Chapter 3

First-Principles Calculations

3.1 Introduction

As mentioned in Chapter 1, for the thermodynamic modeling of the bcc Nb-Ti-V-Zr system, two types of data are required (i) phase diagram data and (ii) thermochemical data. Experimental determination of thermochemical data of the individual phase is difficult. This chapter deals with the calculation of thermochemical data using the DFT. The two major techniques: cluster expansion and special quasi-random structure, are used to calculate the enthalpy of mixing values of binary, ternary, and quaternary subsystems of the Nb-Ti-V-Zr system. Sections 3.2 to 3.7 gives details of binary systems. Sections 3.8 to 3.11 deal with ternary systems, and calculations of the quaternary systems are provided in section 3.12. The computation methodology of these calculations is given in Chapter 2. Results obtained in this chapter are used in subsequent Chapter 4.

3.2 Nb-Ti System

CE results

For the Nb-Ti system, CE calculations were performed for the bcc lattices. Among structures of known energy, actual and predicted ground states agree well. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-1. The convex hull of the calculated and fitted energies of the cluster expansion structures, shown in Figure 3-2(a), underscores the acceptable level of agreement between the two methods.

A total of seven ground-state structures, including five ordered structures, were found in the ground-state search. The formation energies of all the ordered structures are positive, which is consistent with the experimental phase diagram with no ordered intermediate compounds. The energy of the disordered phase was calculated using correlation functions of the disordered (random) phase at various compositions. Calculated CEC vs. cluster diameter plots is given in Figure 3-2(b). Convergence of CECs can be observed. To analyze CECs, the empty, the point, the first two nearest pairs, the first triangle, and tetrahedron clusters, which include the nearest pair, are listed in Table 3-1. The CEC value of the empty cluster corresponds to the energy of the fully-disordered alloy. A negative value of the fully-disordered alloy indicates an ordering tendency in the bcc solution phase. This is coincident with negative values of mixing obtained from SQS calculation. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-2(a). These calculations are comparable with SQS calculations.

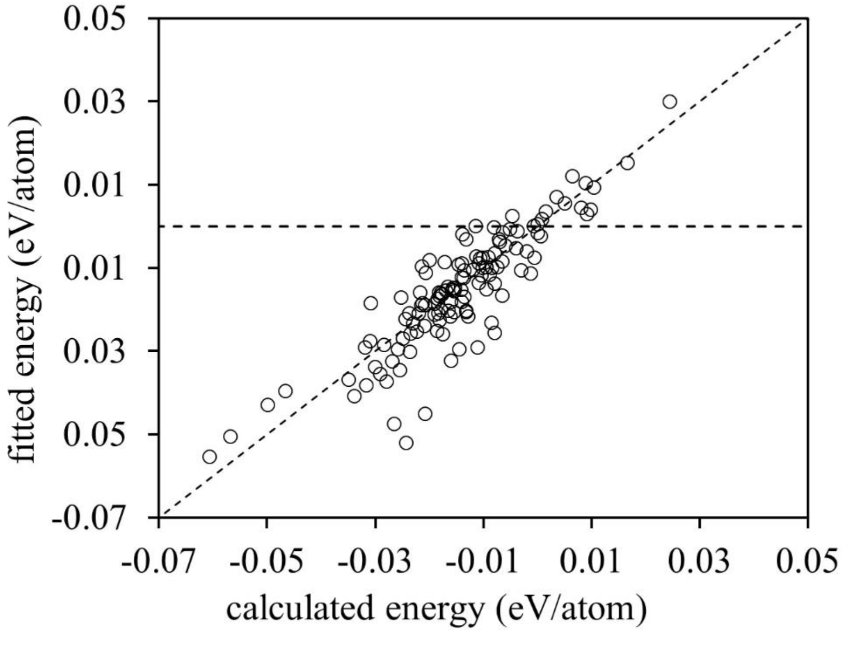
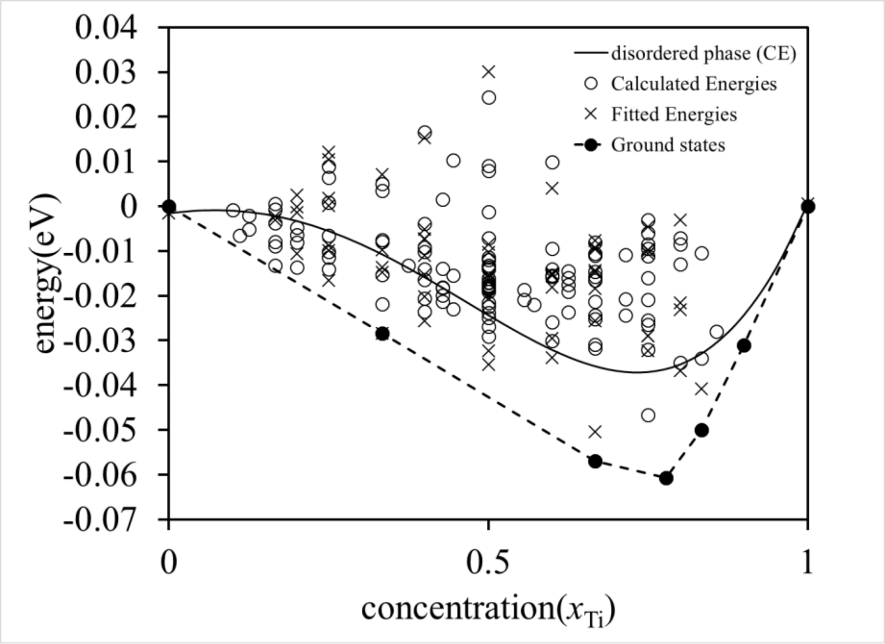
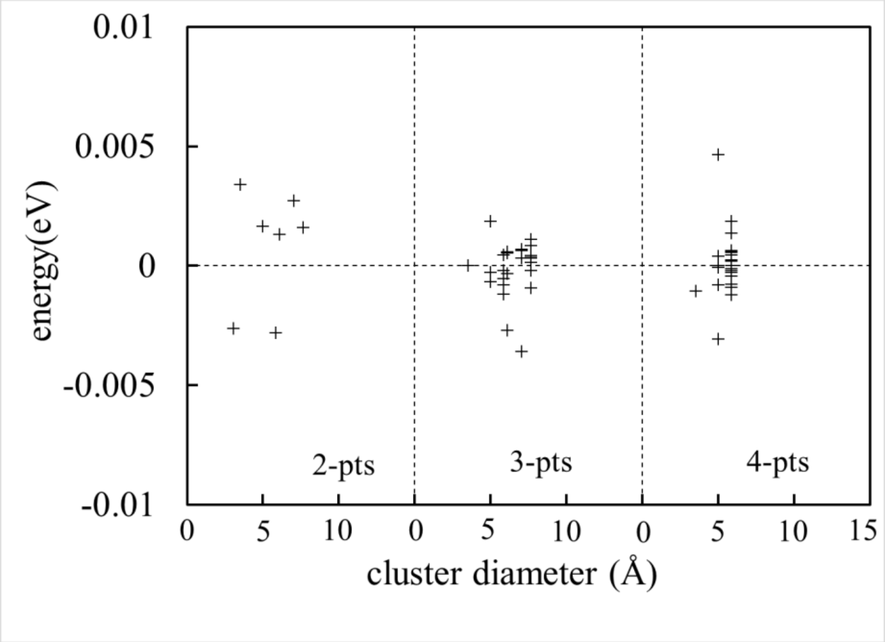


Figure 3-1 Comparison of enthalpies of formation (eV/atom) obtained from FP calculations (calculated) and predicted with CE method (fitted) of Nb-Ti bcc phase.



(a)



(b)

Figure 3-2 (a) Ground-state search for the cluster expansion of Nb-Ti bcc phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the as calculated first principles energies.

Table 3-1 Selected CECs for Nb-Ti bcc system.

num of sites	multiplicity	CEC (eV)
0	1	-0.024347
1	1	-0.042371
2	4	-0.002632
2	3	0.00339
3	12	0.000001
4	6	-0.001049

SQS results

Enthalpy of mixing for the Nb-Ti bcc solutions calculated from SQS are shown in Figure 3-3 along with previous works (Raabe et al. 2007) (Uesugi, Miyamae, and Higashi 2013) (Chandran, Subramanian, and Gigliotti 2013) (Marker et al. 2018). It may be observed that all these works more or less agree with each other and reported negative enthalpy of mixing, except for Marker et al. (2018). The deviation of Marker et al. (2018) results compared to others might be attributed to their use of volume-relaxed SQS, which differs from the full relaxation employed by other studies. No experimental data for this system are available in the literature for comparison. The enthalpies of mixing calculated with SQS results are negative, which implies the bcc solid solution is stable at low temperatures. This is consistent with the experimental observation.

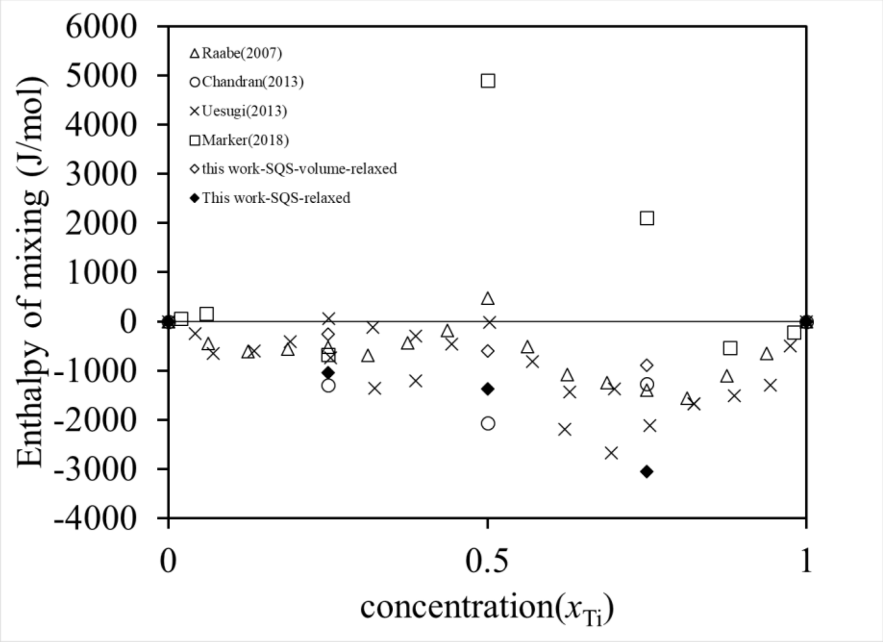


Figure 3-3 Calculated enthalpy of mixing for the bcc phase in the Nb-Ti system

3.3 Ti-V System

CE results

Figure 3-4 compares the enthalpy of formation obtained from the FP calculations and the CE method for the bcc Ti-V system. There is reasonable agreement between these two methods, as shown in the figure. The CV score of the present calculation is 0.021 and sufficiently small for the CE method. Figure 3-5 (a) shows the calculated and fitted energy of the structures used in cluster expansion. A total of four ground-state structures, including two ordered structures, were found in the ground-state search. These structures have a positive enthalpy of formation, suggesting no stable ordered phase with bcc-type symmetry in the Ti-V system. Calculated CEC vs. cluster diameter plots is given in Figure 3-5 (b). Convergence of CECs within atomic distances can be readily observed. The CECs of the empty, the point, the first two nearest pairs, the first triplet, and tetrahedron clusters, which include the nearest pair, are listed in Table 3-2. A positive value of the empty cluster corresponding to a fully-disordered alloy indicates its instability. Similar values of mixing were obtained from SQS calculations. It may be observed from Table 3-2 that the CECs of the nearest and second nearest pair cluster for bcc are negative. This further indicated a tendency for phase separation in the bcc phase. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-5 (a).

The Ti-V system is dynamically unstable at low temperatures and low V concentrations. Skripnyak *et al.*, in their recent work using *ab-initio* Molecular Dynamics (AIMD), found that the enthalpies of mixing calculated at high temperature are positive for all V concentrations, in contrast to the traditional static calculations with full relaxation of atomic positions at T = 0 K, which predict negative values for alloys with low vanadium concentrations. The failure of the accepted zero temperature static approach is linked to the dynamical instability of the bcc phase of Ti and its alloys at 0 K. Our calculations also indicate similar results. The enthalpy of mixing started becoming negative below 35 at. % V.

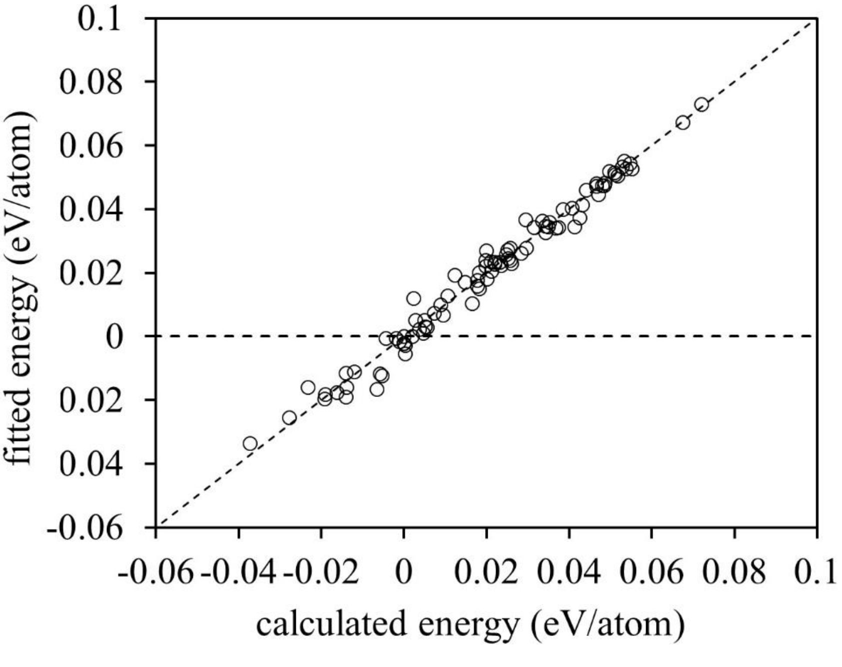
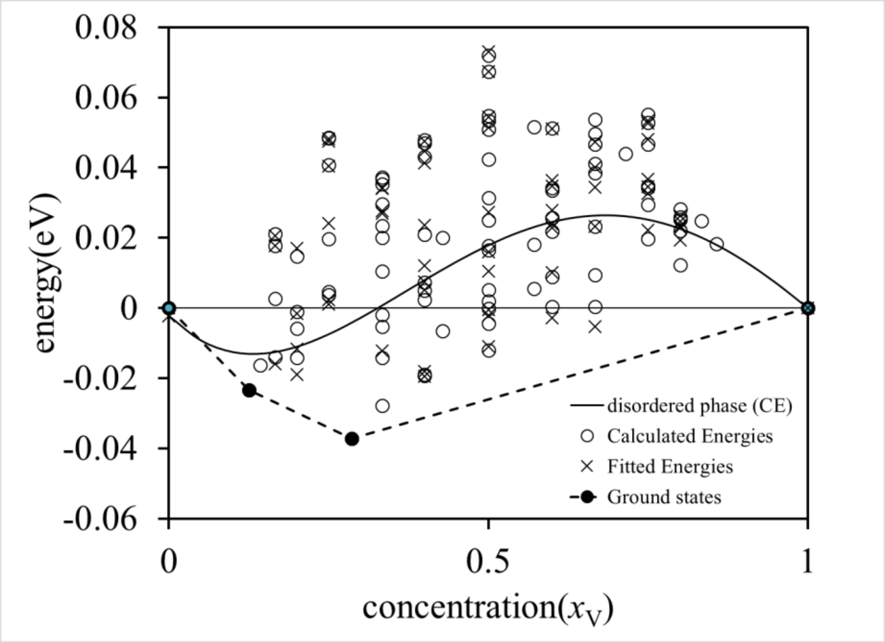
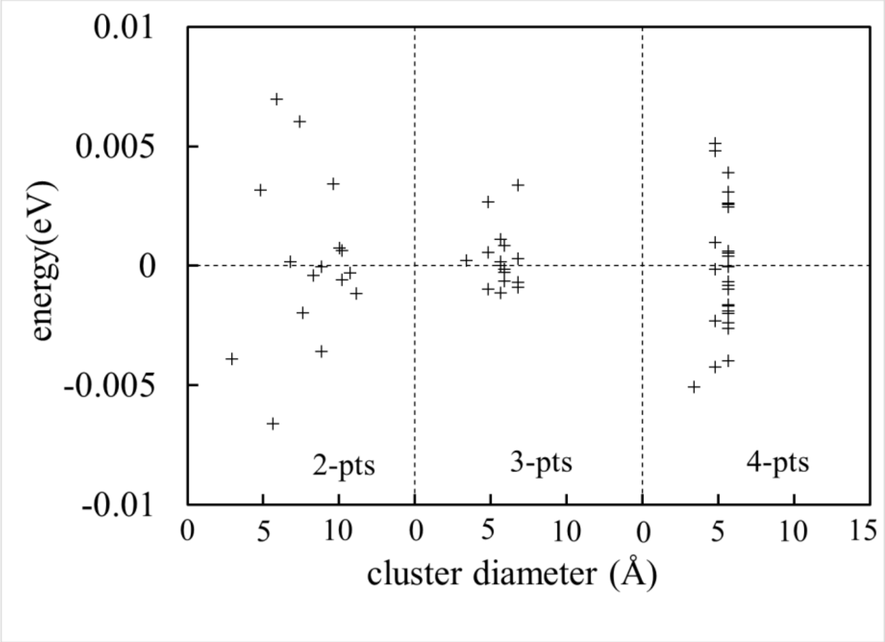


Figure 3-4 Comparison of enthalpies of formation (eV/atom) obtained from FP calculations and predicted with CE method of Ti-V bcc phase.



(a)



(b)

Figure 3-5 (a) Ground-state search for the cluster expansion of Ti-V bcc phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the calculated first principles energies.

Table 3-2 Selected CECs for Ti-V bcc system.

num of sites	multiplicity	CEC (eV)
0	1	0.017886
1	1	0.043157
2	4	-0.003893
2	3	-0.012711
3	12	0.000224
4	6	-0.005084

SQS results

The Enthalpy of mixing for the Ti-V bcc solutions calculated using SQS is shown in Figure 3-6. Results are comparable with those (Skripnyak et al. 2020) and (Uesugi, Miyamae, and Higashi 2013) relaxed SQS. The Ti-V system shows the dynamical instability of the crystal lattice for Ti-rich alloys at low temperatures. While the enthalpy of mixing is positive for V-rich alloys, it becomes negative for Ti-rich alloys. However, these results are inconsistent with experimental data and AIMD results (Skripnyak et al. 2020), which show that the enthalpy of mixing for Ti-V bcc solutions to be positive for all the compositions.

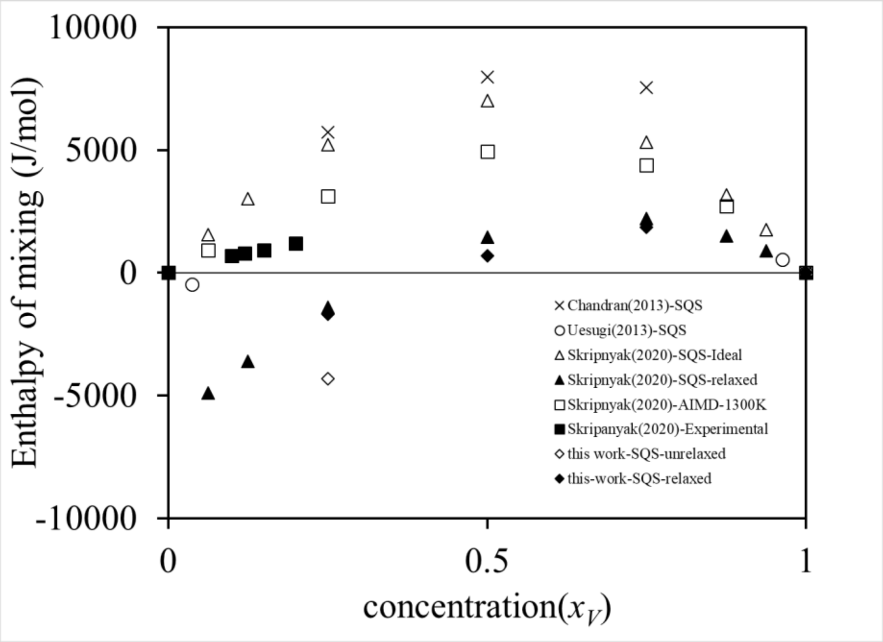


Figure 3-6 Calculated enthalpy of mixing for the bcc phase in the Ti-V system

3.4 Ti-Zr System

CE results

The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-7. Among structures of known energy, actual and predicted ground states agree well. The CV score of the present calculation is 0.023 and sufficiently small for the CE method. The convex hull of the calculated and fitted energies of the cluster expansion structures, shown in Figure 3-8 (a), underscores the acceptable level of agreement between the two methods. A total of five ground-state structures, including three ordered structures, were found in the ground-state search. All these structures have a positive enthalpy of formation, suggesting no stable ordered phase with bcc-type symmetry in the Ti-Zr system. This is consistent with experimental observations. Figure 3-8 (a) also shows the energy of the disordered bcc phase at various compositions calculated using fitted CECs. Convergence of CECs can be readily observed in Calculated CEC vs. cluster diameter plots in Figure 3-8 (b). Table 3-3 lists the CECs of the empty, the point, the first two nearest pairs, the first triplet, and the tetrahedron cluster, which includes the nearest pair. It may be observed that the values of CECs are very small compared to Nb-Ti and Ti-V systems. This indicates less SRO in the bcc phase. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-8 (a). No clear trend is demonstrated by the enthalpy of mixing calculated using CE for the Ti-Zr bcc disordered alloys.

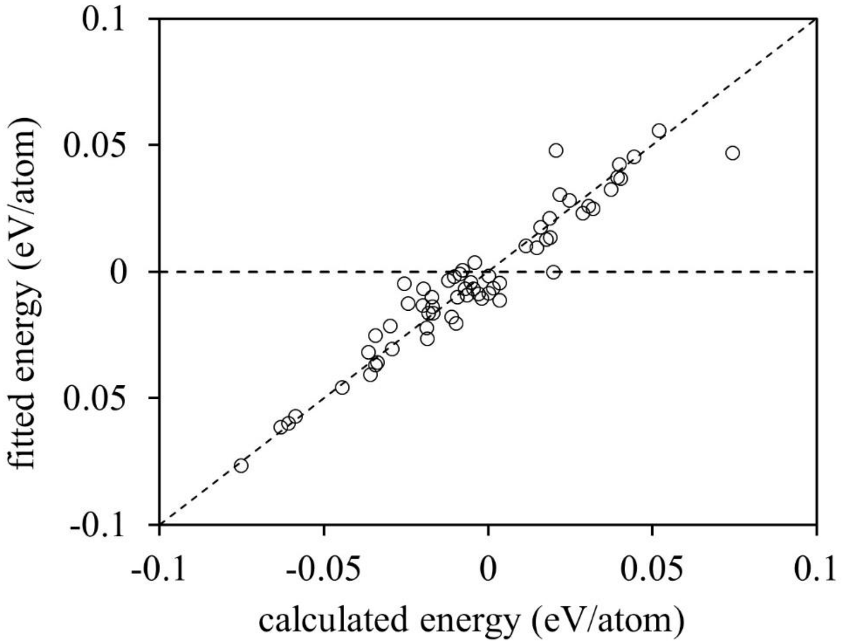
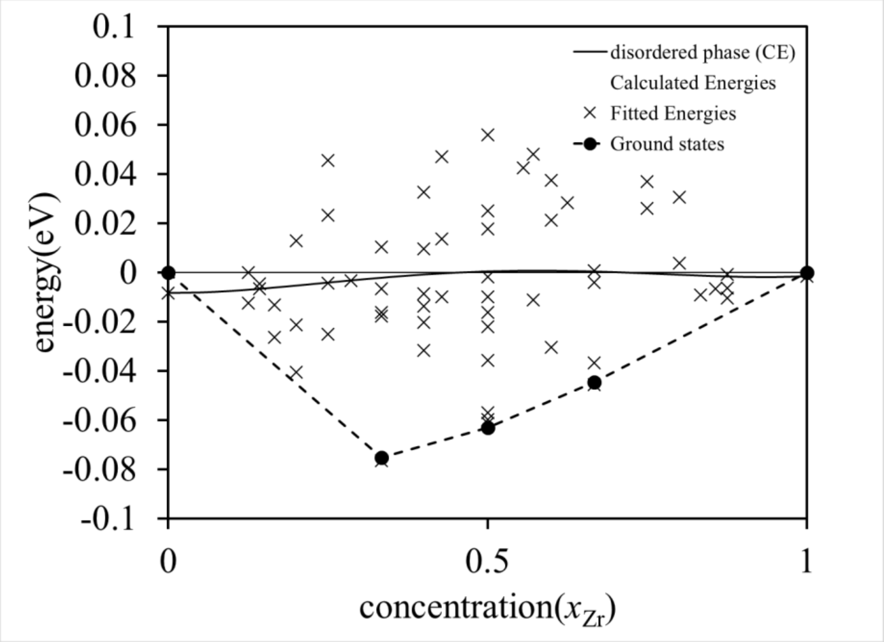
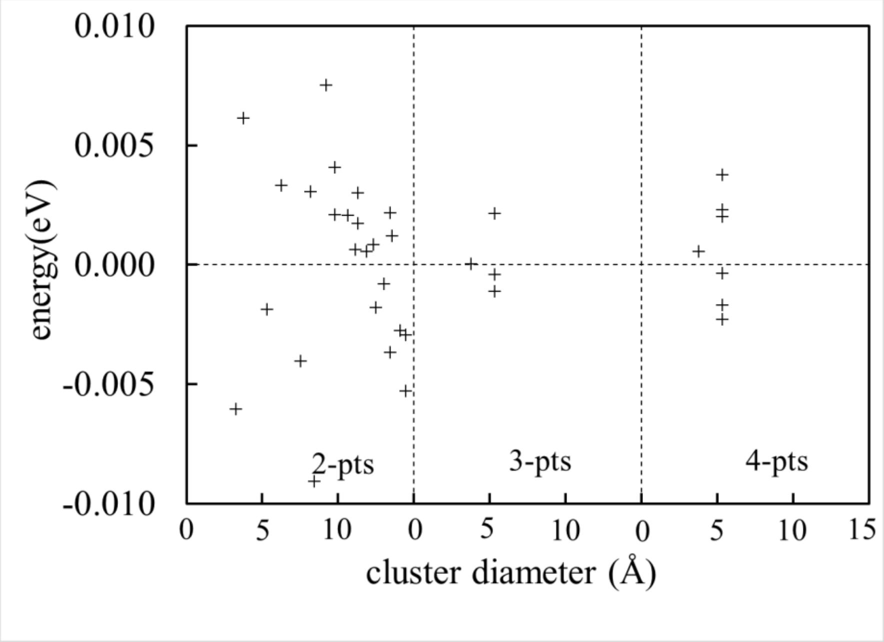


Figure 3-7 Comparison of enthalpies of formation (eV/atom) obtained from FP calculations and predicted with CE method of Ti-Zr bcc phase



(a)



(b)

Figure 3-8 (a) Ground-state search for the cluster expansion of Ti-Zr bcc phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the as calculated first principles energies.

Table 3-3 Selected CECs for Ti-Zr bcc system

num of sites	multiplicity	CEC (eV)
0	1	0.000396
1	1	0.003846
2	4	-0.006044
2	3	0.006127
3	12	0.000032
4	6	0.000546

SQS results

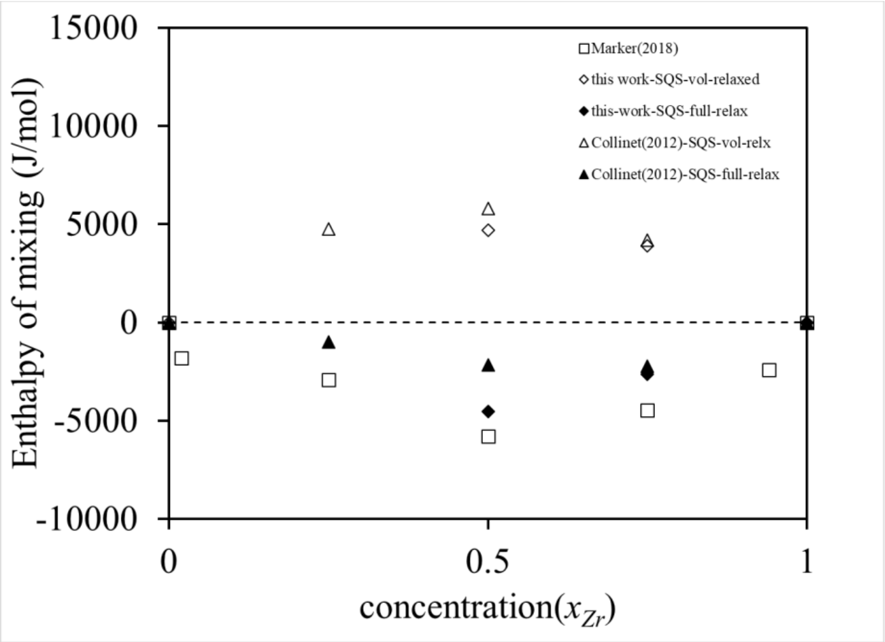


Figure 3-9 shows the results of enthalpy of mixing for the Ti-Zr bcc solutions calculated using SQS. Full relaxed SQS results show a negative enthalpy of mixing for all the compositions. Some researchers (Catherine Colinet and Tedenac 2012) (Marker et al. 2018) indicated a slight ordering tendency of the bcc solution phase at lower temperatures.

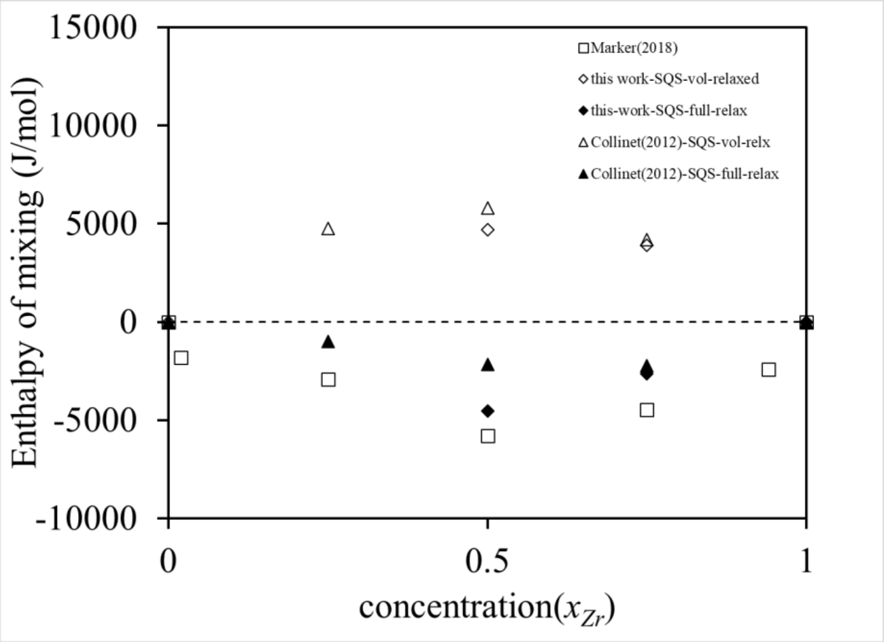


Figure 3-9 Calculated enthalpy of mixing for the bcc phase in the Ti-Zr system.

3.5 Nb-V System

CE results

For the Nb-V system, bcc lattices are chosen to perform CE calculations as parent lattices. Among structures of known energy, actual and predicted ground states agree well. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-10. The CV score of the present calculation is 0.001 and sufficiently small for the CE method. The convex hull of the calculated and fitted energies of the cluster expansion structures, shown in Figure 3-11 (a), underscores the acceptable level of agreement between the two methods. These structures have a positive enthalpy of formation, suggesting no stable ordered phase with bcc-type symmetry in the Nb-V system. Calculated CEC vs. cluster diameter plots is given in Figure 3-11(b). Convergence of CECs can be readily observed. To analyze CECs, the CECs of the empty, the point, the first three nearest pairs, and the first triplet, which includes the nearest pair, are listed in Table 3-4. The CEC value of the empty cluster corresponds to the energy of the fully-disordered alloy. A large positive value of the fully-disordered alloy indicates its instability. This is in coincident positive values of mixing obtained from SQS calculation and observed miscibility gap in the bcc phase. It may be noted from Table 3-4 that the CECs of the nearest and second nearest pair cluster for bcc are negative. This further indicated a tendency for phase separation in the bcc phase. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-11 (b). CEC values of the first triplet are very small compared to Pair CECs suggesting a symmetric behavior of the formation energy. The symmetry of formation energy is reflected in the calculated formation energy plot of the disordered bcc phase Figure 3-11(b).

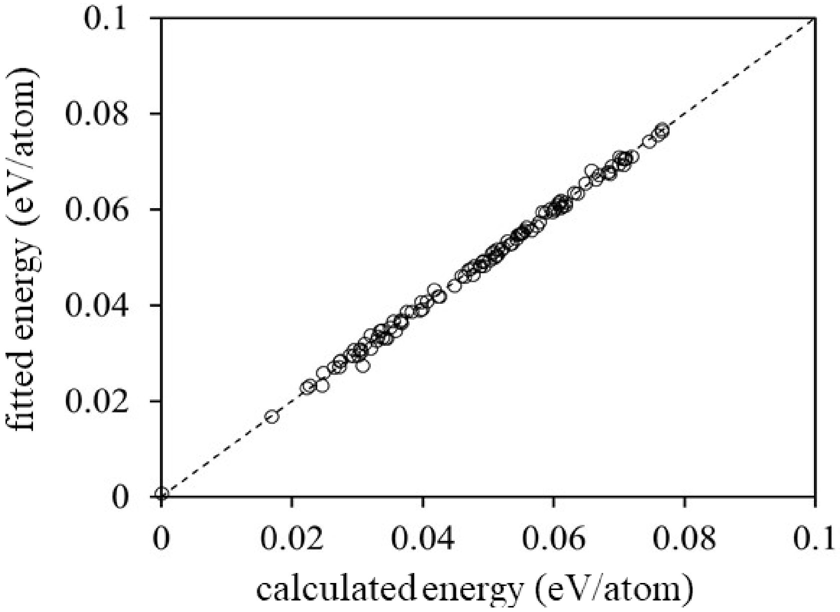
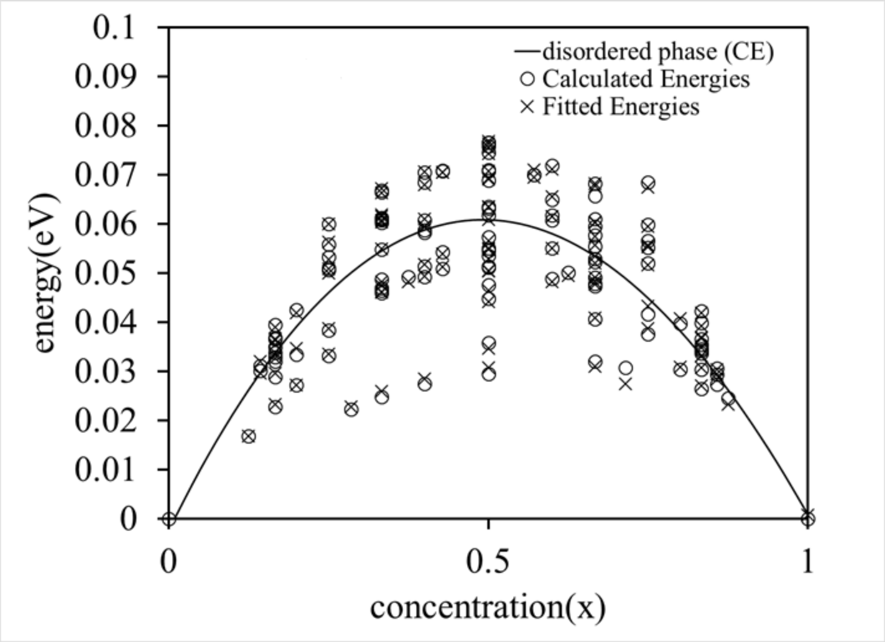
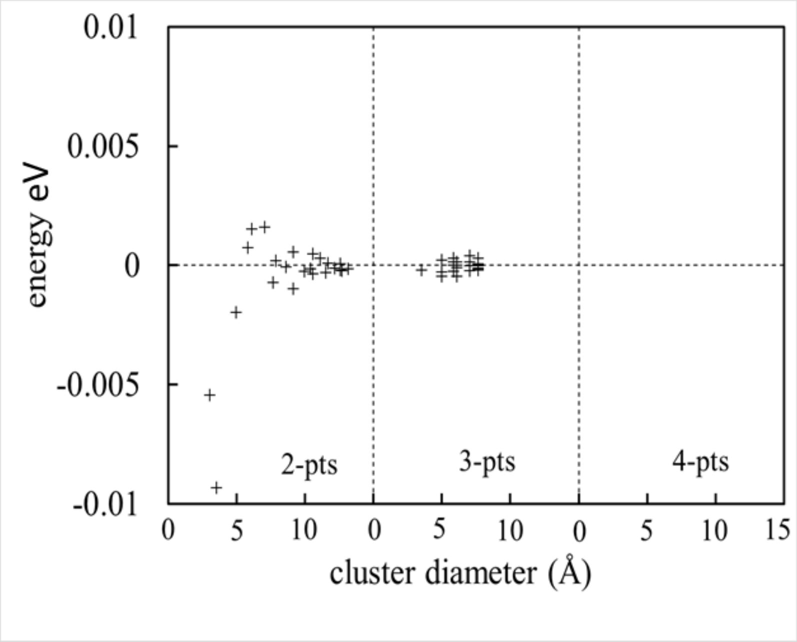


Figure 3-10 Comparison of enthalpies of formation (eV/atom) obtained from FP calculations and predicted with CE method of Nb-V bcc phase.



(a)



(b)

Figure 3-11 (a) Ground-state search for the cluster expansion of Nb-V bcc phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the as-calculated first principles energies

Table 3-4 Selected CECs for Nb-V bcc system

num of sites	multiplicity	CEC (eV)
0	1	0.060809
1	1	-0.002035
2	4	-0.005437
2	3	-0.009328
2	6	-0.001968
3	12	-0.000206

SQS results

Enthalpy of mixing for the Nb-V bcc solutions calculated from first-principles calculations are shown in Figure 3-12 along with earlier work of Jiang et al. (2009). It may be observed that the enthalpy of mixing calculated with fully relaxed SQS structures agrees with (C. Jiang 2009). No experimental data on these structures are available in the literature for comparison. The enthalpies of mixing calculated with SQS results are positive, which implies the bcc solid solution is unstable at low temperatures. This is consistent with the recent results of (J. Gao et al. 2018), which show a miscibility gap in the bcc phase.

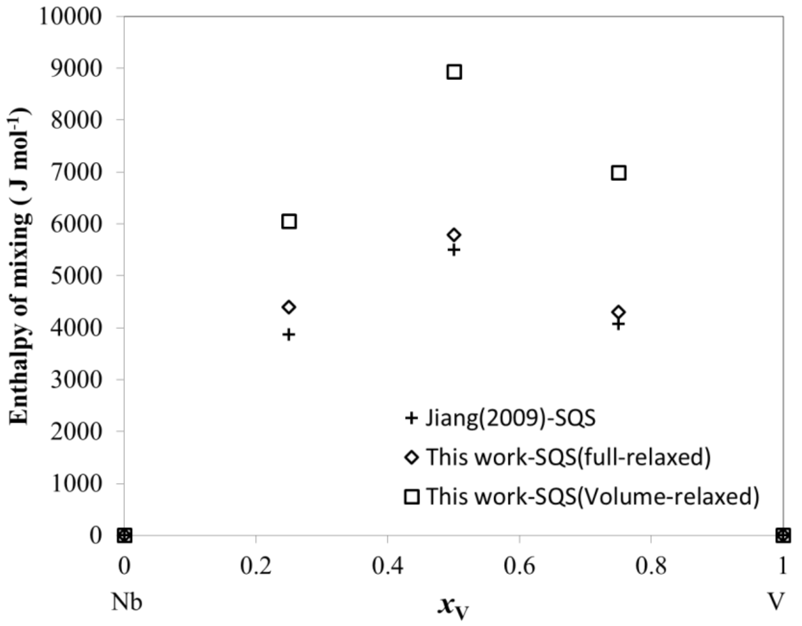


Figure 3-12 Calculated enthalpy of mixing for the bcc phase in the Nb-V system compared with a previous work

3.6 Nb-Zr System

CE results

The bcc_A2 structure is chosen for the Nb-Zr system to perform CE calculations as parent lattices. The comparison of the enthalpy of formation obtained from the DFT calculations and the CE method is shown in Figure 3-13. There is a good agreement between these two methods, as shown in the figure. The CV score of the present calculation is 0.008 and sufficiently small for the CE method. The convex hull of the calculated and fitted energies of the cluster expansion structures, shown in Figure 3-14(a), underscores the acceptable level of agreement between the two methods. The cluster expansion has predicted one ground state belonging to space group C2/m (12). The formation enthalpy of this ground-state is small, less than -16 meV/atom. Calculated CEC vs. cluster diameter plots is given in Figure 3-14(b). Values are three-point, and four-point CECs are smaller than pair CECs, and convergence of CECs can be readily observed. To analyze CECs, The CECs of the empty, the point, the first two nearest pairs, and the first triplet, which includes the nearest pair, are listed in Table 3-5. The CEC value of the empty cluster corresponds to the energy of the fully-disordered alloy. A large positive value of the fully-disordered alloy indicates its instability, which is consistent with positive values of mixing obtained from SQS calculation and the observed miscibility gap in the bcc phase. It may be noted from Table 3-5 Selected CECs for Nb-Zr bcc system that the CECs of the nearest and second nearest pair cluster for bcc are negative. This further indicated a tendency for phase separation in the bcc phase. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-14(a). The predicted mixing enthalpy from CE matches well with the SQS method (Figure 3-15).

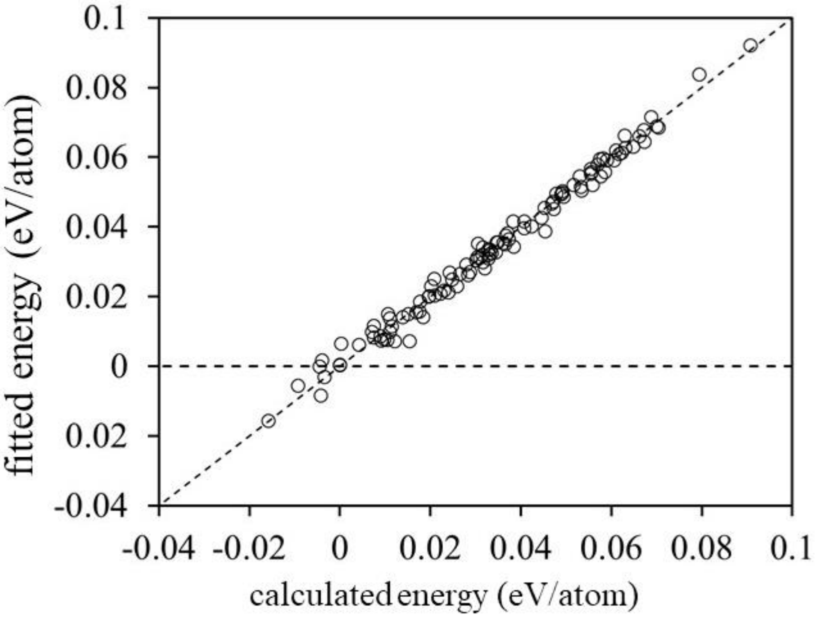
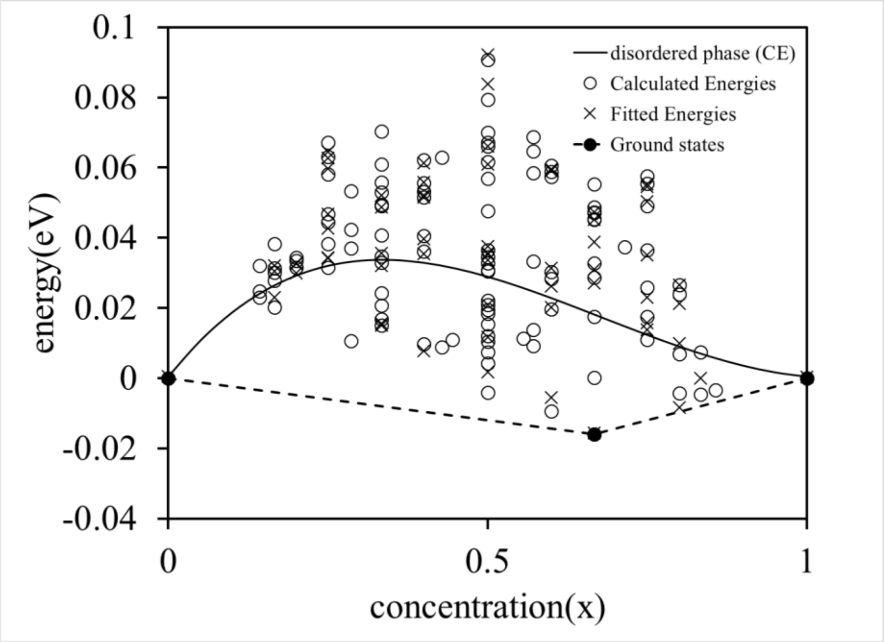
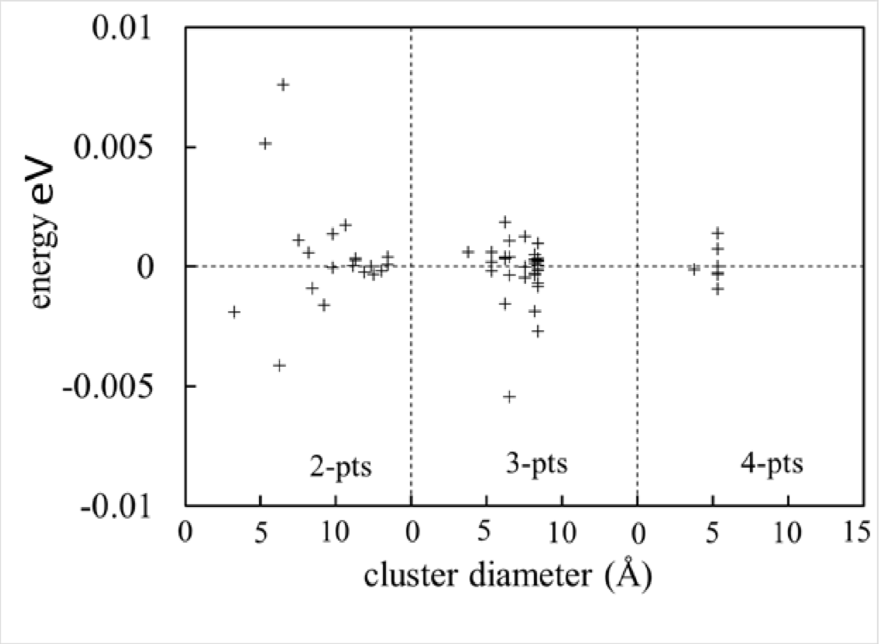


Figure 3-13 Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method in the Nb-Zr system.



(a)



(b)

Figure 3-14 (a) Ground-state search for the cluster expansion of Nb-Zr bcc_A2 phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the as calculated first principles energies

Table 3-5 Selected CECs for Nb-Zr bcc system

num of sites	multiplicity	CEC (eV)
0	1	0.028932
1	1	-0.026241
2	4	-0.001906
2	3	-0.010107
3	12	0.00061
4	6	-0.000116

SQS results

Nb and Zr form a continuous bcc_A2 solid solution with a miscibility gap appearing at low temperatures. Figure 3-15 shows the calculated enthalpies of mixing for random Nb-Zr bcc_A2 alloys using volume-relaxed and fully relaxed SQS structures. As expected, energies for the fully relaxed are found to be lower than volume relaxed structures. Values of relaxed SQS structures compare well with the work of Colinet (C. Colinet, Pasturel, and Hicter 1985), Lafaye et al. (Lafaye et al. 2019), and Zhao et al. (Y. Zhao, Li, and Huang 2021), except near the Zr end. Overall, the enthalpy of mixing is positive and indicates that Nb-Zr is a phase separating-type system. This is consistent with experimental findings where bcc_A2 shows a miscibility gap at lower temperatures. However, enthalpy of mixing for $x_{Zr} = 0.75$ is found to be negative. Zhao et al. (Y. Zhao, Li, and Huang 2021) have also reported similar results near the Zr end. Negative values near the Zr end may be attributed to the bcc Zr-Nb alloy being a dynamically unstable system.

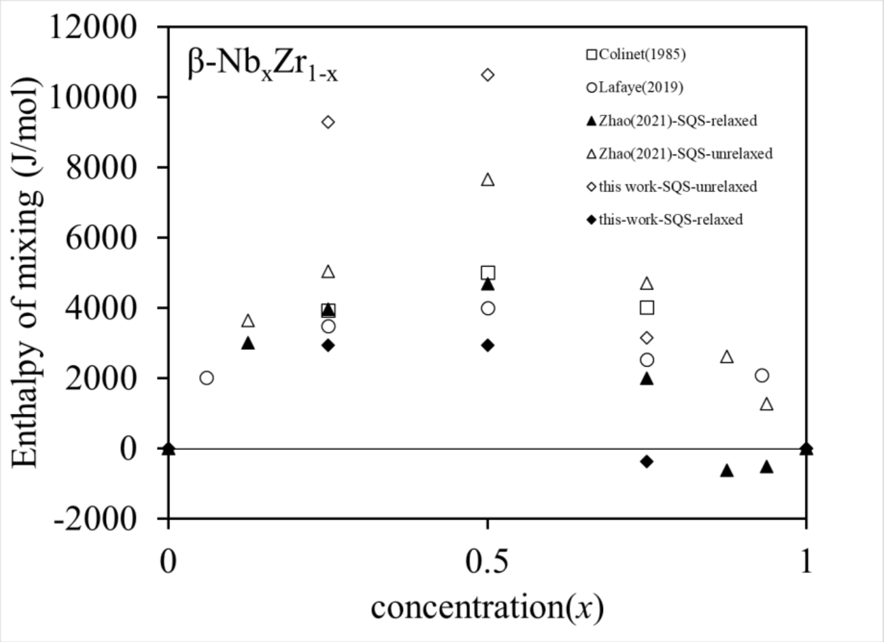


Figure 3-15 Calculated mixing enthalpies of the bcc_A2 solid solutions in the Nb-Zr system compared to data from the literature.

3.7 V-Zr System

CE results

For the V-Zr system, bcc lattices are chosen to perform CE calculations as parent lattices. Actual and predicted ground states agree well Among structures of known energy. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-16. The CV score of the present calculation is 0.018 and sufficiently small for the CE method. Figure 3-17(a) shows the calculated and fitted energy of the structures used in cluster expansion. These structures have a positive enthalpy of formation, suggesting no stable ordered phase with bcc-type symmetry in the V-Zr system. Calculated CEC vs. cluster diameter plots is given in Table 3-6(b).

Convergence of ECIs can be readily observed. The ECIs of the empty, the point, the first three nearest pairs, and the first triplet, which includes the nearest pair, are listed in Table 3-6. A large positive value of the fully-disordered alloy indicates its instability. This is in coincident positive values of mixing obtained from SQS calculation and observed miscibility gap in the bcc phase. It may be noted from Table 3-6 that the CECs of the nearest and second nearest pair cluster for bcc are negative. This further indicated a tendency for phase separation in the bcc phase. The energy of the disordered bcc phase at various compositions has been calculated using fitted CECs, and these results are shown in Figure 3-17(b). CEC values of the first triplet are very small compared to pair CECs suggesting a symmetric behavior of the formation energy. The symmetry of formation energy is reflected in the calculated formation energy plot of the disordered bcc phase Figure 3-17(b).

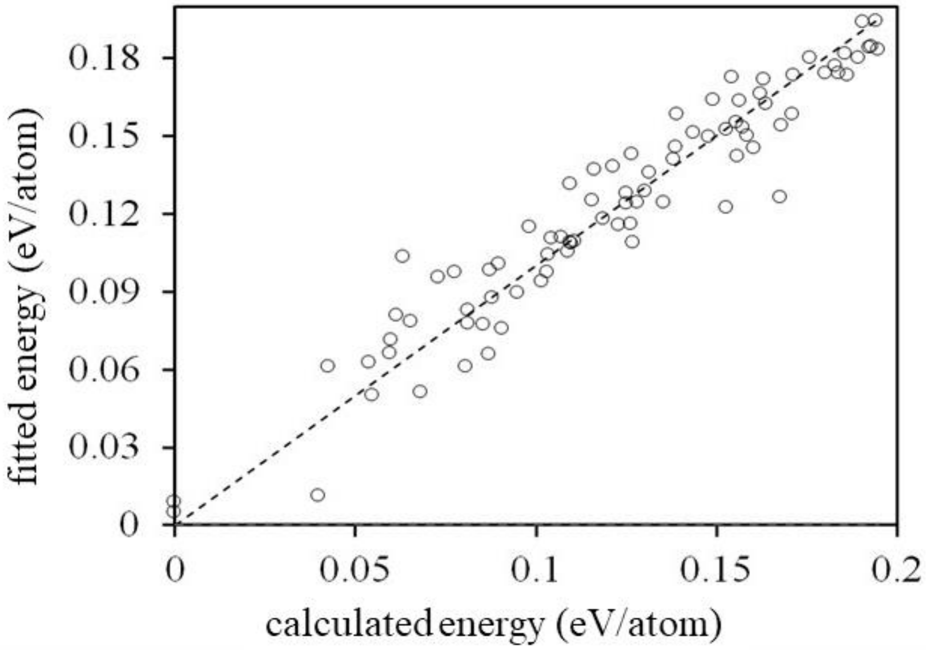
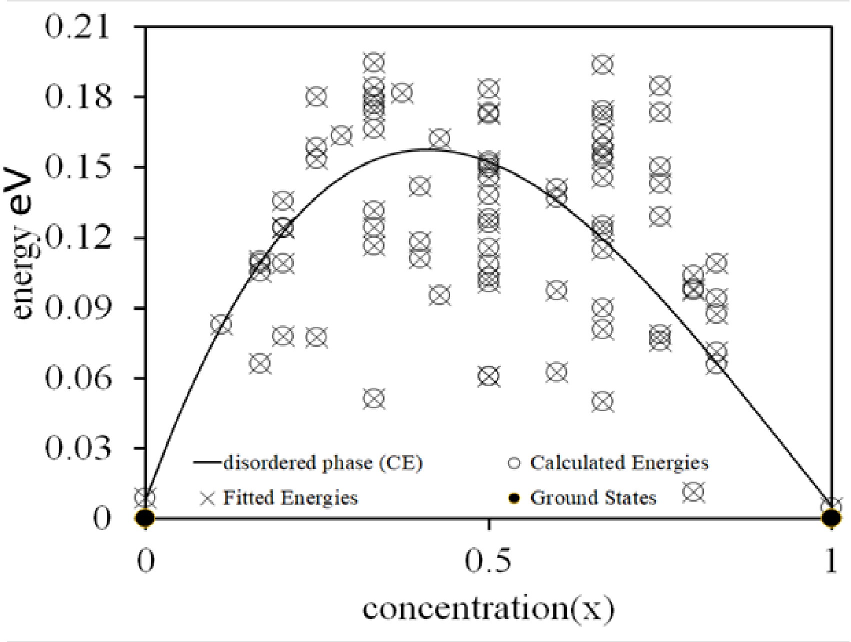


Figure 3-16 Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method.



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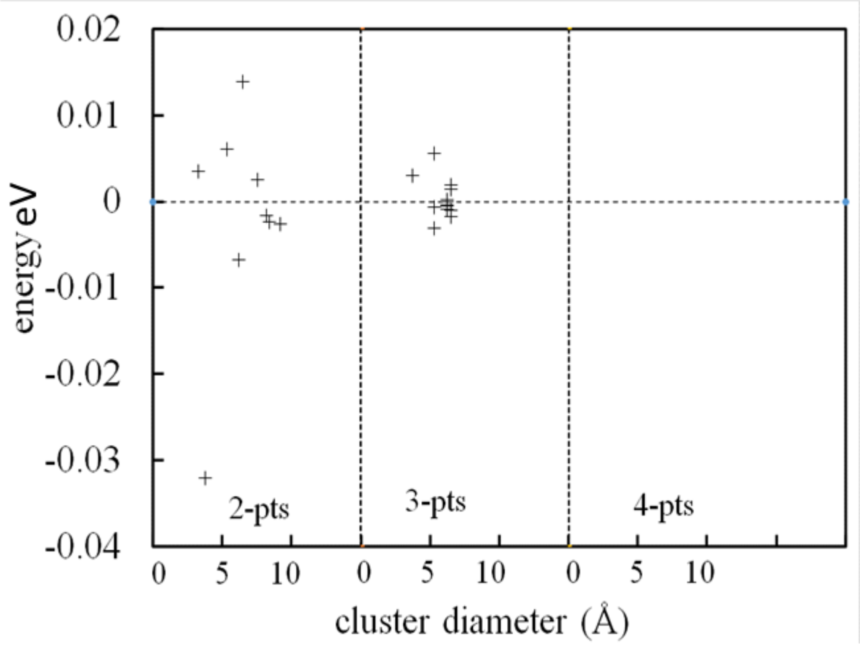


(b)

Figure 3-17 (a) Ground-state search for the cluster expansion of V-Zr bcc_A2 phases in (a) and (b) CEC vs. cluster diameter for a cluster expansion fit to the as calculated first principles energies

Table 3-6 Selected CECs for V-Zr bcc system

num of sites	multiplicity	CEC (eV)
0	1	0.152305
1	1	-0.056853
2	4	-0.003511
2	3	-0.0321
3	12	0.003001
3	12	0.000674

SQS results

The calculated enthalpies of mixing for random V-Zr bcc_A2 alloys using volume-relaxed and fully relaxed SQS structures is shown in Figure 3-18. As expected, energies for the fully relaxed are found to be lower than volume relaxed structures. Overall, the enthalpy of mixing is positive and indicates that V-Zr is a phase separating-type system.

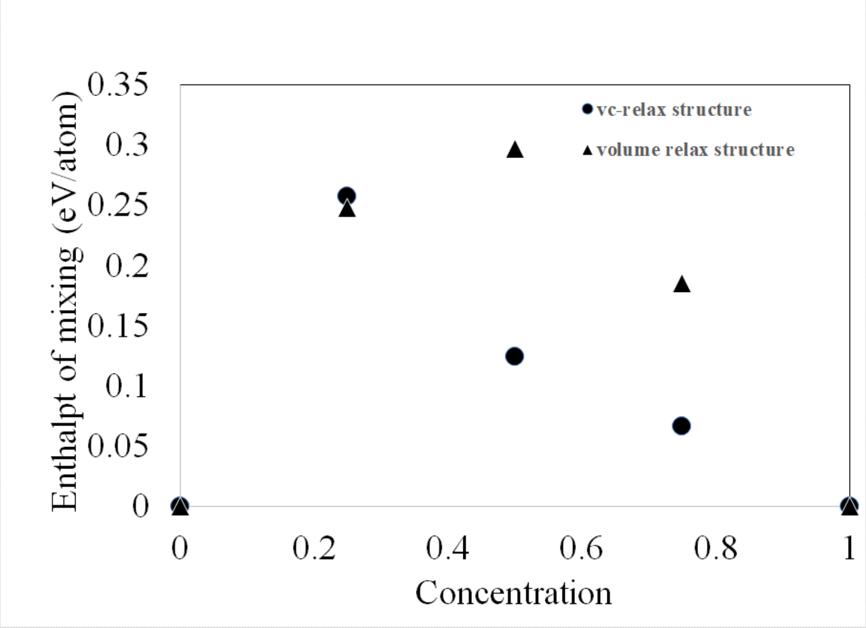


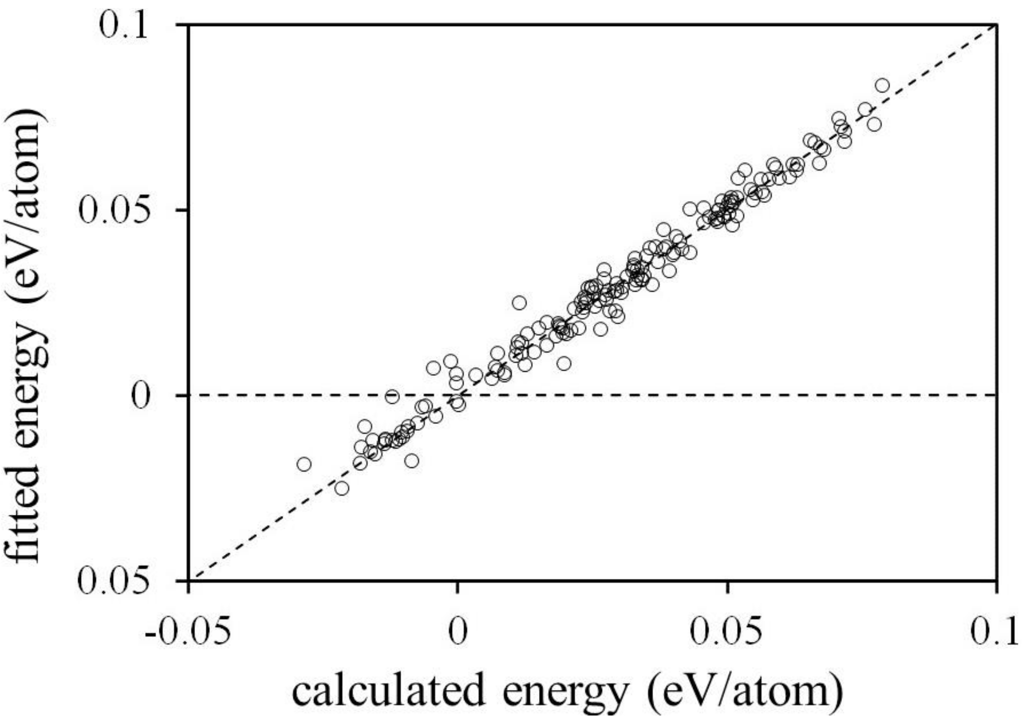
Figure 3-18 Calculated mixing enthalpies of the bcc_A2 solid solutions in the V-Zr system compared to data from volume relax and full relax structure.

3.8 Nb-Ti-V System

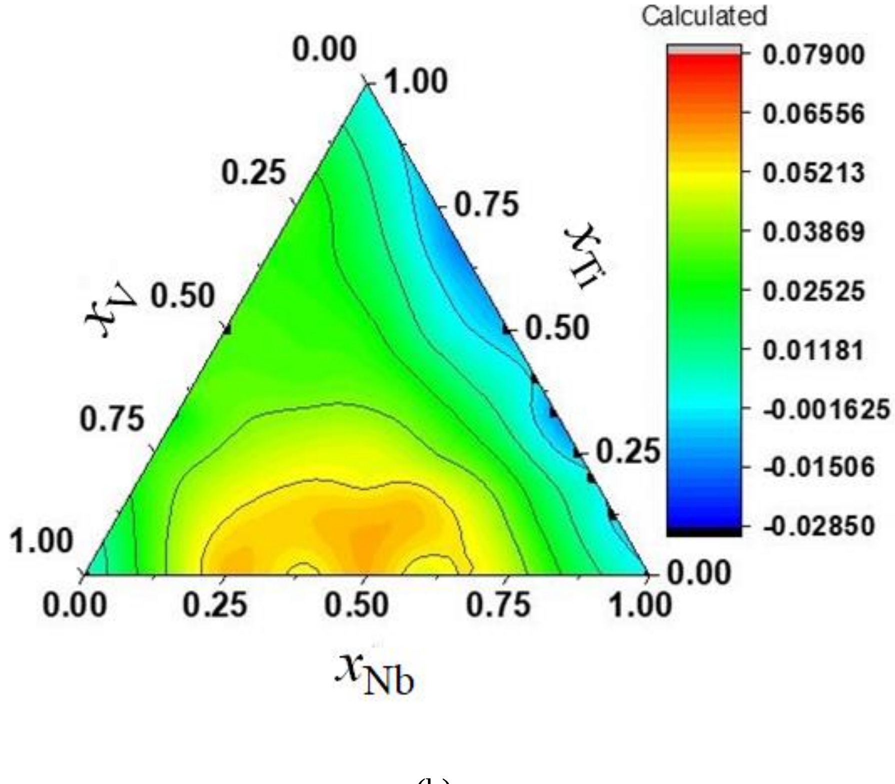
CE results

For the Nb-Ti-V system, CE calculations were performed for the bcc lattice. A total of 166 structures were generated by ATAT software with a maximum of 10 atoms. The CV score was 0.005 eV. Only one structure was removed from the list of structures using the strain criteria. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-19 (a). Figure 3-19 (b and c, respectively) shows a contour plot of calculated and fitted energy after expansion. The calculated and fitted energy agrees well. A total of twelve ground-state structures, including nine ordered structures, were found in the ground-state search. Among structures of known energy, actual and predicted ground states agree well (Figure 3-19). The stability of the Nb-Ti binary end increases with adding V, whereas it decreases for the Ti-V system with the addition of Nb.

The ground state structures of the Nb-Ti system increase from 5 to 6, whereas for Ti-V system decreases from 2 to 1. The Nb-V system remains phase-separating. The enthalpy value of Ti-V in the binary system is negative, whereas Nb addition changes the value from negative to positive in Nb-Ti-V. Figure 3-19(d) shows calculated CEC vs. cluster diameter plots. Convergence of CECs can be observed. The CEC value of the empty cluster corresponds to the energy of the fully-disordered alloy. A positive value of the fully-disordered alloy indicates a phase separation tendency in the bcc solution phase. A list of CECs is given in Table 3-7 Only an 18-pair cluster up to the 5th neighbor is used in the cluster expansion of this system.


0.1
0.05
0
0.05
fitted energy (eV/atom)
-0.05
0
0.05
0.1
calculated energy (eV/atom)

(a)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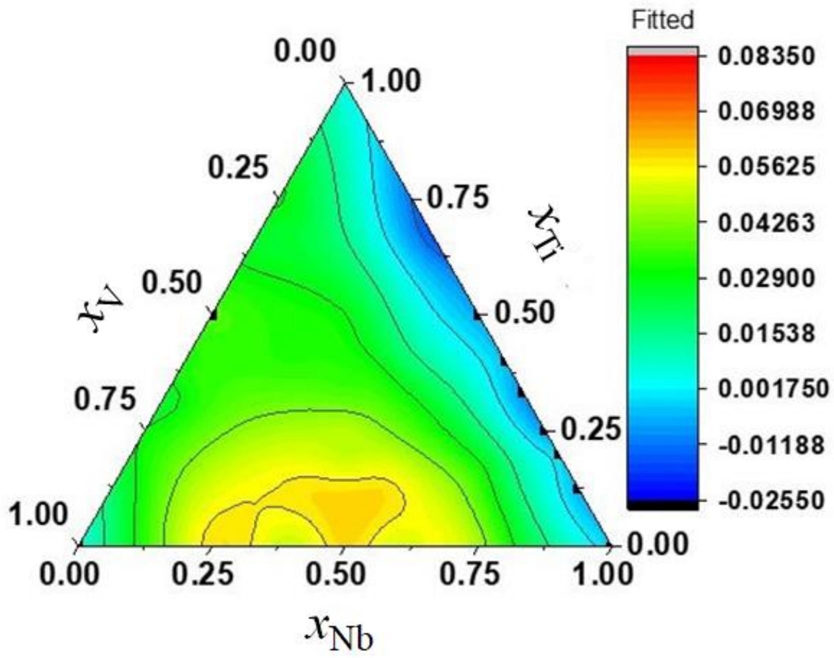
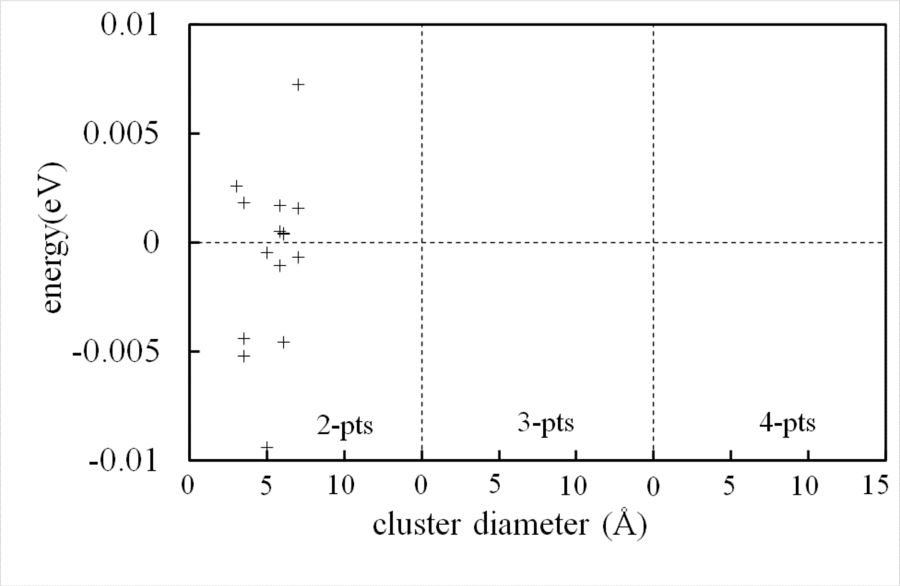
0.05213
0.03869
0.02525
0.01181
-0.001625
-0.01506
-0.02850
0.00
1.00
0.25
0.75
x_V
0.50
0.50
x_{Ti}
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
x_{Nb}

(b)



(c)



(d)

Figure 3-19 (a) Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method (b) The contour plot calculated and (c)fitted Nb-Ti-V β-phase alloys obtained using cluster expansion method. (d) CEC vs. cluster diameter for a cluster expansion fit the as-calculated first principles energies.

Table 3-7 Selected CECs for Nb-Ti-V bcc system

num of sites	distance	multiplicity	CEC (eV)
0		1	0.029863
1		1	0.002567
1		1	0.061879
2	3.045	4	-0.00522
2	3.045	8	-0.00443
2	3.045	4	0.001809
2	3.516063	3	-0.00045
2	3.516063	6	-0.01309
2	3.516063	3	-0.00943

SQS results

The Enthalpy of mixing for the Nb-Ti-V bcc solutions calculated from first-principles calculations are shown in Figure 3-20. The enthalpies of mixing calculated with SQS results are positive, except near the Ti end, which implies the instability of the bcc solid solution. The SQS result of binary ends is similar to these systems' binary SQS. The value of the SQS result at equiatomic composition is similar to the empty cluster value of the cluster expansion result, suggesting good agreement between results obtained from CE and SQS.

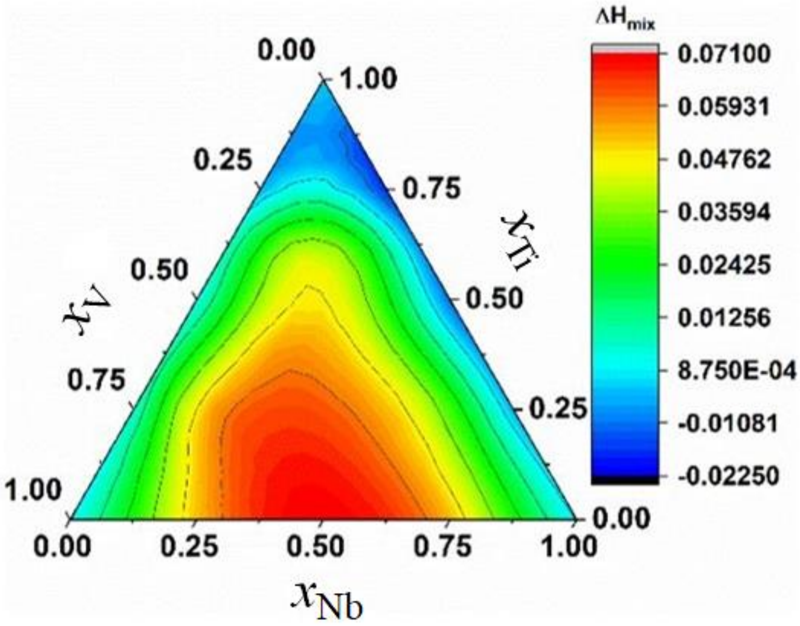


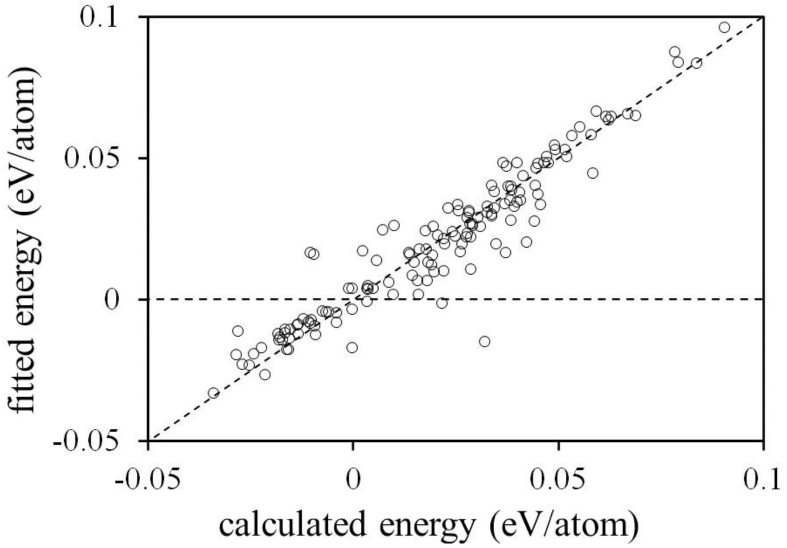
Figure 3-20 Calculated enthalpy of mixing using fully random SQS structure for the bcc phase in the Nb-Ti-V system

3.9 Nb-Ti-Zr System

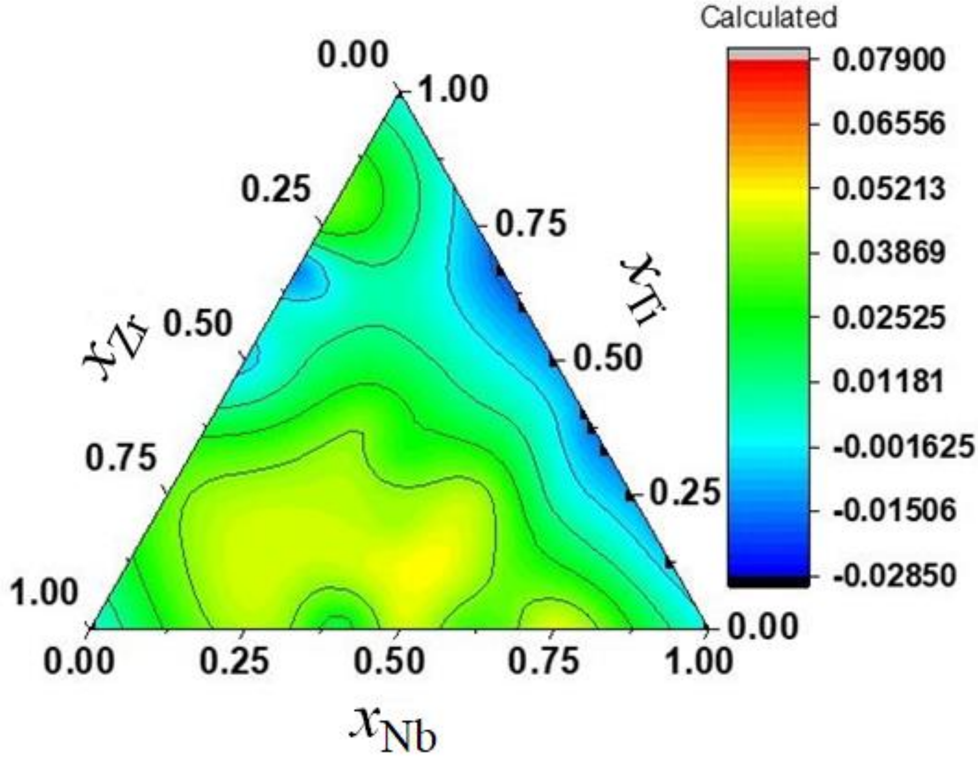
CE results

CE calculations were performed for the bcc lattices to the Nb-Ti-Zr system. A total of 155 structures with a maximum of 10 atoms considered for CE. The CV score was 0.014 eV. Twelve structures having a strain of more than 0.1 were removed from the list of structures. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-21(a). There is a good agreement between these two methods. Figure 3-21 (b and c, respectively) shows a contour plot of calculated and fitted energy after expansion. The calculated and fitted energy agrees well. Among structures of known energy, actual and predicted ground states agree well. A total of eleven ground-state structures, including eight ordered structures, were found in the ground-state search.

The addition of Zr in the Nb-Ti system increases the mixing enthalpy of the system to a positive value. The Nb-Zr system has a negative value of enthalpy of mixing, whereas the addition of Ti changes values from negative to positive. Calculated ECI vs. cluster diameter plots is given in Figure 3-21(d). Convergence of ECIs can be observed. A total of 24 pair clusters with a distance of the 8th nearest neighbor are considered in the CE. The ECIs of the empty, the point, the first three nearest pairs, and the second three nearest pairs are listed in Table 3-8 . A positive value of the fully-disordered alloy indicates a phase-separating tendency in the bcc solution phase.



(a)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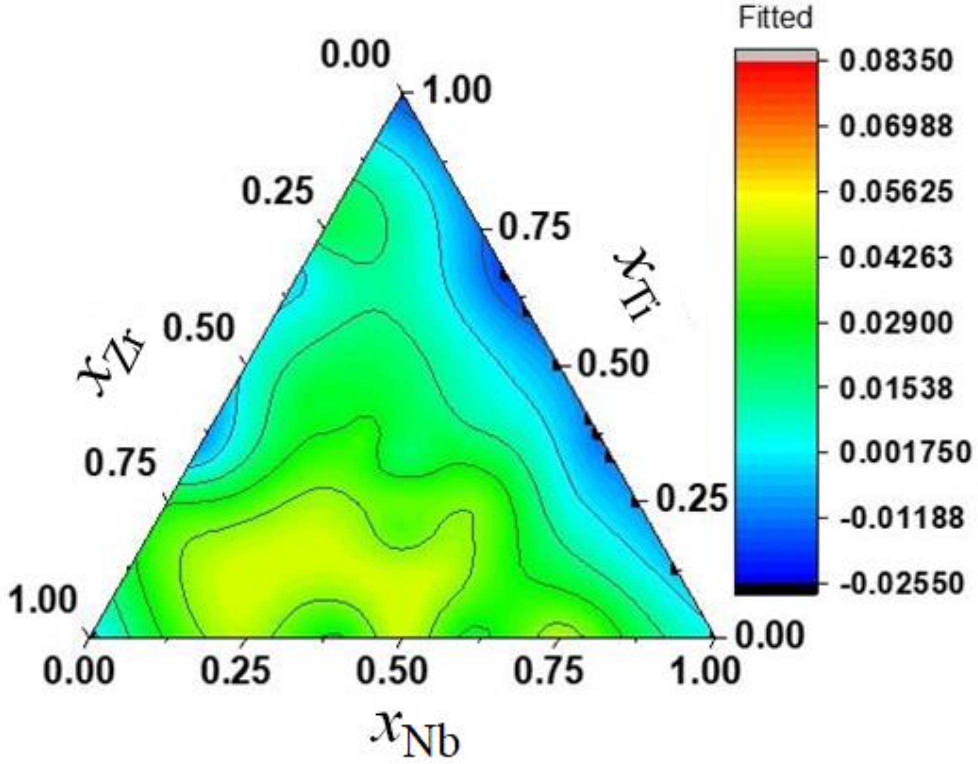
0.06556
0.05213
0.03869
0.02525
0.01181
-0.001625
-0.01506
-0.02850
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_{Ti}
x_{Nb}

(b)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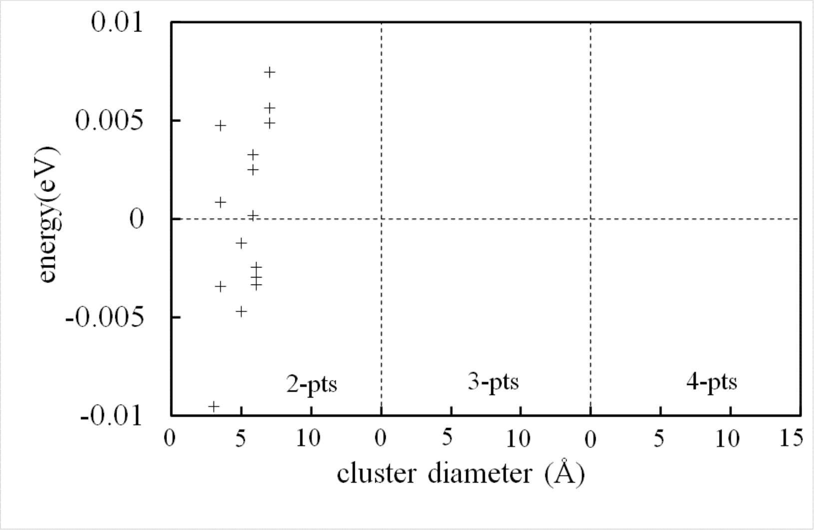
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_{Ti}
x_{Nb}

(c)



(d)

Figure 3-21 (a) Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method (b and c) Ground-state search for the cluster expansion of Nb-Ti-Zr bcc phases. (d) CEC vs. cluster diameter for a cluster expansion fitted to the calculated first principles energies.

Table 3-8 Selected CECs for Nb-Ti-Zr bcc system.

num of sites	distance	multiplicity	CEC (eV)
0		1	0.014542
1		1	-0.009534
1		1	0.044641
2	3.255	4	-0.003424
2	3.255	8	0.000852
2	3.255	4	0.004753
2	3.75855	3	-0.004723
2	3.75855	6	-0.010699
2	3.75855	3	-0.001237

SQS results

The Enthalpy of mixing for the Nb-Ti-Zr bcc solutions calculated from first-principles calculations are shown in Figure 3-22. The enthalpies of mixing calculated with SQS results are positive, implying the bcc solid solution is unstable at higher temperatures. SQS results suggest the addition of Nb in Ti-Zr stabilizes the bcc phase at higher temperatures. The result from CE and SQS agrees well at equiatomic composition, with the empty cluster showing a positive value.

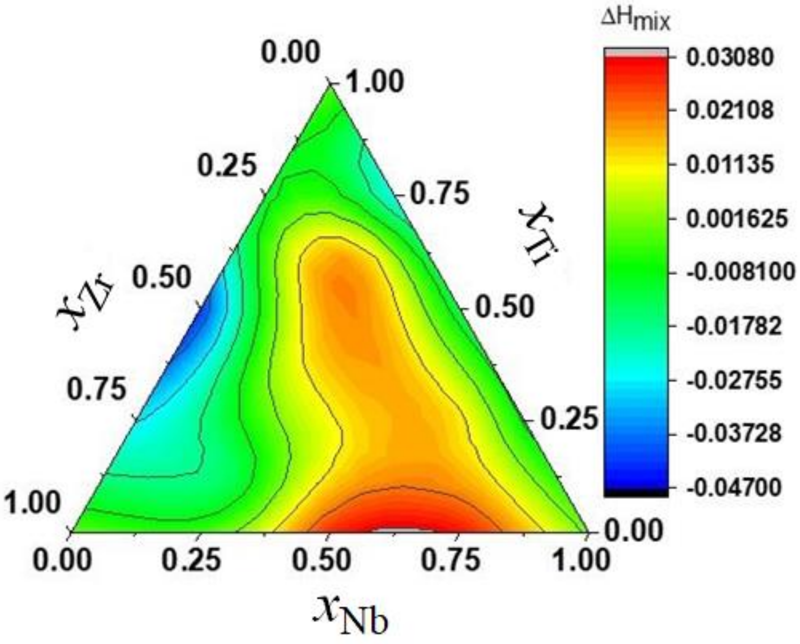


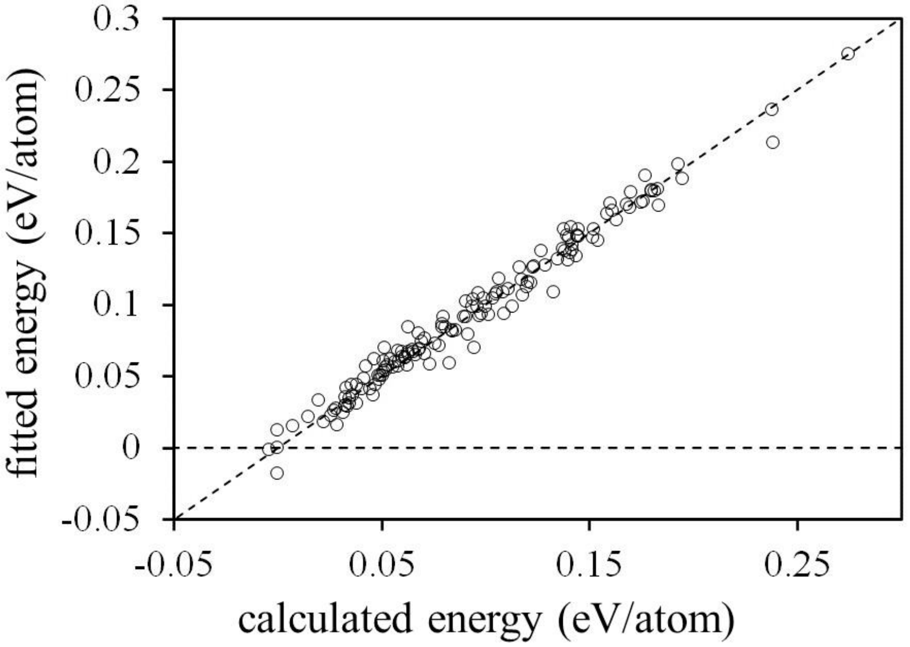
Figure 3-22 Calculated enthalpy of mixing for the bcc phase in the Nb-Ti-Zr system.

3.10 Nb-V-Zr System

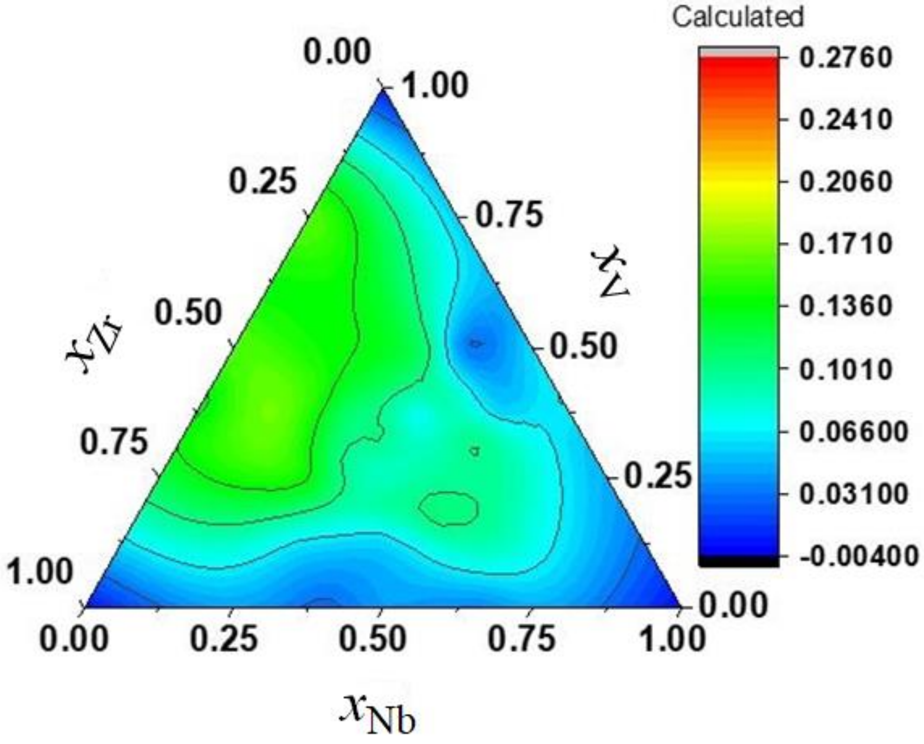
CE results

For the Nb-V-Zr system, 146 structures were generated with a maximum of 10 atoms on the bcc space lattice. The CV score was 0.012 eV. Two structures were removed from the list of structures using the strain criteria. Among structures of known energy, actual and predicted ground states agree well. The comparison of the enthalpy of formation obtained from the FP calculations and the CE method is shown in Figure 3-23(a). Figure

3-23 (b and c) shows a contour plot of calculated and fitted energy after expansion. The calculated and fitted energy agrees well. No ground state was observed in Nb-V and V-Zr in the binary system, whereas Nb-Zr has one ground state in the binary system. In the Nb-V-Zr system, no ground state is observed in the Nb-V and V-Zr binary sides, but the Nb-Zr ground state disappears in the ternary system. The addition of Nb in the V-Zr system decreases the mixing enthalpy of the system to a negative value. Calculated CEC vs. cluster diameter plots is given in Figure 3-23(c). Thirty-nine pair clusters with up to the 12th neighbor distance were considered in the CE process. Convergence of CECs can be observed. The CECs of the empty, the point, and the first six nearest pairs, are listed in Table 3-9 A positive value of the fully-disordered alloy indicates a phase-separating tendency in the bcc solution phase.



(a)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0.1710
0.1360
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0.03100
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0.00
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
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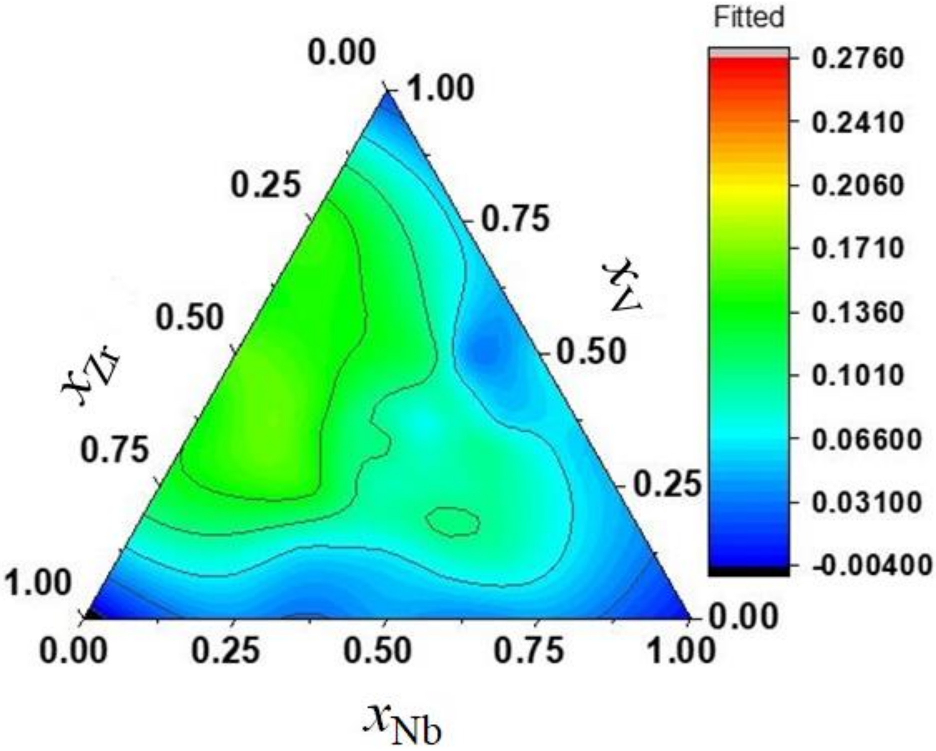
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Nb}

(b)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0.2060
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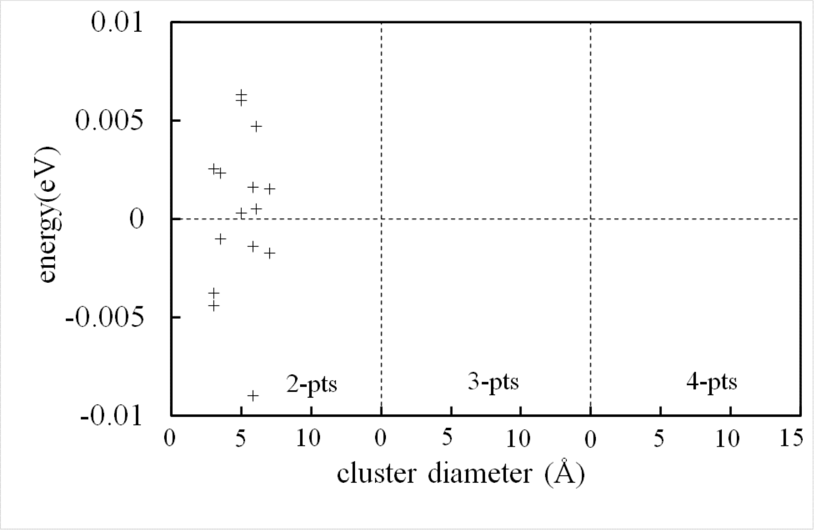
0.1010
0.06600
0.03100
-0.00400
0.00
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Nb}

(c)



(d)

Figure 3-23 (a) Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method (b and c) Ground-state search for the cluster expansion of Nb-V-Zr bcc phases. (d) CEC vs. cluster diameter for a cluster expansion fit the calculated first principles energies.

Table 3-9 Selected CECs for Nb-V-Zr bcc system.

num of sites	distance	multiplicity	CEC (eV)
0		1	0.104245
1		1	0.082202
1		1	-0.029475
2	3.255	4	-0.004411
2	3.255	8	0.002547
2	3.255	4	-0.003760
2	3.75855	3	0.002340
2	3.75855	6	-0.001005
2	3.75855	3	-0.045343

SQS results

The Enthalpy of mixing for the Nb-V-Zr bcc solutions is shown in Figure 3-24. Adding Nb in the V-Zr system decreases the enthalpy of mixing. This result is similar to the result obtained from cluster expansion. At the equiatomic composition, the SQS has a maximum value of mixing enthalpy. In cluster expansion, the maximum value is close to equiatomic composition.

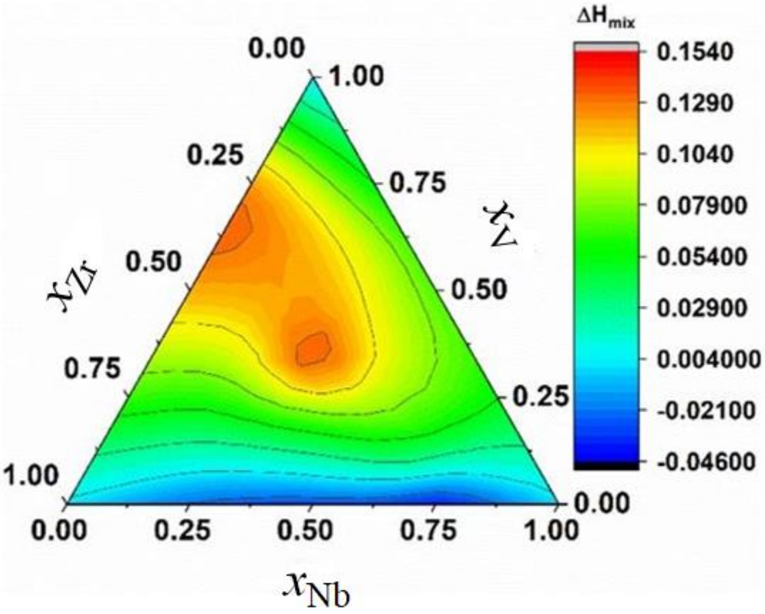
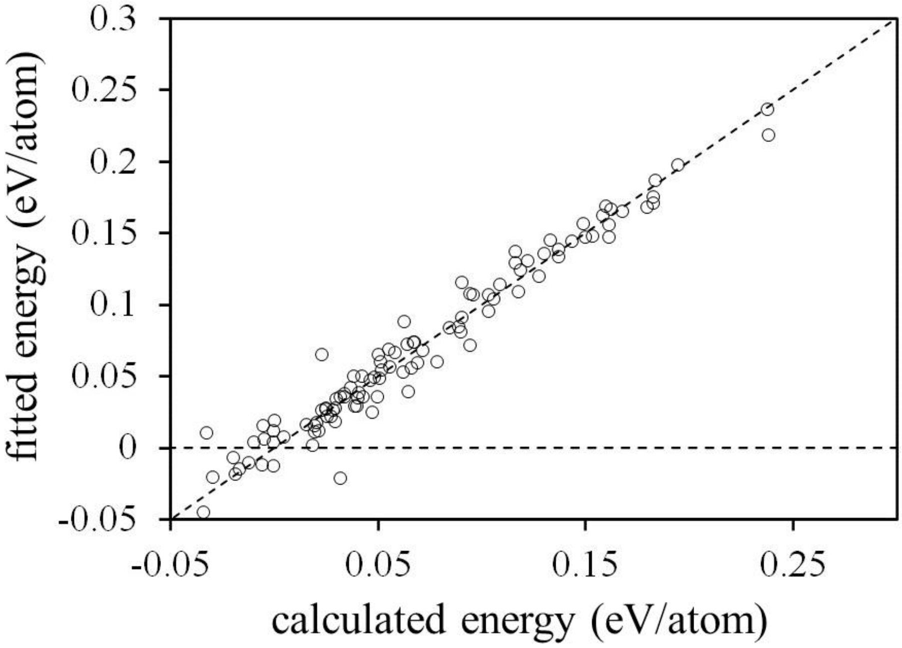


Figure 3-24 Calculated enthalpy of mixing for the bcc phase SQS in the Nb-V-Zr system.

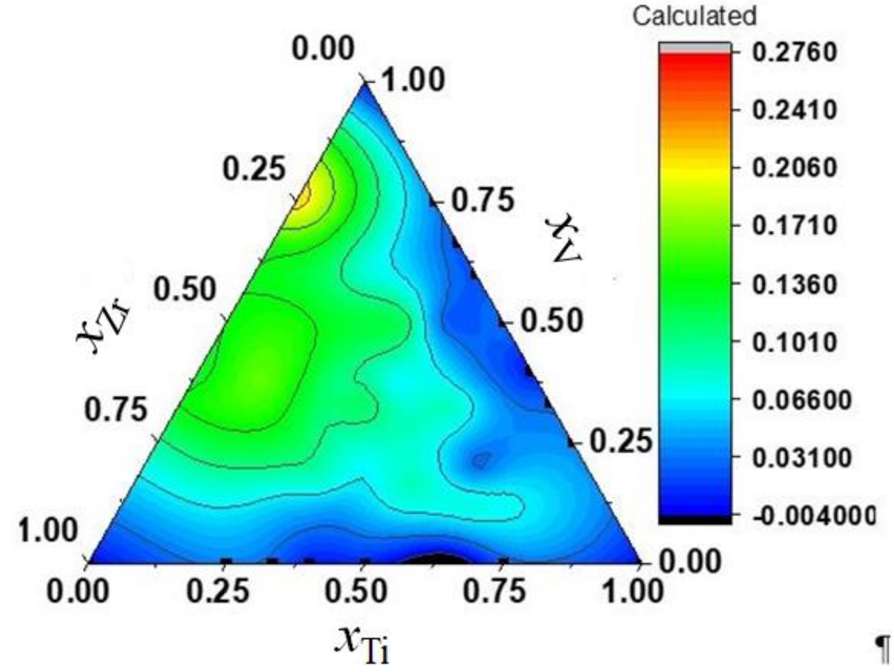
3.11 Ti-V-Zr System

CE results

For the Ti- V-Zr system. one hundred fifty-one structures were generated with a maximum of 10 atoms to perform CE calculation. The CV score was 0.02 eV. Forty-six structures were removed from the list of structures using the strain criteria. Among structures of known energy, actual and predicted ground states agree well. There is a good agreement between these two methods, as shown in Figure 3-25(a). Figure 3-25 (b and c, respectively) shows a contour plot of calculated and fitted energy after expansion. The calculated and fitted energy agrees well. The binary Ti-Zr end has five ground states, and Ti-V has seven. The number of ground states increased in both binary ends. The addition of Zr in the Ti-V system increases the mixing enthalpy of the system to a positive value. Calculated CEC vs. cluster diameter plots is given in Figure 3-25 (d). Convergence of CECs can be observed. The CECs of the empty, the point, and the six-two nearest pairs, which include the nearest pair, are listed in Table 3-10. A total of 27 pairs of clusters were considered in the CE. The clusters of up to 6th neighbors are considered in the CE process. A positive value of the fully-disordered alloy indicates a phase-separating tendency in the bcc solution phase. This coincides with positive mixing values obtained from SQS calculation, especially at the Zr end. The addition of Ti in the V-Zr system decreases the mixing enthalpy.



(a)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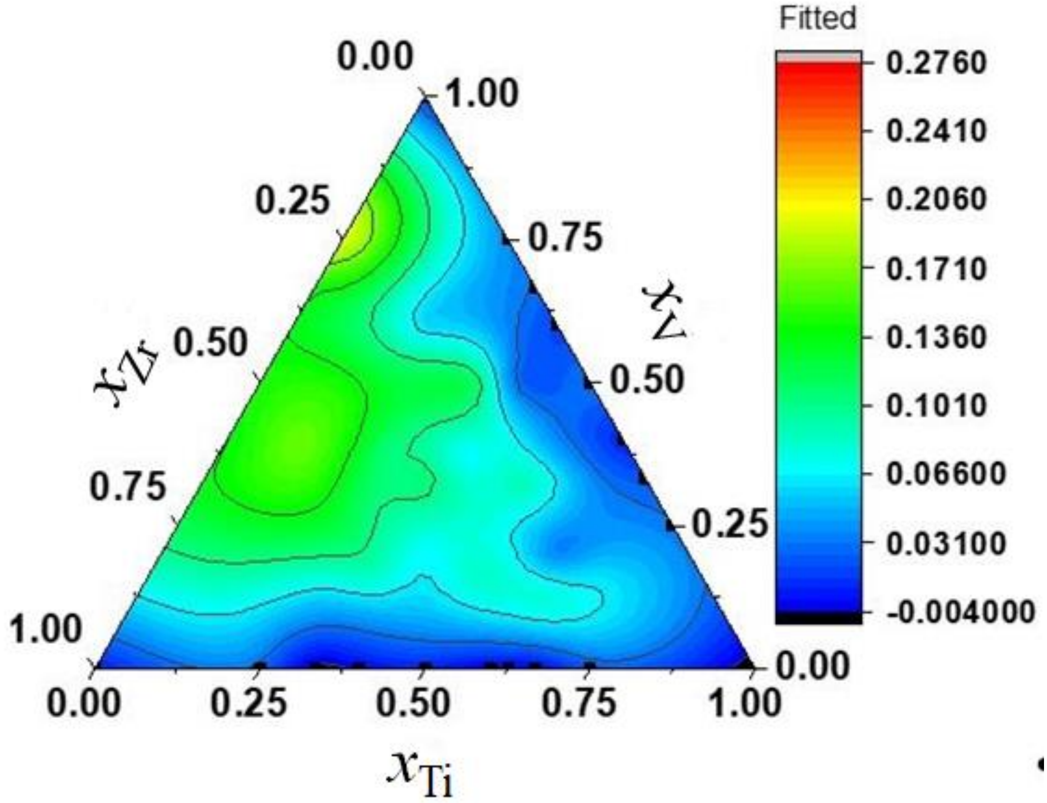
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Ti}
¶

(b)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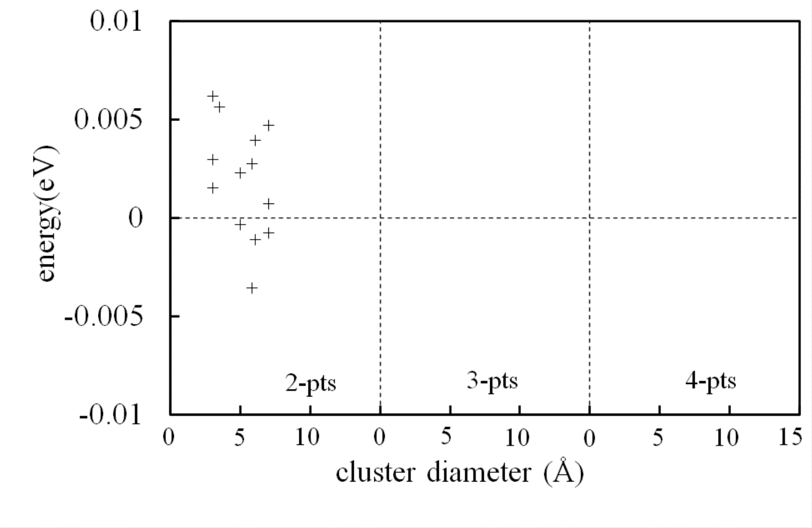
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Ti}

(c)



(d)

Figure 3-25 (a) Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method (b and c) Ground-state search for the cluster expansion of Ti-V-Zr bcc phases (d) CEC vs. cluster diameter for a cluster expansion fit to the calculated first principles energies.

Table 3-10 Selected ECIs for Ti-V-Zr bcc system.

num of sites	distance	multiplicity	CEC (eV)
0		1	0.084855
1		1	0.129393
1		1	-0.027046
2	3.255	4	0.002963
2	3.255	8	0.001536
2	3.255	4	0.006180
2	3.75855	3	0.005648
2	3.75855	6	0.011803
2	3.75855	3	-0.056435

SQS results

The Enthalpy of mixing for the Ti-V-Zr bcc solutions calculated from first-principles calculations are shown in Figure 3-26. The enthalpies of mixing calculated with SQS results are positive, which implies the bcc solid solution is unstable at low temperatures. The value of CE empty cluster and SQS equiatomic composition is similar.

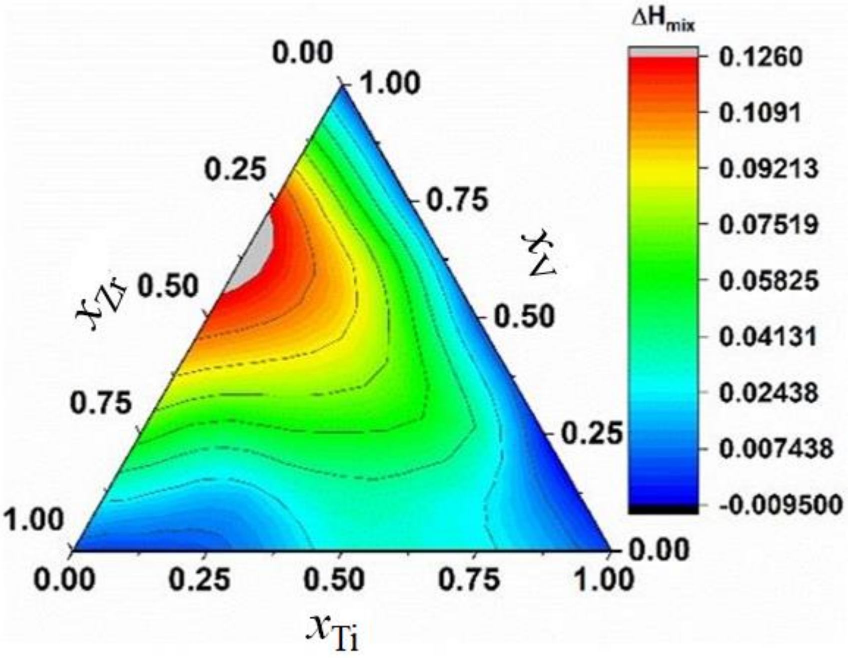
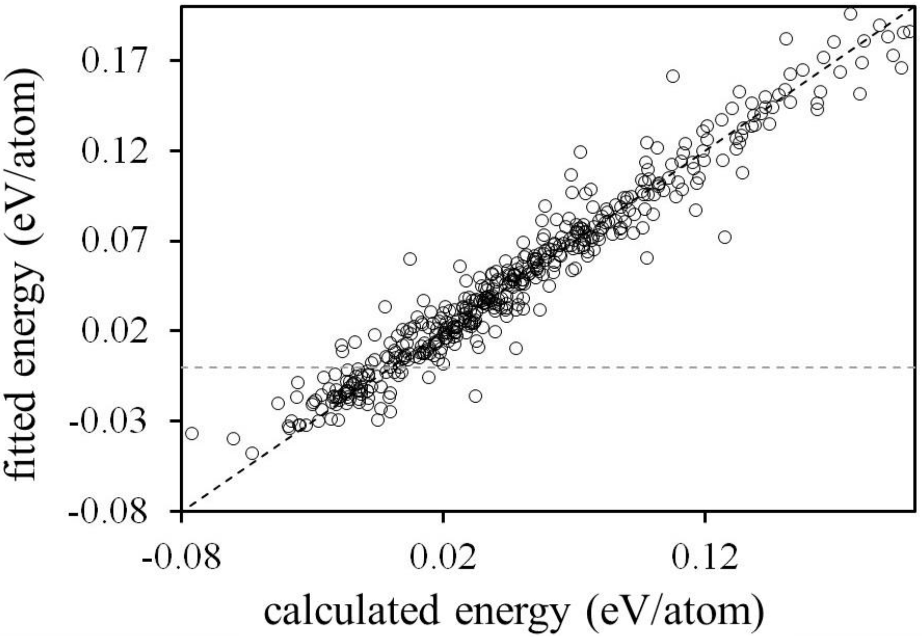


Figure 3-26 Calculated enthalpy of mixing for the bcc phase in the Nb-V-Zr system

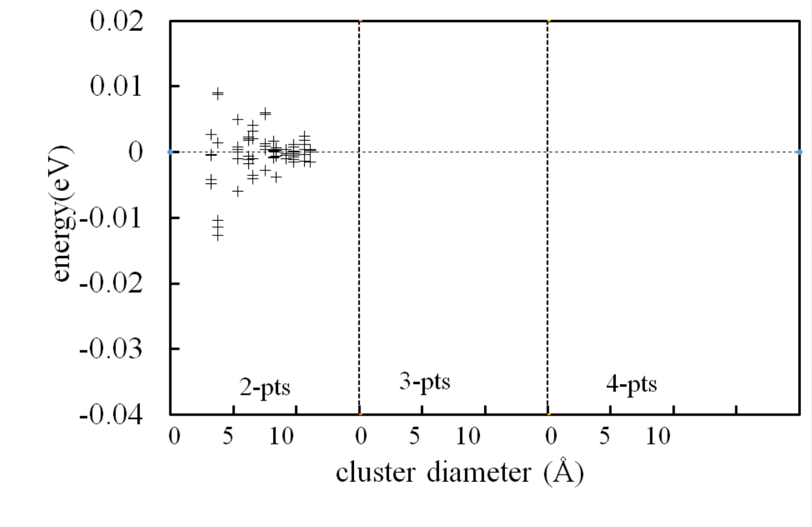
3.12 Nb-Ti-V-Zr system

CE results

For the Nb-Ti-V-Zr system, CE calculations were performed for the bcc lattices. Among structures of known energy, actual and predicted ground states agree well. The comparison of the enthalpy of formation was obtained from the FP calculations and the CE method. There is a good agreement between these two methods, as shown in Figure 3-27(a) A total of seventeen ground-state structures shown in Table 3-12, including thirteen ordered structures, were found in the ground-state search. The cluster expansion model predicts no ternary or quaternary ground state. Calculated CEC vs. cluster diameter plots is given in Figure 3-27(b). Convergence of ECIs can be observed. The ECIs of the empty, the point, and the first twelve nearest pairs, which include the nearest pair, are listed in Table 3-11. No triangle and tetrahedron clusters were obtained in these calculations. The CEC value of the empty cluster corresponds to the energy of the fully-disordered alloy. A positive value of the fully-disordered alloy indicates a phase-separating tendency in the bcc solution phase. This is coincident with negative values of mixing obtained from SQS calculation. These calculations are compared with SQS calculations.



(a)



(b)

Figure 3-27 (a) Comparison of enthalpies of formation (eV/atom) obtained from first principle calculations and predicted with the CE method (b) CEC vs. cluster diameter for a cluster expansion fit to the as calculated first principles energies

Table 3-11 Selected ECIs for Nb-Ti-V-Zr bcc system

num of sites	distance	multiplicity	CEC (eV/atom)
0		1	0.063177
1		1	0.081630
1		1	0.081613
1		1	-0.049619
2	3.255	4	-0.00413
2	3.255	8	0.002756
2	3.255	8	-0.00037
2	3.255	4	-0.00476

2	3.255	8	-0.00043
2	3.255	4	0.001386
2	3.75855	3	-0.01264
2	3.75855	6	0.008996
2	3.75855	6	0.008829
2	3.75855	3	-0.01038
2	3.75855	6	-0.01136
2	3.75855	3	-0.00589

Table 3-12 Ground state structures obtained in the Nb-Ti-V-Zr system.

Nb	Ti	V	Zr	Calculated energy	fitted energy	
1	0	0	0	0	-0.000379	0.000379
0	0	1	0	0	0.012705	-0.01271
0.666667	0.333333	0	0	-0.029616	-0.021334	-0.00828
0	0.8	0	0.2	-0.08593	-0.040132	-0.0458
0	0.714286	0.285714	0	-0.035252	-0.009223	-0.02603
0.333333	0.666667	0	0	-0.026065	-0.024398	-0.00167
0	1	0	0	0	-0.025268	0.025268
0	0.666667	0	0.333333	-0.075615	-0.037106	-0.03851
0.5	0	0	0.5	-0.010381	-0.006368	-0.00401
0	0.4	0	0.6	-0.052552	-0.048066	-0.00449
0.2	0	0	0.8	-0.010868	-0.011621	0.000752
0.142857	0	0	0.857143	-0.008471	-0.005198	-0.00327
0	0	0	1	0	-0.01495	0.01495

SQS Results

The Enthalpy of mixing for the Nb-Ti-V-Zr bcc solutions calculated from first-principles calculations are shown in Table 3-13. The enthalpies of mixing calculated with SQS results are positive. A similar result has been reported by Nataraj et al.(Nataraj, van de Walle, and Samanta 2021) at 2000K.

Table 3-13 Calculated enthalpy of mixing for the bcc phase in the Nb-Ti-V-Zr system

composition				Mixing Enthalpy (eV/atom)
Nb	Ti	V	Zr	
0.375	0.375	0.125	0.125	0.051422
0.375	0.125	0.375	0.125	0.093271
0.125	0.375	0.375	0.125	0.08021
0.125	0.375	0.125	0.375	0.064902
0.375	0.125	0.125	0.375	0.074929
0.25	0.25	0.25	0.25	0.089117
0.125	0.125	0.375	0.375	0.125388

Comparative study of CECs of the binary ternary and quaternary system

CECs are indicators of good cluster expansion. The value of CEC also predicts interaction among elements. The behavior of CEC changes with the addition of elements. The first and second neighbor CECs related Nb-Ti pair clusters are (-0.002632, 0.00339) in the Nb-Ti system, (-0.00522, -0.00045) in the Nb-Ti-V system, (-0.003424, -0.004723) in Nb-Ti-Zr system and (-0.00413, -0.01264) in Nb-Ti-V-Zr system. The nature of the second neighbor changed from positive to negative by adding elements like V and Zr in the Nb-Ti system. In contrast, the value of the first neighbor is decreased with the addition of elements and V addition, making the CEC more negative. The first and second neighbor CECs of Nb-V pair clusters are (-0.005437, -0.009328) whereas (-0.00443, -0.01309) in the Nb-Ti-V system, (-0.004411, 0.002340) in Nb-V-Zr system and (0.002756, 0.008996) in Nb-Ti-V-Zr system. With the addition of Zr, the second neighbor pair becomes positive in the Nb-V-Zr system compared to the Nb-V system. In the quaternary system Nb-Ti-V-Zr, both first and second neighbor CECs become positive. The first and second neighbor CECs of Nb-Zr pair clusters are (-0.001906, -0.010107) whereas (0.000852, -0.010699) in the Nb-Ti-Zr system, (0.002547, -0.001005,) in Nb-V-Zr system and (-0.00037, 0.008829) in Nb-Ti-V-Zr system. The addition of Zr reverts the sign of the second neighbor pair in the Nb-V-Zr system, whereas the Ti addition reverts the sign of the first neighbor in the Nb-Ti-Zr system. The combined effect of Ti and V addition can be seen in the Nb-Ti-V-Zr system with sign reversal of the second neighbor pair and an increase in energy of the first neighbor pair. The first and second neighbor CECs of Ti-V pair clusters are (-0.003893, -0.012711) whereas (0.001809, -0.00943) in the Nb-Ti-V system, (0.002963, 0.005648,) in Ti-V-Zr system and (-0.00476, -0.01038) in Nb-Ti-V-Zr system. The addition of Nb in the Ti-V system changes the nature of the first neighbor from negative to positive. In contrast, Zr addition has an insignificant effect on CECs energies. The addition of Nb and Zr in the Nb-Ti-V-Zr system keeps the sign unchanged of both the first and second neighbor pair and energies are also slightly changed. The first and second neighbor CECs of Ti-Zr pair clusters are (-0.006044, 0.006127) whereas (0.004753, -0.001237) in the Nb-Ti-Zr system, (0.001536, 0.011803) in Ti-V-Zr system and (-0.00043, -0.01136) in Nb-Ti-V-Zr system. The addition of Nb reverts the sign of the first and second neighbor pair, whereas the V addition only changes the sign of the first neighbor pair. The second neighbor pair is stronger than the first neighbor in the quaternary system. The first and second neighbor CECs of V-Zr pair clusters are (-0.003511, -0.0321) whereas (-0.003760, -0.045343) in the Nb-V-Zr system, (0.006180, -0.056435) in Ti-V-Zr system and (0.001386, -0.00589) in Nb-Ti-V-Zr system. The addition of Ti in the V-Zr system changes the sign of the first neighbor pair in the Ti-V-Zr system from the V-Zr system, whereas Nb addition has an insignificant effect. The combined effect of the addition of Nb and Ti in the Nb-Ti-V-Zr system only changes the nature of the first neighbor pair. Whereas the energy of the first neighbor pair has reduced

3.13 Conclusions

Thermochemical data is important for the determination of thermodynamic databases and phase diagrams. Results of the calculations of enthalpy of mixing using CE and SQS for the binary, ternary, and quaternary subsystem of the Nb-Ti-V-Zr system are reported in this chapter. A good match was found in the calculated and CE-fitted energies in all the cases, and ground states were reproduced by the CE calculations. CV score in all the cases was below 0.025 eV. Cluster expansion is obtained on the pair clusters in the ternary and quaternary systems. No ternary and quaternary ground states were found. CE calculation shows that the fully-disordered alloy's energy is found to be positive for all the systems except the Nb-Ti. This indicates an overall phase-separating tendency in the bcc Nb-Ti-V-Zr system. SQS calculations were performed using the SQS structure generated by ATAT software. The disordered energy calculated using the CECs of cluster expansion matches SQS results in binary systems.