Chapter 2

Computational Methodology

2.1 Introduction

This chapter describes the methodology used to achieve the objectives of this work. First principle calculations were used in this work for two purposes (i) to obtain enthalpy of mixing for binary and higher order systems and (ii) to obtain CECs for the ternary and quaternary systems. First, principle calculations were performed using the density functional theory (DFT) (section 2.2) in association with cluster expansion (section 2.3) and a special quasi-random structure model (described in section 2.4). The following section (2.5) gives details of the steps used in the thermodynamic assessments of the binary subsystems. The procedure for calculating various thermodynamic quantities (Gibbs energy of mixing, enthalpy of mixing, entropy of mixing, and SRO parameters) is explained in section 2.6.

2.2 DFT calculations

Many software packages are available for DFT calculations. Lejaeghere *et al.*(Lejaeghere et al. 2016) compared the calculated values for the equation of states for 71 elemental crystals from 15 widely used DFT codes employing 40 different potentials. Among them, Quantum-Espresso with the GBRV pseudo-potentials and VASP with PAW pseudo-potentials performed well. In this work, both these software with the appropriate pseudo-potentials were used.

The ab initio calculations carried out using the VASP code (Kresse and Furthmüller 1996; Kresse and Hafner 1999; Kern et al. 1996). Kresse *et al.* developed Projector augmented wave pseudopotentials (Joubert 1999) as implemented in VASP (Kresse 1996) and an

expansion of the electronic wavefunctions in plane waves with a kinetic-energy cut-off of 500 eV. In this work, PAW pseudopotentials are considered for VASP calculation. All calculated results uses the generalized gradient approximation (GGA) (Paier et al. 2005). Brillouin-zone integrations were performed using Monkhorst–Pack (Pack 1976). For generation of *k*-point meshes the Methfessel–Paxton (Methfessel and Paxton 1989) technique with a smearing parameter of 0.1 eV used. The total energy was converged numerically to less than 1×10^{-6} eV/atom. The electronic, ionic, and unit cell degrees of freedom were relaxed using calculated forces with a preconditioned conjugate gradient algorithm. After structural optimization, calculated energies (which were not identically zero by symmetry) were converged to less than five meV/Å in magnitude. All calculations were performed using the ‘‘high” precision setting within the VASP code. VASP code has been used to calculate the enthalpy of mixing the ternary and quaternary systems using a special quasi-random (SQS) structure.

Electronic structure total energy calculations (Kresse and Furthmüller 1996) of ordered configurations required for the construction of the cluster expansion Hamiltonian are performed using the Quantum-Espresso (P Giannozzi et al. 2022; Paolo Giannozzi et al. 2009, 2020) Simulation Package with the generalized gradient approximation (GGA) (Perdew, Burke, and Ernzerhof 1996) and the ultra-soft pseudopotentials (Walker and Gebauer 2007; Bartók and Yates 2019) is used. The first-order Methfessel-Paxton (Methfessel and Paxton 1989) method of electronic occupancy has been used with a smearing width of 0.2 eV. Brillouin zone integration uses a Monkhorst (Pack 1976)- Pack *k*-point mesh. In this work, KPPRA is set to 46,656, which, for the bcc structure, translates to a 36 × 36 × 36 grid. These basis cut-off and *k*-point grid choices ensure convergence of the total energy within a few meV/atom. The GBRV(Garrity et al. 2014) high-throughput pseudopotentials library developed as all Perdew –Burke-Ernzerhof

PBE potentials in UPF format for Quantum-espresso having Perdew –Burke-Ernzerhof (PBE) parameterization with Koelling – Harmon core and valence scalar relativistic calculation was used as exchange-correlation functional in ultrasoft Pseudopotential (USPP) method. The cut-off energy for the plane wave was 100 Ry, and the density cut-off was 400 Ry. In this work, for calculating the enthalpy of mixing using the cluster expansion technique Quantum-Espresso has been used.

2.3 Cluster Expansion

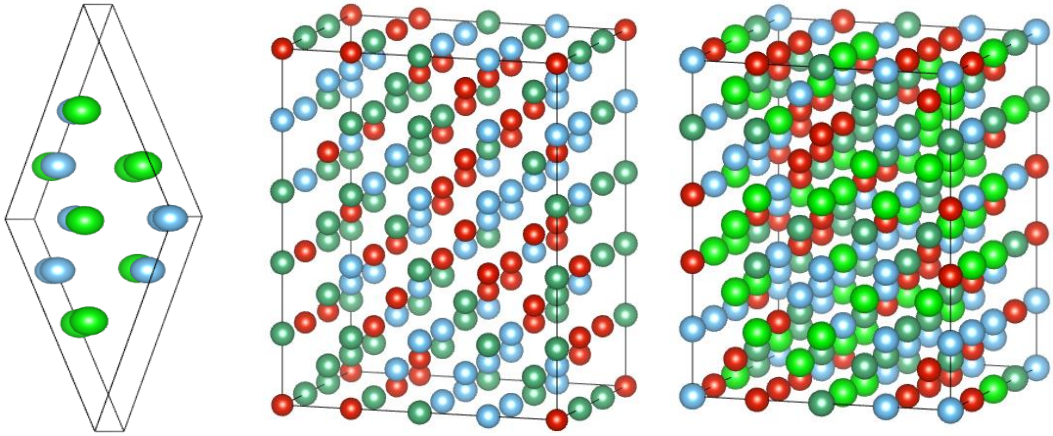
The accuracy of CE parametrization is not determined solely by the piar in the energies predicted by CE compared to those predicted by DFT. Ensuring the CE model predicts the correct lowest energy crystal structures is important. In this work, we used the Alloy Theoretic Automatic Toolkit (ATAT) (van de Walle, Asta, and Ceder 2002), which allows assigning extra weights to certain crystal structures to ensure that the lowest energy structures predicted by CE simulations agree with DFT results. To find the optimum set of ECIs for binary, ternary, and quaternary alloys, we use a database of DFT energies computed for 70 to 100 bcc-like structures for binary, 120 to 170 bcc-like structures for ternary, and 436 bcc-like structures for quaternary systems. DFT calculations involve full atomic relaxations. Full atomic relaxations may strain the structures, and it is possible to leave parent lattice symmetry. Using strain criteria as explained by Yuge and Okawa (Yuge and Okawa 2014) for the Cu-Au system, structures having $strain \geq 0.1$ has to be rejected from CE. The calculated enthalpies of mixing for these crystal structures of binary, ternary and quaternary alloys are explained in chapter 3, where they are labelled as calculated (DFT) and fitted (CE) energies. Another criterion employed for structure consideritation is Born criteria (Born 1940; Born and Huang 1954). In this criteria the elastic constant C_{ij} (namely C_{11}, C_{12}, and C_{44} in the case of bcc structure) must satisfy following conditions. $C_{11} - |C_{12}| > 0$, $C_{11} + 2|C_{12}| > 0$ and $C_{44} > 0$. All the structure

considered in these calculations follows all these criteria. The enthalpies of mixing computed for the initial structures are negative for all alloys (except few). The initial CEC set serves as a starting point for further automatic refinement of CE parameters, which is achieved by generating new structures, hence enabling the verification of accuracy of predictions made using the ATAT method. In this study, the best choice of CE coefficients for all alloys corresponds to the cross validation (C.V.) error between DFT and CE formation enthalpies of 2.5 meV/atom. In order to validate and verify the accuracy of CE parametrization, we use the final CEC sets to calculate the lowest mixing enthalpies of the alloys.

2.4 Generation of special quasi-random structures

In the present study, we generated various SQS-N structures (with N atoms per unit cell) for substitutionally random bcc alloys with compositions for binary $A_{0.25}B_{0.75}$, $A_{0.5}B_{0.5}$, $A_{0.75}B_{0.25}$ with 16 atoms. For ternary alloys, a total of 19 SQS of 120 atoms of the following compositions were generated: $A_{0.25},B_{0.125},C_{0.625}$ and its combinations, $A_{0.2},B_{0.4},C_{0.4}$ and its combinations, $A_{0.3},B_{0.2},C_{0.5}$ and its combinations and $A_{0.333333}B_{0.333333}C_{0.333333}$. Similarly, quaternary $A_{0.375},B_{0.375},C_{0.125,}D_{0.125}$ (and its combinations), and equiatomic composition $A_{0.25},B_{0.25},C_{0.25},D_{0.25}$ SQS of 160 atoms were geneated. Our search criterion was that the pair correlation functions of the SQSs be identical to those of the corresponding random alloys, at least up to the third-nearest neighbor. The most straightforward way to generate the SQSs is to exhaustively enumerate all possible bcc-based structures and then calculate their pair and multisite correlation functions, as the *mcsqs* code implements in the Alloy-Theoretic Automated Toolkit (ATAT)(van de Walle, Asta, and Ceder 2002). For large-sized SQSs, the direct enumeration method becomes time-consuming since the total number of possible candidate structures increases exponentially with N (combinatorial explosion).

Therefore, we employ the Monte Carlo simulated annealing technique (Van de Walle, Asta, and Ceder 2002)(Mäder and Zunger 1995) in generating SQSs with $N > 16$. Different choices of lattice vectors are tested for each alloy composition until the supercell with the lowest periodicity error has been found. The lattice vectors and atomic positions of the obtained SQS-*N* structures in their ideal, unrelaxed forms are given in Tables A.1, A.2, and A.3 of Appendix A, all in Cartesian coordinates, the pair and three-body correlation functions of our generated SQSs in comparison with those of the random alloys. Figure 2-1 shows the generated (a) binary (b) ternary and (c) quaternary SQS.



(a) (b) (c)

Figure 2-1 The SQSs used in this calculation are: (a) an 8-atom SQS for a binary system, (b) a 120-atom SQS for a ternary system, and (c) a 160-atom SQS for a quaternary system. Each color represents a distinct group of atoms.

Enthalpy of mixing calculation

$$\Delta H = E(SQS) - (1 - x_B - x_c - x_D)E(A) - x_B\,E(B) - x_c\,E(c) - x_D\,E(D) \quad 2.1$$

where $E(A)$, $E(B)$, $E(C)$ *and* $E(D)$ are the first-principles calculated total energies (per atom) of the pure constituent *A, B, C,* and *D,* the corresponding SQS, respectively, each

relaxed to their equilibrium geometries. The pure elements in the bcc structure are used as reference states in Eq. 2.1.

2.5 Thermodynamic Assessment

The bcc_A2 and hcp_A3 phases were treated using phenomenological cluster expansion (CE) for configurational enthalpy of mixing and CVM for configurational entropy of mixing (Inden 2001). The tetrahedron and tetrahedron-octahedron approximations of the CE-CVM were used for the bcc_A2 and hcp_A3 phases, respectively. Both these models take into account interactions up to second nearest-neighbor pairs. The Gibbs energy of mixing for the bcc phase is expressed as,

$$G^{\beta,mix} = H^{\beta,mix} - TS^{\beta,mix} \quad 2.2$$

where $H^{\beta,mix}$ and $S^{\beta,mix}$ respectively denote the enthalpy and entropy of mixing shown in Eq. 2.3 and 2.4

$$H^{\beta,mix} = \sum_i C_i^{\beta} m_i^{\beta} u_i^{\beta,mix} \quad 2.3$$

$$S^{\beta,mix} = -R \sum_i \gamma_i^{\beta} m_i^{\beta} \sum_j w_{i,j} \rho_{i,j} \ ln\, \rho_{i,j} \quad 2.4$$

$$C_i^{\beta} = C_{i0}^{\beta} s + C_{i1}^{\beta} T \quad 2.5$$

The C_i^{β} (Eq. 2.5) are phenomenological cluster expansion coefficients (*C.E.C.s*) or effective cluster interactions (*E.C.I.s*), which may be temperature-dependent. The subscript *i* refers to one of the five crystallographically distinct clusters for the tetrahedron approximation. The multiplicity m_i^{β} is equal to the number of clusters of type *i* per atomic site in the structure and $u_i^{\beta,mix} = u_i^{\beta} - x_A u_{i,A}^{\beta} - x_B u_{i,B}^{\beta}$. Here u_i^{β}, $u_{i,A}^{\beta}$ and $u_{i,B}^{\beta}$ represent the correlation functions corresponding to cluster type *i* for the alloy and those for pure component A and B, respectively. These correlation functions are the

average values of site operators or their products. In the orthogonal basis we use, the site operator takes the value –1 or +1, respectively, when component A or B atom occupies the site (Lele and Sarma 2009). These cluster variables are, in turn, functions of correlation functions $\rho_{i,j} = \rho_{i,j}(u_i^{\beta})$. The Gibbs energy of the phase, parameterized by C_i^{β}, can be obtained by minimizing it with respect to the correlation functions (Lele and Sarma 2009) using the Newton–Raphson (*NR*) method. Similar expressions may be written for the hcp_A3 phase as well. The model parameters C_i^{α} and C_i^{β} can be obtained by simultaneous optimization of all available experimental data for the system.

Simultaneous optimization

In the present work, all available phase diagrams and thermodynamic data have been simultaneously optimized (Lele and Sarma 2009). For simultaneous optimization, a figure-of-merit function (χ^2) is defined as the sum of squares of the ratios of the errors ε_i and the respective standard deviations σ_i over all *N* data points.

$$\chi^2 = \sum_{i=1}^{N} \left(\frac{\varepsilon_i}{\sigma_i}\right)^2 \qquad 2.6$$

In general, ε_i corresponds to the difference between the experimental quantity and that calculated using the model under the conditions of experimentation. The χ^2-merit function is minimized with respect to a chosen set of model parameters to determine their values using the Levenberg–Marquardt (*LM*) algorithm (Press et al. 1993). We developed the necessary computer codes for optimization, following the algorithmic considerations discussed by Press et al. (Press et al. 1993). Details of the procedure are given in (Jindal, Sarma, and Lele 2013).

2.6 Calculation of thermodynamic quantities

As mentioned earlier, the binary CECs are to be obtained from thermodynamic assessments. For the ternary and quaternary systems where the thermodynamic

assessment was not feasible, we will use cluster expansion to get CECs related to ternary and quaternary interactions. Later, these CECs are to be combined in a consistent manner to obtain the thermodynamics description of the bcc Nb-Ti-V-Zr system. Recently, Jindal and Lele (Jindal and Lele 2023) have developed a basis (CV basis) by carefully selecting the required number of cluster variables (CVs) as CECs. The advantage of this basis is that CECs of the lower order system remain invariant in this basis and can be straightforwardly extended to multicomponent systems. This work uses this basis to determine the CECs of the multicomponent Nb-Ti-V-Zr system using the CECs of the subsystems. More details of this basis are given in Appendix B. First, CECs corresponding to the binary subsystems were transformed from orthogonal to CV basis (Appendix C). Later, all binary and higher-order CECs were combined to obtain the bcc Nb-Ti-V-Zr system's thermodynamics description consisting of 55 CECs (including 4 points).

CE-CVM model of Gibbs energy for bcc quaternary system is based on 55 CFs. To obtain an equilibrium configuration, Gibbs energy needs to be minimized with respect to these CFs. Minimization has been done using the Newton-Raphson method. For optimization of the correlation function, the code uses random values of the correlation function as initial values. These optimized correlation functions are further used for calculating thermodynamic properties and short-range order calculation.

2.7 Evaluation of Warren Cowley parameters

Cowley-Warren parameters are used to describe the short-range order (SRO) in crystalline alloys. They quantify the probability of finding a specific type of atom at a certain distance from another type of atom in the alloy. These parameters are defined by the following expressions as shown in Eq. 2.7

$$\alpha_{ij}^{AB} = 1 - \frac{P_i^{AB}}{c_A} \quad 2.7$$

where $\boldsymbol{P_i^{AB}}$ is the probability of finding an A atom in the neighborhood of B in the i^{th} shell when B is present at j^{th} site. $\boldsymbol{c_A}$ and $\boldsymbol{c_B}$ are the atomic fractions.

The SRO can also be calculated using correlation function as shown in Eq. 2.8

$$\alpha_i = \frac{u_i - u_0^2}{1 - u_0^2} \quad 2.8$$

Here u_i and u_0 are the equilibrium values of the i^{th} pair and point correlation functions, respectively. Details of obtaining equilibrium correlation functions is given in section 1.6.