Re)_{24}, respectively. The calculated values at 0 Kelvin are compared to previous experiments and calculations at various temperatures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>Diff. (%)</th>
<th>c/a</th>
<th>Diff. (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (hcp)</td>
<td>P6/mmc</td>
<td>2.771</td>
<td>1.613</td>
<td></td>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>Nb (bcc)</td>
<td>Im3m</td>
<td>3.317</td>
<td>1.615</td>
<td>0.43</td>
<td>0.12</td>
<td>DFT[83]</td>
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<tr>
<td>(Re)<em>{10}(Nb)</em>{4}(Nb)_{16} (σ)</td>
<td>P4/mmm (with disorder)</td>
<td>9.779</td>
<td>0.523</td>
<td></td>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>(Re)<em>{24}(Nb)</em>{10}(Re)_{24} (χ)</td>
<td>I43m</td>
<td>9.677</td>
<td>0.521</td>
<td>0.38</td>
<td>0.38</td>
<td>Experiment[52]</td>
</tr>
</tbody>
</table>

Table 3.2: Various properties of the Re, Nb, σ and χ taken from equilibrium equations of state (EOS) fittings. These fittings are derived from the energy vs. volume curves using the 4-parameter Birch-Murnaghan EOS. B₀ and B₀’ denote the bulk modulus and the first derivate of the bulk modulus, respectively. The bulk modulus at room temperature of Re and Nb are also presented, as reported by Kittel[43].

<table>
<thead>
<tr>
<th>Phase</th>
<th>V₀ (Å³/atom)</th>
<th>B₀ (GPa)</th>
<th>B₀’ (GPa)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (hcp)</td>
<td>14.91</td>
<td>369</td>
<td>4.67</td>
<td>Present work</td>
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<tr>
<td></td>
<td></td>
<td>372</td>
<td></td>
<td>Experiment[43]</td>
</tr>
<tr>
<td>Nb (bcc)</td>
<td>18.34</td>
<td>366</td>
<td>4.47</td>
<td>DFT[75]</td>
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<tr>
<td>(Re)<em>{10}(Nb)</em>{4}(Nb)_{16} (σ)</td>
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<td>227</td>
<td>4.12</td>
<td>Present work</td>
</tr>
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<td>(Re)<em>{24}(Nb)</em>{10}(Re)_{24} (χ)</td>
<td>15.68</td>
<td>325</td>
<td>4.89</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Table 3.3: Predicted enthalpies of formation (J/mol-formula units and atom) of σ and χ at 298 K, with the most stable end-members shown in bold text. J/mol-formula units and J/mol-atom are represented as J/mol-f and J/mol-a, respectively.

<table>
<thead>
<tr>
<th>Phase</th>
<th>End-member</th>
<th>$\Delta_f H$ (J/mol-f)</th>
<th>$\Delta_f H$ (kJ/mol-a)</th>
<th>$\Delta_f S$ (J/mol-f/K)</th>
<th>$\Delta_f S$ (J/mol-a/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(σ)</td>
<td>(Re)$_{10}$(Nb)$<em>4$(Re)$</em>{16}$</td>
<td>-67417</td>
<td>-2.247</td>
<td>-2.033</td>
<td>-0.068</td>
</tr>
<tr>
<td>(χ)</td>
<td>(Re)$_{10}$(Nb)$<em>4$(Nb)$</em>{16}$</td>
<td>-407638</td>
<td>-13.588</td>
<td>-0.692</td>
<td>-0.023</td>
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<tr>
<td></td>
<td>(Re)$<em>{24}$(Re)$</em>{10}$(Re)$_{24}$</td>
<td>256567</td>
<td>4.423</td>
<td>25.456</td>
<td>0.439</td>
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<tr>
<td></td>
<td>(Re)$<em>{24}$(Nb)$</em>{10}$(Re)$_{24}$</td>
<td>-785460</td>
<td>-13.542</td>
<td>28.528</td>
<td>0.492</td>
</tr>
<tr>
<td></td>
<td>(Re)$<em>{24}$(Re)$</em>{10}$(Nb)$_{24}$</td>
<td>252829</td>
<td>4.359</td>
<td>51.029</td>
<td>0.880</td>
</tr>
<tr>
<td></td>
<td>(Re)$<em>{24}$(Nb)$</em>{10}$(Nb)$_{24}$</td>
<td>-610088</td>
<td>-10.519</td>
<td>13.751</td>
<td>0.237</td>
</tr>
</tbody>
</table>

Table 3.4: Predicted interaction parameters (J/mol-formula units and atom) of σ and χ end-members at 0 K.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Value (J/mol-f)</th>
<th>Value (kJ/mol-a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ</td>
<td>$^0L_{Re:Nb:Re,Nb}$</td>
<td>-479251</td>
<td>-8.263</td>
</tr>
<tr>
<td>χ</td>
<td>$^0L_{Re:Nb:Re,Nb}$</td>
<td>-1062781</td>
<td>-18.324</td>
</tr>
<tr>
<td></td>
<td>$^0L_{Re:Re,Nb:Re}$</td>
<td>-1023386</td>
<td>-17.645</td>
</tr>
<tr>
<td></td>
<td>$^0L_{Re:Re,Re:Nb}$</td>
<td>-570825</td>
<td>-9.842</td>
</tr>
<tr>
<td></td>
<td>$^0L_{Re:Re,Nb:Nb}$</td>
<td>-352931</td>
<td>-6.085</td>
</tr>
</tbody>
</table>
Table 3.5: Model parameters (in units of J/mol-formula units).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc (Re, Nb)</td>
<td>$u_L^{bcc}$</td>
<td>-101060, +10.568*T</td>
</tr>
<tr>
<td></td>
<td>$L^{bcc}$</td>
<td>-2300</td>
</tr>
<tr>
<td>hcp (Re, Nb)</td>
<td>$u_L^{hcp}$</td>
<td>64957, -33.387*T</td>
</tr>
<tr>
<td>Liquid (Re,Nb)</td>
<td>$L_{Liq}$</td>
<td>-8017, -23.406*T</td>
</tr>
<tr>
<td></td>
<td>$L^{Liq}$</td>
<td>-2001</td>
</tr>
<tr>
<td>fcc (Re,Nb)</td>
<td>$L^{fcc}$</td>
<td>27628</td>
</tr>
</tbody>
</table>

| Interaction | $G^{Re:Nb:Re}$ | $G^{Re:Nb:Nb}$ | $G^{Re:Re:Re}$ |
|            | -67437          | -407760         | 256567          |
| $\sigma$ (Re)$_1$(Nb)$_{10}$(Re,Nb)$_{16}$ | $G^{Re:Re:Re}$ | -758795         | -25.456*T       |
| $\sigma$-interaction | $G^{Re:Re:Re}$ | 252854          | -28.528*T       |
| $\sigma$-interaction | $G^{Re:Re:Re}$ | -610088         | -13.751*T       |
| $\chi$ (Re)$_{24}$(Re,Nb)$_{10}$(Re,Nb)$_{24}$ | $L^{Re:Re:Re}$ | -1648141        | -289.844*T      |
| $\chi$-interaction | $L^{Re:Re:Re}$ | -749989         | +280.032*T      |
| $\chi$-interaction | $L^{Re:Re:Re}$ | -1200286        |                  |
| $\chi$-interaction | $L^{Re:Re:Re}$ | -352931         |                  |

Table 3.6: Calculated invariant reactions compared to the data by Giessen et al.[68].

<table>
<thead>
<tr>
<th>Invariant reaction</th>
<th>Calc. % Re</th>
<th>Expt. % Re</th>
<th>% Diff.</th>
<th>Calc. T</th>
<th>Expt. T</th>
<th>% Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L $\rightarrow$ bcc + $\sigma$ (eutectic)</td>
<td>46</td>
<td>48±1</td>
<td>3.6</td>
<td>2724</td>
<td>2740±10</td>
<td>0.6</td>
</tr>
<tr>
<td>L + $\chi$ $\rightarrow$ $\sigma$ (peritectic)</td>
<td>54</td>
<td>53±0.5</td>
<td>1.8</td>
<td>2831</td>
<td>2843±10</td>
<td>0.4</td>
</tr>
<tr>
<td>$\sigma$ $\rightarrow$ bcc + $\chi$ (eutectoid)</td>
<td>57</td>
<td>54±0.5</td>
<td><strong>5.7</strong></td>
<td>2441</td>
<td>2460±10</td>
<td><strong>0.8</strong></td>
</tr>
<tr>
<td>L $\rightarrow$ $\chi$ + hcp (eutectic)</td>
<td>87</td>
<td>88±0.5</td>
<td>1.6</td>
<td>2982</td>
<td>3004±15</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Figure 3.1 (color online): Calculated thermodynamic properties of $\chi-(\text{Re})_{24}(\text{Nb})_{10}\text{Re}_{24}$ (solid black line) and $\sigma-(\text{Re})_{10}(\text{Nb})_{4}\text{Nb}_{16}$ (red dashed line) using the Debye model for: (a) entropy, (b) enthalpy, (c) heat capacity as a function of temperature.
Figure 3.2: Volume vs. mole fraction of Re for the fcc (■), hcp (♦) and (●) bcc SQS.
Figure 3.3 (color online): Calculated vibrational entropies (solid black line) of SQS at 50% Re using the Debye model for: (a) bcc, (b) hcp plus bcc-Nb (a) and hcp-Re (b) (red dashed line).
Figure 3.4: Solid solution enthalpy of mixing (kJ/mol-atom) calculated in the present work using SQS for hcp (♦), fcc (▲) and bcc (○) compared to the CALPHAD modeling (solid lines) at 298 K.
Figure 3.5: Enthalpies of formation ($\Delta_H$, kJ/mol-atom) calculated in the present work using the Debye model for the end-members of $\sigma$ (●) and $\chi$ (○) at 298K are compared with the CALPHAD modeling (solid black lines) at 298 K and first-principles predictions at 0K (dashed black lines).
Figure 3.6: Enthalpy of formation ($\Delta_H$, kJ/mol-atom) of the Nb-Re system (solid black line) compared to $\sigma$ and $\chi$ end-members calculated in the present work using the Debye model for $\sigma$ (●) and $\chi$ (○) at 298 K.
Figure 3.7: Entropies of formation ($\Delta_f S$, J/mol-atom/K) calculated in the present work using the Debye model for $\sigma$ (●) and $\chi$ (○) are compared to the CALPHAD modeling (solid black lines) at 298 K with the ideal entropy of mixing included.
Figure 3.8: Heat capacities ($C_p$, J/mol-atom/K) of the most stable end-members of $\sigma$ (right) and $\chi$ (left) from the CALPHAD modeling compared to their respective results from the Debye model ($\triangledown$).
Figure 3.9: Composition square for $\chi$ with the equilibrium site fractions (solid black lines) at 500 K and 3000 K for sublattice II and III and the dashed line for a completely random mixture in sublattices II and III.
Figure 3.10: Calculated phase diagram of the Nb-Re system using the CALPHAD method with data from Giessen et al. [68] superimposed for comparison, single-phase regions (▲), two phase regions (▼), invariant reactions (●), melting points (+), no melting observed points (★) and phase boundaries by X-ray techniques (×).
Figure 3.11: Enlarged view of the σ phase region with three invariant reactions and data from Giessen et al. [68]: single-phase regions (▲), two-phase regions (▽), invariant reactions (●), and melting points (+).
Figure 3.12: Data from Knapton[67] is superimposed to the calculated phase diagram of the Nb-Re system: single-phase regions (▲), bcc + χ (◇), χ + hcp (★), melting points (+), and invariant reactions (●).
4 Debye–Grüneisen scaling factor: A case study of the Mg–Zn binary system

Within the fields of applied physics, materials modeling and thermodynamics property predictions, the Debye-Grüneisen model is used extensively due to its simplicity and accuracy in the low temperature regime for crystalline systems, simple and complex. Such an advantage becomes better seen with more complex crystal systems that significantly amplify computation times [29]. However, when the Debye-Grüneisen model is applied in many cases, the predicted Debye temperatures ($\Theta_D$) do not match with experimental values, a consequence of simplifying the speeds of sounds with respect to the bulk modulus ($B$) and density ($\rho$), or $v = \sqrt{B/\rho}$. In such instances, the model requires a semi-empirical multiplicative scaling factor which will help yield the correct $\Theta_D$ [25], [29], [76], [87]. While previous studies have utilized empirical scaling factors successfully for various crystal systems, the agreements with experiments are somewhat coincidental due to the fact that most materials have a Poisson ratio of approximately 1/3 [76]. It is thus desirable to develop an approach to predict the scaling factor.

Typically, the Debye model is described with just a single speed of sound accounted for all acoustic and optical modes, i.e. a linear phonon dispersion that has no directional dependence and is identical for transverse and longitudinal waves. Crystal speed of sound anisotropy is also ignored as Debye acoustic modes are isotropic and non-directional [43]. However, even for an isotropic medium, the assumption of a single speed of sound for transverse and longitudinal waves is incorrect [76], as shown schematically in Figure 4.1. Thus, one actually uses an *effective speed of sound* that incorporates the transverse and longitudinal speeds in the Debye model. As discussed by Anderson [88], for an isotropic solid, this effective speed of sound can be expressed as:
Eq. 4.1: \[ v = \left[ \frac{1}{3} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \]

where \( v \) is the effective speed of sound, \( v_t = \sqrt{S/\rho} \) the transverse speed, \( v_l = \sqrt{L/\rho} \) the longitudinal speed, \( \rho \) the density, \( S \) the shear modulus, and \( L \) the longitudinal modulus. If instead of calculating the effective speed of sound from Eq. 1, one calculates \( v \) by the formula for the speed of sound in a medium (\( v = \sqrt{B/\rho} \)) and obtains the Debye temperature as follows

Eq. 4.2: \[ (\Theta_D)_0 = \frac{\hbar v}{k_B} \left( \frac{6\pi^2N}{\nu} \right)^{1/3} \]

where \( \hbar \) is the reduced Planck constant, \( \nu \) the constant velocity of sound, \( k_B \) the Boltzmann constant, \( N \) the number of particles, and \( V \) the volume [43]. However, thus calculated Debye temperature is significantly different from the ones evaluated from experimental data. Often, this discrepancy is mended by the introduction of a scaling factor \( s \) that scales the predicted \( (\Theta_D)_0 \) to an experimental one, as shown below, which was implemented by Moruzzi et al. [76] and modified by Shang et al. [25]:

Eq. 4.3: \[ \Theta_D = s A V_0^{1/6} \left( \frac{B_0}{M} \right)^{1/2} \left( \frac{V_0}{V} \right)^{\gamma} \]

In this equation, \( s \) is the Debye temperature scaling factor, \( \gamma \) the Grüneisen parameter, \( A \) a constant equal to \( (6\pi^2)^{1/3} \hbar/k_B \) with the equilibrium volume \( V_0 \) given in Å³, the bulk modulus at 0 K represented by \( B_0 \) in GPa, and the atomic mass \( M \) in grams [25]. The averaged atomic mass of an intermetallic compound is taken as the geometric mass to account for large differences in the masses of the pure elements. As shown in previous studies, the logarithmic average of mass can also be used [89]. If the scaling factor is fit from experimental results, then the Debye temperature
is not strictly calculated from “first-principles”. Note that the Grüneisen parameter $\gamma$ scales $(\theta_D)_0$ with the following equation:

$$\theta_D = (\theta_D)_0 \left(\frac{V_0}{V}\right)^\gamma$$

where $V_0$ and $V$ are the volumes of the rigid-lattice equilibrium (separation distance) and the evaluation volume, respectively. There are three commonly used models for the Grüneisen parameter $\gamma$ to account for vibrational anharmonicity: Slater (S) [90], Dugdale-MacDonald (DM) [91], and Vaschenko-Zubarev (VZ) [92]. By expressing the parameter as $\gamma = (1 + B'_0)/2 - x$ and choosing $x = 2/3$, $x = 0$, or $x = 1$, one arrives at the Slater, VZ and DM limits [41]. This formulation captures the linearity of the parameter with respect to the derivative of the bulk modulus [92] and can represent the high and low temperature assumptions of Grüneisen parameter, respectively [25], [29], [76]. Tests must be conducted to select the models for $\gamma$. In this work, as per recommended by Shang et al. [25], the Slater and Dugdale-MacDonald approximations will be evaluated.

Moruzzi et al. [76] and Herper et al. [87] studied the contributions of such a scaling factor in terms of magnetic and non-magnetic cubic elements. It was demonstrated that by fitting the longitudinal and shear moduli with respect to $B$, roughly constant scaling factors can be derived for many cubic transition metals with a few exceptions. The fitted scaling factors are 0.617 and 0.7638 for non-magnetic and magnetic transition metals, respectively. Chen & Sundman [29] and Lu et al. [89], [93] have also studied the scaling contributions for transition metals, cubic carbides, and nitrides.

In this work, we will validate the findings of Lu et al. and extend the method to perform a case study on the Mg-Zn binary system. While Chen & Sundman [29] and Lu et al. [89], [93] have
studied various classes of crystals, a systematic study of the scaling factor for one binary system has not be accomplished. The Mg-Zn system is chosen as a case study because it contains a multitude of stoichiometric intermetallics that have been studied extensively using experiments [94]–[100]. Mg-Zn intermetallics also have very different crystallography including monoclinic, hexagonal Laves, and cubic phases. The data availability, complexities and crystallographic differences make the Mg-Zn a suitable case study.

4.1 Methodology

The Debye model describes the vibrational properties of an isotropic material. Eq. 4.1 shows that the effective speed of sound in a material can be averaged by the transverse and longitudinal speeds of sound $v_t$ and $v_l$. Both moduli can be represented by the Poisson ratio, $\nu$, and bulk modulus, $B$:

Eq. 4.5: $L = \frac{3B(1-\nu)}{1+\nu}$ and $S = \frac{3B(1-2\nu)}{2(1+\nu)}$

Substituting Eq. 4.5 into Eq. 4.1 yields an equation for the scaling factor as a function of the Poisson ratio, which is also shown in Figure 4.2 and in agreement with previous findings [29], [89]:

Eq. 4.6: $s(\nu) = 3^{5/6} \left[ 4\sqrt{2} \left( \frac{1+\nu}{1-2\nu} \right)^{3/2} + \left( \frac{1+\nu}{1-\nu} \right)^{3/2} \right]^{-1/3}$

The validation of this equation can be done with experimental values obtained by Moruzzi et al. [76] and Herper et al. [87]. Moruzzi determined, by fitting cubic non-magnetic metals, that $L$ and $S$ can be represented by $1.42B$ and $0.30B$, respectively. When these values are put into Eq.
4.6, the predicted value of the scaling factor is 0.617 ($\nu = 0.3661$), as found by Moruzzi. The same analysis can be applied to $L$ and $S$ determined for cubic magnetic metals by Herper et al., giving the correct scaling factor of 0.7638 ($\nu = 0.2976$). It should be noted that both values arrive from Poisson ratios of approximately 1/3, as stated in the introduction.

There are some interesting features of Eq. 6 that are worth noting. This function only gives real values for $-1 < \nu \leq \frac{1}{2}$. Outside this range, the function is complex. This is consistent with the rigorously derived mechanical stability limits on Poisson’s ratio for a stable isotropic material, namely that Poisson’s ratio cannot be greater than $\frac{1}{2}$ or less than -1 (the lower limit is sometimes erroneously given as 0 because materials with negative Poisson ratios are very uncommon) [101]. Another interesting feature is that $s(\nu = 0)$ is not equal to 1. Although there is no reason for $s(\nu = 0)$ to be equal to 1, it may be surprising to some due to the misconception that the scaling factor is necessary because of anisotropy and the misconception that Possion’s ratio is a measure of anisotropy. The actual value of $s(\nu = 0)$ is $\frac{3^{5/6}}{(1+4\sqrt{2})^{1/3}}$ or approximately 1.328.

The differences between the present method of predicting the $\Theta_D$ compared to the methods proposed by Alers [102] lie in the treatment of sound velocities in the transverse and longitudinal directions. Alers proposed a method to integrate over the two transverse and one longitudinal speeds of sound, obtained from sound velocity measurements for elastic constants. This treatment gives rise to a 3-frequency Debye model that partially accounts for crystal symmetry. The current treatment accounts for the sound velocity differences after-the-fact and still implements the 1-frequency Debye model as a result. The consequences of this treatment will be discussed in a later section.
4.1.1 First-principles calculations

Electron-ion interactions are described by the projector augmented-wave (PAW) method [77], [78]. In order to describe electron interactions including exchange and correlation, the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE)[22] is used. Plane wave cutoff energies of 420 eV are consistently used for Mg, Zn and Mg-Zn compounds, as recommended by the VASP [79]. For hcp-Mg and hcp-Zn, $25 \times 25 \times 16$ Monkort-Pack $k$-point grids are implemented. For compounds $\text{Mg}_4\text{Zn}_7$, $\text{MgZn}_2$, and $\text{Mg}_2\text{Zn}_{11}$, we use the $8 \times 8 \times 3$, $11 \times 11 \times 6$, and $6 \times 6 \times 6$ $k$-point grids, respectively. The structures are relaxed by implementing the Methfessel-Paxton method[80] in order to calculate the forces acting on the atoms. After relaxations, a final static calculation using the tetrahedral method with Blöch corrections [81] is applied to ensure an accurate total energy, used for the BM4 EOS fittings.

4.2 Results and Discussion

4.2.1 Bcc, fcc, and hcp elements

It is important to compare the differences between the integration methods proposed by Alers [102] and the treatment using a calculated scaling factor. Debye temperatures of pure elements studied by Alers [102] are investigated first with respect to their calculated and measured ($\theta_D)_0$ at the extrapolated low-temperature limit. These are listed alphabetically in Table 4.1 and are represented in terms of simple elemental crystal systems with Figure 4.3. Direct comparisons with results obtained from Alers ($\theta_D$-Elastic) cannot be made as highly accurate sound velocity measurement values are used for the calculation of the Debye temperature. Therefore, elastic constants predicted from first-principles calculations are implemented in the comparison of the
integration and the scaling factor methods. The validity of the scaling factor treatment is shown to be as consistent and accurate as the direct integration method shown by Alers. Figure 4.3 depicts the \((\theta_D)_0\) calculated from \(s(u)\) and \(s = 0.617\). The differences are presented as the absolute % difference between the calculated and measured \((\theta_D)_0\). It is apparent that the most accurate \((\theta_D)_0\) predictions are for bcc and fcc metals. For all bcc and fcc elements, except Ni, the calculated \(s\) shows better agreement with \((\theta_D)_0\) measurements.

These improvements can be attributed to the error in the fittings of \(B\) vs. \(S\) and \(B\) vs. \(L\) in the original work on only 10 non-magnetic bcc metals by Moruzzi et al. [76]; Chen & Sundman show similar findings in their calculations for elements Cu, Mo and Pd [29]. Additionally, elements such as Cr and W, not assessed by Moruzzi et al., deviate strongly from a constant Poisson ratio as fit by Moruzzi et al. [29]. Elements Ni, Au and Pb, however, show large disagreements (13-30%) compared to measured \((\theta_D)_0\). When the calculated \(C_{ij}\)'s for Au and Pb elements are compared to experimental values, the average error is on the order of the error in the predicted \((\theta_D)_0\). Using the experimental \(C_{ij}\)'s for Au and Pb yields \((\theta_D)_0\) in good agreement with the measured value, indicating the deviations arose from the elasticity calculations.

Alers notes that the discrepancy between estimated and calculated values for Ni arise from magnetic spin wave contributions. If these effects are removed from the experiments, the measured \((\theta_D)_0\) would increase [102]. Hcp metals, as shown in Figure 4.3, also demonstrate an improvement from using a constant value of \(s = 0.617\). Figure 4.3 shows that using a constant value of \(s\) yields disagreements in \((\theta_D)_0\) on the order of 25% for all shown hcp metals. This is significantly improved by introduction of a calculated \(s\). Be and Cd are shown to have larger disagreements in comparison to the other metals due to their less accurate \((\theta_D)_0\) extrapolated data [102]. Overall,
our findings are in accordance with previous studies by Alers [102] and Chen & Sundman for hcp Be and Cd [29].

4.2.2 Mg-Zn case study

4.2.2.1 Pure elements Mg and Zn

Mg and Zn are analyzed in greater detail for the case study. Shown in Table 4.2 and Table 4.3 are 0 K predicted equilibrium lattice parameters and bulk modules, $V_0$ and $B_0$, for Mg and Zn in the hcp phase. These values, except for the bulk modulus of Zn, are shown to agree well with literature values. It should be noted that previous first-principles BM4 equations of state fittings for Zn also show this inherent discrepancy in $B$ [28]. Using the equilibrium properties, the elastic constants for Mg and Zn are evaluated according to the methodology presented in Chapter 2 of this thesis, shown in Table 4.4 as compared to previous experimental and predicted values. Mg is seen to have extremely well-predicted $C_{ij}$ values while Zn is not the case, much like in previous DFT studies [28]. $C_{12}$ and $C_{44}$ in both Mg and Zn disagree with experimental measurements due to the uncertainty in measurements for these values, as noted by Ledbetter et al. [103]. Additionally, the calculated Zn $c/a$ ratios, as seen in Table 4.2, also contribute to the low shear $C_{44}$ ($C_{1212}$) predictions. These elastic constants are evaluated using the VRH average [29] to determine $B$, $v$, $s(v)$ and ultimately $\theta_D$. Table 4.5 presents $B$ for Mg and Zn as calculated by BM4-EOS and VRH averaging methods. While Mg shows consistency for both methods, Zn $B$ at 0 K are under-predicted using either method, with the VRH showing better agreement. Hence, the VRH $B$ is used for Zn in the following thermodynamic predictions.
Comparisons of the predicted and measured Debye temperatures extrapolated to 0 K, as presented in Table 4.1 and Table 4.5, show good agreement for Mg and for Zn. Using the predicted Poisson ratios and scaling factors shown in Table 4.5, finite temperature thermodynamic properties for Mg and Zn are subsequently calculated. Figure 4.4 and Figure 4.5 show the predicted $C_p$ and enthalpies, taken with respect to 298 K ($H-H_{298}$), for pure Mg and Zn as well as experimental fittings from Scientific Group Thermodata Europe (SGTE) [50], [104], [105], the National Institute of Standards and Technology JANAF tables [106], Clusius & Vaughen [107], and Martin D. [108]. Neither the EOS nor $C_{ij}$-VRH $B$ values are able to produce the correct thermodynamics for Zn at both temperature limits. By using the EOS $B$ value, low temperature properties are predicted correctly while the opposite is true for $B$ derived from $C_{ij}$-VRH estimations. This problem inherently lies in the inaccurate $c/a$ ratio predicted for Zn using DFT and consequently the $C_{ij}$-VRH prediction is chosen for better agreement.

When the Grüneisen parameters (approximations shown as Debye (S) for Slater and Debye (DM) for Dugdale-MacDonald) are compared in Figure 4.4, the Slater $\gamma$ reproduces the experimental $C_p$ values of Mg better than the DM $\gamma$. However, Zn predictions are better reproduced using the DM $\gamma$. This can be attributed to the extremely low $B$ for Mg where the DM $\gamma$, while more theoretically correct than Slater’s approximations [92], underestimates volumetric effects at higher temperatures. In all cases, a calculated $s(\nu) = 0.790$ reproduces $C_p$ at 298 K that are in much better agreement in contrast to using $s(\nu) = 0.617$. This is especially true in the case of Zn where using the Moruzzi et al. value severely over predicts the $C_p$ of Zn at all temperatures.
4.2.2.2 Intermetallics of the Mg-Zn binary system

The intermetallic compounds, $\text{Mg}_4\text{Zn}_7$ ($\text{Mg}_2\text{Zn}_3$), $\text{MgZn}_2$ (Laves), and $\text{Mg}_2\text{Zn}_{11}$, in the Mg-Zn system are investigated in the current work. Note that the exact stoichiometry for $\text{MgZn}$ is not known, and $\text{Mg}_5\text{Zn}_{20}$ is not of interest as it exists over a minuscule temperature range (598-614 K). Additionally, the stoichiometry for $\text{Mg}_2\text{Zn}_3$ is debated with $\text{Mg}_4\text{Zn}_7$ being accepted as the best model \cite{109}, \cite{110}. We have analyzed $\text{Mg}_4\text{Zn}_7$, $\text{MgZn}_2$, and $\text{Mg}_2\text{Zn}_{11}$ in the same fashion as Mg and Zn. Table 4.2 and Table 4.3 show that the predicted properties at 0 K for all three intermetallics agree with previous theoretical and experimental investigations at 4.2 and 298 K. Calculated $C_{ij}$ values for the intermetallics are shown in Table 4.4 and agreement is seen for $\text{Mg}_4\text{Zn}_7$ and $\text{MgZn}_2$ as compared to previous studies; $C_{ij}$ values of $\text{Mg}_2\text{Zn}_{11}$ could not be found in the literature for comparison. Table 4.5 presents various intermetallic properties after applying the VRH approximation; good agreements are seen for $B_0$, $\nu$, and $\Theta_D$. Further analysis is accomplished by using experimentally measured $C_p$ and $H_H^{298}$ values. Plotted in Figure 4.6, Figure 4.7, and Figure 4.8 are the finite-temperature thermodynamic properties for $\text{Mg}_4\text{Zn}_7$, $\text{MgZn}_2$, and $\text{Mg}_2\text{Zn}_{11}$, respectively. For both $\text{Mg}_4\text{Zn}_7$ and $\text{MgZn}_2$, the thermodynamic predictions are corroborated by experiment. A slight disagreement is seen in the finite-temperature heat capacity of $\text{Mg}_4\text{Zn}_7$, shown in Figure 4.6, as it takes on a slightly different composition than the measured one, $\text{Mg}_2\text{Zn}_3$. Deviations at higher temperatures are also seen as the Debye model does not account for formation of vacancies, anharmonicity and other high temperature effects. In all cases, using $s(t) = 0.617$ severely over predicts the $C_p$ of the intermetallics at all temperatures.

Figure 4.8 shows that the predictions for $\text{Mg}_2\text{Zn}_{11}$ are poor with strong deviations in heat capacity around 50-150 K. Euchner et al. \cite{99}, using neutron scattering techniques as well as \textit{ab initio} calculations, have shown extremely anomalous lattice dynamics in $\text{Mg}_2\text{Zn}_{11}$. By careful
analysis of the phonon density of states (PDOS) spectrum, Van Hove singularities are aplenty and appear for energy as low as 4.5 meV, unusual for a nearly-close-packed metallic phase. Strong acoustic-optical phonon interactions across the whole spectrum also contribute to the anomaly. Therefore, the Debye model cannot capture the complex lattice dynamics of Mg$_2$Zn$_{11}$ due to its strong phonon-phonon interactions and low energy Van Hove singularities. Euchner et al. shows that \textit{ab initio} phonon calculations can somewhat replicate the complex lattice behavior [99]. This phenomenon may be related to the contributions from metastable microstates, resulting in the entropic and thermal expansion anomalies as demonstrated in our recent works [111], [112].

On the other hand, the MgZn$_2$ (Laves) PDOS shows a classical quadratic shape with no irregularities allowing the Debye model to be applied successfully. Predicted enthalpies of formation at 298 K ($\Delta_f H_{298}$) for Mg$_4$Zn$_7$, MgZn$_2$, and Mg$_2$Zn$_{11}$ are shown in Figure 4.9 along with calorimetric data in the literature. The reference enthalpies of Mg and Zn used in these predictions are also from the Debye model and are shown in Figure 4.4 and Figure 4.5. All intermetallic enthalpies of formation show good agreement with previous findings. The DM $\gamma$ is used as the Grüneisen parameter for all intermetallics in this system (shown on plots simply as ‘Debye’) due to the higher $B$ values. While not shown on the plots, Slater’s $\gamma$ over-predicts the $C_p$ values as it incorrectly assumes that $\nu$ is invariant with temperature changes [92]. In Mg$_2$Zn$_{11}$, the agreement at low temperatures for $s(\nu) = 0.617$ is simply a coincidence as there is no physical reason to use the value fit by Moruzzi et al. for pure metals [76].
4.3 Conclusion

Predicted $\theta_D$ for bcc, fcc, and hcp metals, using a calculated scaling factor, show good agreement in comparison with using a single scaling factors given by Moruzzi et al. [76]; this is in agreement with findings by Chen and Sundman [29]. Mg-Zn is used as a case study to investigate the scaling factor treatment for the Debye-Grüneisen model as a means to predict accurate finite temperature vibrational contributions to the free energy. The scaling factor treatment is able to reproduce experimental heat capacities and enthalpies for Mg$_4$Zn$_7$ and MgZn$_2$ very well, but not for the complex Mg$_2$Zn$_{11}$ phase. Mg$_2$Zn$_{11}$ shows anomalous lattice dynamic behavior even at very low temperatures. The use of $s(\nu) = 0.617$ is not appropriate for any of the intermetallics, especially near room temperatures. We believe the true utility of using a calculated scaling factor lies in its use for efficiently predicting finite-temperature properties of crystalline systems.
Tables and Figures

Table 4.1: Predicted Debye temperatures, using two different methods, \((\theta_D\text{-B.}\nu, \theta_D\text{-Int.})\), for pure elements compared to experimental values \((\theta_D\text{-Calor.})\) extrapolated to 0 K adapted from Alers [102]. The elements with the largest disagreements in \(\theta_D\) are bolded. \(\theta_D\text{-Calor.}\) denotes values obtained from calorimetric measurements and extrapolated to 0 K. Also listed in the tables are the \(\theta_D\) values predicted using an integration method \((\theta_D\text{-Elastic})\) using measured elastic constants from Alers [102]. The differences are taken with respect to the calorimetric measurements. Except for Mg and Zn, first-principles elastic constants are taken with permission from Shang et al. [28].

<table>
<thead>
<tr>
<th>Element</th>
<th>(\theta_D\text{-Calor.})</th>
<th>(\theta_D\text{-Elastic})</th>
<th>% Diff.</th>
<th>(\theta_D\text{-Int.})</th>
<th>% Diff.</th>
<th>(\theta_D\text{-B.}\nu)</th>
<th>% Diff.</th>
</tr>
</thead>
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<td>bcc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>445.0</td>
<td>478.1</td>
<td>7.4</td>
<td>465.0</td>
<td>4.5</td>
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<td>5.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>470.0</td>
<td>474.0</td>
<td>0.9</td>
<td>451.9</td>
<td>3.9</td>
<td>457.8</td>
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</tr>
<tr>
<td>Niobium</td>
<td>238.0</td>
<td>276.2</td>
<td>16.1</td>
<td>213.3</td>
<td>10.4</td>
<td>241.8</td>
<td>1.6</td>
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<tr>
<td>Tantalum</td>
<td>240.0</td>
<td>263.8</td>
<td>9.9</td>
<td>243.3</td>
<td>1.4</td>
<td>245.9</td>
<td>2.5</td>
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<tr>
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<td>384.3</td>
<td>1.7</td>
<td>366.3</td>
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<td>366.7</td>
<td>3.0</td>
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<tr>
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<td>399.3</td>
<td>18.1</td>
<td>301.7</td>
<td>10.7</td>
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<tr>
<td>Aluminum</td>
<td>427.7</td>
<td>430.6</td>
<td>0.7</td>
<td>383.8</td>
<td>10.3</td>
<td>385.4</td>
<td>9.9</td>
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<tr>
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<td>345.2</td>
<td>0.2</td>
<td>340.9</td>
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<td>Gold</td>
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<td>161.6</td>
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<td>132.2</td>
<td>19.5</td>
<td>139.2</td>
<td>15.2</td>
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<td>Lead</td>
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<td>105.3</td>
<td>1.3</td>
<td>125.9</td>
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<td>138.6</td>
<td>29.9</td>
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<td>476.7</td>
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<tr>
<td>Silver</td>
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<td>226.4</td>
<td>0.5</td>
<td>212.2</td>
<td>5.8</td>
<td>227.0</td>
<td>0.8</td>
</tr>
<tr>
<td>hcp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beryllium</td>
<td>1160.0</td>
<td>1462.0</td>
<td>26.0</td>
<td>1484.9</td>
<td>28.0</td>
<td>1489.1</td>
<td>28.4</td>
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<td>162.9</td>
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<td>175.1</td>
<td>20.2</td>
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<td>385.9</td>
<td>5.0</td>
<td>348.5</td>
<td>14.2</td>
<td>377.3</td>
<td>7.1</td>
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<td>Yttrium</td>
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<td>256.4</td>
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<td>7.5</td>
<td>252.7</td>
<td>7.5</td>
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<tr>
<td>Zinc</td>
<td>337.0</td>
<td>327.1</td>
<td>2.9</td>
<td>264.8</td>
<td>21.4</td>
<td>306.0</td>
<td>9.2</td>
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Table 4.2: Predicted lattice parameters of Mg, Zn, Mg₄Zn₇, MgZn₂, and Mg₂Zn₁₁. The calculated values at 0 K are compared to previous experiments and calculations at various temperatures (listed if known).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (hcp)</td>
<td>$P6_3/mmc$</td>
<td>3.192</td>
<td>$a$</td>
<td>5.181</td>
<td>1.623</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.189</td>
<td>$a$</td>
<td>5.169</td>
<td>1.621</td>
<td>DFT[83]</td>
</tr>
<tr>
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<td></td>
<td>3.203</td>
<td>$a$</td>
<td>5.199</td>
<td>1.623</td>
<td>Expt. [113]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.210</td>
<td>$a$</td>
<td>5.210</td>
<td>1.623</td>
<td>Expt.[43]</td>
</tr>
<tr>
<td>Zn (hcp)</td>
<td>$P6_3/mmc$</td>
<td>2.654</td>
<td>$a$</td>
<td>5.041</td>
<td>1.900</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.660</td>
<td>$a$</td>
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<td>1.856</td>
<td>DFT[83]</td>
</tr>
<tr>
<td>298 K</td>
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<td>2.665</td>
<td>$a$</td>
<td>4.947</td>
<td>1.856</td>
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</tr>
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<td></td>
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<td>$a$</td>
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<td>Mg₄Zn₇</td>
<td>$C2/m$</td>
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<td>MgZn₂</td>
<td>$P6_3/mmc$</td>
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<td>$a$</td>
<td>8.541</td>
<td>1.639</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.223</td>
<td>$a$</td>
<td>8.566</td>
<td>1.640</td>
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</tr>
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<td>Mg₂Zn₁₁</td>
<td>$Pm\bar{3}$</td>
<td>8.540</td>
<td>$a$</td>
<td>-</td>
<td>-</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.540</td>
<td>$a$</td>
<td>-</td>
<td>-</td>
<td>Expt. [99]</td>
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</table>
Table 4.3: Various properties of the Mg, Zn, Mg$_4$Zn$_7$, MgZn$_2$, and Mg$_2$Zn$_{11}$ taken from equilibrium 4-parameter Birch-Murnaghan equations of state (EOS) fittings. $B_0$ and $B_0'$ denote the bulk modulus and the first derivative of the bulk modulus, respectively. Experimental and previously calculated bulk moduli at low temperatures are also reported. Temperatures for experimentally derived constants, if known, are denoted under ‘Phase’. Note: 0 K values represent extrapolation from low temperatures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_0$ (Å$^3$/atom)</th>
<th>$B_0$ (GPa) - EOS</th>
<th>$B_0'$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (hcp)</td>
<td>22.86</td>
<td>36.4</td>
<td>3.85</td>
<td>Present work</td>
</tr>
<tr>
<td>0 K</td>
<td>22.89</td>
<td>35.7</td>
<td>4.12</td>
<td>DFT[28]</td>
</tr>
<tr>
<td>Zn (hcp)</td>
<td>15.37</td>
<td>55.6</td>
<td>5.38</td>
<td>Present work</td>
</tr>
<tr>
<td>4.2 K</td>
<td>15.40</td>
<td>51.8</td>
<td>7.40</td>
<td>DFT[28]</td>
</tr>
<tr>
<td>Mg$_4$Zn$_7$</td>
<td>16.96</td>
<td>60.6</td>
<td>5.00</td>
<td>Present work</td>
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<td>MgZn$_2$</td>
<td>16.73</td>
<td>61.7</td>
<td>5.20</td>
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</tr>
<tr>
<td></td>
<td>16.01</td>
<td>67.6</td>
<td>5.11</td>
<td>Present work</td>
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Table 4.4: Calculated elastic constants ($C_{ij}$) in Voigt notation and units of (GPa) for Mg, Zn, Mg$_4$Zn$_7$, MgZn$_2$, and Mg$_2$Zn$_{11}$. Experimental and previously calculated results are shown as well (temperatures listed if known). Note: 0 K values represent extrapolation from low temperatures.

<table>
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<th>Phase</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{15}$</th>
<th>$C_{23}$</th>
<th>$C_{25}$</th>
<th>$C_{35}$</th>
<th>$C_{46}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>61.4</td>
<td>65.1</td>
<td>17.7</td>
<td></td>
<td>26.8</td>
<td>21.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>0 K</td>
<td>58.1</td>
<td>64.7</td>
<td>14.2</td>
<td></td>
<td>27.6</td>
<td>21.6</td>
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<td></td>
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<td>Expt. [117]</td>
</tr>
<tr>
<td>Zn</td>
<td>159.4</td>
<td>48.5</td>
<td>24.4</td>
<td></td>
<td>53.7</td>
<td>45.2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Present work</td>
</tr>
<tr>
<td>4.2 K</td>
<td>159.5</td>
<td>57.0</td>
<td>23.2</td>
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<td>56.0</td>
<td>51.8</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td>Expt. [118]</td>
</tr>
<tr>
<td>Mg$_4$Zn$_7$</td>
<td>104.4</td>
<td>122.6</td>
<td>125.4</td>
<td>30.7</td>
<td>27.2</td>
<td>30.8</td>
<td>38.8</td>
<td>55.5</td>
<td>43.2</td>
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<td>0.3</td>
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<td>Present work</td>
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<td></td>
<td>119.0</td>
<td>112.0</td>
<td>100.0</td>
<td>29.0</td>
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<td>32.0</td>
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<td>MgZn$_2$</td>
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<td>58.9</td>
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<tr>
<td>0 K</td>
<td>92.0</td>
<td>126.0</td>
<td>24.0</td>
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<td>37.0</td>
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<td>Mg$<em>2$Zn$</em>{11}$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

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Table 4.5: Various properties of the Mg, Zn, Mg₄Zn₇, MgZn₂, and Mg₂Zn₁₁ calculated using predicted elastic constants. Bulk moduli and Poisson ratios estimated using the Voigt-Reuss-Hill averages are represented by $B₀$ – VRH and $\nu$ – VRH. Previous investigations are shown for comparison. For the listed Debye temperatures, ‘el’ refers to values derived from elastic constants at low temperatures (listed if known). Note: 0 K values represent extrapolation from low temperatures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$B₀$ (GPa) - EOS</th>
<th>$B₀$ (GPa) - VRH</th>
<th>$\nu$ - VRH</th>
<th>$s(\nu)$</th>
<th>$\Theta_D$ (K)</th>
<th>Source</th>
</tr>
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<tr>
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<td></td>
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<td>0.26</td>
<td>0.840</td>
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<td>0.796</td>
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<td></td>
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<td>Expt. [118],</td>
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<td>58.7</td>
<td>0.301</td>
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<td>[121]</td>
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<td>Mg₄Zn₇</td>
<td>60.6</td>
<td>69.3</td>
<td>0.301</td>
<td>0.756</td>
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<td>Present work</td>
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<td></td>
<td>58.7</td>
<td></td>
<td>0.27</td>
<td>0.820</td>
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<td>61.7</td>
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<td>Expt. [94]</td>
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Figure 4.1 (color online): Shown in (a) and (b) are spherical plots of the speeds of sound in units of km/s for the anisotropic and isotropic cases, respectively. Plots (b) and (d) represent the (001)-plane cross-sections of (a) and (b). Red (dot dashed), green (solid) and blue (dashed) represent the longitudinal, transverse 1 and transverse 2 speeds of sound.
Figure 4.2: Scaling factor, $s$, as a function of the isotropic Poisson ratio, $\nu$. Please note that a $\nu=0$ does not denote a $s$ of 1, but rather 1.327.

Figure 4.3: A visual representation of Table 4.1 categorized by crystal structure: bcc (left), fcc (middle), hcp (right). The values predicted with a scaling factor of 0.617 are represented by (●). Variable scaling factor predictions are denoted with (△).
Figure 4.4: Heat capacities ($C_p$, J/mol-atom/K) and enthalpies ($H-H_{298}$, J/mol-atom) of pure hcp-Mg calculated using the Debye-Grüneisen model with a calculated $s(\nu)$. Experimental $C_p$ and $H-H_{298}$ data are obtained from NIST-JANAF [106], SGTE [50], [104], [105], and Clusius & Vaughan [107]. The Debye prediction using a scaling factor of 0.617 uses the Slater $\gamma$. 
Figure 4.5: Heat capacities ($C_p$, J/mol-atom/K) and enthalpies ($H-H_{298}$, J/mol-atom) of pure hcp-Zn calculated using the Debye–Grüneisen and $s(\nu)$. Experimental $C_p$ and $H-H_{298}$ data are obtained from NIST-JANAF [106], SGTE [50], [104], [105], and Martin D. [108]. Debye – $C_{ij}$ and – E.O.S. refer to the bulk moduli values obtained from the elastic constants-VRH method and equations of state fittings, respectively.
Figure 4.6: Heat capacities \((C_p, \text{ J/mol-atom/K})\) and enthalpies \((H-H_{298}, \text{ J/mol-atom})\) of Mg\textsubscript{4}Zn\textsubscript{7} calculated using the Debye-Grüneisen model with a calculated \(s(\nu)\). Experimental \(C_p\) and \(H-H_{298}\) data are obtained from Morishita et al. (2006, 2005) [95], [97].
Figure 4.7: Heat capacities \((C_p, \text{J/mol-atom/K})\) and enthalpies \((H-H_{298}, \text{J/mol-atom})\) of MgZn\(_2\) calculated using the Debye-Grüneisen model with a calculated \(s(\nu)\). Experimental \(C_p\) and \(H-H_{298}\) data are obtained from Morishita et al. [97], Morishita & Koyama [96] and Berche et al. [100].
Figure 4.8: Heat capacities ($C_p$, J/mol-atom/K) and enthalpies ($H-H_{298}$, J/mol-atom) of Mg$_2$Zn$_{11}$ calculated using the Debye-Grüneisen model with a calculated $s(v)$. Experimental $C_p$ and $H-H_{298}$ data are obtained from Morishita et al. [97] and Morishita & Koyama [96].
Figure 4.9: Predicted enthalpies of formation ($\Delta_f H_{298}$, kJ/mol-atom) at 298 K for Mg$_4$Zn$_7$, MgZn$_2$, and Mg$_2$Zn$_{11}$ compared to experimental data from multiple sources: Morishita et al. [97], Schneider et al. [123], Biltz [124], King et al. [125], Berche et al. [100].
5 First-principles calculations, experimental study, and thermodynamic modeling of the Al-Co-Cr system

Computational design of effective MCrAl-based coating compositions necessitates a thermodynamic description methodology which can predict phase compositions and fractions at the temperatures of interest. Limitations are known to exist in the current description of the quaternary Al-Co-Cr-Ni system for Co contents in excess of 20 wt. % [126], [127] which are common in practice [3], [13], [128]. While assessment of the Al-Cr-Ni system has been well documented [1], the thermodynamic properties of the Al-Co-Cr system have not been adequately assessed. Phases important to coating systems are B2 (β, \(Pm\bar{3}m\), simple cubic type) and fcc-Al (γ, \(Fm\bar{3}m\), disordered f.c.c.). However, bcc-A2 (α, \(Im\bar{3}m\), disordered b.c.c.), hcp-A3 (ε, \(P6_3/mmc\), disordered h.c.p.) and sigma (σ, \(P4_2/mmm\), Frank-Kasper) must also be modeled to allow for a complete description. One important feature of the Al-Co-Cr system is the A2/B2 second-order transformation at temperatures above 1373 K [129]. The present study aims to construct a thermodynamic model accounting for the A2/B2 ordering phenomenon, where atoms take on distinct lattice sites in B2. The two phases have vastly different compositions at low temperatures, but merge to similar compositions at higher temperatures which has to be accounted for in the thermodynamic model.

As phase equilibrium data are scarce, especially in the important B2+γ+σ region, experiments are conducted in this study at 1173, 1273, and 1373 K to aid the thermodynamic modeling. Additionally, first-principles calculations based on density functional (DFT) theory are incorporated to supplement the lack of experimentally measured thermochemical data in the ternary system [65] as well as to study the A2+B2 miscibility gap that is prevalent over the entire
phase diagram. Ultimately, this system will be used in the construction of a multicomponent Al-Co-Cr-Ni-Y database. As a result, this database needs to be compatible with previously modeled Al-Co-Ni [130] and Al-Cr-Ni [1] systems.

Ishikawa et al. [129] investigated the Al-Co-Cr system in the temperature range 1273-1623 K using multi-phase alloys and diffusion couples. Isotherms at 1573 and 1623 K showed complete dissolution of $\sigma$ and a particularly large composition range for the B2 phase. The experimental work also provided compositions for the A2/B2 order-disorder transition at 1473 K and above, which are important to the present modeling. Previous models are combined with ternary data from the literature and this work to produce the overall thermodynamic description.

Two Al-Co-Cr ternary models are produced in this thesis. The Co-Cr binary by Oikawa et al. [131] is used in the modeling of Al-Co-Cr in this chapter while the model produced using the binary by Kusoffsky et al. [132] is presented in the following chapter. These differences will be detailed in the following chapter as well.

5.1 Binary systems

A brief overview of all the binary systems used in the modeling of the Al-Co-Cr ternary is presented in this section.

5.1.1 Al-Co

The Al-Co system assessed by Dupin and Ansara [62] showed good agreement with phase-boundary data. Later, Ohtani et al. [133] re-modeled the Al-Co system using a 4-sublattice model
for the bcc phase, instead of the 2-sublattice model applied by Dupin and Ansara [1], but the B2+γ solubility showed discrepancies with measured data; their description is therefore not used in the current work. The Al-Co system originally assessed by Dupin and Ansara [62] is instead updated with the results by Stein et al. [134] who improved the B2 solubilities on both the Al- and Co-rich sides using additional experiments. It should be noted that thermodynamic model by Stein et al. [134] is not used because of incompatibility with the Al-Cr-Ni [1] system adopted in the current work. This stems from the use of interaction parameters involving elements and vacancies that are different in the two descriptions [134][1]. Furthermore, the original Al-Co system as assessed by Dupin and Ansara [62] is compatible with the important Al-Co-Ni ternary, previously modeled by Dupin [130]. In the updated assessment, which is depicted in Figure 5.1, the melting behavior of the B2 was considered carefully, aiding in the extrapolation of the B2 phase for the ternary system.

5.1.2 Al-Cr

Saunders' [135] assessment of the Al-Cr system, shown in Figure 5.2, also agrees well with experimental data, although some intermetallic solubilities have been omitted; these intermetallics are outside the scope of this study and do not affect the ternary assessment. The A2 to B2 transition in the Al-Cr system is currently unknown. Helander and Tolochko cast 4 alloys and found strange XRD peaks at 1158 K and 1178 K for two samples that are possible with B2 ordering. Dupin et al. [1] noted that if this B2 ordering is taken into account, then the A2 phase boundary with AlCr2 will be incorrect and suggested further experiments for confirmation before modification of the phase description. In the current model, the presence of B2 at high temperatures has been suppressed following the assessment by Dupin et al.[1].
5.1.3 Co-Cr

Kusoffsky and Jansson [132] assessed the Co-Cr binary system and achieved good agreement with experimental phase boundary data. Though, the boundary between A2 Cr and $\sigma$ shows some inconsistency. More recently, Oikawa et al. re-modeled the system using newly measured activity data, enthalpy [136] and phase boundary data [131] that are crucial in the extension to the Al-Co-Cr ternary. Both models are shown in Figure 5.3. In the first iteration of modeling Al-Co-Cr, the model by Oikawa et al. is used [131] as it is used in the ternary modeling of Co-Cr-Ni [137], an important ternary in the future modeling of the quaternary Ni-Co-Al-Cr system. In the Co-Cr system, no indications of B2 ordering has been reported, hence the B2 phase is modeled as a metastable phase in this binary. As is shown later, both binaries are tested in the extension of the quaternary system with the model by Kusoffsky and Jansson [132] chosen as the ultimate.

5.2 Materials and Methods

5.2.1 Experimental procedures

From collaborators Thomas Gheno and Brian Gleeson at the University of Pittsburgh:

Ingots of nominal compositions (at. %) Co-20Cr-20Al-0.4Y (A4), Co-26Cr-11Al-0.1Y (A5), Co-35Cr-6Al-0.1Y (A6) and Co-35Cr-11Al-0.1Y (A7) were prepared by arc-melting and drop-cast in a chamber evacuated and back-filled with 0.5 atm of argon. Specimens were cut to
approximate dimensions of 10 x 10 x 1 mm, vacuum-encapsulated in quartz capsules, homogenized for 48 h at 1423 K in a tube furnace, and slowly brought to equilibration temperature. Equilibration treatments were conducted at 1173, 1273 and 1373 K for 500, 200 and 100 h, respectively, followed by water quenching to retain the equilibrated microstructures. Phase constitutions were studied by X-ray diffraction (XRD) with a PANalytical Empyrean instrument, using a Co radiation source (Kα1=1.789 Å).

Polished sections of the heat-treated alloys were prepared by standard metallographic procedures. Phase compositions were determined by electron probe micro-analysis (EPMA) using a JEOL JXA-8530F field emission gun instrument. For each element, measured intensities were converted to concentrations by interpolation via a calibration curve built using a series of standards of known compositions (chemical analysis by inductively coupled plasma mass spectrometry). The probe size used during measurements was about 1 µm, and the alloy microstructures were sufficiently coarse for each phase to be analyzed individually.

5.2.2 CALPHAD thermodynamic models

5.2.2.1 Solution phases: bcc, fcc (γ), hcp (ε), and liquid

To account for the A2/B2 order-disorder transition, the bcc phase is modeled using the partitioning model, which treats the ordered and disordered components separately [56]. Additionally, triple-defect mechanisms are especially important when considering site ordering in B2-aluminide-containing systems such as Al-Co [62], Al-Fe [55] or Al-Ni [1]. To account for this phenomenon [29] when the A2 phase is combined with the B2 phase, vacancies have been
introduced in the substitutional sublattice of the A2 phase model as in Ref. [56]. Ordering of the bcc phase will be described in the following section.

5.2.2.2 Intermetallic phases: B2 and σ

The two ordered phases, B2 and σ, are described using sublattice models based on the compound energy formalism (CEF) [71]. In order to describe the A2/B2 ordering for the bcc phase, both A2 and B2 are modeled using a single Gibbs energy function where the ordered part (B2) is described by a sublattice formula \((\text{Al,Co,Cr,Va})_1(\text{Al,Co,Cr,Va})_1\) and the disordered part (A2) by \((\text{Al,Co,Cr,Va})_1\). Specifically, B2 is appended to the already existing A2 model. Then, as implemented in Thermo-Calc, free energy minimization determines whether A2 and/or B2 are stable depending on the input conditions. In addition, a set of parameterization constraints derived by Dupin and Ansara [56] are used to partition the ordered and disordered parts of the A2/B2 Gibbs energy to allow independent evaluations. The B2 phase contains six stoichiometric compounds, or "end-members" (excluding vacancies) which represent the reference states generated when pure components fully occupy a sublattice; i.e. B2-(Al)(Al), B2-(Al)(Co), B2-(Al)(Cr), B2-(Co)(Cr), B2-(Co)(Co), and B2-(Cr)(Cr). The end-members of the B2 phase in the present system all come from binary systems and as a result, their formation energies are fixed by the previous Al-Co and Al-Cr binary assessments in this model; B2 is not included in the Co-Cr assessment by Oikawa et al. [131] and is therefore modeled in the present work.

The partitioning model describes the A2 and B2 with one single Gibbs energy function and the same sublattice model, \((\text{Al,Co,Cr,Va})_1(\text{Al,Co,Cr,Va})_1\). As a result, the Gibbs energy of A2 combined with B2 is described as:
Eq. 5.1: \[ G^\alpha_\beta^m = G^\beta_m(x_i) + \Delta G^{\text{order}}_m(y_i^{(s)}) \]

to include contributions from the disordered solution, \( G^\beta_m(x_i) \), in A2 as well as from the ordered B2 itself, \( \Delta G^{\text{order}}_m(y_i^{(s)}) \). Here, \( \Delta G^{\text{order}}_m(y_i^{(s)}) \) can be separated into two terms, and the total Gibbs energy of A2 and B2 becomes:

Eq. 5.2: \[ G^\alpha_\beta^m = G^\alpha_m(x_i) + G^{\beta(O)}_m(y_i^{(s)}) - G^{\beta(O)}_m(y_i^{(s)} = x_i) \]

where \( y_i^{(s)} \) denotes the site fraction of element \( i \) on sublattice \( s \). It can be seen that the ordering independent term, \( G^\alpha_m(x_i) \), and the ordering dependent terms \( G^{\beta(O)}_m(y_i^{(s)}) \) and \( G^{\beta(O)}_m(y_i^{(s)} = x_i) \) are separated in a way to allow each to be modeled independently. The term \( G^{\beta(O)}_m(y_i^{(s)}) \) takes on the partitioned form, as described by Dupin and Ansara [56]:

\[
G^{\beta(O)}_m(y_i^{(s)}) = \sum_i \sum_j \left( y_i y_j^* a G^{\beta(O)}_{ij} + y_j^* y_i^* \psi G^{\beta(O)}_{ji} \right) + RT \left[ \sum_i y_i \ln(y_i) + \sum_j y_j^* \ln(y_j^*) \right]
\]

Eq. 5.3: \[
= \sum_i \sum_j \sum_k \left( y_i y_j y_k^* \left( \sum'_v L^{\beta(O)}_{ij,k} (y_i^* - y_j^*)^v \right) \right) + \sum_i \sum_j \sum_k \left( y_k^* y_j y_i^* \left( \sum'_v L^{\beta(O)}_{ki,j} (y_i^* - y_j^*)^v \right) \right)
+ \sum_i \sum_j \sum_k \sum_l \left( y_i y_j y_k y_l^* L^{\beta(O)}_{ij,k,l} + y_j y_i y_k y_l^* L^{\beta(O)}_{ji,k,l} \right)
\]

When the phase becomes disordered, i.e. \( y_i^* = y_j^* = x_i^* \), \( G^{\beta(O)}_m(y_i^{(s)}) - G^{\beta(O)}_m(y_i^{(s)} = x_i) \) equals zero and eliminates the ordering energy contribution. The equivalence of the CEF and partitioned models is obtained using \( 2G^{\text{Partition}}_m(y_i^{(s)}) = G^{\text{CEF}}_m(y_i^{(s)}) \). In Eq. 5.3, \( a G^{\beta(O)}_{ij} \) represents the Gibbs energy of a B2 end-member expressed by Eq. 5.6 with \( i \) and \( j \) in the first and second sublattices, respectively. \( L^{\beta(O)}_{ij,k} \) is the interaction term between end-members of \( i:j \) and \( i:k \) that takes the form
of \( A + B \times T \) where \( A \) and \( B \) are the model parameters to be evaluated in modeling process. Relationships between the interaction parameters used in the CEF and partitioned models exist and are derived by Dupin and Ansara [56]. B2 end-members have both sites equivalent to one another so A2 disordering is possible when those sites have the same disordered occupancy. This crystallographic site equivalency is taken into account with the following expressions [56]:

\[
\text{Eq. 5.4: } \alpha G_{ij}^{\beta} = \alpha G_{ji}^{\beta}, \ \gamma L_{ij,k}^\beta = \gamma L_{ji,k}^\beta, \ \gamma L_{i,j,k}^\beta = \gamma L_{i,j,k}^\beta, \ \text{and } \gamma L_{i,j,k}^\beta = \gamma L_{i,j,k}^\beta
\]

As adopted from the Co-Cr binary [131], \( \sigma \) is modeled with the sublattice formulation \((\text{Al,Co})_8(\text{Al,Co,Cr})_{18}(\text{Cr})_4\). The phase \( \sigma \) contains \( \sigma-(\text{Al})_8(\text{Al})_{18}(\text{Cr})_4, \ \sigma-(\text{Al})_8(\text{Cr})_{18}(\text{Cr})_4, \ \sigma-(\text{Co})_8(\text{Co})_{18}(\text{Cr})_4, \ \sigma-(\text{Co})_8(\text{Cr})_{18}(\text{Cr})_4 \) binary and \( \sigma-(\text{Al})_8(\text{Co})_{18}(\text{Cr})_4, \ \sigma-(\text{Co})_8(\text{Al})_{18}(\text{Cr})_4 \) ternary end-members. To extend the solubility of \( \sigma \) from the binary Co-Cr system, Al must be introduced while keeping consistency with the original model for \( \sigma \). Joubert [52] suggested that Al should only be allowed to mix in the first and second sublattices given its size and electronic characteristics. In accordance with this, a model described as \((\text{Al,Co})_8(\text{Al,Co,Cr})_{18}(\text{Cr})_4\) is established. The Gibbs energy of \( \sigma \) in per mole of formula has the form,

\[
G_m^\sigma = \sum_i \sum_j y_i y_j \alpha G_{ij;Cr}^\sigma + RT \left[ 8 \sum_i y_i \ln(y_i) + 18 \sum_j y_j \ln(y_j) \right]
\]

\[
\text{Eq. 5.5: } + \sum_h \sum_{i_1} \sum_{i_2} \left\{ y_{i_1} y_{i_2} \left[ \sum_k L_{i_1,i_2;Cr}^\sigma (y_{i_1} - y_{i_2})^k \right] \right\}
\]

\[
+ \sum_i \sum_{i_2} \left\{ y_i y_{i_2} \left[ \sum_k L_{i_i,i_2;Cr}^\sigma (y_i - y_{i_2})^k \right] \right\}
\]

where \( y_i' \) and \( y_j' \) represent the site fractions of \( i \) in the first and second sublattices, \( \alpha G_{ij;Cr}^\sigma \) represents the Gibbs energy of particular \( \sigma \) end-members as shown by Eq. 5.6, and \( L_{i,j,k;Cr}^\sigma \) is the interaction term between end-members of \( i;j;\text{Cr} \) and \( i;k;\text{Cr} \).
The described binary and ternary end-members for B2 and σ are modeled as follows,

\[
G_{m}^{Al_{x}Co_{y}Cr_{z}} = x^a G_{Al}^{fcc} + y^a G_{Co}^{hpc} + z^a G_{Cr}^{bcc} + \Delta f G_{Al_{x}Co_{y}Cr_{z}}
\]

where \(\Delta f G_{Al_{x}Co_{y}Cr_{z}} = \Delta f H_{Al_{x}Co_{y}Cr_{z}} - T \Delta f S_{Al_{x}Co_{y}Cr_{z}}\) and represents the Gibbs energy of formation of a particular B2 or σ end-member with the composition \(Al_{x}Co_{y}Cr_{z}\). The Debye-Grüneisen model is used to predict the enthalpy and entropy of the compounds as a function of temperature from 0 K properties obtained by the DFT calculations. Details for these calculations are presented in the following section. The PARROT module within Thermo-Calc [47] is used to assess all model parameters for each phase in the system using the phase equilibrium data from our experimental measurements and the results by Ishikawa et al. [129] as well as first-principles thermochemical data calculated in the present work. PARROT is a thermodynamic data assessment module which has been developed to fit model parameters to experimental data by a least mean square method [45].

5.2.3 First-principles methodologies

The Helmholtz energy \(F(V,T)\) of the condensed phases are calculated using the quasiharmonic approach. A four-parameter Birch-Murnaghan (BM4) equation of state (EOS) [25], [26] is used in the fitting to obtain the Helmholtz energy. Lattice vibrations are modeled with the Debye-Grüneisen model with the benefit of both accuracy and efficiency; the relevant equations have been described in detail in previous publications [75], [138]. The scaling factor is implemented to scale the Debye temperature as a consequence of the differences in transverse and longitudinal phonon modes [102]. It has been shown that the scaling factor is highly dependent on
the crystal structure [29], [89]. This factor can be estimated from elastic constant calculations using DFT and then averaged as an isotropic medium. Elastic constant calculations are implemented in this work for fcc-Al, hcp-Co, bcc-Co, B2, and σ using the method proposed by Shang et al. [27].

In order to predict A2 solution mixing, calculations of the enthalpy of mixing based on special quasirandom structures calculations (SQS) [30] are performed using the 16-atom binary A2 model developed by Jiang et al. [32] and the 32- or 36-atom ternary A2 model developed by Jiang [35]. Additionally, ternary B2 solution mixing calculations are also performed using 8- and 16-atom supercells generated for the isostructural B2-AlNi system by Jiang et al. [36]. SQS calculation procedures for the present work are performed with the method recently implemented by Lieser et al. [82]. The SQS supercells are first relaxed with respect to cell volume only, and then to only cell volume and shape, and finally to cell volume, shape as well as ion positions simultaneously. Radial distribution functions (RDF) of relaxed supercells are compared with the ideal bcc structure after each relaxation step [82]. The structures with the lowest energy that retain the required structural symmetry are used in the present work.

The Vienna *ab-initio* Simulation Package (VASP) [23] is used for spin-polarized DFT calculations due to the ferro- and antiferromagnetic natures of Co and Cr, respectively. Electron-ion interactions are described by the accurate projector augmented-wave (PAW) method [77], [78]. The generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE) [22] is used to describe the electron exchange and correlation. A plane-wave cutoff energy of 400 eV is consistently used to ensure enough basis sets are included, as recommended by the VASP manual [79]. Reciprocal *k*-meshes used for fcc-Al/Co, hcp-Co, bcc-Al/Co/Cr, B2 and σ are $21 \times 21 \times 21$, $23 \times 23 \times 12$, $17 \times 17 \times 17$, $15 \times 15 \times 15$, and $6 \times 6 \times 11$, respectively. The structures are relaxed by implementing the Methfessel-Paxton method [80] to minimize the forces acting on the
atoms. After relaxations, a final calculation using the tetrahedron with Blöchl corrections [81] is applied to ensure an accurate total energy calculation.

5.3 Results and Discussion

5.3.1 Experimental results

From collaborators Thomas Gheno and Brian Gleeson at the University of Pittsburgh:

Alloy phase constitutions were determined through a combination of XRD (selected spectra shown in Figure 5.4) and phase composition analyses (EPMA results given in Table 5.1). At 1173 and 1273 K, the alloys A4, A5 and A7 are within the B2-γ-σ three-phase triangle, which is an invariant equilibrium in a three-component system. Small differences measured between the phase compositions are larger than the experimental standard deviation, and may reflect the slight influence of Y on phase equilibria. Selected microstructures observed after equilibration at 1273 and 1373 K are shown in Figure 5.5. In Figure 5.5 (a) and (b), the dark matrix is B2, the two light phases are γ and σ, and the bright precipitates are Y-containing intermetallics (denoted MY). These phases are identified based on their measured compositions and associated XRD results. This phase constitution is typical for equilibrium at 1173 and 1273 K. At 1373 K, the B2 phase exhibits compositions that vary widely between the four alloys studied. These are substantially different from those measured at 1173 and 1273 K, with Al contents as low as 16.2 at.% and Cr contents as high as 36.9 at.%. Nevertheless, XRD confirmed that the ordered B2 structure is maintained at 1373 K. In the absence of σ reflections, it is concluded that σ has been replaced by A2, which dissolves significantly more Al (Table 5.1). The A2 and B2 phases each have a cubic structure,
and their peaks cannot be resolved with the instrument available. Analysis by EPMA (not shown here) indicated that two types of Co-rich yttrides were present, containing ~ 7 at.% and ~ 9 at.% Y, with 18-25 at.% Cr and 9-14 at.% Al. Due to the low volume fraction of these phases, their structures could not be determined by XRD.

The present experimental results confirm and refine the phase relationships originally documented by Ishikawa et al. [129]. Between 1273 and 1373 K, the B2+γ+σ three-phase region is replaced by an A2+B2+γ triangle, and the solubility of Cr in B2 drastically increases. Both are due to the shrinkage of the A2/B2 miscibility gap as the temperature increases, and to the associated dissolution of σ into A2. Ishikawa et al. [129] observed the A2/B2 order-disorder transition at 1473 K. The present measurements show very close compositions for B2 and A2 in equilibrium with γ at 1373 K and therefore, indicate that the miscibility gap is closed slightly above 1373 K.

5.3.2 First-principles results

To provide a benchmark for the first-principles methodology used in the present work, fundamental properties of Al, Co, Cr and relevant phases, shown in Table 5.2, are compared with previous first-principles calculations [28], [83] and data from various experiments [43], [139]–[142]. Good agreement is seen for these properties for all three elements in their standard element reference (SER) state (pure, most stable at 298 K and 1 bar) [50]. It should be noted that Cr takes on an anti-ferromagnetic state at 0 K. The results agree with previous calculations and experiments [43], [142], [143] for anti-ferromagnetic Cr. The lattice parameters and bulk modulus of B2-(Al)(Co) agree with previous results [144], [145] and hence, the predicted values for B2-(Co)(Cr)
and B2-(Cr)(Al) can be adopted with confidence. No measured bulk moduli for σ-CoCr could be
found in the literature and hence, only experimental lattice parameters are compared. The
calculated values for the end-members σ-(Co)$_8$(Co)$_{18}$(Cr)$_4$ and σ-(Co)$_8$(Cr)$_{18}$(Cr)$_4$ are compared to
the lattice parameter of a σ-Co$_{13}$Cr$_{17}$ alloy and are in good agreement with measurements by
Dickins et al. [139].

Results from our recent study on the Debye-Grüneisen model [146] indicate that using a
calculated scaling factor for the Debye temperature is an accurate and efficient method to predict
thermodynamic properties of pure elements and intermetallic phases in comparison with the more
computationally demanding phonon supercell approach. Table 5.2 shows that the pure-element
properties derived from the EOS fitting match experiments [43], [140], [141] and the DFT
predictions [28], [143]. Therefore, the Debye approximation is used to estimate the thermodynamic
properties for all end-members of B2 and σ. Predicted enthalpies of formation ($\Delta fH$) for each end-
member of B2 and σ are calculated at 298 K and are shown in Table 5.3. Note that the non-SER
reference B2 formation energies are calculated with respect to the bcc phase of the pure elements
and that σ energies are taken with respect to the fcc phase in the first sublattice, bcc in the second
and bcc in the third following Ref. [1], [131]. Experimental thermochemical data for B2 and σ
end-members are unavailable at 298 K and consequently, only previous CALPHAD assessments
and DFT results are compared in Table 5.3. Stein et al. [134] determined values of $\Delta fH_{298}=\text{-64.45}$
kJ/mol-atom and $\Delta fS_{298}=\text{-11.43}$ J/mol-atom of B2 based on modeling of experimental enthalpy
data at 1100 K. The present DFT predictions using the scaling factor Debye-Grüneisen model are
in excellent agreement with these values.

Unfortunately, calorimetric measurements for σ-CoCr have proven unreliable, as reported
measured and calculated enthalpies of formation range from -3 to +10 kJ/mol-atom, shown in Ref.
Also, the stability of $\sigma$ in the Co-Cr system was suggested to range from 30 to 45 at.% Co, which is quite different from the calculated end-member compositions of 26.6 and 86.6 at.% Co. However, Downie and Arslan [149] measured the formation enthalpy of one $\sigma$-CoCr sample close to the composition of the end-member $\sigma$-(Co)$_8$(Cr)$_{18}$(Cr)$_4$ at 473 K and found $\Delta_f H = 6.77$ kJ/mol-atom. While no direct comparison can be made due to the composition and site fractions, the predicted value of $\Delta_f H_{298} = 6.19$ kJ/mol-atom for $\sigma$-(Co)$_8$(Cr)$_{18}$(Cr)$_4$ is in good agreement with the measured value. Table 5.3 shows the final values (non-SER columns) for B2 and $\sigma$ that are used as input for the thermodynamic modeling in the present work.

For all binary and ternary bcc SQS calculations, RDFs indicate that the simultaneous relaxation of cell volume, shape and ion positions reduce the symmetry of the SQS cell environment. Additionally, ternary SQS calculations show symmetry reduction when only cell volume and shape are allowed to relax. Therefore, SQS supercells with the lowest energy and a coordination environment sufficiently close to the ideal bcc structure are used in the analysis. Calculated binary and ternary enthalpies of mixing are shown in Table 5.4, Figure 5.6 and Figure 5.7 for A2 and B2. Along with the symmetry, the magnetism of the SQS supercells is checked. Cobalt is ferromagnetic at 0 K with an average $\mu_B$/atom of 2.2 while Al is non-magnetic. At 0 K, Cr is antiferromagnetic with no net average magnetic moment. Our calculations show that Al and Cr additions, both with no net magnetic moment, decrease the $\mu_B$/atom of Co as a function of composition.

The SQS calculations, shown in Figure 5.7 and Table 5.4, predict the formation of a low-temperature miscibility gap in both Co-Cr and Al-Cr while strong negative mixing is seen in Al-Co. These predictions agree well with experimental observations as well as previous models of the Al-Co [62], [134] and Co-Cr [131] binary systems currently adopted for the thermodynamic
modeling. However, the Al-Cr model adopted in the current work [135] disagrees with current A2 SQS calculations, as is seen in Figure 5.6. However, the ordered B2 value is closer to that of the assessed A2 mixing energy. In the Co-Cr binary modeled by Oikawa et al. [131], a low temperature A2 miscibility gap is seen at 298 K. Furthermore, the predicted A2 Al$_{0.5}$Co$_{0.5}$ mixing enthalpy (Table 5.3) is in good agreement with the Al-Co assessment [62]. However, the Al-Cr model [135] does not produce a low-temperature A2 miscibility gap and hence, disagrees with our current predictions. This is due to a lack of low-temperature thermochemical data available in the literature at the time when Al-Cr was originally modeled. Ternary A2 miscibility gaps are also predicted (Figure 5.7(a)), especially along the Al$_{0.5}$Co$_{0.5}$-Cr cross-section where the composition Al$_{0.5}$Co$_{0.5}$ shows the lowest mixing enthalpy on the whole energy surface. A convex energy surface would produce a tangent from Al$_{0.5}$Co$_{0.5}$ to pure Cr that generates a large miscibility gap across the entire Al$_{0.5}$Co$_{0.5}$-Cr cross-section. When B2 mixing is also taken into account, as shown in Figure 5.7(b), this A2 and B2 miscibility gap becomes more prominent across the Al$_{0.5}$Co$_{0.5}$-Cr cross-section in accordance with the experiments by Ishikawa et al. [129]. The extremely high formation energy of the end-member (Al)(Co) is responsible for this behavior. Additionally, the SQS results show that A2 is more stable than B2 near Cr because $\Delta H_{mix} = -1.17$ kJ/atom for A2 at the composition Al$_{0.25}$Co$_{0.25}$Cr$_{0.5}$ while $\Delta H_{mix} = 8.22$ kJ/atom for B2 at the same composition. These SQS results are in good agreement with measured phase compositions by Ishikawa et al. [129] as well as the present experimental findings. As shown later in Figure 5.8, this A2/B2 miscibility gap is still observed at 1173 K. For use in the following chapter, additional SQS calculations were performed for $\gamma$ and $\gamma'$ phases and compared to results by Wolverton and Ozolins [150], as is shown in Figure 5.6; these results will be discussed in the following chapter.
5.3.3 CALPHAD modeling results

The three binary models, Al-Co [62], Co-Cr [131], and Al-Cr [135], are extrapolated to the ternary system using the partitioning model [56]. In addition, thermodynamic parameters from DFT, listed in Table 5.3, are used as input. The binary B2-(Al)(Co), B2-(Cr)(Al), σ-(Co)₈(Cr)₁₈(Cr)₄ and σ-(Co)₈(Cr)₁₈(Cr)₄ end-members are fixed by previous models and cannot be modified without reassessment of those systems. The initial ternary extrapolation produces a phase diagram with satisfactory phase boundaries for fcc, A2, and B2 at 1173 K compared to experiments, but is at variance with the experimental isothermal sections at all other temperatures [129], [151]. A2/B2 regions do not separate at the order/disorder compositions even at temperatures as high as 1623 K, which is at significant variance with experiments (see experimental Section 6.1 for discussion). The poor extrapolation is a result of fixing the B2-(Cr)(Al) end-member to the value proposed by Dupin et al. [1] in their modeling of the Al-Cr-Ni ternary system. Dupin et al. [1] assessed ΔfH of B2-(Cr)(Al) to be -13.719 kJ/mol-atom, which is much more stable than the value of -7.37 kJ/mol-atom predicted by DFT in the present work. However, modifying this energy will require significant reassessment of Al-Cr-Ni ternary description and is outside the scope of this work. As a consequence of this fixed B2 end-member, additional interaction parameters for the B2 phase are needed to correctly reproduce its miscibility gap.

The binary B2-(Co)(Cr) end-member and the Co-Cr interaction parameters are evaluated by fitting to the present EPMA results at 1173, 1273, and 1373 K (Table 5.1) data from Ishikawa et al. [129] as well as first-principles thermochemical data. Given the complexity of the A2/B2 miscibility gap region, as seen in Figures 4-8, ternary, temperature dependent interaction parameters are needed to describe the B2-(Al)(Co) extension into the ternary as well as the A2/B2
transition temperatures. Interaction parameters for the A2 are also needed to capture the Al and Co solubility. The evaluated parameters are shown in the Appendix and built into a thermodynamic database.

Figure 5.8 shows the calculated isothermal section at 1173 K compared with the present EPMA results as well as experimental data from Moskvitina et al. [151]. A good agreement between calculations and experiments is reached. Figure 5.9 shows the calculated isothermal section at 1273 K, which agrees very well with the present experiments as well as measurements by Ishikawa et al. [129]. Figure 5.10 shows a calculated isothermal section at 1373 K, which agrees well with our experiments, except for the B2 composition in the A2+B2+γ three phase tie-triangle and the A2-B2 tie-line. This is attributed to the fact that the A2/B2 miscibility gap disappears very rapidly with increasing temperature, and as a consequence the morphology of this region of the diagram is extremely sensitive to temperature variations around 1373 K. The A2+B2+γ three phase triangle is predicted to disappear at 1423 K measurements by Ishikawa et al. [129]. Figure 5.11 plots the 1473 K isothermal section, which fits experimental measurements from Ishikawa et al. [129] quite well. At this temperature, the A2/B2 miscibility gap is replaced by a second-order transition represented by a dotted line. The calculation near the transition region shows that the B2 ordering gravitates towards the disordered composition with more Cr additions on the Co-Cr rich side of the phase diagram. This is in good agreement with the experimental results on the order/disorder alloys found by Ishikawa et al. [129]. Figure 5.12 shows the 1573 K isothermal sections. Furthermore, the A2/B2 and B2/γ tie-lines as well as A2/B2 transition points show good agreement at 1573 and 1623 K compared with data from Ishikawa et al.[129] (not included here). An overall good thermodynamic description of Al-Co-Cr, which takes into account predicted first-principles thermochemical data, is produced in this work. We have demonstrated a
model that is able to reproduce the rapid replacement of one three-phase \( \sigma + B_2 + \gamma \) tie-triangle by another and the sharp increase in the solubility of Cr in B2 from 1273 to 1373 K, as observed experimentally (see Section 6.1).

5.4 Conclusions

The Al-Co-Cr system is investigated thoroughly using first-principles calculations, XRD, and EPMA measurements to produce a complete CALPHAD thermodynamic description. First-principles DFT calculations predict a large A2/B2 miscibility gap in the ternary system, which is demonstrated experimentally using phase composition measurements from 1173 to 1373 K. In addition, the experimentally-measured phase compositions for A2, B2, \( \gamma \) and \( \sigma \) are in good agreement with previous experimental results [129]. To aid in the modeling of the ternary system, the Debye-Grüneisen model is used to predict finite-temperature data of B2 and \( \sigma \) such as heat capacities, entropies, and enthalpies. It is found that the complex A2/B2 phase region, which includes an order-disorder transition, can be accurately described with a partitioned bcc model. The calculated B2 ordering compositions are also shown to be in agreement with previous as well as present experimental studies. Overall, a consistent thermodynamic description of the Al-Co-Cr system is produced and its accuracy for predicting thermodynamic properties of all phases relevant for MCrAl-base coatings is confirmed. An alternative Al-Co-Cr model using the Co-Cr by Kusoffsky et al. [132] is presented in the following chapter.
Acknowledgement

The author would like to acknowledge collaborators Dr. Thomas Gheno and Dr. Brian Gleeson for preparing the experimental sections of this chapter.
Tables and Figures

Table 5.1: Phase compositions of the CoCrAlY alloys measured by EPMA (at.%).

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<th></th>
<th></th>
<th>σ</th>
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Table 5.2: Various properties of the Al, Co, Cr, and the end-members of B2 and σ. These properties are derived from the energy vs. volume curves using the 4-parameter Birch-Murnaghan EOS. $B_0$ denotes the bulk modulus. The bulk modulus at room temperature of Al, Co, and Cr are also presented, as reported by Kittel [43]. Other experimental temperatures are shown if known; reported 0 K values are extrapolated from low temperature data.

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Table 5.3: Predicted enthalpies and entropies of formation of B2 and σ end-members at 298 K. Energies are shown in units of J/mol-formula and atom with the most stable end-members shown in bold text. Also, energies taken with respect to standard states are denoted with SER. Energies used for CALPHAD modeling are taken with different reference states depending on the sublattice models used. B2 formation energies are calculated with respect to the bcc phase of the pure elements. For σ, energies are taken with respect to the fcc phase in the first sublattice, bcc in the second and bcc in the third; same as the sublattice model implemented in the current work.

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<th>$\Delta_f H$ (SER) (kJ/mol)</th>
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Table 5.4: Calculated enthalpies of mixing for solution A2 and B2. These calculations are based on binary and ternary SQS calculations at 0 K with references taken as bcc-A2 for Al, Co, and Cr.

<table>
<thead>
<tr>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>SQS prototype</th>
<th>$\Delta H_{\text{mix}}$ (kJ/mol-atom)</th>
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<tr>
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<th>$\Delta H_{\text{mix}}$ (kJ/mol-atom)</th>
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<td>(Cr)(Al)-(Al)(Co) section</td>
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Figure 5.1: Al-Co binary as assessed by Dupin and Ansara [62] and converted to the partitioned model with the modification of one parameter in B2. Note that ferromagnetic $\gamma$ undergoes a magnetic transition into paramagnetic $\gamma$ at higher temperatures (- - -).
Figure 5.2: Al-Cr binary assessed by Saunders as a part of the COST 507 project [135]. The circled region denotes possible B2 ordering, as found by Helander and Tolochko [152].
Figure 5.3: Co-Cr binary as assessed by Kusoffsky et al. [132] (solid) and by Oikawa et al. [131] (---). Note that $\gamma$- and $\varepsilon$-undergo transitions into $\gamma$- and $\varepsilon$-paramagnetic at higher temperatures, respectively. The $\gamma$ transition is shown as (···).
Figure 5.4: XRD analysis of selected alloy phase constitutions at 1273 K and 1373 K. Note that preferential orientations inherent to cast microstructures were still present after annealing. Specimens were rotated in-plane to ensure that all phases were detected.

Figure 5.5: Microstructure of alloys (a,c) A6 and (b,d) A7 equilibrated at (a,b) 1273 K and (c,d) 1373 K. The bright precipitates are Y-containing intermetallics (noted MY).
Figure 5.6: Predicted enthalpies of formation in the three binary systems Al-Co (a), Al-Cr (b), and Co-Cr (c) for fcc-γ (○) and A2 (∆, blue) from SQS calculations at 0 K. 16-atom SQS γ calculations by Wolverton and Ozolins [150] are represented by (□). Ordered L_{12}/L_{10} (●) and B2 (▲, blue) formation energies are also shown. Formation enthalpies at 298 K from the individual models by Dupin et al. [62] (a), Saunders [135] (b), Kusoffsky et al. [132] (c), and Oikawa et al. [131] (c-red) are plotted: γ (- - -), γ’ (- - -), A2 (· · ·,blue), and B2 (——,blue). Additionally, the Co-Cr system is plotted in (d) with SER reference states to show the large lattice stability differences for Cr between DFT and CALPHAD. B2 in Al-Co with modified vacancy interactions are shown in (—,red).
Figure 5.7: Predicted A2 (a) and B2 (b) enthalpies of mixing. These calculations are based on 16-atom binary and 32/36-atom ternary SQS supercells at 0 K. Grey points in (a) represent distinct A2 SQS compositions and black points in (b) represent B2 SQS compositions. A color map is added to guide the reader in viewing the energy surface.
Figure 5.8: Al-Co-Cr Isothermal section at 1173 K. Shown with phase equilibria data from Moskvitina et al. [151]: single phase (□), 2-phase (▽), and 3-phase (†). Phase equilibria data from the present work: 2-phase (●), 3-phase (▲).

Figure 5.9: Al-Co-Cr Isothermal section at 1273 K. Shown with phase equilibria data from Ishikawa et al. [129]: 2-phase (○), and 3-phase (△). Experimental phase equilibria data from the present work: 2-phase (●), 3-phase (▲).
Figure 5.10: Al-Co-Cr Isothermal section at 1373 K. Shown with phase equilibria data from the present work: 2-phase (●), 3-phase (▲).

Figure 5.11: Al-Co-Cr isothermal section at 1473 K. Phase equilibria data from Ishikawa et al. [129]: 2-phase (○), order-disorder transition (★). The calculated order-disorder transition is shown with (∙ ∙ ∙).
Figure 5.12: Al-Co-CrIsothermal section at 1573 K. Phase equilibria data from Ishikawa et al. [129]: 2-phase (○), order-disorder transition (★). The calculated order-disorder transition is shown with (⋯).
6 First-principles calculations and thermodynamic modeling of Al-Co-Ni, Co-Cr-Ni ternary alloys with re-modeling of Al-Co-Cr

In the previous chapter, on CoCrAlY alloys, the effectiveness of a computational approach in predicting accurate phase diagrams of higher order systems by implementing the CALPHAD method (Calculation of Phase Diagrams) has been demonstrated. In the literature, there is no complete description of the Al-Co-Cr-Ni alloy system. The current work combines the previous model for the Al-Co-Cr coating system with the models of the Al-Cr-Ni [1], Al-Co-Ni, and Co-Cr-Ni systems in order to build a coherent quaternary database. It is important to note that some modifications are made in the description of the Al-Co-Cr [153] system and are discussed in detail later in the manuscript. The intermetallic L12 (γ', Pm3m, simple cubic type) phase is accounted for in the current work in addition to the phases shown in the previous chapter as it appears in the Al-Co-Ni and Al-Cr-Ni ternaries.

The present work focuses on evaluating and modeling the important ternary alloy systems found in the Al-Co-Cr-Ni quaternary in order to produce meaningful extrapolations without the need of extraneous higher order parameters. First-principles calculations based on density functional theory (DFT) are performed to supplement the lack of experimentally measured thermochemical data and by effectively combining these results with experimental information, energetically accurate parameters in the lower order systems are evaluated. Ultimately, this model will be used in the construction of a multicomponent Al-Co-Cr-Ni database in future work.
6.1 Binary systems

A brief overview of the binary systems used in the modeling of the Al-Co-Cr-Ni quaternary is presented in this section. Those used in the Al-Co-Cr subsystem are presented in the previous chapter.

6.1.1 Al-Ni

The Al-Ni system modeled by Ansara et al. [59] and later modified by Dupin et al. [1] is used in the current work (Figure 6.1). This system is widely adopted in the literature as its energetics have been refined numerous times due to its importance for Ni-base superalloys. It was first modeled by Ansara et al. [57] in 1988 using an order-disorder model for the fcc-based phase to describe γ’-Ni₃Al ordering. It was subsequently modified by Dupin [130] and by Ansara et al. [59] with new optimizations of certain parameters. In the re-assessment of the Al-Cr-Ni by Dupin et al. [1] in 2001, the bcc-based phases A2 and B2 are also demonstrated using the order-disorder model. Due to the numerous refinements, this binary reproduces all experimental measurements extremely well.

6.1.2 Co-Ni and Cr-Ni

The Co-Ni and Cr-Ni binary descriptions are adopted from SGTE [154], based on works by Guillermet F. [155] and Lee B.-J. [156], respectively. In addition, the present Cr-Ni description includes a modification of the σ phase as suggested by Kattner [157] following the work by
Gustafson [158] in the ternary Ni-Cr-W system. The Co-Ni and Cr-Ni phase diagrams are shown in Figure 6.2 and Figure 6.3, respectively.

6.2 Ternary systems

A summary of the experimental techniques for the ternary systems is shown in Table 6.1. Phase equilibria data gathering techniques include optical microscopy (OM), scanning electron microscopy (SEM), electron probe microanalyzer (EPMA), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS/XDS), wavelength-dispersive X-ray spectroscopy (WDS), and X-ray diffraction (XRD). Thermochemical and thermophysical properties of alloys are often obtained using adiabatic calorimetry, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), Knudsen effusion mass spectrometry (KEMS), and electrochemical measurements.

6.2.1 Al-Co-Cr

In previous work, the Al-Co-Cr model was modeled using experimental findings from Ishikawa et al. [129] supplemented with new phase equilibrium experiments and first-principles data. The previous model implemented the following binary models: Al-Co binary by Dupin and Ansara [62], Al-Cr by Saunders [135], and Co-Cr by Oikawa et al. [131]. The model by Oikawa et al. [131] was chosen because the calculated A2+σ phase boundaries describe measurements more accurately. However, the description by Oikawa et al. [131] fails to reproduce our calculated
formation energies for the σ end-members and consequently, the previous Al-Co-Cr description is remodeled implementing the Co-Cr binary by Kusoffsky et al. [132]. The Co-Cr model by Kusoffsky et al. [132] reproduces the formation energies measured by Downie and Arslan [149] well.

### 6.2.2 Al-Co-Ni

The Al-Co-Ni ternary system was first modeled by Dupin [130] and reproduces experimental phase equilibria from Schramm [159] and Jia et al. [160] as well as enthalpies from Kek et al. [161] faithfully. This system has been remodeled recently by Zhu et al. [162] for incorporation into a Al-Co-Ni-W quaternary database. However, in both cases, the A2 (metastable in Al-Co-Ni) and B2 phases are modeled using two separate Gibbs energy functions and are thus not compatible with the order-disorder transition seen in the Al-Co-Cr ternary system. To be able to model such an order/disorder transition, the A2 and the B2 phases must be modeled using one single Gibbs energy function. Since this transition is expected to be present in the quaternary Al-Co-Cr--Ni system, the Al-Co-Ni system needs to be remodeled in the present work for compatibility reasons.

This work also includes a remodeling of the Al-Co-Ni ternary using new experimental phase equilibria on the γ, γ' and B2 from Kainuma et al. [163] and Albers et al. [164] as well as enthalpies of formation data from Grün et al. [165]. Schramm [159] also investigated isothermal/vertical sections pertaining to γ, γ' and B2 from room temperature to 1350 °C and Gödecke et al. [166]–[169] studied the Al-rich corner of the Al-Co-Ni phase diagram in a series of experiments focusing on Al-rich intermetallics. In addition to this experimental information available in literature, first-principles calculations of the solution phases performed in the present work aid in the modeling.
6.2.3 Al-Cr-Ni

The Al-Cr-Ni ternary by Dupin et al. [1] is adopted in the current work and is shown in Figure 6.4 for temperatures 1173 to 1573 K. Both the A2/B2 and γ/γ’ phases use partitioned Gibbs energy models which is compatible with previous Al-Co-Cr ternary model. All experimental data found in the literature is well produced except for the A2/B2 phase boundary near the Cr-rich region of the system at 1423 K compared to EPMA measurements by Oforka and Argent [170]. This was recently investigated, using diffusion couples and EPMA, by Cutler [171] at 1473 K and the A2/B2 phase boundary is found to disagree with those found by by Oforka and Argent [170]. More experiments must be performed to determine the phase boundaries in this region at temperatures above 1373 K. A summary of experiments relevant to this ternary can be found in Dupin et al. [1] and is not covered in detail in the present manuscript. The model by Dupin et al. [1] describes only the Cr-Ni rich region of the phase diagram. In order for this system to be compatible with the other ternary subsystems within the Al-Co-Cr-Ni quaternary system, σ is introduced as a metastable ternary phase.

6.2.4 Co-Cr-Ni

Yang et al. [137] modeled the Co-Cr-Ni ternary using binary descriptions different from the current work as well as excessive ternary interaction parameters. Here, the system is remodeled using the following binary models due to ternary compatibility with the Al-Co-Cr, Al-Co-Ni and Al-Cr-Ni systems: Co-Cr by Kusoffsky et al. [132], Co-Ni by Guillerm F. [155], and Cr-Ni by Lee B.-J. [156]. Phase equilibria by Zhmurko et al. [172], Omori et al. [173], and Zhanpeng J.
are accounted for in the evaluation. Additionally, A2, γ, and σ formation enthalpies measured by Kubaschewski and Hack [175] are also used. First-principles calculations of the solution phases are performed and accounted for in the modeling work.

6.3 Materials and Methods

No experiments are performed for this chapter of the thesis.

6.3.1 CALPHAD thermodynamic models

The thermodynamic modeling methodology remains the same as in previous work on Al-Co-Cr. However, in that description of the Al-Co-Cr system, γ’ was not modeled as it is only a metastable phase. In the current work γ’ is stable in the Al-Co-Ni and Al-Cr-Ni ternary extensions of the Al-Ni binary and hence, γ’ must be included also in the Al-Co-Cr system. To account for the A2/B2 order-disorder transition and γ’ ordering from γ, the bcc and fcc phases are modeled using partitioning models, which treat the ordered and disordered components separately and with the same Gibbs energy functions [56]. Ordering of the bcc phase was described in detail previously in the work on the Al-Co-Cr system and the ordering of the fcc phase is similar. Some bond energies relevant to the ordering of the fcc are fixed from the binary and ternary assessments including $U_{AlNi}$, $U_{AlCr}$, and $U_{CrNi}$ from the Al-Cr-Ni description by Dupin et al. [1]. The bond energies $U_{AlCo}$, $U_{CoCr}$, $U_{CoNi}$ are assessed in the current work by utilizing first-principles calculations and experimental results.
When adding Ni to the Al-Co-Cr systems, the A2, B2, \( \sigma \), \( \epsilon \), and liquid phases need to be modified accordingly. The model for \( \sigma \) is adapted to accommodate Ni in the first and second sublattices: \((\text{Al,Co,Ni})_8(\text{Al,Co,Cr,Ni})_{18} (\text{Cr})_4\), and the ternary end-members that describe \( \sigma \) now include: \( \sigma-(\text{Al})_8(\text{Co})_{18}(\text{Cr})_4 \) and \( \sigma-(\text{Co})_8(\text{Al})_{18}(\text{Cr})_4 \) in Al-Co-Cr, \( \sigma-(\text{Al})_8(\text{Ni})_{18}(\text{Cr})_4 \) and \( \sigma-(\text{Ni})_8(\text{Al})_{18}(\text{Cr})_4 \) in Al-Cr-Ni, as well as \( \sigma-(\text{Co})_8(\text{Ni})_{18}(\text{Cr})_4 \) and \( \sigma-(\text{Ni})_8(\text{Co})_{18}(\text{Cr})_4 \) in Co-Cr-Ni. No \( \sigma \) end-members exist for the Al-Co, Al-Ni, and Co-Ni binary systems in the confines of the current model.

The PARROT module within Thermo-Calc [45]–[47] is used to assess all model parameters for each phase in the system using phase equilibrium data from the experimental measurements listed in Table 6.1 as well as first-principles data calculated in the present work. The resulting thermodynamic parameters are all included in the Appendix. It is important to note that Al-Co-Cr-Ni quaternary data from the following chapter is used in the assessment of the ternaries as well. During optimization it is possible to obtain various sets of optimized parameters which represent the thermodynamics of the system well. However, some sets of optimized parameters produce better extrapolations in higher order systems and these are the finalized sets [176].

### 6.3.2 First-principles methodologies

First-principles approaches remain the same as the previous chapter on Al-Co-Cr. Additional special quasirandom structures calculations (SQS) [30] are performed to predict mixing energies in the A2, B2, \( \gamma \) and \( \gamma' \) phases. The calculations for \( \gamma \) utilizes binary 16-atom cells developed by Wolverton C. [31] and ternary 24/32-atom cells by Shin et al. [34]. The supercell generated by Jiang [36], is used for the B2 ternary calculations of the A\(_{0.5}\)B\(_{0.5}\)C composition.
sections, see Figure 6.5 (b). To enable the γ' SQS calculations along certain composition sections, such as Ni₃Al to Co₃Al, a 24-atom ternary SQS supercell (Figure 6.5 (c)) is generated using the Alloy Theoretic Automated Toolkit (ATAT) [39] together with the Monte Carlo method developed recently by van de Walle et al. [38]. Other cell sizes are tested to ensure that the selected cell size is sufficient. Other SQS settings for these calculations and the relaxation requirements in obtaining a final structure remain the same as in previous work [153]. To obtain the scaling factors to be used in the Debye-Grüneisen model for finite-temperature thermodynamic properties or B2, γ’ and σ end-members, elastic constant calculations are performed. The effectiveness and accuracy of using a scaling factor for the Debye-Grüneisen model has been demonstrated previously [146].

First-principles DFT calculations are performed using the Vienna *ab-initio* Simulation Package (VASP) [23] with spin-polarization due to the ferromagnetic nature of Co and Ni as well as the antiferromagnetic nature of Cr. The Project augmented-wave (PAW) method is used to describe electron-ion interactions while the Perdew, Burke, and Ernzerhof (PBE) [22] implementation of the generalized gradient approximation (GGA) is used to describe electron exchange and correlation. To ensure that enough basis sets are included in the calculation, a plane-wave cutoff energy of 400 eV is consistently used for all calculations. Reciprocal k-meshes used for fcc-Al/Co/Cr/Ni, hcp-Co, and bcc-Al/Co/Cr/Ni are $21 \times 21 \times 21$, $23 \times 23 \times 12$ and $17 \times 17 \times 17$, respectively. For the intermetallic B2, γ’ and σ, the reciprocal k-meshes $15 \times 15 \times 15$, $21 \times 21 \times 21$, and $6 \times 6 \times 11$ are used, respectively.
6.4 Results and discussion

6.4.1 First-principles results

The results of the first-principles calculations for the B2 and γ’ end-members are shown in Table 6.2. This includes elastic stiffness constants ($C_{ij}$), volume/atom ($V_0$), bulk modulus ($B_0$), Poisson’s ratio (Voigt-Reuss-Hill effective medium), the Debye model scaling factor as well as the Debye temperatures for each end-member. These results are crucial properties necessary for accurate finite temperature predictions. End-members B2-CoNi and γ’-Cr$_3$Al are shown to be mechanically unstable due to the stability criteria $C_{11}>|C_{12}|$, $C_{44}>0$, and $C_{11}+2C_{12}>0$ for cubic structures [177]. B2-CoAl, NiAl and γ’-Ni$_3$Al are the only stable end-members and experimental results for these are included in Table 6.2. Current $C_{ij}$ and $B_0$ results for B2-CoAl and NiAl agree well with experimental findings [178]–[182] at various temperatures as well as other first-principles calculations [183], [184]. It should be noted that $C_{ij}$ decreases as a function of temperature and hence, room temperature values are expected to be lower than their first-principles counterparts by a few percent. The $C_{ij}$ and $B_0$ results for γ’-Ni$_3$Al [185], [186] also are shown to agree with experimental data and other calculations [41], [184]. Elastic and equation of state calculations for other end-members are not available in the literature and thus are not compared.

In Table 6.3 are the elastic stiffness constants for the end-members of σ are listed. The end-member σ-(Al)$_8$(Al)$_{18}$(Cr)$_4$ can be concluded to be mechanically unstable as its $C_{44}<0$ breaks the necessary elastic stability requirements for a tetragonal (I) crystal class [177]. In the case of the σ phase, elastic stiffness constants have only been calculated for a Fe-V alloy [187] previously. These results are included in Table 6.3 for comparison and similarity with the present calculations can be concluded given the differences in elemental composition.
Table 6.4 includes the enthalpies ($\Delta fH^{298}$, kJ/mol-atom), entropies ($\Delta fS^{298}$, J/mol-atom/K) and Gibbs energies ($\Delta fG^{298}$, kJ/mol-atom) of formation at 298 K relative to standard reference states for the pure elements. The formation energies for fcc-Al, hcp-Co, bcc-Cr and fcc-Ni. B2-CoAl and NiAl are in good agreement with experiments at 298 K and other temperatures. The formation enthalpy of B2-CoAl predicted in the current work at 1100 K is -59.911 kJ/mol-atom, between the experimental value of -59.5 by Henig et al. [188] at 1100 K and the compilation value of -60.7±0.5 by Rzyman and Moser [189] at 1073 K. The experimental formation energy of B2-NiAl varies from -58.3 to -67 kJ/mol-atom according to Rzyman et al. [190] while the value at 298 K predicted in the current work is -64.211 kJ/mol-atom. Current results also agree with previous DFT predictions by Arroyave et al. [24] at 298 K. In the case of Ni$_3$Al, the calculated formation enthalpy ($\Delta fH^{298}$) of -42.126 kJ/mol-atom agrees with the measured values -40.6±1.0 by Kek et al. [161] and -41.3±1.3 by Rzyman et al. [191]. Additional experimental values compiled by Rzyman et al. [191] indicate formation enthalpies between -47 and -37.6 kJ/mol-atom at various temperatures for Ni$_3$Al. Other first-principles calculations by Ohtani et al. [192] and Arroyave et al. [24] produced values of -42.38 and -46.39 kJ/mol-atom. Results for the formation entropy (-3.252 J/mol-atom/K) and Gibbs energy (-39.809 kJ/mol-atom) agree with measured values by Róg et al. [193] at 900 K for Ni$_3$Al. Additionally, the Gibbs energy of formation at 900 K vary between -34.2 to -47.5 kJ/mol-atom according to other experiments compiled by Róg et al. [193]. Al$_3$Co, Al$_3$Ni, Co$_3$Al end-member formation energies calculated by Ohtani et al. [192] at 0 K are also in agreement with the current results. Concludingly, the overall good agreement reported above validates the method of the current work for prediction of finite temperature thermodynamic properties.
As is shown in Table 6.5, calculated formation enthalpy at 0 K by Pavlů et al. [147] for both σ-CoCr end-members are more positive than the predictions in the present work. This is due to the use of LMTO energies for σ end-members and discrepant DFT energies for the magnetic elements by Pavlů et al. [147]. Unfortunately, calorimetric experiments for σ-CoCr prove to be unreliable as enthalpies of formation range from -3 to +10 kJ/mol-atom [147]–[149]. Also, the stability range of σ in the Co-Cr system goes from 30 to 45 at.% Co, which differs from the calculated end-member composition range from 26.6 to 86.6 % at. Co. However, Downie and Arslan [149] studied the formation enthalpy of one σ–CoCr sample close to the composition of the end-member σ-(Co)8(Cr)18(Cr)4 at 473 K and measured formation enthalpies of 6.77 kJ/mol-atom. While no direct comparison can be made due to the different compositions, the predicted value of 6.19 kJ/mol-atom for σ-(Co)8(Cr)18(Cr)4 is in good agreement with the measured value for a similar composition. It can be seen that all binary σ end-members have rather positive formation enthalpies at 298 K with (Al)8(Al)18(Cr)4 being mechanically unstable. In the Co-Cr case, positive formation entropies can be seen for both end-members indicating potential stabilization of σ at higher temperatures as it is not stable on the convex hull at 0 K [147].

SQS calculations from A2, γ, B2 and γ’ are shown in Table 6.6, Table 6.7, Table 6.8, and Table 6.9, respectively. Binary SQS calculations are also shown in Figure 6.6 along with binary energies from the CALPHAD models adopted in the current work. These results are compared to the ternary CALPHAD modeling as well as experimental measurements in Figure 6.8, Figure 6.9 and Figure 6.10 for Al-Co-Cr, Figure 6.14 and Figure 6.15 for Al-Co-Ni and Figure 6.19 for Co-Cr-Ni and is discussed in the following section. In the case of Cr-containing systems, the huge difference in Cr lattice stability between DFT and CALPHAD makes SQS calculations for γ difficult to interpret. Comparing to the SER reference states (bcc-Cr, fcc-Ni), as seen in Figure 6.6
(d) for Cr-Ni, shows better agreement compared to the mixing reference (fcc-Cr,Ni) states shown in Figure 6.6 (c). Wolverton and Ozolins have noted similar problems for calculations involving Cr in fcc structures [150]. By and large, taking the fcc reference state for Cr will produce mixing energies that are too negative near the Cr-rich portion of the phase diagram. This will be discussed in greater detail in section relating to the modeling results for the Co-Cr-Ni. For Al-containing systems, Wolverton and Ozolins [150] performed 16-atom SQS calculations similar to the current work and found mixing energies lower than the current work and the CALPHAD models presented. In the Al-Co, Al-Cr, and Al-Ni systems, the energies from the CALPHAD models lie between the values calculated by Wolverton and Ozolins [150] and the current work.

It can be seen that Al-rich B2-CoAl and NiAl, similarly, have the largest ordering and formation energies relative to their respective A2 disordered states (Table 6.6). This is unexpected given the strong presence of B2 in both the Al-Co and Al-Ni systems. It can also be concluded that B2-CrAl has a much lower ordering energy compared to CoAl and NiAl. Furthermore, B2-CoNi and CrNi all have positive ordering energies relative to their disordered states with CoNi being mechanically unstable which can be attributed to the extremely small and almost ideal mixing behavior in the A2 for Co-Ni; between -0.81 and 0.2 kJ/mol-atom. B2-CoCr also presents an interesting case as its ordering energy is nearly 0. Much like with B2, in the γ/γ’ case, γ’-Al₃Co, Co₃Al, Al₃Ni, and Ni₃Al have the largest ordering tendencies, see Table 6.7. In the Al-Cr system, γ’-Al₃Cr has a large ordering energy while Cr₃Al is mechanically unstable given its elastic stiffness constants. For Co-Cr and Cr-Ni, small ordering energies are seen for γ’-Co₃Cr, Cr₃Co, Cr₃Ni, and Ni₃Cr end-members. Interestingly, the current results for ordering in the Cr-Ni binary is in agreement with the bond energy assessed by Dupin et al. [1]. The calculations for γ Co-Ni
demonstrate its similarity with A2 which mixing behavior almost is ideal. Ordering energies in Co-Ni binary are negligible given the current results.

6.4.2 CALPHAD modeling results

6.4.2.1 Al-Co-Cr

The previous modeling of the Al-Co-Cr system included the Co-Cr binary by Oikawa et al. [131]. While a satisfactory phase diagram was obtained, the formation energy of one σ end-member, \( \sigma-(Co)_{8}(Cr)_{18}(Cr)_{4} \), was -8.55 kJ/mol-atom. This corresponds to formation energies much lower than those measured by Downie et al. at 473 K [149], which range between 2-7 kJ/mol-atom at stable σ compositions. Additionally, present calculations indicate that the formation energies of the end-members \( \sigma-(Co)_{8}(Co)_{18}(Cr)_{4} \) and \( \sigma-(Co)_{8}(Cr)_{18}(Cr)_{4} \) are 9.62 and 6.29 kJ/mol-atom at 298 K, respectively. The modeling by Kusoffsky et al. [60] resulted in end-member energies of 9.83 and 0.003 kJ/mol-atom at 298 K for \( \sigma-(Co)_{8}(Co)_{18}(Cr)_{4} \) and \( \sigma-(Co)_{8}(Cr)_{18}(Cr)_{4} \), which is in much better alignment with current calculations and the measurements by Downie et al. [149]. This justifies the selection of the Co-Cr description by Kusoffsky et al. [60] in the current work.

In the previous work, ordered B2 phase parameters are linked to disordered A2 \( ^0L \), \( ^1L \), and \( ^2L \) parameters. Kusoffsky et al. [60] showed that the disordered phase can be modeled independently of the ordered phase as a separate contribution that has no order dependence (with careful selection of parameters). The modified sublattice model (MSL) is still retained in the current work for B2 but with fewer, decoupled, interaction parameters, such as in the modeling of Al-Ru by Prins et al. [194]. As seen in Figure 6.7 (a) and (b), the 1173 and 1273 K isotherms remain nearly identical to previous work. The important A2+B2, B2+γ, and B2+γ+σ regions are
described well with the new models when compared to measurements from Mosktivina et al. [151] and Ishikawa et al. [129].

At 1373 K (Figure 6.7 (c)) the new model reproduces B2+γ, and A2+B2+γ regions better than previous calculations. Similarly, results at 1473 K for the A2+γ and B2+γ regions are also improved (Figure 6.7 (d)). These improvements will prove crucial in the quaternary system as most MCrAlY alloys are of the B2+γ variety. Previous modeling efforts also attempted to capture the complex A2+B2 phase boundary curvature seen especially at 1473 K (Figure 6.7 (d)) and it has been determined that additional asymmetrical B2 interaction parameters were needed to reproduce the curvature. This is omitted in the current model as more experiments are needed to confirm these phase boundaries, and over-fitting may produce strange results in the quaternary extrapolation. Even without the asymmetrical parameters, the A2+B2 regions are reproduced well at 1373, 1473, and 1573 K, respectively (Figure 6.7 (c), (d), and (e)).

The current model also reproduces A2 and B2 energies predicted using first-principles methods. Figure 6.8 shows the Co0.5Al0.5-Cr vertical section at 298 K with predicted SQS solution mixing enthalpies for A2 and the formation energy for B2-CoAl. Figure 6.9 depicts a similar calculated Co0.5Cr0.5-Co0.5Al0.5 vertical section in comparison to SQS results (Table 6.6 and Table 6.8). It can be seen that in both cases the calculated CALPHAD results coordinate well with first-principles predicted results. In Figure 6.10 the calculated γ and γ’ enthalpies of formation for the (CrxCo1-x)0.75Al0.25 vertical section at 298 K are compared to their respective SQS calculations (Table 6.7 and Table 6.9). The Cr3Al end-member (Figure 6.10) is not mechanical stable, as proven by current elastic constant calculations, indicating that its true formation energy is not well-defined. Given the instability, the ordered state has the same energy as a disordered γ at this composition since any ordering energy contribution is not to be expected. The bond energy term
$U_{CoCr}$ is not assessed in the current ternary modeling as it is metastable in all ternaries. It will be modeled using quaternary data alongside with the current DFT calculations.

6.4.2.2 Al-Co-Ni

The binary subsystems adopted in the current work produces a ternary extrapolation of the Al-Co-Ni system that agrees quite well with B2+γ, B2+γ', and γ+γ' phase boundaries as well as enthalpies [159]–[161], [163]–[165]. Bond energies $U_{AlCo}$ and $U_{CoNi}$ are modeled using experimental information as well as first-principle results, including SQS mixing energies. It should be noted that, given the age of the data by Schramm (1941) [159] and the accuracy of measurements from 73 years ago, more recent data from Jia et al. [160], Kainuma et al. [163] and Albers et al. [164] are primarily used in the modeling.

Al-Co-Ni isotherms at 1173 up to 1573 K are shown in Figure 6.11 (a) through (e). The important regions B2, γ and γ' appear at all temperatures and hence, only slight variation with temperature is concluded. At 1173 K (Figure 6.11 (a)), the present calculations agree well with measurements from Jia et al. [160], Kainuma et al. [163] and Schramm [159]. This agreement is also seen at 1273, 1373, 1473, and 1573 K (Figure 6.11 (a) to (e)). Data on single-phase γ' and two-phase γ'+B2 and γ+γ' alloys equilibrated at 1473 K by Albers et al. [164] also match the current results (Figure 6.11 (d)). No composition measurements in the γ+γ'+B2 region have been performed at any temperatures for comparison. However, given the good agreement for the single and two phase regions around the ternary region, it is expected to be accurate. Figure 6.12 shows calculated Co$_x$Ni$_{1-x}$-Al vertical sections at Ni:Co ratios of 90:10, 80:20, 50:50, and 20:80 in comparison to experimental data by Schramm [159]. Good agreement is seen at all Ni:Co ratios
for single-, two- and three-phase regions. The data from Schramm [159] are utilized to determine liquid interaction parameters as no liquidus measurements have been reported for this region of the ternary.

Figure 6.13 shows the Gibbs energies of formation for B2-CoAl, initially modeled by Dupin and Ansara [62] but modified in the current work, and for B2-NiAl modeled by Dupin et al. [1]. First-principles predictions using the Debye-Grüneisen model are also included and good agreement is seen for both B2 end-members. Figure 6.14 shows the calculated A2 and B2 enthalpies of formation compared to enthalpy measurements by Grun et al. [165] at 1073 K as well as first-principles SQS results (Table 6.6 and Table 6.8). Satisfactory agreement is obtained although the metastable A2 mixing enthalpy at Ni0.5Al0.5 deviate slightly from the current SQS results. This can be attributed to the MSL conversion of the Al-Ni system by Dupin et al. [1] which was performed without the availability of these new SQS calculations. Due to the metastable nature of the A2, such a deviation does not warrant the re-assessment of Al-Ni binary.

Figure 6.15 shows γ and γ' enthalpies of formation compared with measurements by Kek et al. [161] at 298 K and current SQS results (Table 6.7 and Table 6.9). Similar to A2 in Al-Ni, good agreement is seen for γ’ at Ni0.75Al0.25 but not for the metastable γ at this composition. Shown in Figure 6.16 are the excess Al, Co and Ni partial enthalpies and entropies measured along the composition (Ni3Al)1-xCox at 1473 K plotted with KEMS measurements by Albers et al. [164]. Good agreement is seen for each species, indicating correct thermodynamics along this composition. Lack of information on the mixing behavior of γ in the Al-Co description by Dupin and Ansara [62] also creates an uncertainty in energy compared to current SQS results for Co0.75Al0.25. Calculations in the current work give a Co3Al ordering energy of -5.09 kJ/mol-atom, which is different than that produced by Dupin [130] due to differences in bond energy parameters.
$U_{AlCo}$ and $U_{CoNi}$. Dupin assessed values of $U_{AlCo} = -9870 + 3.068 \times T$ and $U_{CoNi} = 4000$. Using these bond energies, the enthalpy of formation for Co$_3$Al at 298 K is -28.64 kJ/mol relative to the disordered solution, which is -21.24 kJ/mol (order energy of -7.4 kJ/mol). Current DFT calculations yield values of -18.62 kJ/mol for the ordered Co$_3$Al relative to -13.54 kJ/mol disordered solution from SQS, as seen in Table 6.4. It can be seen that the calculated values are smaller in magnitude in terms of absolutes as well as the ordering energy. Previous results on the formation energy of Co$_3$Al, which is -19.9 kJ/mol [192], also agree with the current results. Therefore, the updated value for $U_{AlCo} = -4872$ is smaller in magnitude and omits the temperature dependence by the addition of a $U4_{AlCo} = 3023$ term, similar to Al-Ni [1], [59]. Using this new value, the formation enthalpy of Co$_3$Al at 298 K is calculated to be -23.77 kJ/mol. Additionally, $U_{CoNi}$ is set to 0 due to small differences in energies between the ordered and disordered states of Co$_3$Ni and Ni$_3$Co calculated in the present work, as is shown in Table 6.4 and Table 6.7.

6.4.2.3 Co-Cr-Ni

The ternary extrapolation produced with the Co-Cr binary by Kusoffsky et al. [132] is better than that produced by Oikawa et al. [131]. If the description by Oikawa et al. [131] is used, 0L, 1L and 2L interaction parameters are required for the A2 and γ phases in order to reproduce the formation enthalpies measured by Kubaschewski and Hack [175] as well as first-principles predictions. Additional excess entropy terms and ternary σ end-members are then required to reproduce phase boundary data from Zhmurko et al. [172], Omori et al. [173], and Zhanpeng J. [174]. On the other hand, with the binary description by Kusoffsky et al. [132], formation enthalpies [175] and phase boundaries [172]–[174] are well produced at 1073-1373 K without the
introduction of any ternary interaction parameters. Symmetrical ternary interaction parameters are simply used to improve the phase boundary agreement at 1473-1573 K.

As seen in Figure 6.17 (a) and (b), the current description agrees well with EPMA measurements by Omori et al. [173] at 1173 and 1273 K. Tie-line compositions and directions match measured values well for the A2+σ, γ+σ, and A2+γ regions. Figure 6.17 (c) and (d) show the rapid decomposition of σ in accordance with data by Omori et al. [173] and Zhanpeng J. [174] at 1373 to 1473 K. The agreement is good between the calculated values and EPMA measurements from both experiments, especially at 1473 K where the calculated A2+σ boundary matches the loop measured by Zhanpeng J. [174]. At 1573 K (Figure 6.17 (e)), only the A2+γ region remains as σ has decomposed at this temperature. Calculated tie-lines in this region are in good agreement with measurements by Omori et al. [173]. Figure 6.18 shows the calculated liquidus and solidus temperatures at 10-40 % Cr compared with DSC measurements by Omori et al. [173]. Disagreement arises primarily from the Co-Cr binary where melting temperatures suggested by Omori et al. [173] are consistently about 20 K higher than the model by Kusoffsky et al. [132]. It should be noted that the way Omori et al. [173] determined the liquidus and solidus based on DSC should be called into question as little information is presented on the actual heating curves. Given the small amount of melting data in the Co-rich region of the Co-Cr phase diagram, more experiments need to be performed in order to adjust the parameters in the Co-Cr model by Kusoffsky et al. [132].

In Figure 6.19, the calculated enthalpies of formation for the A2 and γ at 1523 K are compared to measured enthalpies by Kubachewski and Hack [175] and to SQS calculations for the solution phases (Table 6.6 and Table 6.7). Reference states are taken to be γ-Co, A2-Cr and γ-Ni in order to enable direct comparison with calorimetric values. Enthalpies of formation values for
A2 agree with experiments as well as the "s" shape predicted by first-principles which reaches a maximum at 50 % Cr. Agreement for γ compared to the measured values are also good. However, first-principles results show some deviation. This can be attributed to the large difference in lattice stability for γ-Cr between CALPHAD and DFT, which is 31 kJ/mol-atom. Overall, this work has produced a thermodynamic description of the Co-Cr-Ni system that agrees well with measured and first-principles predicted energies in addition to experimental phase equilibria.

6.5 Conclusions

The Al-Co-Cr, Al-Co-Ni, and Co-Cr-Ni ternary systems are reviewed and investigated thoroughly in the present work. Due to the lack of thermochemical data and the metastability of phases in the ternary systems, first-principles calculations are performed. SQS calculations and Debye-Grüneisen predictions are used to predict energies for the important A2, B2, γ, and γ' phases. These results are used to produce CALPHAD models that agree well with all experimental results including a number of isotherms at temperatures ranging from 1173 to 1573 K. The ternary system modeled in this work are to be combined into a Al-Co-Cr-Ni quaternary description for use in predicting the thermodynamics of MCrAl coatings.
### Tables and Figures

Table 6.1: Summary of relevant experimental information used in the modeling

<table>
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<tr>
<th>References</th>
<th>Exp. method</th>
<th>Exp. data</th>
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</thead>
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<td><strong>Al-Co-Cr</strong></td>
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<td>Moskvitina et al.</td>
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<td>Isothermal section at 1173 using cast alloys; no phase compositions</td>
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<td>Ishikawa et al.</td>
<td>EDS, TEM</td>
<td>Isothermal sections at 1273, 1473, 1573 and 1623 K determined using cast alloys and diffusion couples, order-disorder transition; phase compositions given</td>
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<td>Schramm</td>
<td>OM, XRD</td>
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<td>γ’ formation enthalpies for various Co additions</td>
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<td>Jia et al.</td>
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Table 6.2: Calculated elastic stiffness constants and various properties of the end-members of B2 and γ’ compared to experimental data and calculations available in the literature. Stable end-members CoAl, NiAl, and Ni$_3$Al are bolded while mechanically unstable CoNi and Cr$_3$Al are italicized.

<table>
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<tr>
<th>End-member</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$V_0$ (Å$^3$/atom)</th>
<th>$B_0$ (GPa)</th>
<th>$\nu$</th>
<th>Scaling factor</th>
<th>$\Theta_0$ (K)</th>
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<td>73.2</td>
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<td>90 K</td>
<td>227</td>
<td>148</td>
<td>129</td>
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<td></td>
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<td>125.4</td>
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<td>470 Expt. [196]</td>
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<td>231</td>
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</table>
Table 6.3: Calculated elastic stiffness constants and various properties of the end-members of $\sigma$. Experiments and calculations from literature are also shown with relevant temperatures given if available.

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<th>End-member</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$V_0$ (Å$^3$/atom)</th>
<th>$B_0$ (GPa)</th>
<th>$\nu$</th>
<th>Scaling factor</th>
<th>$\Theta_D$ (K)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>(Al)$_3$(Al)$_3$(Cr)$_4$</td>
<td>118.4</td>
<td>110.8</td>
<td>50.6</td>
<td>175.2</td>
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<td>27.6</td>
<td>15.704</td>
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<td>156.5</td>
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<td>469.0</td>
<td>108.6</td>
<td>147.9</td>
<td>12.369</td>
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<td>0.273</td>
<td>0.815</td>
<td>674</td>
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<td>342.8</td>
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<td>141.0</td>
<td>475.2</td>
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<td>11.451</td>
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<td>0.763</td>
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<td>(Al)$_3$(Co)$_3$(Cr)$_4$</td>
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<td>113.6</td>
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<td>365.3</td>
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<td>277.2</td>
<td>65.7</td>
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<td>13.072</td>
<td>141</td>
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<td>(Al)$_3$(Ni)$_3$(Cr)$_4$</td>
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<td>332.4</td>
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<td>11.834</td>
<td>173</td>
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<td>0.696</td>
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<td>245.0</td>
<td>75.3</td>
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<td>13.249</td>
<td>135</td>
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<td>(Ni)$_3$(Co)$_3$(Cr)$_4$</td>
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<td>10.757</td>
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<td>0.717</td>
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<td>Fe-V $\sigma$</td>
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<td></td>
<td></td>
<td></td>
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<td>Calc. [187]</td>
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Table 6.4: Calculated enthalpies, entropies and Gibbs energies of formation of B2 and γ' end-members at 298 K. Energies taken with respect to the standard reference states. Experiments and calculations at various temperatures, including 298 K, are included for comparison; temperature information is given when available. Mechanically unstable end-members have 0 K formation enthalpies shown in italics. Asterisks denote data from compilations by other authors.

<table>
<thead>
<tr>
<th>End-member</th>
<th>$\Delta H^{298}$ (kJ/mol-atom)</th>
<th>$\Delta S^{298}$ (J/mol-atom/K)</th>
<th>$\Delta G^{298}$ (kJ/mol-atom)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
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<td>-55.220</td>
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</tr>
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<td>1100 K</td>
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</tr>
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<td></td>
</tr>
<tr>
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<td></td>
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<tr>
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<td></td>
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</table>
Table 6.5: Calculated enthalpies, entropies and Gibbs energies of formation of σ end-members at 298 K. Energies taken with respect to the standard reference states. Experiments and calculations at various temperatures, including 298 K, are included for comparison; temperature information is given when available. Mechanically unstable end-members have 0 K formation enthalpies shown in italics.

<table>
<thead>
<tr>
<th>End-member</th>
<th>$\Delta_fH^{298}$ (kJ/mol-atom)</th>
<th>$\Delta_fS^{298}$ (J/mol-atom/K)</th>
<th>$\Delta_fG^{298}$ (kJ/mol-atom)</th>
<th>Ref.</th>
</tr>
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<td></td>
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</tr>
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</tr>
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<td></td>
<td></td>
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<td>Co$<em>{39.3}$Cr$</em>{60.7}$ 473 K</td>
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Table 6.6: Calculated enthalpies of mixing for A2. The results are based on binary and ternary SQS calculations at 0 K with reference states taken as bcc-A2 for Al, Co, and Cr, and Ni. B2 end-members with the same reference states are included. Energies for mechanically unstable ordered structures are shown in italics. Values for Al-Co, Al-Cr, Co-Cr, and Al-Co-Cr and adapted from previous work [153] and are indicated with an asterisk *.

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<th>System</th>
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<th>Co</th>
<th>Cr</th>
<th>Ni</th>
<th>SQS prototype</th>
<th>$\Delta H_{\text{mix}}$ (kJ/mol-atom)</th>
<th>$\Delta H_{B2-\beta}$ (kJ/mol-atom)</th>
<th>$\Delta H_{\text{order}}$ (kJ/mol-atom)</th>
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</thead>
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Table 6.7: Calculated enthalpies of mixing for γ. These calculations are based on binary and ternary SQS calculations at 0 K with references taken as fcc-γ for Al, Co, and Cr, and Ni. γ' end-members with the same reference states are also shown. Energies for mechanically unstable ordered structures are shown in italics.

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Table 6.8: Calculated enthalpies of mixing for B2. The results are based on ternary SQS calculations at 0 K with reference states taken as bcc-A2 for Al, Co, and Cr, and Ni. Energies for mechanically unstable binary ordered structures are shown in italics. Values for Al-Co, Al-Cr, Co-Cr, and Al-Co-Cr and adapted from previous work [153] and are indicated with an asterisk *.

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Table 6.9: Calculated enthalpies of mixing for $\gamma'$. The results are based on ternary SQS calculations at 0 K with reference states taken as fcc-$\gamma$ for Al, Co, and Cr, and Ni. Energies for mechanically unstable binary ordered structures are shown in italics.

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Figure 6.1: Al-Ni binary as assessed by Ansara et al. [59] which is later converted to the partitioned model and used in the Al-Cr-Ni ternary by Dupin et al. [1]. Note that ferromagnetic $\gamma$ undergoes a magnetic transition into paramagnetic $\gamma$ at higher temperatures (- - -).
Figure 6.2: The Co-Ni description is adopted from SGTE [154], based on work by Guillermet F. [155]. Note that ferromagnetic $\gamma$ undergoes a magnetic transition into paramagnetic $\gamma$ at higher temperatures (- - -).
Figure 6.3: The Cr-Ni binary description is adopted from SGTE [154], based on work by Lee B.-J. [156]. Note that ferromagnetic $\gamma$ undergoes a magnetic transition into paramagnetic $\gamma$ at higher temperatures (- - -).
Figure 6.4: Calculated Al-Cr-Ni isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e) from Dupin et al. [1].
Figure 6.5: The atomic structures for the $\sigma$-sigma end-member(s) (a), 8-atom B2 (b) and the SQS for the 24-atom $\gamma'$ (c). The different colors denote different atomic species and some bonds have been added to aid in the visualization of the unit cell crystal structures.
Figure 6.6: Predicted enthalpies of formation in the three binary systems Al-Ni (a), Co-Ni (b), and Cr-Ni (c) for fcc-γ (◯) and A2 (△, blue) from SQS calculations at 0 K. 16-atom SQS γ calculations by Wolverton and Ozolins [150] are represented by (□). Ordered L12/L10 (●) and B2 (▲, blue) formation energies are also shown. Formation enthalpies at 298 K from the individual models by Dupin et al. [1] (a), SGTE [154] (based on work by Guillermet F. [155]) (b), and SGTE [154] (based on work by Lee B.-J. [156]) are plotted: γ (− − −), γ′ (− · −), A2 (· · ·, blue), and B2 (—, blue). Additionally, the Cr-Ni system is plotted in (d) with SER reference states to show the large lattice stability differences for Cr between DFT and CALPHAD.
Figure 6.7: Calculated Al-Co-Cr isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental phase equilibrium data by Moskvitina et al. [151] is included for comparison: single phase (□), 2-phase (▽), and 3-phase (+).and by Ishikawa et al. [129]: 2-phase (○), order-disorder transition (★). Phase equilibria data from the present work: 2-phase (●), 3-phase (▲). The calculated order-disorder transition is also shown (⋯).
Figure 6.8: Calculated A2 (---) and B2 (—) formation energy of the Co$_{0.5}$Al$_{0.5}$-Cr vertical section compared to first-principles results for the A2 (○) and B2 phases (●) at 298 K. Reference states are taken as A2 for Al, Co and Cr.
Figure 6.9: Calculated A2 (---) and B2 (——) formation energy of the Co$_{0.5}$Cr$_{0.5}$-Co$_{0.5}$Al$_{0.5}$ vertical section compared to first-principles results for the A2 (○) and B2 phases (●) at 298 K. Reference states are taken as A2 for Al, Co and Cr.
Figure 6.10: Calculated $\gamma$ (---) and $\gamma'$ (—) enthalpies of formation for the $(\text{Cr}_x\text{Co}_{1-x})_{0.75}\text{Al}_{0.25}$ vertical section compared at 298 K compared to first-principles SQS results for $\gamma$ (○) and $\gamma'$ (●). Reference states are taken as $\gamma$ for Al, Co and Cr.
Figure 6.11: Calculated Al-Co-Ni isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental data from Jia et al. [160] (△), Kainuma et al. [163] (○), and Albers et al. [164] (1-phase ◊, 2-phase □) are included for comparison. Equilibrated alloys from Schramm [159] are also shown: 1-phase (●), γ’+B2 (×), γ+γ’ (+), and γ+B2 (▽).
Figure 6.12: Calculated Al-Co-Ni vertical sections at Ni:Co ratios of 90:10, 80:20, 50:50, and 20:80 compared to equilibrated alloys from Schramm [159]: 1-phase (\(\times\)), \(\gamma'+B2(\times)\), \(\gamma+\gamma'(\times)\), \(\gamma+B2(\nabla)\), 3-phase (\(\varphi\)), and Curie temperature (\(\bar{X}\)). The \(\gamma\) ferromagnetic-paramagnetic transition is also shown with (\(\cdot\cdot\cdot\)).
Figure 6.13: Gibbs energies of formation for B2-CoAl (—) and B2-NiAl ( - - - ) from the CALPHAD modeling compared to their respective results from the Debye-Grüneisen model (○ and △).
Figure 6.14: Calculated B2 (—) enthalpies of formation for the (Ni$_{0.5}$Co$_{0.5}$)$_0$Al$_{0.5}$ vertical section compared to measurements from Grun et al. (▲) [165] at 1073 K (error bars approximately size of symbols). Experimental reference states are liquid Al, solid γ-Co, and solid γ-Ni. Enthalpies of formation for A2 (○) and B2 (●) with all A2 reference states at 298 K are shown in comparison to first-principles SQS results for A2 (○) and B2 (●).
Figure 6.15: Calculated γ’ (—) enthalpies of formation for the (Ni₃Co₁₋ₓ)₀.₇₅Al₀.₂₅ vertical section compared to measurements from Kek et al. (▲) [161] at 298 K. Experimental reference states are solid γ for Al, Co, and Ni. The enthalpy of formation for the γ (- - -) with all γ reference states at 298 K are shown in comparison to first-principles SQS results for γ (○) and γ’ (●).
Figure 6.16: Al (—), Co (· · ·, blue) and Ni (- - -, red) excess partial enthalpies and entropies of γ’ along the composition \((\text{Ni}_3\text{Al})_{1-x}\text{Co}_x\) at 1473 K plotted with KEMS measurements by Albers et al. [164].
Figure 6.17: Calculated Co-Cr-Ni isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental results of investigations of the 2-phase equilibria by Omori et al. [173] (○) and Zhanpeng J. [174](△) are included as comparison. A2/σ phase boundaries measured by Zhanpeng J. [174] are also shown (+).
Figure 6.18: Calculated liquidus and solidus temperatures (—) compared to measurements from Omori et al. [173] at various Cr concentration levels: 0.1Cr (○), 0.2Cr (△), 0.3Cr (□), 0.4 (◇)
Figure 6.19: Calculated $\gamma$ (—) and A2 (- - -) formation enthalpies of the Co$_{0.5}$Ni$_{0.5}$-Cr vertical section compared to measured $\gamma$ (●) and A2 (▲) enthalpies from Kubachewski and Hack [175] at 1523 K. Experimental reference states are solid $\gamma$-Co, A2-Cr and $\gamma$-Ni. First-principles SQS results for the $\gamma$ (○) and A2 phases (△) at 298 K with the same reference states as the experimental measurements are also included.
7 Thermodynamic modeling of the Al-Co-Cr-Ni quaternary

While many phase stability studies exist on the Al-Co-Cr-Ni quaternary, few thermodynamic modeling efforts have been performed. As a result, additional alloys were prepared for the current work to supplement the modeling efforts along with some literature data. Broz et al. [197], [198] and Bursik et al. [199] studied the Al-Co-Cr-Ni system experimentally and theoretically using CALPHAD models for Ni-rich alloys (~60 at. % Ni). Broz et al. [197], [198] produced and analyzed a series of Ni-rich $\gamma+\gamma'$ alloys and at 1173 and 1273 K, respectively. Additionally, they developed a quaternary CALPHAD description using models from Dupin [130], similar to the current work [197], [198]. Unfortunately, these models are not presented in detail and are not available in the literature so it is not possible to compare directly with the present work. Bursik et al. [199] annealed alloys at 1273 and 1373 K to study their phase stabilities using XRD. In the current work, data from Broz et al. [198] and Bursik et al. [199] are used while those from Broz et al. [197] are not used due to inconsistencies in the sets. The constructed quaternary database, henceforth named CR-AL DFT-Amended Database (CRALDAD), will provide a foundation for the theoretical study of MCrAIY type coatings.

7.1 Materials and Methods

7.1.1 Experimental procedures

From collaborators Thomas Gheno and Brian Gleeson at the University of Pittsburgh:
Ingots of nominal compositions given in Table 7.1 were prepared by Ar arc melting, drop cast into 10 mm diameter rods, and homogenized 6 h at 1473 K and 48 h at 1423 K in vacuum at the Materials Preparation Center of Ames Laboratory (Materials Preparation Center, Ames Laboratory USDOE, Ames IA, USA). Specimens (approximately 1 mm thick) were vacuum-encapsulated in quartz capsules, further homogenized 48 h at 1423 K in a tube furnace, and slowly brought to equilibration temperature. Equilibration heat treatments were conducted at 1173, 1373 and 1473 K for 525, 100 and 50 h, respectively, followed by water quenching to retain the equilibrium microstructures. Phase constitutions were studied by X-ray diffraction (XRD) with a PANalytical Empyrean instrument, using a Co radiation source (\(K_{\text{A2}}=1.789 \ \text{Å}\)). Metallographic preparation and characterization were performed in the same way as for CoCrAlY alloys shown in Chapter 5.

### 7.1.2 CALPHAD thermodynamic models

Al-Co-Cr, Al-Co-Ni and Co-Cr-Ni ternary models from the previous chapter were combined with the Al-Cr-Ni model by Dupin et al. [1] to produce a quaternary Al-Co-Cr-Ni extrapolation. It should be noted that the ternary models developed in the previous chapter involved quaternary data presented in this chapter. Optimized ternary parameters are systematically extrapolated to the quaternary to determine a set of parameters that describes the quaternary phase equilibria best. Only after this is optimization performed. This is done as disagreements in higher order systems often stem from lower systems where poor parameter choices may have been made [176]. The quaternary system demonstrating its four ternary faces in ‘origami’ form is shown in Figure 7.3.
To successfully extrapolate $\gamma'$, ternary interaction parameters in the quaternary based on bond energies $U$ for $\gamma'$ must be introduced that allow the phase to disorder [16], [130]: $^{0}L'_{Al,Co,Cr;Ni}$, $^{0}L'_{Al,Co,Nil;Cr}$, $^{0}L'_{Al,Co,Ni;Co}$, $^{0}L'_{Co,Cr,Ni;Al}$. Details on the implementation of such parameters are shown in Chapter 2 and result from work by Dupin [130]. One additional quaternary parameter is required for $\sigma$ and this will be discussed later in the chapter. Due to the metastability of certain phases, such as B2 and $\gamma'$ in the Co-Cr-Ni ternary, only quaternary alloys provide an experimental avenue in determining their interaction parameters alongside with DFT calculations. The PARROT module within Thermo-Calc [45]–[47] is used to assess the parameters in the system using phase equilibrium data from the experimental measurements listed in Table 7.2 and from ref. [198], [199]. The resulting thermodynamic parameters are included in Appendix C.

### 7.2 Results and Discussion

#### 7.2.1 Experimental results

*From collaborators Thomas Gheno and Brian Gleeson at the University of Pittsburgh:*

Alloy phase constitutions were determined through a combination of XRD (selected spectra shown in Figure 7.1), phase composition analysis (EPMA results given in Table 7.2), and visual examination of the microstructures (selected micrographs shown in Figure 7.2). In Figure 7.2, the dark matrix is B2, the grey phases are A2, $\gamma$ and $\sigma$ (by increasing brightness), and the bright precipitates are Y-containing intermetallics. All alloys exhibit a primary B2-$\gamma$ microstructure typical of MCrAlY alloys. At 1473 K, alloys with high Cr contents (A3, A5) produce A2 in
addition to B2 and γ. The A2 and B2 phases both have a cubic structure, and their XRD signals cannot be resolved with the instrument available. However, the phases exhibit very distinct compositions (Table 7.2). In Cr-lean alloys (A6, A7), NiAl martensite, noted L10, is found instead of B2. Martensite is identified by XRD from its L10 tetragonal structure (see alloy A6 in Figure 7.1), and presents a typical twinned microstructure (Figure 7.2). Its presence does not affect phase equilibrium since it is formed by a diffusionless transformation during cooling. At 1373 K, the Cr-rich phase is either A2 or σ, depending on alloy composition. The two phases differ in their composition, with σ dissolving more Co and slightly less Al than A2. Further, XRD clearly identifies the D8b tetragonal structure of σ (see alloys A2 and A5 versus A3 in Figure 7.1). The σ phase is stabilized at the expense of A2 in alloys with higher Co (A4, A5 versus A3) or lower Cr content (A2 v. A3). The B2 → L10 transformation is observed for Cr-lean alloys equilibrated at 1373 K, but not at 1173 K (see alloy A6 in Figure 7.2). At 1173 K, the Cr-rich alloys precipitate σ, and no A2 is found. Precipitation of γ’ in γ is observed in the micrographs for the Cr-lean alloys (A6 and A7). Precipitates of γ’ could however, not be distinguished from γ using the XRD instrument available. The γ’ precipitates were also too small for accurate composition measurements by EPMA. Qualitatively, the precipitates were found to have less Cr and more Al than the matrix, and the cuboidal microstructure is typical of γ-γ’ equilibria.

If Y is disregarded and we consider the quaternary Al-Co-Cr-Ni system, three-phase equilibria are univariant, which explains the slight variations of the γ-B2-A2 or γ-B2-σ equilibria in the different alloys. At 1473 K, the difference between the compositions of A2 and B2 reflects a significant miscibility gap. This is to be compared with the previous work on the Al-Co-Cr system, which showed that the A2-B2 miscibility gap is suppressed and replaced by an order-disorder transition between 1373 and 1473 K. In contrast, Dupin et al. [1] showed that the mutual
solubilities of A2 and B2 remained very limited up to melting in the NiAl-Cr pseudo-binary system. Thus in terms of the A2-B2 phase relationship, the Al-Co-Cr-Ni system exhibits an intermediate behavior between those of Al-Co-Cr and Al-Cr-Ni. The tendency to a disordering of the B2 structure with increasing temperature is observed here as the Al and Cr contents of the B2 phase show large variations at 1473 K (Table 7.2). Higher Co contents favor an increase of Cr solubility and decrease of Al content in B2, as could be expected from the behavior of the Al-Cr-Ni and Al-Co-Cr systems. As the temperature decreases to 1373 and 1173 K, the range of Al and Cr concentrations in B2 becomes more limited.

In terms of alloy microstructures, A2 precipitation mainly occurred within B2, as expected considering the similar crystal structure of these two cubic phases. Precipitation of σ is seen in Figure 7.2 to have occurred both from A2, reflecting the replacement of A2 by σ in the three-phase equilibrium as the temperature decreases, and at the expense of γ at the B2-γ interface, driven by the decrease of Cr solubility in γ. In the latter case, heterogeneous nucleation reflects the lack of compatibility between the tetragonal σ and the other phases of the system. In contrast, γ' is exclusively found within γ. Coherent precipitation is typically observed for these two cubic phases. Similarly, σ also precipitates out of A2 in the subsystems Al-Co-Cr [129] and Co-Cr-Ni [174] near the Co-Cr binary.

7.2.2 CALPHAD modeling results

The extrapolated quaternary model reproduces phase stabilities and compositions of the measured alloys well. However, σ compositions indicate an excess of Co and Cr at the expense of both Al and Ni, especially at 1173 K. Given the good agreement seen in the ternary systems
containing $\sigma$, Al-Co-Cr and Co-Cr-Ni, the low solubility could be due to the energy contributions from metastable $\sigma$ existing in Al-Cr-Ni. However, alteration of binary and ternary parameters in the Cr-Ni and Al-Cr-Ni systems for $\sigma$ induces full stability of this phase in these subsystems. The formation of $\sigma$ in the Cr-Ni binary and the Al-Cr-Ni ternary would then contradict experiments and models [1], [156]. A quaternary reciprocal parameter relating binary interactions in two sublattices was therefore chosen to introduce greater Al and Ni content in $\sigma$ ($L_{Co,Ni:Al,Co:Cr}^\sigma$) without stabilizing $\sigma$ in Cr-Ni and Al-Cr-Ni. An additional metastable binary B2 interaction ($L_{Co,Ni:Cr}^{B2}$) in the Co-Cr-Ni ternary was included in the evaluation to improve phase compositions for Co and Cr in B2. Additionally, the bond energy term $U_{CoCr}$, relating to ordering of $\gamma'$, can be modeled using quaternary data as $\gamma'$ is no longer metastable. DFT calculations shown in the previous chapter indicate that Co$_3$Cr and Cr$_3$Co have ordering energies of -4.15 and -3.62 kJ/mol relative to the disordered phase. A temperature dependent term is also introduced for $U_{CoCr}$ to better describe the $\gamma'$ phase compositions. By the introduction of these parameters, a satisfactory quaternary description is obtained.

Figure 7.4, Figure 7.5, and Figure 7.6 show the calculated quaternary isotherms at various Co to Ni contents and temperatures with nominal alloy compositions overlaid on Figure 7.4. Note that alloys on the x(Co)=0.19 isotherm have nominal compositions only close to 19 at. % and the figure is plotted for easy viewing. Phase stabilities are well predicted for all alloys for the nominal compositions. For A6 and A7, $\gamma'$ stability are also predicted, in agreement with the current measured results shown in Table 7.2. The important Al-Co-Cr (a) and Al-Cr-Ni (b) subsystems at 1373 K are shown in Figure 7.5 with additional phase boundaries produced by varying Co:Ni ratios from 10:90 to 90:10. The destabilizing effects of Co on $\gamma'$ can clearly been seen in Figure 7.5 (b),
resulting in $\gamma$+B2 at a Co:Ni ratio of 40:60. Figure 7.6 provides a 3-dimension view of the B2+$\gamma$ region at 1373 K for 10-40 at. % Co concentrations.

Figure 7.7 and Figure 7.8 includes the calculated phase compositions for alloys A1 (a) and A4 (b) as well as A5 (a) and A6 (b), respectively, compared to EPMA measurements in Table 7.2. Overall, at 1173, 1373, and 1473 K, phase compositions are well reproduced using the current model for B2 and $\gamma$. Additionally, note that the A2 to $\sigma$ transition temperature is predicted to be approximately 1374 K with the current measurements being $\sigma$ at 1373 K. In the case of $\sigma$, Cr and Ni contents still disagree with measured compositions even with the addition of the quaternary $\sigma$ reciprocal parameter; at 1373 K, all compositions are better reproduced. This particular effect has been attributed to the unphysical nature of the sublattice model implemented in this work for $\sigma$ [52] where Cr can take on a maximum composition of 73.3 at. % at the end-member (A)$_8$(Cr)$_{18}$(Cr)$_4$. The true $\sigma$ model would include 5 distinct sublattices relating to Wyckoff positions with Al, Co, Cr, and Ni going into each one since no element is truly forbidden from any particular site; (Al,Co,Cr,Ni)$_2$(Al,Co,Cr,Ni)$_4$(Al,Co,Cr,Ni)$_8$(Al,Co,Cr,Ni)$_8$(Al,Co,Cr,Ni)$_8$ [52], [200]. By using this model, an astonishing 1024 end-members would have to be defined. Simplifications were thus made by combining certain sites and restricting their contents [52] with the model implemented in the current model being the most common [52]. If a more physical model, i.e. how Wyckoff positions (crystallographic sites) are combined [52], is adopted for $\sigma$, the maximum Cr composition is 66.7 at. % at the end-member (A)$_{10}$(Cr)$_{16}$(Cr)$_4$. With similar site occupations, this would yield Cr compositions closer to experimental measurements and increase the amount of Al and Ni in the phase. Interestingly, this discrepancy is also seen in other Ni-base superalloy databases which adopt the old model, such as TTN18 (Thermotech) [201]. However, changing sublattice models require partial or complete remodeling of the important Co-Cr binary, which is
outside the scope of the current work as all subsequent ternaries must also then be remodeled. Given the focus of the current work, the phase compositions of \( \gamma \) and \( B2 \) are deemed most important and well described. Changing the \( \sigma \) model will be investigated in future work.

It can be seen in Figure 7.8 (b) that the predictions for alloy A6 deviate slightly from EPMA measurements at 1173 K. One possible explanation could be that complete equilibrium is not reached. Given the non-equilibrium appearance of the microstructure shown in Figure 7.2 where \( \gamma-\gamma' \) are separated by large regions of \( B2 \), it is difficult to ascertain the true three-phase equilibrium, especially for \( \gamma \) and \( \gamma' \). Predictions show a large change in \( \gamma \) composition with the precipitation of \( \gamma' \); this is expected due to strong partitioning effects between \( \gamma \) and \( \gamma' \) [160]. With the accurate predictions seen at 1373 and 1473 K, the predictions at 1173 K are expected to be accurate if true 3-phase equilibrium is reached.

### 7.2.3 Database comparisons and conclusions

*TCNI6 and TTNI8 calculations from collaborators Thomas Gheno and Brian Gleeson at the University of Pittsburgh:*

Shown in Figure 7.9 and Figure 7.10 are bar chart phase composition comparisons of two alloys, A4 and A5, at 1173, 1373 and 1473 K. These alloys were chosen for their high Co contents (~ 30 at. %) in order to demonstrate the accuracy of the current predictions. Results calculated using CRALDAD are compared to results from experimental measurements as well as calculations using other databases from Thermo-Calc (TCNI6) [16], Thermotech (TTNI8) [201], and NIST [157] designed for Ni-base superalloys. Overall, the new predictions show an improvement for all phases compared to the previous descriptions. This is especially true for alloy A5 at 1473 K where
only CRALDAD and TTNI8 predict the formation of A2, in agreement with current experimental results. Overall, CRALDAD and TTNI8 show good agreement with EPMA results for MCrAlY compositions.

The current results demonstrate the robustness of the ternary models developed in the previous chapter. With the addition of only two excess parameters and one bond energy term, all predicted quaternary phase stabilities and compositions are shown to agree with measured alloys. Phase composition predictions at 1173 K for σ deviate slightly from experimental results. However, predictions at 1373 K match better with measured values. Overall, an accurate thermodynamic description of the Al-Co-Cr-Ni quaternary is produced for the first time. This Al-Co-Cr-Ni quaternary description provides a fundamental basis for studying MCrAlYs of various compositions (without Y) including CoCrAlY, CoNiCrAlY, NiCrAlY and NiCoCrAlY alloys. With the main phases accurately described, such as γ and B2, additional models based on the current description can focus on modeling reactive element effects [13].

Acknowledgement

The author would like to acknowledge collaborators Dr. Thomas Gheno and Dr. Brian Gleeson for preparing the experimental sections of this chapter.
Tables and Figures

Table 7.1: Nominal compositions (at. %) of the NiCoCrAlY alloys used for experimental study. All alloys contained an additional 0.1 at. % Y.

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Table 7.2: Phase compositions of the NiCoCrAlY alloys measured by EPMA (at. %).

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Note: γ’ was formed in A6 and A7 at 1173 K but was too finely dispersed to be analyzed.
Figure 7.1: XRD analysis of phase constitution of selected alloys. The insert indicates ICSD card numbers.
Figure 7.2: Microstructure of alloys A3, A5 and A6 equilibrated at 1173, 1373 and 1473 K.
Figure 7.3: The 4 ternaries from the previous chapter at 1273 K are combined to create an ‘origami’ plot to represent the four faces of the Al-Co-Cr-Ni quaternary tetrahedron. Data points shown are identical to ones shown in the isotherms in the previous chapter.
Figure 7.4: Al-Co-Cr-Ni isothermal sections at 19 (a), 26 (b), 30 (c) at. % Co and at 1473 K. Shown with nominal compositions of the quaternary alloys used in this study (symbols). Note that some alloys shown in (a) are not in the true plane of the calculation as their Co contents vary slightly.
Figure 7.5: Changes in the $\gamma$, $\gamma'$ and B2 phase boundaries as a function of Co:Ni ratios (shown in legend) for the base Al-Co-Cr (a) and Al-Cr-Ni (b) systems calculated in the current work at 1373 K. Please note the two images can be superimposed to describe the full change from Al-Co-Cr to Al-Cr-Ni as a function of Co:Ni ratios (color bars and lines).
Figure 7.6: 3D vertical isotherms at 1373 K for varying Co contents on the Z axis (10 to 40 at. % Co shown). Please note that tie-lines are out of the plane of the contours as this may be misleading.
Figure 7.7: Calculated alloy A1 and A4 phase compositions for Al (—), Co (· · ·), Cr (— · —), and Ni (— · -) (γ-black, B2-red, σ-blue) compared to measured compositions for Al (○), Co (□), Cr (△), and Ni (○) (γ-open, B2-filled in). Compositions for σ are shown as: Al (+), Co (×), Cr (∗), Ni (∇).

Figure 7.8: Calculated alloy A5 and A6 phase compositions with the same labels as the previous figure for Al, Co, Cr, and Ni (γ-black, γ’-orange, A2-green, B2-red, σ-blue). Compositions for A2 and σ are shown as: Al (+), Co (×), Cr (∗), Ni (∇).
Figure 7.9: Phase composition (at.%) comparisons for alloy A4 at 1173 (a), 1373 (b) and 1473 K (c) compared to current experimental results as well as other Ni-base superalloy databases.
Figure 7.10: Phase composition (at. %) comparisons for alloy A5 at 1173 (a), 1373 (b) and 1473 K (c) compared to current experimental results as well as other Ni-base superalloy databases.
Effects of ternary alloying elements on the interfacial energy of coherent \( \gamma/\gamma' \) interfaces in the Ni-Al system: A study using first-principles

Single-crystal (SX) nickel-base superalloys, one of the most important gas turbine ‘hot section’ materials, derive their excellent high temperature mechanical properties from the strengthening \( \gamma' \)-Ni\(_3\)Al (L\(_{12}\)) phase in its \( \gamma \)-Ni (face-centered cubic, fcc) matrix [3]. To improve their creep resistances, precipitate hardened SX superalloys, such as CMSX-4, can contain up to 70 volume \% \( \gamma' \) after aging treatments [202]. The often cuboidal \( \gamma/\gamma' \) microstructure is ultimately responsible for strengthening previous and current generations of SX superalloys [203]. These cuboidal \( \gamma' \) precipitates create \( \gamma/\gamma' \) interfaces that have predominantly \{100\} orientations after aging [5]. Due to the very small differences in lattice constants of the ordered \( \gamma' \) phase and the disordered \( \gamma \) matrix (less than 0.5\% in lattice parameters in most cases), lattice misfits are quite small [3]. This small lattice misfit creates \( \gamma/\gamma' \) interfaces which are highly coherent in the microstructure.

Prediction of interfacial energies \( (\sigma_{\gamma/\gamma'}) \) at the \( \gamma/\gamma' \) interface will help determine precipitate growth mechanisms, rates and sizes. These factors are highly influential on the final bulk mechanical properties of the SX superalloy [204]. Microstructure evolutions in metallic alloys dictate their usefulness as materials [205]. Attempts to model phase transformations such as solidification, coarsening and grain growth require kinetic as well as thermodynamic data. In terms of thermodynamics, coarsening is driven by lowering the overall energy of the system, which is strongly affected by the interfacial properties. Investigating atomic level interactions, such as the interface itself, has always been challenging due to lengthscales limitations. High resolution techniques such as transmission electron microscopy, grazing incident X-ray scattering [206] and
atom probe tomography [207] can only examine certain aspects of interfaces; leaving theoretical quantitative ab initio atomistic simulations as the main methodology [208].

Benedek et al. [208] demonstrates the ability to investigate heterophase interfaces, such as those existing between the TiAl and Ti₃AlC systems. Benedek et al. [208] outlines that the sharp interface model, where a distinct atomic layer bounds one phase, are the most quantitatively important. As a result, atomistic models lend themselves to be the best methodology for looking at atomically sharp interfaces. Atomistic simulations using ab-initio density functional theory (DFT) have been implemented in the study of coherent interfaces such as those that exist between the γ and γ’ phases in Ni-base superalloys [207]. These simulations present an alternative to experiments where important properties, such as interfacial energy, must be calculated differently from coarsening theories that are often inaccurate due to the averaging over all crystallographic planes.

Currently, interfacial energies are mostly estimated from experiments and parametrically studied. Atomistic models have been used to look at only binary Ni-Al systems. Interfacial energies at 0 K between pristine (only Al and Ni considered) γ and γ’ interfaces have been calculated by several research groups [204], [207], [209], [210] using various computational techniques. Experimental interfacial energy values are back-calculated using Lifshitz-Slyozov-Wagner (LSW) and trans-interface diffusion-controlled (TIDC) theories [211] for averaged precipitate interface orientations. These prediction methods produce interfacial energy values between 6.9 to 60 mJ/m² [210]. First-principles calculations recently performed by Mao et al. [207] includes detailed analysis of {100}, {011}, and {111} orientations of the γ/γ’ interface as well as vibrational effects. Woodward et al. [212] recently performed a similar study and found similar conclusions as Mao et al. concerning sharp γ/γ’ interfaces at low temperatures. The present work
will attempt to shed light on dilute ternary element effects on the $\gamma/\gamma'$ interface. Very few experimental coarsening studies relating to interfacial energies have been performed on Ni-Al systems with minute additions of a ternary element. Some of these studies include the Ni-Al-Co [213], [214] and Ni-Al-Ti [215] systems. Davies et al. studied multiple Ni-Al-Co samples and found that small additions of Co decreased the coarsening rate slightly when compared to a binary Ni-Al sample [213]. Additionally, studies performed on Ni-Al-Ti alloys show retardation of the coarsening process. Njah & Dimitrov found deceleration of coarsening in a Ni-10.6% Al-2.5% Ti alloy [215]. On another note, transition metal additions to the Ni-Al system imparts partitioning/segregation effects where elemental preference for either $\gamma$ or $\gamma'$ is seen [160]. Jia et al. found, in a series of Ni-Al-X (dilute X) alloys, that Ti, Ta, and Nb strongly segregate to the $\gamma'$ while Co, Cr, and Fe have slight preferences for the $\gamma$ across 900-1300 °C. Also, it was shown that Mo and W prefer $\gamma'$ at lower temperatures and $\gamma$ at higher temperatures [160]. Therefore, it is important to understand how the interfacial energies change when elements partition to either phase. This work attempts to systematically study ternary alloying effects on the interfacial energy when dilute elements reside in $\gamma$ or $\gamma'$.

8.1 Methodology

In order to create a chemical sharp interface between $\gamma/\gamma'$ particles, a simplification of geometry must be implemented. Currently, DFT simulations are limited in size to a few nm’s and a few hundred atoms. It is impractical to model, with accurate DFT methods, entire $\gamma'$ particles and the $\gamma$ matrix/channels as they are on the order of tens to hundreds of nanometers. In the present study, 96-atom supercells, consisting of repeating $\gamma$ and $\gamma'$ phases, are used; each half of the
supercells consists of the γ and γ’ phases, respectively. The resulting supercells contain periodic slabs and two interfaces due to boundary constraints. There are no misfit dislocations at the interface due to forced coherency, unlike in a real interface [208].

In this study, the interfacial energy (mJ/m²) is calculated using [216]:

Eq. 8.1: \[
\sigma_{\gamma/\gamma'} = \left\{ E_{\gamma/\gamma'}(a, b, c) - \frac{1}{2} \left[ E_{\gamma}(a, b, c) + E_{\gamma'}(a, b, c) \right] \right\} / 2A
\]

where \( E_{\gamma/\gamma'}(a, b, c) \) is the bulk energy of a 96-atom supercell (with lattice parameters a, b and c) constructed of γ and γ’ phases with two interfaces separating them. \( E_{\gamma}(a, b, c) \) and \( E_{\gamma'}(a, b, c) \) denote the bulk energies of 96-atom supercells that consist of only γ and γ’, respectively. \( A \) is the cross-sectional area of the supercell as interfacial energies are defined on a per unit area basis (e.g. mJ/m²). Given the current setup, an overall composition of 12.5% at. Al is achieved, which is representative of many experimental Ni-Al alloys [217]–[220].

This methodology is modified for supercells that contain alloying atoms near the interface. Four supercells are required for the calculation; alloying atoms are placed symmetrically and equivalently in relation to the two interfaces due to symmetry. For alloyed interfaces, the interfacial energy of γ/γ’ with an alloying element X \( (\sigma_{\gamma/\gamma'}^X) \) is using the following equation. For alloying atoms in the γ phase, the interfacial energy is defined as:

Eq. 8.2: \[
\sigma_{\gamma/\gamma'}^X = \left\{ E_{\gamma/\gamma'}(a, b, c) - \frac{1}{2} E_{\gamma}(a, b, c) - \left[ E_{\text{Alloyed,\gamma}}(a, b, c) - \frac{1}{2} E_{\gamma}(a, b, c) \right] \right\} / 2A
\]

The additional \( E_{\text{Alloyed,\gamma}}(a, b, c) \) term is required to calculate the interaction effects on the bulk energy of the phase γ that the alloying atom is placed in. Effectively, Eq. 8.2 shows that the chemical potential contributions of the alloying atom will be effectively removed. Otherwise,
energies between the interface supercell and the reference cells cannot be compared. This is done by replacing the bulk energies between the two interacting atoms with the bulk energies of a supercell that does not have the alloying atoms or interactions. The same approach is used for dilute additions to $\gamma'$. In both cases, an overall composition of 12.5 % Al and 1% X (ternary element) is achieved. This composition corresponds to an equivalent phase fraction of $\gamma$ and $\gamma'$ at 0 K. Ta and Ti are special cases in this study as they have extremely strong tendencies to partition to Al-sites in $\gamma'$ [160], [221]. Therefore, calculations are performed for the cases where Ta and Ti substitute for either Al or Ni in $\gamma'$.

Lattice misfit between the $\gamma/\gamma'$ phases must be accounted for in the relaxation scheme. The scheme for the current calculations are implemented using suggestions from Wang et al. [216], Benedek et al. [208] and Christensen & Wahnström [222]. Woodward et al. [212] has also proven the effectiveness of this method for calculating the energetics of the $\gamma/\gamma'$ interface. Interface-supercells with bulk energies $E_{\gamma/\gamma'}(a, b, c)$ are relaxed in all directions to the equilibrium volume. Lattice parameters for the interface-supercell will have $a$ and $b$ in between that of the pure $\gamma$ and $\gamma'$ phases. Once the equilibrium volume of these interface-supercells have been found, the lattice parameters are used as input for the $E_\gamma(a, b, c)$, $E_{\gamma'}(a, b, c)$, and $E_{\text{Alloyed,}\gamma}(a, b, c)$. These supercells are only allowed to be optimized perpendicular to the interface, or only in the $c$ direction with $a$ and $b$ fixed. Such a relaxation scheme is used to eliminate the need to calculate elastic strain that is built up along the interface in order to investigate the interfacial properties in terms of pure thermodynamics. Previously, multiple supercells must be calculated and extrapolated to a 0-atom supercell size in order to determine the interfacial energy [210] that do not contain strain effects. As noted by Benedek et al., it is possible to constrain the chemical potentials of the alloying element by precluding strain-related contributions as well [208].
8.2 Calculation details

In the present work, spin-polarized DFT calculations are performed using the Vienna *ab-initio* Simulation Package (VASP)[23]. The electron-ion interactions are described by the projector augmented-wave (PAW) method [77], [78]. The generalized gradient approximation (GGA), as implemented by Perdew, Burke, and Ernzerhof (PBE) [22], is used as the electron exchange-correlation approximation. Additionally, the spin-state dependent correlation is described using the Vosko, Wilk and Nusair interpolation for a homogenous electron gas to accurately capture ferromagnetism. A plane-wave cutoff energy of 350 eV is consistently used, a value that is more than 1.3 times of the highest plane wave energy cutoff of the elements in the system [79]. Due to the large sizes of the supercells and convergence considerations, Γ-centered k-points scheme is consistently employed. The structures are relaxed by utilizing the Methfessel-Paxton method [28] in order to minimizing the forces acting on the atoms. Spin-polarization is applied to account for the ferromagnetic nature of Ni and Ni$_3$Al. While the Curie temperature of Ni and Ni$_3$Al are 633 and 48 K, respectively, Woodward et al. emphasizes the importance of spin-polarization. Magnetic fluctuations within the alloy still persist even at temperatures higher than the Curie temperature [212].

Necessary equilibrium volumes and energies are obtained using an equation of state. $E_{0K} (V)$ is obtained using a four parameter Birch-Murnaghan (BM4) equation of state (EOS) fitting [25], [26]. Calculations for five volumes are used in fitting the EOS using the following procedure. An initial supercell is relaxed with respect to ion positions, cell shape and cell size. Thereafter,
four additional volumes with up to 6% difference in lattice parameter in expansion and compression are constructed. These additional supercells with fixed volumes are relaxed with respect to ion positions and cell shape (fixed volume). A similar technique is implemented for cells that are only relaxed in the $c$ direction (fixed volume and shape). The $E_{0K}(V)$ data, energies and pressures, are extracted from each volume. By fitting the extracted data to the $BM4$ equation, the energy ($E-V$) and pressure ($P-V$) vs. volume relationships are found. Once the equilibrium volume is determined from the $BM4$ fitting, a supercell is relaxed to this volume to determine the corresponding lattice parameters.

8.3 Results and Discussion

8.3.1 Ni-Al system

It is important to first validate the calculated results for the binary Ni-Al system and investigate how the interface affects the adjacent atomic layers (bulk phases). Differential charge density analysis indicates that the atomic Ni layer shared by $\gamma$ and $\gamma'$ is the interface layer and suggests that energy convergence is achieved in the center of the slabs as the interface interactions are localized to the atomic layers adjacent to it. Figure 8.1 and Table 8.1 compares the calculated lattice parameters with previous computational and experimental investigations [204], [207], [209]–[211], [223]–[225]. Good agreement is seen for the pure phases as well as for the $\gamma/\gamma'$ interface. It is shown that the calculated in-plane lattice parameters of the interface supercell are between those calculated for the pure $\gamma$ and $\gamma'$ phases; i.e. $\gamma$ is in tension and $\gamma'$ compression. According to Eq. 8.1, the spin-polarized calculations for the sharp unalloyed $\gamma/\gamma'$ interface results
\[ \sigma_{\gamma'/\gamma} = 19 \text{ mJ/m}^2. \] This is in line with previous first-principles investigations [204], [207], [209], [210], [212] which are in the ranges of 20-60 mJ/m\(^2\). Lattice parameters of the interface supercell show a 0.68% increase compared to pure Ni and 0.64% decrease compared to pure Ni\(_3\)Al. While not directly comparable, the current results for the supercell in-plane lattice parameter compares favorably to measured lattice parameters in the \(\gamma+\gamma'\) region of the Ni-Al phase, as seen in Figure 8.1.

Experiments [211], [223]–[225] on Ni-Al systems have also attempted to study the thermodynamics of the \(\gamma'/\gamma'\) interface. Ardell [223] implemented a magnetic technique to measure the coarsening rates of two Ni-Al alloys with Al compositions of 12.85 and 13.14 at. %. Coarsening data at high temperatures is fit to the LSW diffusion-controlled coarsening equation, which has been shown to work exceptionally well for Ni-Al systems, in order to back calculate the interfacial energies. The calculated energies, using both alloys, are 14.4 and 14.2 mJ/m\(^2\) at 898 K and 988 K, respectively [223]. Chellman & Ardell [224] conducted additional studies on four Ni-Al alloys with 14.07, 15.91, 17.70, and 19.46 at. % Al at 1073 K and found corresponding interfacial energy values of 6.2, 8.9, 11.9, and 8.3 mJ/m\(^2\). Marsh & Chen [225] found energy values of 16.9, 21.7, 16.6, and 10.3 mJ/m\(^2\) at 823, 873, 923, and 973 K, respectively, for an alloy with an Al composition of 12.5 at. %. Recent studies using a trans-interface diffusion-controlled model by Ardell & Ozolins [211] indicate the interfacial energy may be as low as 3.71–4.29 mJ/m\(^2\) for an alloy containing 12.86 at. % Al at higher temperatures. The most recent values calculated by Ardell take into account Gibbs energy corrections for intermetallics by Calderon et al. [226], yielding values of 20 and 30 mJ/m\(^2\) for the TIDC and LSW cases. In this approach, the second derivative of the Gibbs energy for the Ni-Al system is calculated using the CALculation of PHAse Diagrams (CALPHAD) approach for the real, non-ideal, case [59], [227]. While there is no “accepted” value,
it can be seen that most interfacial energies hover around 10-20 mJ/m\(^2\) for this interface at 800-1000 K.

For this work, the binary systems Ni-Si and Ni-Ti are also investigated in the same fashion to validate the current methods. Ardell predicted, using the methods previously described, that the Ni-Si and Ni-Ti \(\gamma/\gamma'\) interfaces would have energies higher than that of Ni-Al (84-109 and 56-84 mJ/m\(^2\), respectively) [227]. Current results for the Ni-Si interface (162 mJ/m\(^2\)), shown in Table 8.2, agrees exceptionally well with predictions by Ardell (84-109 mJ/m\(^2\)) [227]. However, due to the meta-stability of L\(_{12}\)-Ni\(_3\)Ti and its decomposition path to an ordered-hexagonal \(\eta\) phase, direct comparison with real alloy data is difficult [227]. Albeit, the calculated Ni-Ti \(\gamma/\gamma'\) interfacial energy seen in Table 8.2 is stiller slightly higher than that of Ni-Al.

It is seen that distinct differences exist in the calculated interfacial values in this work and values derived from coarsening data, which takes into account diffuse interfaces at finite temperatures. As noted by Ardell [227], the sharp interface implemented in the current work at 0 K would represent the upper bound of the interfacial energy since interface widening and entropic contributions above 0 K will cause the interfacial excess free energy to decrease. Recent studies by Woodward et al., using Monte Carlo methods, find that configuration entropy near the interface and interface widening can decrease the 0 K \{100\} interfacial energy from approximately 41 mJ/m\(^2\) to 11 mJ/m\(^2\) at 800-1000 K. A supplementary Ni-Al supercell was constructed with the addition of an Al atom near the interface in the \(\gamma\) to study its effects on the interfacial energy (13.5 % Al in Figure 8.1). The dilute addition of Al is shown to decrease the interfacial energy to 15 mJ/m\(^2\). While this is not representative of a diffuse interface, the disruption of the completely sharp interface with perfect ordering actually decreases the interfacial energy. This effect becomes
amplified with the disordering of the interface at higher temperatures as the interfacial width increases [212].

8.3.2 Ni-Al-X systems

It is necessary to first rectify dilute ternary effects on the interfacial energy before studying higher concentrations. This work includes studies on 16 elements commonly found in Ni-base superalloys with their interfacial energies shown in Table 8.3. Amongst the investigated are refractory and platinum group metals which encompass the latest development in superalloys.

8.3.2.1 3-d transition metals: Ti, Cr, Fe, Co, Ni

Of the utmost importance is to ensure that the alloying elements expand or contract the phase it resides in reasonably. Otherwise, the produced interfacial energies may be false even though volume-dependent strain effects are removed. The effects of 3-d transition metals on the $\gamma/\gamma'$ in-plane lattice parameters are presented in Figure 8.2 and Figure 8.3. Experimental measurements on Ni-X solid solutions with dilute transition metal additions by c are also plotted for comparison in Figure 8.3 (a). It can be seen that Ti increases the in-plane lattice parameter of the supercell by 0.5 % when alloyed in $\gamma$, in agreement with experimental Ni-Ti solid solutions [228]. Note that the magnitude of the increase is larger for the experimental Ni-X solid solutions as $\gamma'$ is absent in those systems. Cr, Fe and Co are shown to have small effects on the supercell lattice parameters, which is in agreement with solid solution measurements by Mishima et al. [228]. In $\gamma'$, however, Ti, Cr, and Fe that substitute for Ni all increase the in-plane lattice
parameters with Ti having the largest effect. For Ti, this is no longer the case when it favorably substitutes for an Al atom due to site preference [221]. Figure 8.4 (a) and Figure 8.5 (a) show that when a ternary dilute atom resides γ, there is no direct correlation between the lattice expansion induced by the alloying element and its effects on the interfacial energy. It can be seen that Co and Fe decrease the interfacial energy by only 1-2 mJ/m². On the other hand, Cr and Ti in γ can lower the interfacial energy to around 10 mJ/m².

Shown in Figure 8.4 (b) and Figure 8.5 (b), Ti increases the interfacial energy when it resides in γ’ when substituting for an Al or Ni atom. Interestingly, the interfacial energy is higher when it substitutes for Al, which is the favorable site for Ti [221]; the energies are expectedly different due to different site occupations. Cr, Fe, and Co all increase the interfacial energy slightly in γ’ when substituting for Ni with Cr having the smallest effect. It is also important to note that no atomistic level experimental values for interfacial energies exist on these systems. However, qualitative comparisons can be made with energies calculated using coarsening theories for the few experiments that do exist. Ardell found, by applying TDIC theory to coarsening data, that a Ni-7.5Al-8.5Cr alloy yields an interfacial energy of 15 mJ/m² for the γ/γ’ interface[229]. Unfortunately, given the high Cr and low Al contents of this alloy, it is difficult to delineate the direct contribution of Cr in relation to the current results.

8.3.2.2 4-d transition metals: Y, Zr, Nb, Mo, Ru, Pd

Similar effects on in-plane lattice parameters are seen Figure 8.2 and Figure 8.3 for the 4-d transition metals as is seen for the 3-d. Elements Y and Zr, given their large atomic sizes, distort the interface supercell the greatest. Figure 8.3 (b) shows that the relative change in in-plane lattice
parameter caused by the ternary addition in $\gamma$ is in good agreement with measurements by Mishima et al. [228]. Figure 8.5 (a) again indicates that the interfacial energy is not directly attributed to lattice expansion effects caused by the addition of the alloying elements. Pd and Mo introduce similar atomic volumes to the lattice but have opposite effects on the interfacial energy. Pd increases the interfacial energy slightly while Mo, Nb, Zr and Y all decrease it. Mo is shown to have the greatest effect on the interfacial energy as it can decrease the interfacial energy to as low as 4 mJ/m$^2$. Figure 8.4 (b) and Figure 8.5 (b) show that Y, Zr, Nb, and Mo all increase the interfacial energy when in $\gamma'$. Ru and Pd are shown to have minor effects. It is seen that expansions caused by the ternary additions in the in-plane lattice parameters generally increase the interfacial energies accordingly for $\gamma'$.

8.3.2.3 5-d transition metals: Hf, Ta, W, Re, Pt

Much like the 3-d and 4-d transition metals, larger atoms increase the lattice parameters of the interface supercells in $\gamma$. These effects are shown in Figure 8.2 and Figure 8.3 and are in agreement with measurements by Mishima et al. [228]. Figure 8.5 (a) also present no direct correlation between the lattice expansion induced by the ternary element and the apparent interfacial energy. For example, Pt increases the interfacial energy while Re, W, Ta, and Hf all decrease this value. With the alloying element in $\gamma'$, only Pt is shown to decrease the interfacial energy. This can be attributed to the fact that the Pt-Al binary is the only system other than Ni-Al that forms stable $\gamma'$ [230]. Ternary additions to $\gamma'$ increase the interfacial energy as a function of lattice expansion (Figure 8.5 (b)). In fact, as seen in Figure 8.5 (b), Hf is shown to increase the interfacial energy to 37 mJ/m$^2$. Much like Ti, Ta sitting on its preferred Al-site produces a higher interfacial energy. Few data points are available for comparison in these ternary systems as well.
Atom probe tomography (APT) experiments were used to investigate W effects on a SX \{100\} oriented superalloy. Amouyal et al. show that W can effectively decrease the $\sigma_{\gamma/\gamma'}$ by approximately 6 mJ/m$^2$ [231], consistent with the present DFT calculations.

### 8.3.2.4 Magnetic effects on the $\gamma/\gamma'$ interface

Initial calculations that did not employ spin-polarization resulted in negative interfacial energies, denoting the interfaces are more stable than the bulk [231]. Previous calculations by Price & Cooper [204] also show that removing spin-polarization lowers the energy to a point of infinite interfaces, which is unphysical. From the performed calculations, it quickly becomes apparent that magnetic spin contributes strongly to the interfacial energy. Woodward et al. states that the interfacial energies are extremely sensitive to local spin moments often induced by bad optimization of the electronic structure in elongated supercells [212]. Therefore, special attention is paid to the magnetic convergence of each cell where the overall magnetic moment of a supercell is checked [232]. Mao et al. has shown that ferromagnetism can change the average magnetic moment of Ni atoms across the interface and decrease the \{100\} interfacial energy by 15 mJ/m$^2$ [207]. In this study, this effect has been analyzed by looking at how alloying elements can affect the average Ni magnetic moment in $\gamma$. The change in average Ni magnetic moment is shown in Figure 8.6. It is seen that ferromagnetic elements Fe and Co increase the average Ni magnetic moment and magnetic spin is not disturbed across the interface, resulting in a small change in the interfacial energy. However, elements that are paramagnetic or antiferromagnetic will alter and disrupt the magnetic ordering across the interface. Elements such as Mo, Re, and W that decreases
the average Ni magnetic moment greatly will also drop the interfacial energy. Elements such as Ru and Pt are seen to have little effect on the average Ni magnetic moment and all increase the interfacial energy. Disregarding the ferromagnetic elements, there is a linear trend, for each row of elements, which exists between the interfacial energy and how the average Ni magnetic moment is changed with respect to the alloying element. It can be seen from this analysis that one of the strongest contributions to the interfacial energy is indeed the magnetic spin moments present in the system. Elements which induce the largest changes in the Ni magnetic moment near the interface lead to rapid decreases in the interfacial energy.

8.4 Conclusions

- A methodology for determining the effects of alloying elements on a coherent interface has been investigated according to recommendations by Wang et al. [216], Benedek et al. [208], Christensen & Wahnström [222] and Woodward et al. [212].
- First-principles calculations for the Ni-Al γ/γ' interface yields a value of 19 mJ/m², which is in agreement with previous atomistic investigations findings in ref. [204], [207], [209], [210], [212] which range from 20-60 mJ/m².
- Calculations show that Mo, W, and Re have the largest effect on the interfacial energy by decreasing it to 4-5 mJ/m² when partitioned to γ. Ru and Pt are shown to increase the interfacial energy the greatest amount, up to 25-28 mJ/m² when partitioned to γ.
- In γ', all ternary additions substituting for Ni increase the interfacial energy except for Pt, which decreases it to 16 mJ/m². Hf is seen to increase this value to 37 mJ/m².
• For Ti and Ta, which segregate strongly to $\gamma'$ and substitute for Al, interfacial energies increase to 32 and 35 mJ/m$^2$, respectively.

• It is found that the interfacial energy is the lowest when the ternary alloying element is in $\gamma$ and decrease the average Ni magnetic moment the most, such as Mo, Re, and W.

• Ternary additions to $\gamma'$ increase the interfacial energies as a function of in-plane lattice expansion.
Tables and Figures

Table 8.1: Calculated lattice parameters for the pure phases as well as the interface supercell compared to previous publications and experiments in the Ni-Al system. Calculated interfacial energies are shown as well. Additional experimental data points are shown in Figure 8.1.

<table>
<thead>
<tr>
<th>Phase (s)</th>
<th>Lattice parameters</th>
<th>This work (Å)</th>
<th>Calc. (Å)</th>
<th>Expt. (Å)</th>
<th>$\sigma_{\gamma'/\gamma}$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma^+\gamma'$ Ni-Ni$_3$Al</td>
<td>$a, b$ (in-plane)</td>
<td>3.548</td>
<td>3.545 [209]</td>
<td>3.546 [234]</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Table 8.2: Calculated lattice parameters for the pure phases as well as the interface supercell compared to previous publications and experiments in the Ni-Si and Ni-Ti systems.

<table>
<thead>
<tr>
<th>Phase (s)</th>
<th>Lattice parameters</th>
<th>This work (Å)</th>
<th>Calc. (Å)</th>
<th>Expt. (Å)</th>
<th>$\sigma_{\gamma'/\gamma}$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma'$-Ni$_3$Si</td>
<td>$a, b, c$</td>
<td>3.507</td>
<td>3.512 [235]</td>
<td>3.506 [236] 3.510 [234]</td>
<td></td>
</tr>
<tr>
<td>$\gamma'$-Ni$_3$Ti</td>
<td>$a, b, c$</td>
<td>3.612</td>
<td>3.618 [237]</td>
<td>3.589 [238] (metastable)</td>
<td></td>
</tr>
<tr>
<td>$\gamma^+\gamma'$ Ni-Ni$_3$Si</td>
<td>$a, b$ (in-plane)</td>
<td>3.525</td>
<td>3.518 [234]</td>
<td></td>
<td>161.9</td>
</tr>
<tr>
<td>$\gamma^+\gamma'$ Ni-Ni$_3$Ti</td>
<td>$a, b$ (in-plane)</td>
<td>3.577</td>
<td></td>
<td></td>
<td>22.1</td>
</tr>
</tbody>
</table>
Table 8.3: Calculated Ni-Al-X ternary interfacial energies for dilute additions in \( \gamma \) or \( \gamma' \) (units of mJ/m\(^2\)).

<table>
<thead>
<tr>
<th></th>
<th>3-d</th>
<th>( \gamma )</th>
<th>( \gamma' )</th>
<th>4-d</th>
<th>( \gamma )</th>
<th>( \gamma' )</th>
<th>5-d</th>
<th>( \gamma )</th>
<th>( \gamma' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>9.3</td>
<td>22.4</td>
<td>Y</td>
<td>8.4</td>
<td>28.8</td>
<td>Hf</td>
<td>7.8</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>7.4</td>
<td>19.6</td>
<td>Zr</td>
<td>7.6</td>
<td>26.2</td>
<td>Ta</td>
<td>6.8</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>18.2</td>
<td>22.6</td>
<td>Nb</td>
<td>6.6</td>
<td>26.2</td>
<td>W</td>
<td>5.3</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>17.8</td>
<td>21.1</td>
<td>Mo</td>
<td>4.0</td>
<td>25.3</td>
<td>Re</td>
<td>5.6</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>19.0</td>
<td></td>
<td>Ru</td>
<td>27.7</td>
<td>19.9</td>
<td>Pt</td>
<td>25.4</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pd</td>
<td>22.0</td>
<td>20.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti (Al)</td>
<td>31.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ta (Al)</td>
<td>35.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>14.9</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Figure 8.1: Calculated 0 K DFT lattice parameters for pure γ-Ni, γ′-Ni₃Al, and two sharp γ/γ′ interface superlattices at different compositions of Al (12.5 % and 13.5 %). Measured lattice parameters at various compositions and temperatures are shown for comparison. In addition, γ (short dashed) and γ′ (long dashed) phase boundaries from 300 to 1000 K are shown using the CALPHAD method from Dupin et al. [1]. Lattice parameters are taken from Aoki and Izumi [239], Bradley and Taylor [240], Kamara et al. [234], Mishima et al. [228], Noguchi et al. [241], and Taylor and Floyd [242].
Figure 8.2: Supercell in-plane lattice parameter \((a,b)\) change (Å) when a ternary element \(X\) (plotted with respect to atomic number) substitutes for a Ni atom in the \(\gamma\) phase.
Figure 8.3: Supercell in-plane lattice parameter ($a, b$) change (%) when a 3-d (a), 4-d (b), or 5-d (c) ternary element X (plotted with respect to atomic number) substitutes for a Ni atom in the $\gamma$ phase. Also shown are lattice parameter changes in $\gamma$ Ni-X solid solutions with dilute X additions as measured by Mishima et al. [228].
Figure 8.4: The $\gamma/\gamma'$ interfacial energy change when a ternary element X (plotted with respect to atomic number) is in $\gamma$ or $\gamma'$. 
Figure 8.5: The $\gamma/\gamma'$ interfacial energy change when a ternary element X (plotted with respect to atomic size) is in $\gamma$ or $\gamma'$. 
Figure 8.6: The $\gamma/\gamma'$ interfacial energy change when a ternary element X (plotted with respect to change in average Ni magnetic moment) is in $\gamma$ or $\gamma'$. 
9 Conclusions and Future Work

9.1 Conclusions

The CALPHAD technique, coupled with first-principles calculations, is demonstrated in this thesis for systems relevant to the design of Ni-base superalloys and MCrAlY coatings.

1. First, the phase stabilities of detrimental phases in superalloys are explored using the metallic Nb-Re binary system. Due to a lack of data, first-principles calculations based on density functional theory (DFT) are employed to supplement missing thermochemical information in this binary system for all the phases. It is found that first-principles predictions, especially using the special quasi-random structures method and the Debye–Grüneisen model, are a necessary part of phase diagram evaluations. Predicted energies are then used in the modeling of the thermodynamics. The compound energy formalism is demonstrated to describe the stability of the topologically close-packed solutions phases $\sigma$ and $\chi$ well. Experimentally measured phase boundaries and equilibria data are then used to refine the predicted energies to produce a self-consistent, optimized, thermodynamic description of the Nb-Re system. The resulting phase diagram agrees well with experimentally measured alloys, especially when considering the phase stability of the detrimental phase $\sigma$. With the addition of this model to the literature, TCP predictions in Nb and Re containing superalloys are improved.

2. During the analysis of the predicted thermochemical data for Nb-Re, it is realized that a crucial component of the Debye-Grüneisen model, used for vibrational contributions
to the finite heat capacity, should be predicted using first-principles methods rather than from experimentally fit data. It is demonstrated that crystal elasticity predictions from first-principles, more specifically the Poisson’s ratio, can be used effectively to predict accurate 0 K Debye temperatures. This is the so called Debye ‘scaling factor’. Mg-Zn is used as a benchmark due to a wealth of information about its thermodynamics and crystallographic characteristics. Predicted Debye temperatures and consequent thermodynamic properties are shown to agree well with calorimetric experiments. The small increase in complexity of the calculations required yields much more accurate and physically sound predictions for all of the phases demonstrated in Mg-Zn. However, the limitations of the Debye-Grüneisen model are also shown for an intermetallic Mg$_2$Zn$_{11}$ which exhibits anomalous vibrational modes in the lattice. These effects are rare and not expected to contribute to predictions in the remaining work. By using the predicted Debye scaling factor method, the thermodynamic properties of any elastically stable phase can be predicted accurately without the need of experimental fittings.

3. The important workhorse Al-Co-Cr coating alloy has been modeled, for the first time, in the literature. This system is investigated in detail, extending the methodologies from the modeling of Nb-Re and predictions from the Debye–Grüneisen model with a scaling factor. In order to account for the second order order-disorder transition that occurs in one of the cubic phases, the solution A2 and ordered B2 phases are modeled using an extended sublattice model. The so called “two sublattice order-disorder model” treats A2 and B2 Gibbs energies as the same function and energy minimization
at specific compositions determine the stable phase(s); i.e. a miscibility gap is seen in an A2/B2 two-phase region. First-principles calculations are performed to predict the thermodynamic properties of A2, B2, γ and σ phases necessary to the modeling efforts. The resulting thermodynamic description is refined and validated using equilibrated alloys fabricated for the present work as well as alloys from the literature. The order-disorder model, coupled with first-principles calculations, proves effective in modeling the A2/B2 transitions seen in the system.

4. The developed Al-Co-Cr model is extrapolated, along with models for the Al-Co-Ni, Al-Cr-Ni and Co-Cr-Ni ternaries, to produce the Al-Co-Cr-Ni quaternary. The order-disorder model is adopted for the fcc phase as well from the Al-Ni system in order to describe L12 ordering. It was realized that the σ energies in the Co-Cr binary model produced bad quaternary extrapolations, especially in terms of the Co content in σ. The Al-Co-Ni and Co-Cr-Ni models were also found to give poor extrapolations in the quaternary. B2, γ and σ phase compositions did not agree well with quaternary measurements performed for this study, which included characterization using XRD as well as EPMA. The introduction of quaternary parameters increased the complexity of the models without significant improvements in calculated phase compositions. As a result, the Al-Co-Cr model was modified to include a different Co-Cr binary model that produces more reasonable σ energies. The ternaries Al-Co-Ni and Co-Cr-Ni were also remodeled using new experimental data in the literature as well as the methods described for the Al-Co-Cr system. These new ternaries include far fewer interaction parameters than the original models with the aid of first-principles results.
5. The Al-Co-Cr, Al-Co-Ni, and Co-Cr-Ni ternaries were once again combined with the Al-Cr-Ni system to produce a quaternary description. Phase stabilities and compositions predicted using the new ternaries agree very well with experimental measurements. Only one quaternary interaction parameter for σ is needed to account for Al solubility at lower temperatures. Critical remodeling of the Al-Co-Cr, Al-Co-Ni and Co-Cr-Ni ternaries produced a quaternary model that is validated with experimental alloys. Yet, the current σ model should be updated with a model that better takes into account crystal symmetry. Such a model will yield end-members that can be more accurately described by first-principles calculations. It is shown in the current work that similarities and differences between Al-Co-Cr and Al-Cr-Ni type of coatings. Al-Cr-Ni alloys are characterized by the formation of stable γ’ even at temperatures as high as 1373 K while it is not the case for Al-Co-Cr alloys. Consequently, it is shown that the addition of Co to Al-Cr-Ni destabilizes γ’ and introduces greater Cr solubility in B2.

6. The stability of the {100} coherent interface in Ni-base superalloys is investigated using first-principles calculations. This is important in the understanding and ultimately prediction of γ’ coarsening rates for multi-component Ni-base superalloy systems. The calculated Ni-Al γ/γ’ interfacial energy, 19 mJ/m², is found to agree well with literature experimental and theoretical values. The method used to calculate the binary interfacial energy is modified to accommodate a dilute ternary addition when it partitions to either γ or γ’. Calculations show that Mo, W, and Re have the largest effect on the interfacial
energy by decreasing it to 4-5 mJ/m² when partitioned to γ. Ru and Pt are shown to increase the interfacial energy the greatest amount, up to 25-28 mJ/m² when partitioned to γ. In γ’, all ternary additions substituting for Ni increase the interfacial energy except for Pt, which decreases it to 16 mJ/m². Hf is seen to increase this value to 37 mJ/m². For Ti and Ta, which segregate strongly to γ’ and substitute for Al, interfacial energies increase to 32 and 35 mJ/m², respectively. It is found that the interfacial energy is the lowest when the ternary alloying element is in γ and decrease the average Ni magnetic moment the most, such as Mo, Re, and W. Ternary additions to γ’ increase the interfacial energies as a function of in-plane lattice expansion.

This thesis, overall, contributes to the literature a comprehensive thermodynamic foundation for the important Al-Co-Cr-Ni system pertinent to MCrAlY coatings. This modeling and analysis in this work will be crucial for subsequent studies involving microstructural evolutions, thermal stabilities, and other phenomena.
9.2 Future work

Additional work should be taken in the following areas to improve on the work presented here:

- The addition of hafnium (Hf) and yttrium (Y) to the Al-Co-Cr-Ni system is important in studying the so-called “reactive element” (RE) effect found to be beneficial in many MCrAlY-type coatings. Hf and Y contents in the amount of less than 0.5 % at. can drastically aid in the formation of adherent $\alpha$-$\text{Al}_2\text{O}_3$ scales on the coating surface. Nonetheless, doping content control is somewhat of a ‘black magic’ as the optimal content of reactive elements that should be added in the base alloy is unknown. In fact, slight over-doping can be extremely detrimental to the alloy. With changing alloy compositions, this becomes an even more complex problem. Simultaneous doping of Hf+Y have also yield phenomenological improvements in the oxidation and corrosion behavior of these alloys. It has been proposed that the interplay between Hf, Y, and the base alloy, in terms of activities, will be an important guide in the understanding of RE effects. While some of the constituent systems required to augment the current database with Hf and Y exist, a comprehensive study of the literature is required to correctly model solubilities (Hf and Y in the base alloy) and phase stabilities. Hf- and Y-base intermetallics (hafnides and yttrides) have not been characterized especially well in the literature mainly due to their complexity and difficulty of synthesis. However, the computational methods presented in this thesis can be utilized in the investigations of these intermetallics along with carefully designed experiments.

- The addition of silicon (Si) to the Al-Co-Cr-Ni system can also yield benefits similar to Hf and Y. This can be attributed to the similarities between Al and Si, especially in the
formation of intermetallics with 3-d transition metals. Si plays a key role in the modification of Hf and Y activities and needs to be investigated thoroughly.

- The addition of refractory elements tantalum (Ta), rhenium (Re), and tungsten (W) can prevent interdiffusion between the coating and the alloy during service. These heavy elements act as “diffusion barriers” near the alloy-coating interface but can also be detrimental as they are significant TCP formers. Understanding the limits of these refractory additions can be taken in the same approach as the Nb-Re system.

- Development of the accompanying Al-Co-Cr-Ni kinetic database is necessary to study microstructural variations that can occur during processing or service. Diffusion in the B2 must be investigated carefully due to the high vacancy concentrations present at certain compositions. Co diffusivities in B2, γ and γ’ should be evaluated, validated and coupled to the existing Al-Cr-Ni thermodynamic/kinetic database to produce a full Al-Co-Cr-Ni description. Then, it is possible to study interdiffusion between the MCrAlY and the substrate alloy.

- With the addition of O to the current description, the growth of α-Al₂O₃ relative to other unfavorable oxides, such as spinels, can be studied for various MCrAlY compositions. Ideally, the introduction of O₂ and the relevant transition metal oxides would allow evolutionary studies of bond coats when exposed to O₂ environments. Work has been performed in this area for the Al-Ni-Fe-O system.
References


Appendix A (Nb-Re Database)

As is compiled on NIMS (http://www.nims.go.jp/cmsc/pst/database/nb-elem/nbre/nbre.htm):

$ ---------------------------------------------------------$
$ PARAMETERS ARE TAKEN FROM$
$ First-principles aided thermodynamic modeling of the NB-RE system,
$ ---------------------------------------------------------$

$ ELEMENT /- ELECTRON_GAS  0.0000E+00  0.0000E+00  0.0000E+00!
$ ELEMENT VA  VACUUM                    0.0000E+00  0.0000E+00  0.0000E+00!
$ ELEMENT RE  HCP_A3                    1.8621E+02  5.3555E+03  3.6526E+01 !
$ ELEMENT NB  BCC_A2                    9.2906E+01  5.2200E+03  3.6270E+01 !
$ $---------------------------------------------------------$

$ Lattice stability$
$---------------------------------------------------------$

FUNCTION GHSERRE 298.15 -7695.279+128.421589*T-24.348*T*LN(T)
-2.53505E-3*T**2+0.192818E-6*T**3+32915*T**(-1); 1200 Y
-15775.989+194.667426*T-33.586*T*LN(T)+2.24565E-3*T**2-0.281835E-6*T**3
+1376270*T**(-1); 2400 Y
-70882.739+462.110749*T-67.956*T*LN(T)+11.84945E-3*T**2-0.788955E-6*T**3
+13075200*T**(-1); 3458 Y
34635.888+1211.371859*T+140.8316548*T*LN(T)-33.764567E-3*T**2
+1.053726E-5*T**3-13458866*T**(-1); 5000 Y
-78564.296+346.997842*T-49.519*T*LN(T); 6000 N !

FUNCTION GLIQRE 298.15 16125.604+122.076209*T
-24.348*T*LN(T)-2.53505E-3*T**2+0.192818E-6*T**3+32915*T**(-1); 1200 Y
8044.885+188.322047*T-33.586*T*LN(T)+2.24565E-3*T**2-0.281835E-6*T**3
+1376270*T**(-1); 2000 Y
56884.665+2527.838455*T+314.1788975*T*LN(T)-89.39817E-3*T**2
+3.92854E-6*T**3-163100987*T**(-1); 3458 Y
-39044.888+335.723691*T-49.519*T*LN(T); 6000 N !

FUNCTION GBCCRE 298.15 11000-1.5*T+GHSERRE; 6000 N !
FUNCTION GFCCRE 298.15 17000-3.7*T+GHSERRE; 6000 N !

FUNCTION GHSERNB 298.15 -8519.353+142.045475*T-26.4711*T*LN(T)
-2.53505E-3*T**2+0.192818E-6*T**3+32915*T**(-1); 1200 Y
-37669.3+271.720843*T-41.77*T*LN(T)+1528.238E29*T**(-9); 6000.00 N !
FUNCTION GLIQNB 298.15 29781.555-10.816418*T-306.096E-25*T**7+GHSERNB; 2750 Y
-7499.398+260.754618*T-41.77*T*LN(T); 6000.00 N !
FUNCTION GCFCNB 298.15 13500+1.7*T+GHSERNB; 6000 N !
FUNCTION GCPCNB 298.15 10000+2.4*T+GHSERNB; 6000 N !

$---------------------------------------------------------$

TYPE_DEFINITION % SEQ *!
DEFINE_SYSTEM_DEFAULT ELEMENT 2 !
DEFAULT_COMMAND DEF_SYS_ELEMENT VA /- !
$---------------------------------------------------------$

$ PARAMETERS FOR  BCC_RENB$
$---------------------------------------------------------$

PHASE  BCC_RENB % 1 1. !
CONSTITUENT  BCC_RENB : RE, NB : !
PARAMETER G( BCC_RENB,RE;0) 298.5 GBCCRE; 6000 N !
PARAMETER G( BCC_RENB,NB;0) 298.5 GHSERNB; 6000 N !
PARAMETER G( BCC_RENB,RE,NB;0) 298.5 -101060+10.568*T ; 6000 N !
PARAMETER G( BCC_RENB,RE,NB;1) 298.5 -2300 ; 6000 N !

$---------------------------------------------------------$
$ PARAMETERS FOR HCPRENB$
$---------------------------------------------------------$


$----------------------------------------$
PHASE HCP_RENB  % 1 1. !
CONSTITUENT HCP_RENB : RE, NB : !
PARAMETER G(HCP_RENB,RE;0) 298.5 GHSERRE; 6000 N !
PARAMETER G(HCP_RENB,NB;0) 298.5 GHCPNB; 6000 N !
PARAMETER G(HCP_RENB,RE, NB;0) 298.5 64957-33.387*T ; 6000 N !
$----------------------------------------$
$ PARAMETERS FOR LIQUID_RENB$
$----------------------------------------$
PHASE LIQUID_RENB % 1 1. !
CONSTITUENT LIQUID_RENB : RE, NB : !
PARAMETER G(LIQUID_RENB,RE;0) 298.5 GLIQRE; 6000 N !
PARAMETER G(LIQUID_RENB,NB;0) 298.5 GLIQNB; 6000 N !
PARAMETER G(LIQUID_RENB,RE,NB;0) 298.5 8017-23.406*T; 6000 N !
PARAMETER G(LIQUID_RENB,RE,NB;1) 298.5 -2001; 6000 N !
$----------------------------------------$
$ PARAMETERS FOR FCC_RENB$
$----------------------------------------$
PHASE FCC_RENB % 1 1. !
CONSTITUENT FCC_RENB : RE, NB : !
PARAMETER G( FCC_RENB,RE;0) 298.5 GFCCRE; 6000 N !
PARAMETER G( FCC_RENB,NB;0) 298.5 GFCCNB; 6000 N !
PARAMETER G( FCC_RENB,RE,NB;0) 298.5 27628 ; 6000 N !
$----------------------------------------$
$ PARAMETERS FOR SIGMARENB$
$----------------------------------------$
PHASE SIGMARENB % 3 10 4 16 !
CONSTITUENT SIGMARENB :RE:NB:RE:NB:RE:!
PARAMETER G(SIGMARENB,RE:NB:RE;0) 298.5 67437+2.033*T+10*GHSERRE+4*GHSERNB+16*GHSERRE; 6000 N !
PARAMETER G(SIGMARENB,RE:NB:NB;0) 298.5 407760 +0.692*T+8.769*0.001*T**2+10*GHSERRE+4*GHSERNB+16*GHSERNB; 6000 N !
PARAMETER G(SIGMARENB,RE:NB:RE,NB;0) 298.5 479251 -498.110*T; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE;0) 298.5 256567 -25.456*T ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE;0) 298.5 +256567 -25.456*T+24*GHSERRE+10*GHSERRE+24*GHSERRE; 6000 N !
PARAMETER G(SIGMARENB,RE:NB:RE;0) 298.5 758795 -28.528*T+24*GHSERRE+10*GHSERNB+24*GHSERRE; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:NB;0) 298.5 -758795 -28.528*T+24*GHSERRE+10*GHSERNB+24*GHSERRE ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 +252854+24*GHSERRE+10*GHSERRE+24*GHSERNB ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 -610088 -13.751*T+24*GHSERRE+10*GHSERNB+24*GHSERRE ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 -1648141 -289.844*T ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 -749989 +280.032*T ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 -1200286 ; 6000 N !
PARAMETER G(SIGMARENB,RE:RE:RE,NB;0) 298.5 -352931 ; 6000 N !
$----------------------------------------$
$ PARAMETERS FOR CHI_RENB$
$----------------------------------------$
PHASE CHI_RENB % 3 24 10 24 !
CONSTITUENT CHI_RENB :RE:RE,RE:NB:NB,RE:!
$PARAMETER G(CHI_RENB,RE:RE:RE;0) 298.5 256567 -25.456*T ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE;0) 298.5 +256567 -25.456*T+24*GHSERRE+10*GHSERRE+24*GHSERRE; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE;0) 298.5 -758795 -28.528*T+24*GHSERRE+10*GHSERNB+24*GHSERRE ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 +252854+24*GHSERRE+10*GHSERRE+24*GHSERNB ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 -610088 -13.751*T+24*GHSERRE+10*GHSERNB+24*GHSERRE ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 -1648141 -289.844*T ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 -749989 +280.032*T ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 -1200286 ; 6000 N !
PARAMETER G(CHI_RENB,RE:RE:RE,NB;0) 298.5 -352931 ; 6000 N !
$----------------------------------------$
$RE-NB End
Appendix B (Al-Co-Cr Database)

IMPORTANT: Co-Cr binary from Oikawa et al. [131] used, different from Appendix C

Al-Co with revised parameters due to presence of B2 with vacancies at high temperatures can be found in Eq. 2.94 in Chapter 2. Discussion on the value of $G_{Va, Va}^{42}$ is also discussed.

$ AL$-$CO$-$CR$ BOND COAT DATABASE
$ Database built by Xuan Liu
$ Dec. 2014
$ *Thermodynamic modelling of the Al-Co-Cr system*
$ Works with BIN AND TERN modules
$ 1473, 1573, and 1623 isotherms may require many starting
$ points to map correctly, we apologize for this
$ inconvenience

ELEMENT /- ELECTRON_GAS 0.0000E+00 0.0000E+00 0.0000E+00!
ELEMENT VA VACUUM 0.0000E+00 0.0000E+00 0.0000E+00!
ELEMENT AL FCC_A1 2.6982E+01 4.5773E+03 2.8321E+01!
ELEMENT CO HCP_A3 5.8933E+01 4.7656E+03 3.0040E+01!
ELEMENT CR BCC_A2 5.1996E+01 4.0500E+03 2.3560E+01!

DATABASE_INFO '''
ALCOCR, version Dec 2014'
'
ELEMEENTS : Al, Co, Cr'
'
ASSESSED SYSTEMS :
'
BINARIES'
  Al-Co, Co-Cr, Al-Cr'
TERNARIES'
  Al-Co-Cr'
'
MODELLING ORDER/DISORDER:'
'
A2/B2 Partitioning'
!

ASSESSED_SYSTEMS
AL-CR(;G5 MAJ:BCC_B2/CR:VA ;P3 STP:.75/1200/1)
AL-CO(;P3 STP:.75/1200/1)
CO-CR(;G5 MAJ:BCC_B2/CR:VA ;P3 STP:.5/1200/2)
  ;P3 STP:.45/.01/1/2)
!!

$$--SIGMA--PARAMETERS---------------------------------------------
$$$$$$--BINARY--CR-AL--$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
FUNCTION VV1 298.15 161148; 6000 N !
FUNCTION VV7 298.15 47886; 6000 N !

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FUNCTION VV3  298.15  -931861.59; 6000 N!
FUNCTION VV5  298.15  -617537.34; 6000 N!
FUNCTION VV11  298.15  -78970.431; 6000 N!
FUNCTION VV34  298.15  -78970.431; 6000 N!
FUNCTION VV35  298.15  -617537.34; 6000 N!

FUNCTION VV40  298.15  -35909; 6000 N!
FUNCTION VV41  298.15  -16.474; 6000 N!
FUNCTION VV44  298.15  -4000; 6000 N!
FUNCTION VV54  298.15  -13276.116; 6000 N!
FUNCTION VV90  298.15  -28320; 6000 N!
FUNCTION VV91  298.15  -16.474; 6000 N!
FUNCTION VV92  298.15  -46432.157; 6000 N!
FUNCTION VV96  298.15  -17295.477; 6000 N!
FUNCTION VV98  298.15  -25000; 6000 N!

FUNCTION GHSERAL  298.15  -7976.15+137.093038*T-24.3671976*T*LN(T)
-0.001884662*T**2+74092*T**3; 7.00000E+02  Y
-11276.24+223.048446*T-38.5844296*T*LN(T)+0.18531982*T**2
-5.764227E+06*T*3+74092*T**3-9.33600E+02  Y
FUNCTION GALBCC  298.15  +10083-4.813*T+GHSERAL#; 6000 N!
FUNCTION GHSERCO  298.15  +310.241+133.36601*T-25.0861*T*LN(T)
-0.002654739*T**2+1.7348E-07*T**3+72526.9*T**3; 1.76800E+03  Y
-11278.378+188.684153*T-31.748192*T*LN(T)-1.234E+28*T**(-9); 6000 N!
FUNCTION GCOBCC  298.15  +2938-3.7138*T+GHSERCO#; 6000 N!
FUNCTION GCRHCP  298.15  +7284+.163*T+GHSERCR#; 6000 N!
FUNCTION UN_ASS  298.15  0.0 ;  3.00000E+02  N !

$$=-BCC_B2-FUNCTIONS-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~$

$$-VACANCY-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

FUNCTION GB2ALVA  298.15  +10000-T;  6000  N !
FUNCTION LB2ALVA  298.15  10000;  6000  N !

FUNCTION GB2COVA  298.15  +145000-35.62*T;  6000  N !
FUNCTION LB2COVA  298.15  +45000-34.47*T;  6000  N 98DUP !

FUNCTION GB2CRVA  298.15  0;  6000  N !
FUNCTION LB2CRVA  298.15  0;  6000  N !

$$=--BINARY--~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

FUNCTION GB2ALCO  298.15  -138500+34.62*T;  6000  N 98DUP !
FUNCTION LB2ALCO  298.15  +54531-37.04*T;  6000  N 14LIU !
FUNCTION BU1ALCO  298.15  -.5*LB2ALCO#;  6000  N !

FUNCTION GB2COCR  298.15  +VV40#+VV41*T;  6000  N !

FUNCTION GB2CRLA  298.15  +VV44#;  6000  N !

$$--TERNARY--A2-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

FUNCTION LALCO2CR  298.15  +VV34#+VV35#*T;  6000  N !

FUNCTION BCOCRMAL  298.15  +VV90#+VV91#*T;  6000  N !

FUNCTION CRALMCO1  298.15  +VV54#;  6000  N !

FUNCTION BALCOMCR  298.15  +VV92#;  6000  N !

$-$-L0(LIQUID:AL,CO,CR)  0

$-$-L1(CO:AL,CO,CR)
FUNCTION LALCO2CR  298.15  +VV34#+VV35#*T;  6000  N !

$-$-L2(CR:AL,CO,CR)  0

$-$-L0(AL:CO,CR)  L1 is 0
FUNCTION BCOCRMAL  298.15  +VV90#+VV91#*T;  6000  N !

$-$-L0(CO:AL,CR)  L0 is 0
FUNCTION CRALMCO1  298.15  +VV54#;  6000  N !

$-$-L1(CR:AL,CO)  L1 is 0
FUNCTION BALCOMCR  298.15  +VV92#;  6000  N !

$-$-L0(AL,CO,CR)  L0 is 0
FUNCTION BCOCRMAL  298.15  +VV90#+VV91#*T;  6000  N !

$-$-L1(CR:AL,CO)  L1 is 0
FUNCTION BALCOMCR  298.15  +VV92#;  6000  N !

$-$-L2(CR:AL,CO,CR)  0

$-LIQUID-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~$

PHASE LIQUID:L %  1  1.0  !
CONSTITUENT LIQUID:L :AL,CO,CR :  !

PARAMETER G(LIQUID,AL;0)  298.15  +11005.029-11.841867*T
+7.934E-20*T**7+GHSERAL#;  9.33600E+02  Y
+10482.282-11.253974*T+1.231E+28*T**(-9)+GHSERAL#;  6000  N 91DIN !

$-$-UNARY-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
PARAMETER G(LIQUID,CO;0)  298.15 +15085.037-8.931932*T
-2.19801E-21*T**7+GHSERCO#;  1.76800E+03 Y
+16351.056-9.683796*T-9.3488E+30*T**(-9)+GHSERCO#;  6000 N 91DIN !

PARAMETER G(LIQUID,CR;0)  298.15 +24339.955-11.420225*T
+2.37615E-21*T**7+GHSERCR#;  2.18000E+03 Y
+18409.36-8.563683*T+2.88526E+32*T**(-9)+GHSERCR#;  6000 N 91DIN !

PARAMETER G(LIQUID,AL,CO;0)  298.15 -152470+40.259*T;   6000 N 98DUP !
PARAMETER G(LIQUID,AL,CO;1)  298.15 -57527.5+27.0453*T;   6000 N 98DUP !
PARAMETER G(LIQUID,AL,CO;2)  298.15 +30494-8.0518*T;   6000 N 98DUP !
PARAMETER G(LIQUID,AL,CO;3)  298.15 +24655-11.591*T;   6000 N 98DUP !

PARAMETER G(LIQUID,AL,CR;0)  298.15 -29000;   6000 N 91SAU1 !
PARAMETER G(LIQUID,AL,CR;1)  298.15 -11000;   6000 N 91SAU1 !

PARAMETER G(LIQUID,CO,CR;0)  3.00000E+02 -12008.6239+2.2019*T;
3.00000E+03 N 02OIK !
PARAMETER G(LIQUID,CO,CR;1)  3.00000E+02 -5836.4696+1.1402*T;
3.00000E+03 N 02OIK !

PARAMETER G(LIQUID,AL,CO,CR;0)  298.15 +VV66#;   6000 N 14LIU !

TYPE_DEFINITION & GES A_P_D BCC_A2 MAGNETIC

PHASE BCC_A2 %& 2 1 3 !
CONSTITUENT BCC_A2 :AL,CO,CR,VA : VA : !

PARAMETER G(BCC_A2,AL:VA;0)  298.15 +GALBCC#;   6000 N 91DIN !
PARAMETER G(BCC_A2,CO:VA;0)  298.15 +GCOBCC#;   6000 N 91DIN !
PARAMETER TC(BCC_A2,CO:VA;0)  298.15 1450;   6000 N 91DIN !
PARAMETER BMAGN(BCC_A2,CO:VA;0)  298.15 1.35;   6000 N 91DIN !
PARAMETER G(BCC_A2,CR:VA;0)  298.15 +GHSERCR#;   6000 N 91DIN !
PARAMETER TC(BCC_A2,CR:VA;0)  298.15 -311.5;   6000 N 91DIN !
PARAMETER BMAGN(BCC_A2,CR:VA;0)  298.15 -.01;   6000 N 91DIN !

PARA G(BCC_A2,VA:VA;0)  298.15 0;   6000 N!
PARAMETER G(BCC_A2, AL, CO: VA; 0) 298.15 +GB2ALCO# +LB2ALCO#; 6000 N 14LIU!

PARAMETER G(BCC_A2, AL, CR: VA; 0) 298.15 -54900 +10*T; 6000 N 14LIU!

PARAMETER G(BCC_A2, CO, CR: VA; 0) 298.15 +1033.2829 - 1.4808*T; 3.0000E+03 N 02OIK!

PARAMETER G(BCC_A2, CO, CR: VA; 1) 298.15 +11971.5008 - 13.3741*T; 3.0000E+03 N 02OIK!

PARAMETER G(BCC_A2, AL, VA: VA; 0) 298.15 +GB2ALVA# +LB2ALVA#; 6000 N 14LIU!

PARAMETER G(BCC_A2, CO, VA: VA; 0) 298.15 +GB2COVA# +LB2COVA#; 6000 N 14LIU!

PARAMETER G(BCC_A2, CR, VA: VA; 0) 298.15 100000; 6000 N 14LIU!

PARAMETER G(BCC_A2, AL, CO, CR: VA; 0) 298.15 -59367 +20.56600*T; 6000 N 14LIU!

PARAMETER G(BCC_A2, AL, CO, CR: VA; 1) 298.15 -151614 +109.68941*T; 6000 N 14LIU!

PARAMETER G(BCC_A2, AL, CO, CR: VA; 2) 298.15 -85919 +20.56600*T; 6000 N 14LIU!

PARAMETER G(BCC_A2, AL, VA: VA; 0) 298.15 0; 6000 N 14LIU!

PARAMETER G(BCC_B2, AL, CO: VA; 0) 298.15 0; 6000 N 14LIU!

PARAMETER G(BCC_B2, AL, CR: VA; 0) 298.15 0; 6000 N 14LIU!

PARAMETER G(BCC_B2, CR, VA: VA; 0) 298.15 0; 6000 N 14LIU!

PARAMETER G(BCC_B2, VA: VA; 0) 298.15 0; 6000 N 14LIU!

PARAMETER GC(BCC_B2, CO: AL, VA; 0) 298.15 -1450; 6000 N 14LIU!

PARAMETER TC(BCC_B2, CO: AL, VA; 0) 298.15 -1450; 6000 N 14LIU!

PARAMETER BMAGN(BCC_B2, CO: AL, VA; 0) 298.15 -1.35; 6000 N 14LIU!

PARAMETER BMAGN(BCC_B2, AL: CO, VA; 0) 298.15 -1.35; 6000 N 14LIU!

PARAMETER GC(BCC_B2, AL: CO, VA; 0) 298.15 +.5*GB2ALCO# -.5*LB2ALCO#;
PARAMETER G(BCC_B2,CO:AL:VA;0)  298.15  +.5*GB2ALCO#-.5*LB2ALCO#;
PARAMETER G(BCC_B2,AL:CR:VA;0)  298.15  +.5*GB2CRAL#;
PARAMETER G(BCC_B2,CO:CR:VA;0)  298.15  +.5*GB2COCR#;
PARAMETER G(BCC_B2,CR:CO:VA;0)  298.15  +.5*GB2COCR#;

PARAMETER G(BCC_B2,AL:VA:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,VA:AL:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,CO:VA:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,VA:CO:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,CR:VA:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;
PARAMETER G(BCC_B2,VA:CR:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;

PARAMETER G(BCC_B2,CO:AL,CO,CR:VA;0)  298.15  +.5*LALCO2CR#;
PARAMETER G(BCC_B2,AL,CO,CR:CO:VA;0)  298.15  +.5*LALCO2CR#;
PARAMETER G(BCC_B2,CR:AL,CO:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;
PARAMETER G(BCC_B2,AL,CO:CR:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;

PARAMETER G(BCC_B2,CO:AL,CR:VA;1)  298.15  +.5*CRALMCO1#;
PARAMETER G(BCC_B2,AL,CR:CO:VA;1)  298.15  +.5*CRALMCO1#;

PARAMETER G(BCC_B2,CO:AL:VA;0)  298.15  +.5*GB2ALCO#-.5*LB2ALCO#;
PARAMETER G(BCC_B2,AL:CR:VA;0)  298.15  +.5*GB2CRAL#;
PARAMETER G(BCC_B2,CO:CR:VA;0)  298.15  +.5*GB2COCR#;
PARAMETER G(BCC_B2,CR:CO:VA;0)  298.15  +.5*GB2COCR#;

PARAMETER G(BCC_B2,AL:VA:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,VA:AL:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,CO:VA:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,VA:CO:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,CR:VA:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;
PARAMETER G(BCC_B2,VA:CR:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;

PARAMETER G(BCC_B2,CO:AL,CO,CR:VA;0)  298.15  +.5*LALCO2CR#;
PARAMETER G(BCC_B2,AL,CO,CR:CO:VA;0)  298.15  +.5*LALCO2CR#;
PARAMETER G(BCC_B2,CR:AL,CO:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;
PARAMETER G(BCC_B2,AL,CO:CR:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;

PARAMETER G(BCC_B2,CO:AL,CR:VA;1)  298.15  +.5*CRALMCO1#;
PARAMETER G(BCC_B2,AL,CR:CO:VA;1)  298.15  +.5*CRALMCO1#;

$-----------------------------------VACANCY-----------------------------------$

PARAMETER G(BCC_B2,AL:VA:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,VA:AL:VA;0)  298.15  +.5*GB2ALVA#-.5*LB2ALVA#;
PARAMETER G(BCC_B2,CO:VA:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,VA:CO:VA;0)  298.15  +.5*GB2COVA#-.5*LB2COVA#;
PARAMETER G(BCC_B2,CR:VA:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;
PARAMETER G(BCC_B2,VA:CR:VA;0)  298.15  +.5*GB2CRVA#-.5*LB2CRVA#;

$-----------------------------------TERNARY (X:AL,CO,CR)-----------------------------------$

PARAMETER G(BCC_B2,CO:AL,CO,CR:VA;0)  298.15  +.5*LALCO2CR#;
PARAMETER G(BCC_B2,AL,CO,CR:CO:VA;0)  298.15  +.5*LALCO2CR#;

$-----------------------------------TERNARY 0TH ORDER (X:Y,Z)-----------------------------------$

PARAMETER G(BCC_B2,AL:CO,CR:VA;0)  298.15  +.5*BCOCRML#;
PARAMETER G(BCC_B2,CO,CR:AL:VA;0)  298.15  +.5*BCOCRML#;
PARAMETER G(BCC_B2,CR:AL,CO:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;
PARAMETER G(BCC_B2,AL,CO:CR:VA;0)  298.15  +.5*BALCOMCR#+BU1ALCO#;

$-----------------------------------TERNARY 1ST ORDER (X:Y,Z)-----------------------------------$

PARAMETER G(BCC_B2,CO:AL,CR:VA;1)  298.15  +.5*CRALMCO1#;
PARAMETER G(BCC_B2,AL,CR:CO:VA;1)  298.15  +.5*CRALMCO1#;

$-----------------------------------FCC_A1-----------------------------------$
TYPE_DEFINITION (GES A_P_D FCC_A1 MAGNETIC -3.0 2.80000E-01 !
PHASE FCC_A1 %( 2 1 1 !
    CONSTITUENT FCC_A1 :AL,CO,CR : VA :

$\$\$\$-------------------------------------------------------UNARY------------------------------------------------------$

PARAMETER G(FCC_A1,AL:VA;0) 298.15 +GHSERAL#; 6000 N 91DIN !
PARAMETER G(FCC_A1,CO:VA;0) 298.15 +GCOFCC#; 6000 N 91DIN !
PARAMETER TC(FCC_A1,CO:VA;0) 298.15 1396; 6000 N 91DIN !
PARAMETER BMAGN(FCC_A1,CO:VA;0) 298.15 1.35; 6000 N 91DIN !
PARAMETER G(FCC_A1,CR:VA;0) 298.15 +GCRFCC#; 6000 N 91DIN !
PARAMETER TC(FCC_A1,CR:VA;0) 298.15 -1109; 6000 N 91DIN !
PARAMETER BMAGN(FCC_A1,CR:VA;0) 298.15 -2.46; 6000 N 91DIN !

$\$\$\$-------------------------------------------------------BINARY------------------------------------------------------$

PARAMETER G(FCC_A1,AL,CO:VA;0) 298.15 -122840+22.925*T; 6000 N 98DUP !
PARAMETER G(FCC_A1,AL,CO:VA;2) 298.15 +24568-4.585*T; 6000 N 98DUP !
PARAMETER TC(FCC_A1,AL,CO:VA;0) 298.15 -1830; 6000 N 98DUP !
PARAMETER TC(FCC_A1,AL,CO:VA;1) 298.15 970; 6000 N 98DUP !
PARAMETER BMAGN(FCC_A1,AL,CO:VA;0) 298.15 10; 6000 N 98DUP !
PARAMETER G(FCC_A1,AL,CR:VA;0) 298.15 -45900+6*T; 6000 N 91SAU1 !
PARAMETER G(FCC_A1,CO,CR:VA;0) 3.00000E+02 -24052.09+8.1884*T; 3.00000E+03 N 02OIK !
PARAMETER G(FCC_A1,CO,CR:VA;1) 3.00000E+02 +5331.8252-6.9059*T; 3.00000E+03 N 02OIK !
PARAMETER TC(FCC_A1,CO,CR:VA;0) 3.00000E+02 -9392.5259; 3.00000E+03 N 02OIK !
PARAMETER TC(FCC_A1,CO,CR:VA;1) 3.00000E+02 8383.0424; 3.00000E+03 N 02OIK !

$\$\$\$-------------------------------------------------------TERNARY------------------------------------------------------$

PARAMETER G(FCC_A1,AL,CO,CR:VA;0) 298.15 +VV96#; 6000 N 14LIU !
PARAMETER G(HCP_A3,CO:VA;0) 298.15 +GHSERCO#; 6000 N
PARAMETER TC(HCP_A3,CO:VA;0) 298.15 1396; 6000 N 91DIN!
PARAMETER BMAGN(HCP_A3,CO:VA;0) 298.15 1.35; 6000 N

PARAMETER G(HCP_A3,CR:VA;0) 298.15 +GCRHCP#; 6000 N
PARAMETER TC(HCP_A3,CR:VA;0) 298.15 -1109; 6000 N 91DIN!
PARAMETER BMAGN(HCP_A3,CR:VA;0) 298.15 -2.46; 6000 N

PARAMETER TC(HCP_A3,AL,CO:VA;0) 298.15 -1830; 6000 N
PARAMETER TC(HCP_A3,AL,CO:VA;1) 298.15 970; 6000 N 98DUP!
PARAMETER BMAGN(HCP_A3,AL,CO:VA;0) 298.15 10; 6000 N

PARAMETER G(HCP_A3,AL,CR:VA;0) 298.15 -45900+6*T; 6000 N 91SAU1!
PARAMETER G(HCP_A3,CO,CR:VA;0) 3.00000E+02 -28673.6824+15.5105*T; 3.00000E+03 N 02OIK!
PARAMETER G(HCP_A3,CO,CR:VA;1) 3.00000E+02 -12673.5606-14.8392*T; 3.00000E+03 N 02OIK!

PARAMETER TC(HCP_A3,AL,CO,CR:VA;0) 298.15 +VV98#; 6000 N 14LIU!
PARAMETER G(SIGMA_SGTE,CO:CO:CR;0) 298.15 -16898.7187-29.814*T+8*GCOFCC#+18*GCOBCC#; 3.00000E+03 N 02OIK!
PARAMETER G(SIGMA_SGTE,CO:CR:CR;0) 298.15 -259935.807+85.0966*T+8*GCOFCC#+18*GHSERCR#; 3.00000E+03 N 02OIK!
PARAMETER G(SIGMA_SGTE,AL:AL:CR;0) 298.15 +VV1#+8*GHSERAL#+18*GALBCC#*4*GHSERCR#; 6000 N 14LIU!
PARAMETER G(SIGMA_SGTE,AL:AL:CR;0) 298.15 +VV7#*8*GHSERAL#+22*GHSERCR#; 6000 N 14LIU!
PARAMETER G(SIGMA_SGTE,CO:AL:CR;0) 298.15 +VV3#+8*GCOFCC#
   +18*GALBCC#; 6000  N 14LIU !
PARAMETER G(SIGMA_SGTE,AL:CO:CR;0) 298.15 +VV5#+8*GHSERAL#
   +18*GCOBCC#; 6000  N 14LIU !
PARAMETER G(SIGMA_SGTE,CO:AL,CR:CR;0) 298.15 +VV11#;
   6000  N 14LIU !

$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdotted
**PHASE AL8CR5_L % 2 8 5**

**CONSTITUENT AL8CR5_L :AL : CR :**

**PARAMETER G(AL8CR5_L,AL:CR;0) 298.15 \(-229515+8*GHSERAL#+5*GHSERCR#;\)**

6000 N 91SAU1 !

**PHASE AL9CO2 % 2 9 2**

**CONSTITUENT AL9CO2 :AL : CO :**

**PARAMETER G(AL9CO2,AL:CO;0) 298.15 \(-391800+103.77*T+9*GHSERAL#+2*GHSERCO#;\)**

6000 N 98DUP !

**PHASE AL9CR4_H % 2 9 4**

**CONSTITUENT AL9CR4_H :AL : CR :**

**PARAMETER G(AL9CR4_H,AL:CR;0) 298.15 \(-134433-56.16*T+9*GHSERAL#+4*GHSERCR#;\)**

6000 N 91SAU1 !

**PHASE AL9CR4_L % 2 9 4**

**CONSTITUENT AL9CR4_L :AL : CR :**

**PARAMETER G(AL9CR4_L,AL:CR;0) 298.15 \(-230750+16.094*T+9*GHSERAL#+4*GHSERCR#;\)**

6000 N 91SAU1 !

**PHASE ALCR2 % 2 1 2**

**CONSTITUENT ALCR2 :AL : CR :**

**PARAMETER G(ALCR2,AL:CR;0) 298.15 \(-32700-8.79*T+GHSEAL#+2*GHSERCR#;\)**

6000 N 91SAU1 !

$\$$

**LIST_OF_REFERENCES**

**NUMBER SOURCE**

89DIN  'Alan Dinsdale, SGTE Data for Pure Elements, NPL Report DMA(A)195 September 1989'

91SAU1 'Nigel Saunders, 1991, based on N. Saunders, V.G. Rivlin Z. metallkd, 78 (11), 795-801 (1987); Al-Cr'


98DUP 'N. Dupin, I. Ansara Thermodynamic Assessment of the System Al-Co, Revue de Metallurgie, 95 (9), 1121-1129 (1998); Al-Co'

01DUP 'N. Dupin, I. Ansara, B. Sundman Thermodynamic Re-Assessment of the Ternary System Al-Cr-Ni, Calphad, 25 (2), 279-298 (2001); Al-Cr-Ni'

02OIK 'K. Oikawa, G.W. Qin, T. Ikeshoji, R. Kainuma, K. Ishida Direct evidence of magnetically induced phase separation in the fcc phase and thermodynamic calculations of phase equilibria of the Co-Cr system, Acta Materialia, 50 (9), 2223-2232 (2002); Co-Cr'

14LIU  'Xuan L. Liu, Thomas Gheno, Bonnie Lindahl, Greta Lindwall, Brian Gleeson, Zi-Kui Liu First-principles calculations, experimental study, and thermodynamic modeling of the Al-Co-Cr system PLOS ONE (2014); Al-Co-Cr'
Appendix C (Al-Co-Cr-Ni Database, CRALDAD V1)

IMPORTANT: Co-Cr binary from Kusoffsky et al. [132] used, different from Appendix B

Al-Co with revised parameters due to presence of B2 with vacancies at high temperatures can be found in Eq. 2.94 in Chapter 2. Discussion on the value of $G_{va:va}^{42}$ is also discussed.

$\\$}
$\\$$ Al-Co-Cr-Ni Quaternary
$\\$$ CRALDAD VERSION 1
$\\$$ ChRome Aluminun D(ensity functional theory)-Amended Database
$\\$$ Database developed by:
$\\$$ Xuan L. Liu, Thomas Gheno
$\\$$ Greta Lindwall, Bonnie Lindahl
$\\$$ Zi-Kui Liu, Brian Gleeson
$\\$$ 4-1-2015
$\\$$ Database based off of work by (using same layout):
$\\$$ N. Dupin, I. Ansara, B. Sundman,
$\\$$ Thermodynamic Re-Assessment of the Ternary System Al-Cr-Ni,
$\\$$ Calphad, 25 (2), 279-298 (2001); Al-Cr-Ni'
$\\$$
$\\$ELEMENT / - ELECTRON_GAS               .0000E+00   .0000E+00   .0000E+00!
$\\$ELEMENT VA   VACUUM                     .0000E+00   .0000E+00   .0000E+00!
$\\$ELEMENT AL   FCC_A1                    2.6982E+01  4.5773E+03  2.8322E+01!
$\\$ELEMENT CO   HCP_A3                    5.8933E+01  4.7656E+03  3.0040E+01!
$\\$ELEMENT CR   BCC_A2                    5.1996E+01  4.0500E+03  2.3560E+01!
$\\$ELEMENT NI   FCC_A1                    5.8690E+01  4.7870E+03  2.9796E+01!
$\\$SPECIES AL1CO1                      AL1CO1!
$\\$SPECIES AL1NI1                      AL1NI1!
$\\$SPECIES AL1NI3                      AL1NI3!
$\\$SPECIES AL2                         AL2!
$\\$SPECIES AL3CO1                      AL3CO1!
$\\$SPECIES AL3NI1                      AL3NI1!
$\\$SPECIES AL3NI2                      AL3NI2!
$\\$SPECIES AL5CO2                      AL5CO2!
$\\$SPECIES AL9CO2                      AL9CO2!
$\\$SPECIES CO2                         CO2!
$\\$SPECIES CR2                         CR2!
$\\$SPECIES NI2                         NI2!
$\\$FUNCTION UNASS      298.15  0;,,N !
$\\$TYPE_DEFINITION % SEQ *
$\\$DEFINE_SYSTEM_DEFAULT E 2 !
$\\$DEFAUL_COMMAND DEF_SYS_ELEMENT VA !
$\\$DATABASE_INFO ''
$\\$CRALDAD1, version 2-16-2015'
ELEMENTS : Al, Co, Cr, Ni

ASSESSED SYSTEMS :

BINARIES'
Al-Co, Al-Cr, Al-Ni, Co-Cr, Co-Ni, Cr-Ni,

TERNARIES'
Al-Co-Cr, Al-Co-Ni, Al-Cr-Ni, Co-Cr-Ni,

MODELLING ORDER/DISORDER:
A2/B2 Partitioning

ASSESSED_SYSTEMS
AL-CO:(P3 STP:.75/1200/1)
AL-CR:(G5 MAJ:BCC_B2/CR:CR:VA ;P3 STP:.75/1200/1)
AL-NI:(P3 STP:.75/1200/1)
CO-NI:(P3 STP:.75/1200/1)
;P3 STP:.45/.01/1/2)
;P3 STP:.01/.8/2)
AL-CO-NI:(P3 STP:.01/.8/2)
CO-CR-NI:(P3 STP:.01/.8/2)

DEFAULT_COMMAND REJECT_PHASE GAS !

PHASE GAS:G % 1 1.0 !
CONST GAS:G :AL,AL2,CO,CO2,CR,CR2,NI,NI2 :

PHASE LIQUID:L % 1 1.0 !
CONST LIQUID:L :AL,CO,CR,NI :

PHASE FCC_A1 %A 2 1 1 !
CONST FCC_A1 :AL,CO,CR,NI% : VA% : 

PHASE BCC_A2 %B 2 1 3 !
CONST BCC_A2 :AL,CO,CR%,NI,VA : VA : 

PHASE HCP_A3 %A 2 1 .5 !
CONST HCP_A3 :AL,CO,CR,N : VA% : 

PHASE BCC_B2 %BCW 3 .5 .5 3 !
CONST BCC_B2 :AL,CO,CR,N,VA : AL%,CO,CR,N,VA : VA : 

PHASE L12_FCC %ADG 3 .75 .25 1 !
CONST L12_FCC :AL,CO,CR,NI : AL,CO,CR,NI : VA : 

PHASE SIGMA_SGTE % 3 8 18 4 !
CONST SIGMA_SGTE :AL,CO,NI : AL,CO,CR,NI : CR : 

TYPE_DEFINITION A GES A_P_D @ MAGNETIC -3.0 .28 !
TYPE_DEFINITION B GES A_P_D @ MAGNETIC -1.0 .40 !

TYPE_DEFINITION C GES A_P_D BCC_B2 DIS_PART BCC_A2 !
TYPE_DEFINITION D GES A_P_D L12_FCC DIS_PART FCC_A1 !
TYPE_DEFINITION G IF (AL AND NI) THEN
GES A_P_D L12_FCC C_S 2 NI:AL:VA !

TYPE_DEFINITION G IF (NI) THEN
GES A_P_D L12_FCC MAJ 1 NI:NI:VA !

TYPE_DEFINITION W IF (CR AND AL AND NI) THEN
GES A_P_D BCC_B2 C_S,, NI:AL:VA !

TYPE_DEFINITION W IF (CR AND AL AND CO) THEN
GES A_P_D BCC_B2 C_S,, CO:AL:VA !

TYPE_DEFINITION W IF (CR) THEN
GES A_P_D BCC_B2 MAJ 1 CR:CR:VA !

FUNCTION ZERO       298.15  0;,,N !
FUNCTION DP         298.15  +P-101325;,,N !
FUNCTION TROIS 298.15 3;,,N !
FUNCTION UNTIER 298.15 TROIS**(-1);,,N !

$$FRANKE (2014)$$
$$PARAMETER G(BCC_A2,VA:VA;0)  298.15  2*R*T;,,N 15LIU !$$

FUNCTION F154T 298.15
+323947.58-25.1480943*T+20.859*T*LN(T)
+4.5665E-05*T**3-24275.5*T**(-1);
4300.0  Y
+342017.233-54.0526109*T+6.822E-05*T**2
-1.9111667E-08*T**3-14782200*T**(-1);
8200.0  Y
+542396.07-411.214335*T+22.2419*T*LN(T)+6.822E-05*T**2
-1.9111667E-08*T**3-2.0366965E+08*T**(-1); 1.00000E+04  N !

FUNCTION F625T 298.15
+496408.232+35.479739*T-41.6397*T*LN(T)
+.00249636*T**2-4.9050733E-07*T**3+85390.3*T**(-1);
900.00  Y
+497613.221+17.368131*T+22.2419*T*LN(T)+6.822E-05*T**2
-9.4091E-08*T**3-2.0366965E+08*T**(-1); 2.80000E+03  N !

FUNCTION GHSHERAL 298.15
-7976.15+137.093038*T-25.1480943*T*LN(T)
-4.5665E-05*T**3-24275.5*T**(-1);
700.00  Y
-11276.24+223.048446*T-38.5844296*T*LN(T)
+.018531982*T**2-5.764227E-06*T**3+74092*T**(-1);
933.60  Y
-11278.378+188.684153*T-31.748192*T*LN(T)
-1.231E+28*T**(-9);,, N !
FUNCTION GHCPAL 298.15 +5481-1.8*T+GHSERAL;,,N ! $
FUNCTION GBCCAL 298.15 +10083-4.813*T+GHSERAL;,,N !
FUNCTION GALECC 298.15 +10083-4.813*T+GHSERAL;,,N !$
FUNCTION GLIQAL 298.14 +11005.029-11.841867*T+7.934E-20*T**7+GHSERAL;  
933.59 Y +10482.282-11.253974*T+1.231E+28*T**(-9)+GHSERAL;,,N !$
FUNCTION GALHCP 298.15 +5481-1.8*T+GHSERAL;,,N !$
GAS PHASE
PARAMETER G(GAS,AL;0) 298.15 +F154T+R*T*LN(1E-05*P);,,N REF184 !
PARAMETER G(GAS,AL2;0) 298.15 +F625T+R*T*LN(1E-05*P);,,N REF448 !$
LIQUID PHASE
PARAMETER G(LIQUID,AL;0) 298.13 +11005.029-11.841867*T+7.934E-20*T**7+GHSERAL;  
933.60 Y +10482.382-11.253974*T+1.231E+28*T**(-9)+GHSERAL;,,N 91DIN !$
FCC_A1 PHASE
PARAMETER G(FCC_A1,AL;VA;0) 298.15 +GHSERAL;,,N 91DIN !$
BCC_A2 PHASE
PARAMETER G(BCC_A2,AL;VA;0) 298.15 +GBCCAL;,,N 91DIN !
  FUNC B2ALVA 295.15 10000-T;,,N !
  FUNC LB2ALVA 298.15 15000;,,N !
PARAMETER L(BCC_A2,AL,VA:VA;0) 298.15 B2ALVA+LB2ALVA;,,N 99DUP !$
HCP_A3 PHASE
PARAMETER G(HCP_A3,AL;VA;0) 298.15 +GHCPAL;,,N 91DIN !$
BCC_B2 PHASE
PARAMETER G(BCC_B2,AL;VA:VA;0) 298.15 .5*B2ALVA-.5*LB2ALVA;,,N 99DUP !
PARAMETER G(BCC_B2,VA:AL;VA;0) 298.15 .5*B2ALVA-.5*LB2ALVA;,,N 99DUP !$
FUNCTIONS
FUNCTION F7439T 298.15 +416729.448-35.265807*T-20.78*T*LN(T)  
-.0080941*T**2+1.95473333E-06*T**3+68440*T**(-1);  
6.00000E+02 Y +415600.439-4.47823809*T-25.919*T*LN(T)-3.217E-04*T**2+1.228E-08*T**3  
+69800*T**(-1);  
1.60000E+03 Y +404059.608+60.9456563*T-34.475*T*LN(T)+.00226985*T**2  
-1.11743333E-07*T**3+2845480*T**(-1);  
5.30000E+03 Y +619409.166+455.183402*T+25.674*T*LN(T)-.00531515*T**2  
+7.0418333E-08*T**3-1.4391985E+08*T**(-1);  
1.00000E+04 N !
FUNCTION F7591T  298.15 +739344.57+228.270513*T -75.86201*T*LN(T) +.02653785*T**2+3.82613167E-06*T**3-589055*T**(-1);
9.00000E+02 Y +766271.806-69.2721015*T-32.277*T*LN(T)-.0051345*T**2+.002654739*T**2 -1.7348E-21*T**7+72526.9*T**(-1); 2.50000E+03 Y +1148759.49-821.285064*T+51.18*T*LN(T)-.0082646*T**2 +1.76621667E+03 Y +16351.056-9.683796*T-9.3488E+30*T**(-9)+GHSERCO; 1.76800E+03 Y +0.5875727*T-58.296*T*LN(T)+.0049326*T**2 -1.2219167E-07*T**3-1487375*T**(-1); 5.80000E+03 Y +1148759.49-821.285064*T+51.18*T*LN(T)-.0082646*T**2 +1.76621667E+03 Y +16351.056-9.683796*T-9.3488E+30*T**(-9)+GHSERCO;,,N !

FUNCTION GHSERCO  298.15 +310.241+133.36601*T -25.0861*T*LN(T) -.002654739*T**2-1.7348E-07*T**3+72526.9*T**(-1); 1.76800E+03 Y -1717.666+253.28374*T-40.5*T*LN(T)+9.3488E+30*T**(-9)+GHSERCO;,,N !

FUNCTION GCOFCC  298.15 +427.59-.61525*T+GHSERCO;,,N !

FUNCTION GCOBCC  298.15 +2938-.7138*T+GHSERCO;,,N !

FUNCTIONS FROM DUPIN 98, PRODUCES B2 AT HIGH TEMP
FUNCTION GB2COVA  298.15 +148500-35.62*T;,,N 15LIU !
FUNCTION LB2COVA  298.15 +45030-34.47*T; 3000 Y 0; 6000 Y 15LIU !

PARAMETER G(BCC_A2,CO:VA;0)  298.15 +GB2COVA+LB2COVA;,,N 15LIU !
FUNCTION G(BCC_B2,CO:VA:VA;0)  298.15 +.5*GB2COVA-.5*LB2COVA;,,N 15LIU !
FUNCTION G(BCC_B2,VA:CO:VA;0)  298.15 +.5*GB2COVA-.5*LB2COVA;,,N 15LIU !

FUNCTION G(BCC_A2,CO,VA:VA;0)  298.15 +GB2COVA+LB2COVA;,,N 15LIU !
FUNCTION G(BCC_B2,CO,VA:VA;0)  298.15 +.5*GB2COVA-.5*LB2COVA;,,N 15LIU !
FUNCTION G(BCC_B2,VA,CO:VA;0)  298.15 +.5*GB2COVA-.5*LB2COVA;,,N 15LIU !

FUNCTION GHSERCO  298.15 +310.241+133.36601*T -25.0861*T*LN(T) -.002654739*T**2-1.7348E-07*T**3+72526.9*T**(-1); 1.76800E+03 Y -1717.666+253.28374*T-40.5*T*LN(T)+9.3488E+30*T**(-9)+GHSERCO;,,N !
FUNCTION F7454T 298.15
+390765.331-31.5120154*T*LN(T)
\quad +7.253215E-04*T**2-1.588679E-07*T**3+10285.15*T**(-1); 1100.0 Y
\quad +393886.928-44.107465*T-19.9603*T*LN(T)+.001513089*T**2
\quad -4.23648333E-07*T**3-722515*T**(-1); 2000.0 Y
\quad +412172.003+3.6829866*T+5.628866*T*LN(T)-.00848877*T**2
\quad +2.984635E-07*T**3-6015405*T**(-1); 3300.0 Y
\quad +305164.698+251.019831*T-55.20304*T*LN(T)+.005324585*T**2
\quad -2.850405E-07*T**3+34951485*T**(-1); 5100.0 Y
\quad +871952.838+1686.47356*T-204.5589*T*LN(T)+.007475225*T**2
\quad -4.6276355E+08*T**(-1); 6.00000E+03 N !

FUNCTION F7735T 298.15 +598511.402+41.5353219*T-40.56798*T*LN(T)
\quad +.004961847*T**2-1.612167E-06*T**3+104422.85*T**(-1); 800.00 Y
\quad +613345.232-104.20799*T-19.7643*T*LN(T)-.007085085*T**2
\quad -4.69883E-07*T**3+1738066.5*T**(-1); 1400.0 Y
\quad +642608.843-369.286259*T+17.64743*T*LN(T)-.02767321*T**2
\quad +1.605906E-06*T**3-5831655*T**(-1); 2300.0 Y
\quad +553119.895+159.188556*T-52.07969*T*LN(T)-.004229401*T**2
\quad +1.5939925E-07*T**3-14793625*T**(-1); 3900.0 Y
\quad +347492.339+623.137624*T-105.0428*T*LN(T)+.39699545E-04*T**2
\quad +1.51783483E-07*T**3+.1843765E+08*T**(-1); 5800.0 Y
\quad -484185.055+2598.25559*T-334.7145*T*LN(T)+.028597625*T**2
\quad -4.97520167E-08*T**3+1.35805E+09*T**(-1); 6.00000E+03 N !

FUNCTION GHSERCR 298.14
-8856.94+157.48*T-26.908*T*LN(T)
\quad +.00189435*T**2-1.97721E-06*T**3+139250*T**(-1); 2180.0 Y
\quad -34869.344+344.18*T-50*T*LN(T)-2.88526E+32*T**(-9);,,N !

FUNCTION GCRLIQ 298.15 +24339.955+11.420225*T+2.37615E-07+GHSERCR; 2180.0 Y
\quad -16459.984+335.616316*T-50*T*LN(T);,,N !

FUNCTION GFCCCR 298.15 +7284+.163*T+GHSERCR;,,N !

FUNCTION GHCPCR 298.15 +4438+GHSERCR;,,N !

FUNCTION ACRBCC 298.15 +1.7E-05*T+9.2E-09*T**2;,,N !
FUNCTION BCRBCC 298.15 +1+2.6E-11*P;,,N !
FUNCTION CCRBCC 298.15 2.08E-11;,,N !
FUNCTION DCRBCC 298.15 +1*LN(BCRBCC);,,N !
FUNCTION VCRBCC 298.15 +7.188E-06*EXP(ACRBC);,,N !
FUNCTION ECRBCC 298.15 +1*LN(CCRBCC);,,N !
FUNCTION XCRBCC  298.15 +1*EXP(.8*DCRBCC)-1;,,N !
FUNCTION YCRBCC  298.15 +VCRBCC*EXP(-ECRBCC);,,N !
FUNCTION ZCRBCC  298.15 +1*LN(XCRBCC);,,N !
FUNCTION GPCRBCC  298.15 +YCRBCC*EXP(ZCRBCC);,,N !

FUNCTION ACRLIQ  298.15 +1.7E-05*T+9.2E-09*T**2;,,N !
FUNCTION BCRLIQ  298.15 +1+4.65E-11*P;,,N !
FUNCTION CCRLIQ  298.15 3.72E-11;,,N !
FUNCTION DCRLIQ  298.15 +1*LN(BCRLIQ);,,N !
FUNCTION VCRLIQ  298.15 +7.653E-06*EXP(ACRLIQ);,,N !
FUNCTION ECRLIQ  298.15 +1*LN(CCRLIQ);,,N !
FUNCTION XCRLIQ  298.15 +1*EXP(.8*DCRLIQ)-1;,,N !
FUNCTION YCRLIQ  298.15 +VCRLIQ*EXP(-ECRLIQ);,,N !
FUNCTION ZCRLIQ  298.15 +1*LN(XCRLIQ);,,N !
FUNCTION GPCRLIQ  298.15 +YCRLIQ*EXP(ZCRLIQ);,,N !

PARAMETER G(GAS,CR;0)  298.15 +F7454T+R*T*LN(1E-05*P);,,N REF4465 !
PARAMETER G(GAS,CR2;0)  298.15 +F7735T+R*T*LN(1E-05*P);,,N REF4591 !

PARAMETER G(LIQUID,CR;0)  298.15 +GCRLIQ+GPCRLIQ;,,N 91DIN !

PARAMETER G(FCC_A1,CR:VA;0)  298.15 +GFCCCR+GPCRBCC;,,N 89DIN !
PARAMETER TC(FCC_A1,CR:VA;0)  298.15 -1109;,,N 89DIN !
PARAMETER BMAGN(FCC_A1,CR:VA;0)  298.15 -2.46;,,N 89DIN !

PARAMETER G(BCC_A2,CR:VA;0)  298.15 +GHSERCR+GPCRBCC;,,N 91DIN !
PARAMETER TC(BCC_A2,CR:VA;0)  298.15 -311.5;,,N 89DIN !
PARAMETER BMAGN(BCC_A2,CR:VA;0)  298.15 -.008;,,N 89DIN !
PARAMETER L(BCC_A2,CR,VA:VA;0)  298.15 100000;,,N 01DUP !

PARAMETER G(HCP_A3,CR:VA;0)  298.15 +GHPCR;,,N 90DIN !
PARAMETER TC(HCP_A3,CR:VA;0)  298.15 -1109;,,N 90DIN !
PARAMETER BMAGN(HCP_A3,CR:VA;0)  298.15 -2.46;,,N 90DIN !

PARAMETER G(BCC_B2,CR:VA:VA;0)  298.15 0;,,N 01DUP !
PARAMETER G(BCC_B2,VA:CR:VA;0)  298.15 0;,,N 01DUP !

FUNCTION F13191T  298.15 +417658.868-44.7777921*T-20.056*T*LN(T)
+1.24774E-06*T**3-16320*T**(-1); 800.0 Y
+413885.448+9.41787679*T+28.332*T*LN(T)+.00173115*T**2
+8.399E-08*T**3+289050*T**(-1); 3900.0 Y
+440866.732-62.5810038*T-19.819*T*LN(T)+5.067E-04*T**2
-4.93233333E-08*T**3-15879735*T**(-1);  
7600.0 Y  
+848806.287-813.398164*T+64.69*T*LN(T)-.00731865*T**2  
+8.71833333E-08*T**3-3.875846E+08*T**(-1);  10000. N  
$\text{FUNCTION F13265T} \quad 298.15  
+638073.279-68.1901928*T-24.897*T*LN(T)  
-.0313584*T**2+5.9355333E-06*T**3-14215*T**(-1);  
800.00 Y  
+611401.772+268.084821*T-75.25401*T*LN(T)+.01088525*T**2  
-7.08741667E-07*T**3+2633835*T**(-1);  
2100.0 Y  
+37459.339+72.0712678*T-48.587*T*LN(T)+.07.98E-05  
+9.12933333E-08*T**3-481755*T**(-1);  
4500.0 Y  
+56450.781+329.599011*T-80.11301*T*LN(T)+.00578085*T**2  
-1.08841667E-07*T**3+29137900*T**(-1);  6000.0 N  
$\text{FUNCTION GHSERNI} \quad 298.14  
-5179.159+117.854*T-22.096*T*LN(T)  
-.0048407*T**2;  
1728.0 Y  
-27840.655+279.135*T-43.1*T*LN(T)+1.12754E+31*T**(-9);  
N  
$\text{FUNCTION GHCPNI} \quad 298.15  
+9715.084-3.556*T+GHSERNI;  
N  
$\text{FUNCTION GBCCNI} \quad 298.15  
+8715.084-3.556*T+GHSERNI;  
N  
$\text{FUNCTION GNIBCC} \quad 298.15  
+8715.084-3.556*T+GHSERNI;  
N  
$\text{GAS PHASE}  
$\text{PARAMETER G(GAS,NI;0)} \quad 298.15  
+F13191T+R*T*LN(1E-05*P);  
N \text{ REF7504}  
$\text{PARAMETER G(GAS,NI2;0)} \quad 298.15  
+F13265T+R*T*LN(1E-05*P);  
N \text{ REF7553}  
$\text{LIQUID PHASE}  
$\text{PARAMETER G(LIQUID,NI;0)} \quad 298.13  
+16414.686-9.397*T-3.82318E-21*T**7+GHSERNI;  
1728.0 Y  
+18290.88-10.537*T-1.12754E+31*T**(-9)  
+GHSERNI;  
N \text{ 91DIN}  
$\text{FCC_A1 PHASE}  
$\text{PARAMETER G(FCC_A1,NI:VA;0)} \quad 298.15  
+GHSERNI;  
N \text{ 91DIN}  
$\text{PARAMETER TC(FCC_A1,NI:VA;0)} \quad 298.15  
633;  
N \text{ 89DIN}  
$\text{PARAMETER BMAGN(FCC_A1,NI:VA;0)} \quad 298.15  
.52;  
N \text{ 89DIN}  
$\text{BCC_A2 PHASE}  
$\text{PARAMETER G(BCC_A2,NI:VA;0)} \quad 298.15  
+GBCCNI;  
N \text{ 91DIN}  
$\text{PARAMETER TC(BCC_A2,NI:VA;0)} \quad 298.15  
575;  
N \text{ 89DIN}  
$\text{PARAMETER BMAGN(BCC_A2,NI:VA;0)} \quad 298.15  
.85;  
N \text{ 89DIN}  
$\text{FUNC B2NIVA} \quad 295.15  
+162397.3  
$\text{FUNC LB2NIVA} \quad 298.15  
-64024.38+26.49419*T;  
N  
$\text{PARAMETER L(BCC_A2,NI,VA:VA;0)} \quad 298.15  
B2NIVA+LB2NIVA;  
N \text{ 99DUP}  
$\text{HCP_A3 PHASE}  
$\text{PARAMETER G(HCP_A3,NI:VA;0)} \quad 298.15  
+GHCNI;  
N \text{ 90DIN}  
$\text{PARAMETER TC(HCP_A3,NI:VA;0)} \quad 298.15  
633;  
N \text{ 88GUI}  
$\text{PARAMETER BMAGN(HCP_A3,NI:VA;0)} \quad 298.15  
.52;  
N \text{ 88GUI}  
$
**BCC_B2 PHASE**

PARAMETER G(BCC_B2,VA:NI:VA;0)  298.15  .5*B2NIVA-.5*LB2NIVA;,,N 99DUP !
PARAMETER G(BCC_B2,NI:VA:VA;0)  298.15  .5*B2NIVA-.5*LB2NIVA;,,N 99DUP !

**BINARY PARAMETERS**

From Dupin & Ansara (1998)
A2/B2 implemented, LB2ALCO changed slightly in the current work

**LIQUID PHASE**

PARAMETER G(LIQUID,AL,CO;0)  298.15 -152470+40.259*T;,,N 98DUP !
PARAMETER G(LIQUID,AL,CO;1)  298.15 -5752.5+27.0453*T;,,N 98DUP !
PARAMETER G(LIQUID,AL,CO;2)  298.15 +30494-8.0518*T;,,N 98DUP !
PARAMETER G(LIQUID,AL,CO;3)  298.15 +24655-11.591*T;,,N 98DUP !

**FCC_A1 PHASE**

PARAMETER G(FCC_A1,AL,CO:VA;0)  298.15 -122840+22.925*T;,,N 98DUP !
PARAMETER G(FCC_A1,AL,CO:VA;2)  298.15 +24568-4.585*T;,,N 98DUP !
PARAMETER TC(FCC_A1,AL,CO:VA;0)  298.15 -1830;,,N 98DUP !
PARAMETER TC(FCC_A1,AL,CO:VA;1)  298.15 90;,,N 98DUP !
PARAMETER BMAGN(FCC_A1,AL,CO:VA;0)  298.15 10;,,N 98DUP !

**BCC_A2 PHASE**

PARAMETER G(BCC_A2,AL:CO:VA;0)  298.15  +GB2ALCO+LB2ALCO;,,N 15LIU !

**HCP_A3 PHASE**

PARAMETER G(L12_FCC,CO:AL:VA;0)  298.15  +ALCO3;,,N 01DUP !

Present work: 2015 CRALDAD
FUNCTION GB2ALCO 298.15 -138500+34.62*T;,,N 98DUP !
FUNCTION LB2ALCO 298.15 +56531-37.04*T;,,N 15LIU !
PARAMETER G(BCC_B2,AL:CO:VA;0)  298.15  +.5*GB2ALCO-.5*LB2ALCO;,,N 15LIU !
PARAMETER G(BCC_B2,CO:AL:VA;0)  298.15  +.5*GB2ALCO-.5*LB2ALCO;,,N 15LIU !

Present work: 2015 CRALDAD
Using the same interaction constraints shown by Dupin for Al-Cr-Ni
FUN U1ALCO 298.15 -4872;,,N 01DUP !
FUN U3ALCO 298.15 0.0; 6000.00 01DUP !
FUN U4ALCO 298.15 3023; 6000.00 N 01DUP !
FUNCTION L04ALCO 298.15 U3ALCO;,,N !
FUNCTION L14ALCO 298.15 U4ALCO;,,N !
FUNCTION ALCO3 298.15 3*U1ALCO;,,N !
FUNCTION AL2CO2 298.15 4*U1ALCO;,,N !
FUNCTION AL3CO 298.15 3*U1ALCO;,,N !
PARAMETER G(L12_FCC,CO:AL:VA;0)  298.15 +ALCO3;,,N 01DUP !
PARAMETER G(L12_FCC,AL:CO:VA;0) 298.15 +AL3CO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO:AL:VA;0) 298.15
  -1.5*ALCO3+1.5*AL2CO2+1.5*AL3CO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO:VA;0) 298.15
  +1.5*ALCO3+1.5*AL2CO2-1.5*AL3CO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO(AL:VA;1) 298.15
  +0.5*ALCO3-1.5*AL2CO2+1.5*AL3CO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO:CO;0) 298.15
  -1.5*ALCO3+1.5*AL2CO2-0.5*AL3CO;,, N 01DUP !
PARAMETER L(L12_FCC,*:AL:CO:VA;0) 298.15 +L04ALCO;,, N 01DUP !
PARAMETER L(L12_FCC,*:AL:CO:VA;1) 298.15 +L14ALCO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO:*:VA;0) 298.15 +3*L04ALCO;,, N 01DUP !
PARAMETER L(L12_FCC,AL:CO:*:VA;1) 298.15 +3*L14ALCO;,, N 01DUP !

PARAMETER G(AL13CO4,AL:CO;0) 298.15 -711760+170.4*T+13*GHSERAL
  +4*GHSERCO;,, N 98DUP !

PARAMETER G(AL3CO,AL:CO;0) 298.15 -174490+41.735*T+3*GHSERAL
  +GHSERCO;,, N 98DUP !

PARAMETER G(AL5CO2,AL:CO;0) 298.15 -335100+81.65*T+5*GHSERAL
  +2*GHSERCO;,, N 98DUP !

PARAMETER G(AL9CO2,AL:CO;0) 298.15 -391800+103.77*T+9*GHSERAL
  +2*GHSERCO;,, N 98DUP !

$---------------------------------------------------------------------$
$ Al-Co without high temp B2
$$_$$PRELIMINARY TO CORRECT VACANCIES IN B2, 2015 LIU
$$FRANKE (2014)$$
PARAMETER G(BCC_A2,VA:VA;0) 298.15 2*R*T;,, N 15LIU !
PARAMETER G(LIQUID,AL,CO;0) 298.15 -130953.594+30.5*T;,, N 15LIU !
PARAMETER G(LIQUID,AL,CO;1) 298.15 -19501.3177+4.83164418*T;,, N 15LIU !
PARAMETER G(LIQUID,AL,CO;2) 298.15 1117.30262-1.0799941*T;,, N 15LIU !
PARAMETER G(LIQUID,AL,CO;3) 298.15 0;,, N 15LIU !
$$_$$FUNCTION LB2COVA 298.15 -15000+30*T;,, N 15LIU !
\[ \text{PARAMETER } G(\text{AL13CO4,AL:CO};0) \quad 298.15 \quad -711760+176.814357^*T+13^*\text{GHSERAL} \]
\[ +4^*\text{GHSERCO};,,N \quad 15LIU! \]
\[ \]
\[ \text{PARAMETER } G(\text{AL3CO,AL:CO};0) \quad 298.15 \quad -174490+43.4573128^*T+3^*\text{GHSERAL} \]
\[ +4^*\text{GHSERCO};,,N \quad 15LIU! \]
\[ \]
\[ \text{PARAMETER } G(\text{AL5CO2,AL:CO};0) \quad 298.15 \quad -335100+86.3253498^*T+5^*\text{GHSERAL} \]
\[ +2^*\text{GHSERCO};,,N \quad 15LIU! \]
\[ \]
\[ \text{PARAMETER } G(\text{AL9CO2,AL:CO};0) \quad 298.15 \quad -391800+106.598758^*T+9^*\text{GHSERAL} \]
\[ +2^*\text{GHSERCO};,,N \quad 15LIU! \]

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Mainly from Saunders (COST507)

Metastable B2 and L12 from revision of Al-Cr-Ni

<table>
<thead>
<tr>
<th>Phase</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIQUID PHASE</td>
<td>[ L(\text{LIQUID, AL, CR};0) \quad 298.15 \quad -29000;,,N \quad 91SAU1! ]</td>
</tr>
<tr>
<td>FCC_A1 PHASE</td>
<td>[ G(\text{FCC_A1, AL, CR};0) \quad 298.15 \quad -45900+6^*T;,,N \quad 91SAU1! ]</td>
</tr>
<tr>
<td>BCC_A2 PHASE</td>
<td>[ G(\text{BCC_A2, AL, CR};0) \quad 298.15 \quad -54900+10^*T;,,N \quad 91SAU1! ]</td>
</tr>
<tr>
<td>BCC_B2 PHASE</td>
<td>metastable</td>
</tr>
</tbody>
</table>

Present work: july 1999, study of Al-Cr-Ni, revision of NDTH. The B2 phase is not stabilized enough to become stable in the Al-Cr. It is thus not in agreement with "T. Helander, and O. Tolochko, J. of Phase Eq, 20 (1) 1999, 57-60." Further study on the extension of the B2 phase towards AlCr in Al-Cr-Ni would be desirable.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>L12_FCC PHASE</td>
<td>metastable</td>
</tr>
</tbody>
</table>

Present work: july 1999, study of Al-Cr-Ni, revision of NDTH.
PARAMETER L(L12_FCC,*:AL,CR:*:VA;0) 298.15 +L04ALCR;,,N 01DUP !
PARAMETER L(L12_FCC,*:AL,CR:*:VA;1) 298.15 +L14ALCR;,,N 01DUP !
PARAMETER L(L12_FCC,AL,CR:*:VA;0) 298.15 +3*L04ALCR;,,N 01DUP !
PARAMETER L(L12_FCC,AL,CR:*:VA;1) 298.15 +3*L14ALCR;,,N 01DUP !

$AL11CR2 PHASE$

PHASE AL11CR2 % 3 10 1 2 !
PARAMETER G(AL11CR2,AL:AL:CR;0) 298.15
  +11*GHSERAL+2*GHSERCR-175500+25.805*T;,,N 91SAU1 !

$AL13CR2 PHASE$

PHASE AL13CR2 % 2 13 2 !
CONST AL13CR2 :AL : CR : !
PARAMETER G(AL13CR2,AL:CR;0) 298.15
  +13*GHSERAL+2*GHSERCR-174405+22.2*T;,,N 91SAU1 !

$AL4CR PHASE$

PHASE AL4CR % 2 4 1 !
CONST AL4CR :AL : CR : !
PARAMETER G(AL4CR,AL:CR;0) 298.15
  +4*GHSERAL+GHSERCR-89025+19.05*T;,,N 91SAU1 !

$AL8CR5_H PHASE$

PHASE AL8CR5_H % 2 8 5 !
CONST AL8CR5_H :AL : CR : !
PARAMETER G(AL8CR5_H,AL:CR;0) 298.15
  +8*GHSERAL+5*GHSERCR-147732-58.5*T;,,N 91SAU1 !

$AL8CR5_L PHASE$

PHASE AL8CR5_L % 2 8 5 !
CONST AL8CR5_L :AL : CR : !
PARAMETER G(AL8CR5_L,AL:CR;0) 298.15
  +8*GHSERAL+5*GHSERCR-229515;,,,N 91SAU1 !

$AL9CR4_H PHASE$

PHASE AL9CR4_H % 2 9 4 !
CONST AL9CR4_H :AL : CR : !
PARAMETER G(AL9CR4_H,AL:CR;0) 298.15
  +9*GHSERAL+4*GHSERCR-134433-56.16*T;,,N 91SAU1 !

$AL9CR4_L PHASE$

PHASE AL9CR4_L % 2 9 4 !
CONST AL9CR4_L :AL : CR : !
PARAMETER G(AL9CR4_L,AL:CR;0) 298.15
  +9*GHSERAL+4*GHSERCR-230750+16.094*T;,,N 91SAU1 !

$ALCR2 PHASE$

PHASE ALCR2 % 2 1 2 !
CONST ALCR2 :AL : CR : !
PARAMETER G(ALCR2,AL:CR;0) 298.15
  +GHSERAL+2*GHSERCR-32700-8.79*T;,,N 91SAU1 !

SIGMA_SGTE PHASE

SIGMA_H GHSERAL metastable
PARAMETER G(SIGMA_SGTE, AL:AL:CR;0)  298.15 +161148*GHERAL+18*GALBCC+4*GHERCR;,,N 15LIU!
PARAMETER G(SIGMA_SGTE, AL:CR:CR;0)  298.15 +4786+8*GHERAL+22*GHERCR;,,N 15LIU!

$----------------------------------------$
$   Al-Ni
$   Mainly from ND thesis,
$   slightly revised to get better solvus at low temperature
$----------------------------------------$

LIQUID PHASE

PARAMETER L(LIQUID, AL, NI;0)  298.15 -207109.28+41.31501*T;,,N 95DUP3!
PARAMETER L(LIQUID, AL, NI;1)  298.15 -10185.79+5.8714*T;,,N 95DUP3!
PARAMETER L(LIQUID, AL, NI;2)  298.15 +81204.81-31.95713*T;,,N 95DUP3!
PARAMETER L(LIQUID, AL, NI;3)  298.15 +4365.35-2.51632*T;,,N 95DUP3!

PARAMETER L(LIQUID, AL, NI;4)  298.15 -22101.64+13.16341*T;,,N 95DUP3!

FCC_A1 PHASE

PARAMETER TC(FCC_A1, AL, NI:VA;0)  298.15 -1112;,,N 95DUP3!
PARAMETER TC(FCC_A1, AL, NI:VA;1)  298.15 1745;,,N 95DUP3!
PARAMETER G(FCC_A1, AL, NI:VA;0)  298.15 -162407.75+16.212965*T;,,N 95DUP3!
PARAMETER G(FCC_A1, AL, NI:VA;1)  298.15 +73417.798-34.914168*T;,,N 95DUP3!
PARAMETER G(FCC_A1, AL, NI:VA;2)  298.15 +33471.014-9.8373558*T;,,N 95DUP3!
PARAMETER G(FCC_A1, AL, NI:VA;3)  298.15 -30758.01+10.25267*T;,,N 95DUP3!

BCC_A2 PHASE

BCC_B2 PHASE

L12_FCC PHASE
PARAMETER L(L12_FCC,AL,NI:*:VA;0) 298.15 +3*L04ALNI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,NI:*:VA;1) 298.15 +3*L14ALNI;,,N 01DUP !

AL3NI1 PHASE

PHASE AL3NI1 % 2 .75 .25 !
CONST AL3NI1 :AL : NI : !
PARAMETER G(AL3NI1,AL:NI;0) 298.15
\[ -48483.73 + 12.29913 \times T + .75 \times \text{GHSERAL} + .25 \times \text{GHSERNI};,,N \ 95DUP3 !

AL3NI2 PHASE

PHASE AL3NI2 % 3 3 2 1 !
CONST AL3NI2 :AL : AL,NI% : NI,VA% !
PARAMETER G(AL3NI2,AL:AL:NI;0) 298.15 +5*GBCCAL+GBCCNI
\[ -39465.978 + 7.89525 \times T;,,N \ 95DUP3 !
PARAMETER G(AL3NI2,AL:NI:NI;0) 298.15 +3*GBCCAL+3*GBCCNI
\[ -42191.9 + 79.21725 \times T;,,N \ 95DUP3 !
PARAMETER G(AL3NI2,AL:AL:VA;0) 298.15 +5*GBCCAL
\[ + 30000 - 3 \times T;,,N \ 95DUP3 !
PARAMETER G(AL3NI2,AL:NI:VA;0) 298.15 +3*GBCCAL+2*GBCCNI
\[ -35725.92 + 68.322 \times T;,,N \ 95DUP3 !
PARAMETER G(AL3NI2,AL:AL:VA;0) 298.15 +5*GBCCAL
\[ + 30000 - 3 \times T;,,N \ 95DUP3 !

AL3NI5 PHASE

PHASE AL3NI5 % 2 .375 .625 !
CONST AL3NI5 :AL : NI : !
PARAMETER G(AL3NI5,AL:NI;0) 298.15 +.375*GHSERAL+.625*GHSERNI
\[ -55507.7594 + 7.2648103 \times T;,,N \ 95DUP3 !

LIQUID PHASE

PARAMETER G(LIQUID,CO,CR;0) 3.00000E+02 -3034-5.614*T;,,N 97KUS !
PARAMETER G(LIQUID,CO,CR;1) 3.00000E+02 909;,,N 97KUS !

FCC_A1 PHASE

PARAMETER G(FCC_A1,CO,CR:VA;0) 3.00000E+02 +1500-9.592*T;,,N 97KUS !
PARAMETER TC(FCC_A1,CO,CR:VA;0) 3.00000E+02 -1795;,,N 97KUS !

BCC_A2 PHASE

PARAMETER G(BCC_A2,CO,CR:VA;0) 298.15 +17208-13.519*T;,,N 97KUS !
PARAMETER G(BCC_A2,CO,CR:VA;1) 298.15 -5470;,,N 97KUS !

HCP_A3 PHASE

PARAMETER G(HCP_A3,CO,CR:VA;0) 3.00000E+02 -6436;,,N 97KUS !
PARAMETER TC(HCP_A3,CO,CR:VA;0) 3.00000E+02 -1795;,,N 97KUS !

BCC_B2 PHASE

Mainly from Kusoffsky
Metastable B2 and L12 from the current work
Present work: 2015 CRALDAD

FUNCTION GB2COCR 298.15 -6.148723*T;,,N 15LIU!

PARAMETER G(BCC_B2,CO:CR:VA;0) 298.15 +.5*GB2COCR;,,N 15LIU!
PARAMETER G(BCC_B2,CR:CO:VA;0) 298.15 +.5*GB2COCR;,,N 15LIU!

L12_FCC PHASE metastable

Using the same interaction constraints shown by Dupin for Al-Cr-Ni
U1COCR optimized to gamma prime data from current work and Broz (2002)
Some disagreement with SQS calculations for U1COCR, but may be due to
FCC_A1 disagreement (SQS vs. Assessment)
SQS calculations indicate that Co3Cr and Cr3Co are more energetically
 Favorable than FCC_A1 at these compositions

FUN U1COCR 298.15 -5616+9.250*T;,,,N 01DUP!
FUN U1COCR 298.15 5520;,,,N 01DUP!
FUNCTION L04COCR 298.15 U3COCR;,,N 01DUP!
FUNCTION L14COCR 298.15 U4COCR;,,N 01DUP!
FUNCTION COCR3 298.15 +3*U1COCR;,,N 01DUP!
FUNCTION CO2CR2 298.15 +4*U1COCR;,,N 01DUP!
FUNCTION CO3CR 298.15 +3*U1COCR;,,N 01DUP!
PARAMETER G(L12_FCC,CR:CO:VA;0) 298.15 +CO3CR;,,,N 01DUP!
PARAMETER G(L12_FCC,CO:CR:VA;0) 298.15 +CO3CR;,,,N 01DUP!
PARAMETER L(L12_FCC,CO,CR:CO:VA;0) 298.15 +3*L04COCR;,,N 01DUP!
PARAMETER L(L12_FCC,CO,CR:*:VA;0) 298.15 +3*L14COCR;,,N 01DUP!

SIGMA_SGTE PHASE

PARAMETER G(SIGMA_SGTE,CO:CO:CR;0) 298.15 +17077-30.518*T+8*GCOFCC+18*GCOBCC+4*GHSERCR;,,N 97KUS!
PARAMETER G(SIGMA_SGTE,CO:CR:CR;0) 298.15 -7466-104.215*T+8*GCOFCC+22*GHSERCR;,,N 97KUS!

SIGMA_SGTE PHASE

Co-Ni
Mainly from SGTE
Metastable B2 and L12 from the current work

LIQUID PHASE

PARAMETER G(LIQUID,CO,NI;0) 298.15 1331;,,N 87GU3!

FCC_A1 PHASE

PARAMETER G(FCC_A1,CO,NI:VA;0) 298.15 -800+1.2629*T;,,N 87GU3!
PARAMETER TC(FCC_A1,CO,NI:VA;0) 298.15 411;,,N 87GU3!
PARAMETER TC(FCC_A1,CO,NI:VA;1) 298.15 -99;,,N 87GU3!
PARAMETER BMAGN(FCC_A1,CO,NI:VA;0) 298.15 1.046;,,N 87GU3!
PARAMETER BMAGN(FCC_A1,CO,NI:VA;1) 298.15 .165;,,N 87GU3 !

BCC_A2 PHASE

PARAMETER G(BCC_A2,CO,NI:VA;0) 298.15 2000;,,N 87GU3 !
PARAMETER TC(BCC_A2,CO,NI:VA;0) 298.15 556;,,N 87GU3 !
PARAMETER TC(BCC_A2,CO,NI:VA;1) 298.15 -288;,,N 87GU3 !
PARAMETER BMAGN(BCC_A2,CO,NI:VA;0) 298.15 .474;,,N 87GU3 !

HCP_A3 PHASE

PARAMETER G(HCP_A3,CO,NI:VA;0) 298.15 -1620-.385*T;,,N 87GU3 !
PARAMETER TC(HCP_A3,CO,NI:VA;0) 298.15 411;,,N 87GU3 !
PARAMETER TC(HCP_A3,CO,NI:VA;1) 298.15 -99;,,N 87GU3 !
PARAMETER BMAGN(HCP_A3,CO,NI:VA;0) 298.15 1.046;,,N 87GU3 !
PARAMETER BMAGN(HCP_A3,CO,NI:VA;1) 298.15 .165;,,N 87GU3 !

BCC_B2 PHASE

FUNCTION GB2CONI 298.15 +7728-3.328*T;,,N 15LIU !
PARAMETER G(BCC_B2,CO:NI:VA;0) 298.15 +.5*GB2CONI;,,N 15LIU !
PARAMETER G(BCC_B2,NI:CO:VA;0) 298.15 +.5*GB2CONI;,,N 15LIU !

L12_FCC PHASE

FUNCTION L04CONI 298.15 U3CONI;,,N 01DUP !
FUNCTION L14CONI 298.15 U4CONI;,,N 01DUP !
FUNCTION CONI3 298.15 +3*U1CONI;,,N 01DUP !
FUNCTION CO2NI2 298.15 +4*U1CONI;,,N 01DUP !
FUNCTION CO3NI 298.15 +3*U1CONI;,,N 01DUP !
PARAMETER G(L12_FCC,NI:CO:VA;0) 298.15 +CONI3;,,N 01DUP !
PARAMETER G(L12_FCC,CO:NI:VA;0) 298.15 +CO3NI;,,N 01DUP !
PARAMETER L(L12_FCC,CO,NI:CO:VA;0) 298.15 -1.5*CONI3+1.5*CO2NI2+1.5*CO3NI;,,N 01DUP !
PARAMETER L(L12_FCC,CO,NI:NI:VA;0) 298.15 +1.5*CONI3+1.5*CO2NI2-1.5*CO3NI;,,N 01DUP !
PARAMETER L(L12_FCC,CO,NI:CO:VA;1) 298.15 +0.5*CONI3-1.5*CO2NI2+1.5*CO3NI;,,N 01DUP !
PARAMETER L(L12_FCC,CO,NI:NI:VA;1) 298.15 -1.5*CONI3+1.5*CO2NI2-0.5*CO3NI;,,N 01DUP !
PARAMETER L(L12_FCC,*,CO,NI:VA;0) 298.15 +L04CONI;,,N 01DUP !
PARAMETER L(L12_FCC,*,CO,NI:VA;1) 298.15 +L14CONI;,,N 01DUP !
PARAMETER L(L12_FCC,*,CO,NI:*,VA;0) 298.15 +3*L04CONI;,,N 01DUP !
PARAMETER L(L12_FCC,*,CO,NI:*,VA;1) 298.15 +3*L14CONI;,,N 01DUP !

LIQUID PHASE

PARAMETER L(LIQUID,CR,NI;0) 298.15 +318-7.3318*T;,,N 91LEE !
PARAMETER L(LIQUID,CR,NI;1) 298.15 +16941-6.3696*T;,,N 91LEE !
PARAMETER G(FCC_A1,CR,NI:VA;0)  298.15  +8030-12.8801*T;,,N 91LEE !  
PARAMETER G(FCC_A1,CR,NI:VA;1)  298.15  +33080-16.0362*T;,,N 91LEE !  
PARAMETER TC(FCC_A1,CR,NI:VA;0)  298.15  -3605;,,N 86DIN !  
PARAMETER EMAGN(FCC_A1,CR,NI:VA;0)  298.15  -1.91;,,N 86DIN !  

PARAMETER G(BCC_A2,CR,NI:VA;0)  298.15  +17170-11.8199*T;,,N 91LEE !  
PARAMETER G(BCC_A2,CR,NI:VA;1)  298.15  +34418-11.8577*T;,,N 91LEE !  
PARAMETER TC(BCC_A2,CR,NI:VA;0)  298.15  2373;,,N 86DIN !  
PARAMETER TC(BCC_A2,CR,NI:VA;1)  298.15  617;,,N 86DIN !  
PARAMETER BMAGN(BCC_A2,CR,NI:VA;0)  298.15  4;,,N 86DIN !  

PARAMETER G(BCC_B2,CR:NI:VA;0)  298.15  4000;,,N 01DUP !  
PARAMETER G(BCC_B2,NI:CR:VA;0)  298.15  4000;,,N 01DUP !  

PARAMETER G(L12_FCC,NI:CR:VA;0)  298.15  +CRNI3;,,  N 01DUP !  
PARAMETER G(L12_FCC,CR:NI:VA;0)  298.15  +CR3NI;,,  N 01DUP !  
PARAMETER L(L12_FCC,CR,NI:CR:VA;0) 298.15  -1.5*CRNI3+1.5*CR2NI2+1.5*CR3NI;,,N 01DUP !  
PARAMETER L(L12_FCC,CR,NI:NI:VA;0) 298.15  +1.5*CRNI3+1.5*CR2NI2-1.5*CR3NI;,,N 01DUP !  
PARAMETER L(L12_FCC,CR,NI:CR:VA;1) 298.15  -0.5*CRNI3-1.5*CR2NI2+1.5*CR3NI;,,N 01DUP !  
PARAMETER L(L12_FCC,CR,NI:NI:VA;1) 298.15  -1.5*CRNI3+1.5*CR2NI2-0.5*CR3NI;,,N 01DUP !  
PARAMETER L(L12_FCC,*:CR,NI:VA;0) 298.15  +L04CRNI;,,N 01DUP !  
PARAMETER L(L12_FCC,*:CR,NI:VA;1) 298.15  +L14CRNI;,,N 01DUP !  
PARAMETER L(L12_FCC,*:CR,NI:*:VA;0) 298.15  +3*L04CRNI;,,N 01DUP !  
PARAMETER L(L12_FCC,*:CR,NI:*:VA;1) 298.15  +3*L14CRNI;,,N 01DUP !  

PARAMETER G(SIGMA_SGTE,NI:CR:CR;0) has been modified by  
Ursula R. Kattner, NIST, Gaithersburg, MD, USA  
Which gives better results in Co-Cr-Ni  
Parameter shown below by Gustafson  
PARAMETER G(SIGMA_SGTE,NI:CR:CR;0)  298.15  +173460-188*T+8*GHSERNI+18*GHSERCR+4*GHSERC;,,N 88GUS1 !  
PARAMETER G(SIGMA_SGTE,NI:NI:CR;0)  298.15  +175400+8*GHSERNI+18*GNIBCC+4*GHSERC;,,N 88GUS1 !  

SIGMA_SGTE PHASE  
metastable

**************************************************************************
TERNARY PARAMETERS

Mainly from the current work (2015)

Co-Cr from Kusoffsky used instead of Oikawa as energies
are shown to be better for sigma. Also produces a better
Co-Cr-Ni extrapolation

LIQUID PHASE

Simple parameter to suppress liquid formation a 1573 K

FCC_A1 PHASE

BCC_A2 PHASE

BCC_B2 PHASE

L12_FCC PHASE
PARA L(L12_FCC,CO,CR:AL:VA;0) 298.15
  +1.5*ALCOCR2+1.5*ALCO2CR-1.5*ALCO3-1.5*ALCR3;,,N 01DUP !
PARA L(L12_FCC,AL,CO:CR:VA;1) 298.15
  -1.5*ALCO2CR+1.5*AL2COCR-0.5*AL3CR+0.5*C03CR;,,N 01DUP !
PARA L(L12_FCC,AL,CR:CO:VA;1) 298.15
  -1.5*ALCOCR2+1.5*AL2COCR-0.5*AL3CO+0.5*COCR3;,,N 01DUP !
PARA L(L12_FCC,CO,CR:AL:VA;1) 298.15
  -1.5*ALCO2CR-1.5*ALCO2CR-0.5*ALCO3+0.5*ALCR3;,,N 01DUP !

SIGMA_SGTE PHASE

PARAMETER G(SIGMA_SGTE,CO:AL:CR;0)  298.15
  -931862+8*GCOFCC+18*GALBCC+4*GHSERCR;,,N 15LIU !
PARAMETER G(SIGMA_SGTE,AL:CO:CR;0)  298.15
  -617537+8*GHSERAL+18*GCOBCC+4*GHSERCR;,,N 15LIU !
PARAMETER G(SIGMA_SGTE,CO:AL,CR:CR;0)  298.15  -200000;,,N 15LIU !

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Mainly from the current work (2015)
Update of Al-Co-Ni from NDTH by Dupin

LIQUID PHASE

PARAMETER G(LIQUID,AL,CO,NI;0)  298.15  20000;,,N 15LIU !

FCC_A1 PHASE

FUNCTION BALCOMNI  298.15  -43538;,,N 15LIU !

BCC_A2 PHASE

FUNCTION BALCOMNI  298.15  +.5*BALCOMNI;,,N 15LIU !
PARAMETER G(BCC_A2,NI:AL,CO:VA;0)  298.15  +.5*BALCOMNI;,,N 15LIU !

BCC_B2 PHASE

Present work: 2015 CRALDAD
Using the same interaction constraints shown by Dupin for Al-Cr-Ni
FUN U1ALCONI 298.15 0;,,N 01DUP !
FUN U2ALCONI 298.15 0;,,N 01DUP !
FUN U3ALCONI 298.15 0;,,N 01DUP !
FUN ALCONI2 298.15 U1ALCO+2*U1ALNI+2*U1CONI+U1ALCONI;,,N 01DUP !
FUN ALCO2NI 298.15 2*U1ALCO+U1ALNI+2*U1CONI+U2ALCONI;,,N 01DUP !
FUN AL2CONI 298.15 2*U1ALCO+2*U1ALNI+U1CONI+U3ALCONI;,,N 01DUP !
PARA L(L12_FCC,AL,CO,NI:AL:VA;0) 298.15
  -1.5*ALCONI2-1.5*ALCO2NI+ALCO3+ALNI3+6*AL2CONI
  -1.5*AL2CO2-1.5*AL2NI2-1.5*AL3CO-1.5*AL3NI;,,N 01DUP !
PARA L(L12_FCC,AL,CO,NI:CO:VA;0) 298.15
  -1.5*ALCONI2+6*ALCO2NI-1.5*ALCO3-1.5*AL2CONI
  -1.5*AL2CO2+AL3CO+CONI3-1.5*CO2NI2-1.5*CO3NI;,,N 01DUP !
PARA L(L12_FCC,AL,CO,NI:NI:VA;0) 298.15
  +6*ALCONI2-1.5*ALCO2NI-1.5*ALNI3-1.5*AL2CONI
  -1.5*AL2NI2+AL3NI-1.5*CONI3-1.5*CO2NI2+CO3NI;,,N 01DUP !
PARAMETER L(LIQUID,AL,Cr,NI;0) 298.15
+1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !
PARAMETER L(FCC_A1,AL,Cr,NI;0) 298.15
+1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !
PARAMETER L(BCC_A2,AL,Cr,NI;0) 298.15
+1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !
PARAMETER L(BCC_A1,AL,Cr,NI;0) 298.15
+1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;0) 298.15
-1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !

Al-Cr-Ni

July 1999, ND
Revision. Main changes:
- description of the A2/B2
- new liquidus data taken into account
- simpler ternary interaction parameters

LIQUID PHASE

PARAMETER L(LIQUID,AL,Cr,NI;0) 298.15 16000;,,N 01DUP !

FCC_A1 PHASE

PARAMETER G(FCC_A1,AL,Cr,NI;VA;0) 298.15 30300;,,N 01DUP !

BCC_A2 PHASE

PARAMETER G(BCC_A2,AL,Cr,NI;VA;0) 298.15 42500;,,N 01DUP !

L12_FCC PHASE

$-------------------------------------$
$FUN U1ALCrNI 298.15 6650;,,N 01DUP !$
$FUN U2ALCrNI 298.15 0;,,N 01DUP !$
$FUN U3ALCrNI 298.15 0;,,N 01DUP !$
$FUN ALCrNi2 298.15 U1ALCr+2*U1ALNI+2*U1CrNi+U1ALCrNi;,,N 01DUP !$
$FUN ALCr2NI 298.15 2*U1ALCr+U1ALNI+2*U1CrNi+U2ALCrNi;,,N 01DUP !$
$FUN ALCr2NI 298.15 2*U1ALCr+2*U1ALNI+U1CrNi+U3ALCrNi;,,N 01DUP !$
PARAMETER L(L12_FCC,AL,Cr,NI;AL;VA;0) 298.15
-1.5*AL2CrNI-1.5*AL3Cr-1.5*AL3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;CR;VA;0) 298.15
-1.5*AL2CrNI+6*ALCr2NI-1.5*ALCr3-1.5*AL2CrNI
-1.5*AL2Cr2+AL3Cr+CrNi3-1.5*Cr2Ni2-1.5*Cr3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;NI;VA;0) 298.15
+6*ALCrNi2-1.5*ALCr2NI-1.5*AL3NI-1.5*AL2CrNI
-1.5*AL2Ni2+AL3Ni-1.5*CrNi3-1.5*Cr2Ni2-1.5*Cr3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;VA;0) 298.15
+1.5*ALCr2NI+1.5*AL2CrNI-1.5*AL3NI-1.5*Cr3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;CR;VA;0) 298.15
+1.5*ALCr2NI+1.5*AL2CrNI-1.5*AL3Cr-1.5*CrNi3;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;AL;VA;1) 298.15
+1.5*ALCr2NI+1.5*AL2CrNI-1.5*AL3Cr-1.5*CrNi3;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;CR;VA;1) 298.15
-1.5*ALCr2NI-0.5*AL3Cr+0.5*Cr3NI;,,N 01DUP !
PARAMETER L(L12_FCC,AL,Cr,NI;AL;VA;1) 298.15
-1.5*ALCr2NI-0.5*AL2CrNI-0.5*AL3Cr+0.5*Cr3NI;,,N 01DUP !
SIGMA_SGTE PHASE

metastable

PARAMETER G(SIGMA_SGTE,AL:N1:CR;0)  298.15
-1045169+8*GHSERAL+18*GNIBCC+4*GHSERCR;,,N 15LIU !
PARAMETER G(SIGMA_SGTE,N1:AL:CR;0)  298.15
-1169367+8*GHSERNI+18*GALBCC+4*GHSERCR;,,N 15LIU !

----------------------------------------------------------------------------

Co-Cr-Ni

Mainly from the current work (2015)
Extrapolations from binaries are slightly improved

LIQUID PHASE

PARAMETER G(LIQUID,CO,CR,N1;0)  298.15  -16000;,,N 15LIU !

FCC_A1 PHASE

PARAMETER G(FCC_A1,CO,CR,N1:VA;0)  298.15  -40710+13.5334*T;,,N 15LIU !

BCC_A2 PHASE

PARAMETER G(BCC_A2,CO,CR,N1:VA;0)  298.15  -60134+17.699513*T;,,N 15LIU !

BCC_B2 PHASE

Metastable parameter assessed from quaternary data
FUNCTION BCONIMCR  298.15  72707.735-48.325581*T;,,N 15LIU !

PARAMETER G(BCC_B2,CR:CO,N1:VA;0)  298.15  +.5*BCONIMCR;,,N 15LIU !
PARAMETER G(BCC_B2,CO,N1:CR:VA;0)  298.15  +.5*BCONIMCR;,,N 15LIU !

L12_FCC PHASE

Present work: 2015 CRALDAD
Using the same interaction constraints shown by Dupin for Al-Cr-Ni
FUN U1COCRNI 298.15 0;,,N 01DUP !
FUN U2COCRNI 298.15 0;,,N 01DUP !
FUN U3COCRNI 298.15 0;,,N 01DUP !
FUN COCRNI2 298.15  U1COCR+2*U1CONI+2*U1CRNI+U1COCRNI;,,N 01DUP !
FUN COCR2NI 298.15  2*U1COCR+U1CONI+2*U1CRNI+U2COCRNI;,,N 01DUP !
FUN CO2CRNI 298.15  2*U1COCR+2*U1CONI+U1CRNI+U3COCRNI;,,N 01DUP !
PARA L(L12_FCC,CO,CR,N1:CO:VA;0)  298.15
-1.5*COCRNI2+1.5*COCR2NI+1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+1.5*COCR2NI+1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+1.5*COCR2NI+1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+1.5*COCR2NI+1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+1.5*COCR2NI+1.5*COCR3+1.5*CO2CRNI

PARA L(L12_FCC,CO,CR,N1:CR:VA;0)  298.15
-1.5*COCRNI2+6*COCR2NI-1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+6*COCR2NI-1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+6*COCR2NI-1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+6*COCR2NI-1.5*COCR3+1.5*CO2CRNI
-1.5*COCRNI2+6*COCR2NI-1.5*COCR3+1.5*CO2CRNI

PARA L(L12_FCC,CO,CR,N1:N1:VA;0)  298.15
+6*COCRNI2+1.5*COCR2NI-1.5*COCR3+1.5*CR2NI+1.5*CR3NI
+6*COCRNI2+1.5*COCR2NI-1.5*COCR3+1.5*CR2NI+1.5*CR3NI
+6*COCRNI2+1.5*COCR2NI-1.5*COCR3+1.5*CR2NI+1.5*CR3NI
+6*COCRNI2+1.5*COCR2NI-1.5*COCR3+1.5*CR2NI+1.5*CR3NI
+6*COCRNI2+1.5*COCR2NI-1.5*COCR3+1.5*CR2NI+1.5*CR3NI

PARA L(L12_FCC,CO,CR,N1:NI:VA;0)  298.15
+1.5*COCR2NI+1.5*COCRNI+1.5*CO2NI+1.5*CO3NI+1.5*CO3NI+1.5*CO3NI
+1.5*COCR2NI+1.5*COCRNI+1.5*CO2NI+1.5*CO3NI+1.5*CO3NI+1.5*CO3NI
+1.5*COCR2NI+1.5*COCRNI+1.5*CO2NI+1.5*CO3NI+1.5*CO3NI+1.5*CO3NI
+1.5*COCR2NI+1.5*COCRNI+1.5*CO2NI+1.5*CO3NI+1.5*CO3NI+1.5*CO3NI
+1.5*COCR2NI+1.5*COCRNI+1.5*CO2NI+1.5*CO3NI+1.5*CO3NI+1.5*CO3NI

PARA L(L12_FCC,CO,CR:N1:VA;1)  298.15

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-1.5*COCR2NI+1.5*CO2CRNI-0.5*CO3NI+0.5*CR3NI;,,N 01DUP !
PARA L(L12_FCC,CO,NI:CR:VA;1) 298.15
-1.5*COCR2NI+1.5*CO2CRNI-0.5*CO3NI+0.5*CR3NI;,,N 01DUP !
PARA L(L12_FCC,CR,NI:CO:VA;1) 298.15
-1.5*COCR2NI+1.5*CO2CRNI-0.5*CO3NI+0.5*CR3NI;,,N 01DUP !
$
$ SIGMA_SGTE PHASE
$ Phase boundaries well reproduced without the need of ternary end-members
$ extra energies
PARAMETER G(SIGMA_SGTE,NI:CO:CR;0) 298.15
+8*GHSERNI+18*GCOBCC+4*GHSERCR;,,N 15LIU !
PARAMETER G(SIGMA_SGTE,CO:NI:CR;0) 298.15
+8*GCOFCC+18*GNIBCC+4*GHSERCR;,,N 15LIU !
$
$-------------------------------------------------------
$----------------------------------------------------------------------------------
$----------------------------------------------------------------------------------
$----------------------------------------------------------------------------------
$----------------------------------------------------------------------------------
$ Al-Co-Cr-Ni
$ Extrapolations from ternaries only need slight modification
$ Co-Cr-Ni B2 parameter and Sigma quaternary parameter are
$ Assessed from quaternary data
$
$PARATOR G(SIGMA_SGTE,NI:CO:CR;0) 298.15 0.0;,,N 15LIU !
PARAMETER G(L12_FCC,AL,CO,CR:NI:VA;0) 298.15 +AL3NI+CO3NI+CR3NI
-1.5*AL2CONI-1.5*ALCR2NI-1.5*AL2CRNI-1.5*ALCO2NI
-1.5*AL2CO2NI+6*ALCOCRNI;,,N 15LIU !
PARAMETER G(L12_FCC,AL,CO,NI:CR:VA;0) 298.15 +AL3CR+CO3CR+CRNI3
-1.5*ALCO2CR-1.5*ALCR2NI-1.5*AL2COCR-1.5*AL2CRNI-1.5*ALCO2NI
-1.5*AL2CRNI-6*ALCOCRNI;,,N 15LIU !
PARAMETER G(L12_FCC,AL,CR,NI:CO:VA;0) 298.15 +AL3CO+CO3CR+CRNI3
-1.5*ALCOCR2-1.5*ALCONI2-1.5*AL2COCR-1.5*AL2CRNI-1.5*ALCRNI2
-1.5*AL2COCR+6*ALCOCRNI;,,N 15LIU !!!
PARAMETER G(L12_FCC,CO,CR,NI:AL:VA;0) 298.15 +ALCO3+ALCR3+ALNI3
-1.5*ALCOCR2-1.5*ALCONI2-1.5*ALCO2CR-1.5*ALCO2NI-1.5*ALCRNI2
-1.5*ALCR2NI+6*ALCOCRNI;,,N 15LIU !
SIGMA_SGTE PHASE

Use -1075000 if NIST G(SIGMA_SGTE,NI:CR;0) is used
Use -1175000 if Gustafson G(SIGMA_SGTE,NI:CR;0) is used
PARAMETER G(SIGMA_SGTE,CO,NI:AL,CR:CR;0) 298.15 -1175000;,,N 15LIU !

LIST_OF_REFERENCES

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>SOURCE</th>
</tr>
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<td>REF448</td>
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<td>REF4591</td>
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Xuan Liu was born on June 25, 1989 in Taigu, Shanxi Province, China and spent the next decade bouncing around the world from China to Israel in 1998 and then finally the United States in 2000. After graduating in 2007 from East Lyme High School, Xuan enrolled at the University of Virginia. He spent the 4 years of his life in Charlottesville, Virginia studying Chemical Engineering and learning to play the 5-string banjo. In 2011, he graduated with a Bachelor of Science degree in Chemical Engineering and decided to pursue graduate studies. After joining Dr. Zi-Kui Liu’s research group at the Pennsylvania State University in 2011, he has focused his research on Ni-base superalloys and their protective coatings. Outside of research, Xuan spends his time playing in various bluegrass bands around Central PA.

Listed below are his publications during his Ph.D. study:


