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Interplay of ordering and spinodal decomposition in the formation of ordered precipitates in binary fcc alloys: Role of second nearest-neighbor interactions

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In this paper, the possible interaction of ordering and phase separation tendencies in the formation of an ordered precipitate phase ($A_3B/L1_2$) within a binary supersaturated fcc solid solution is investigated using computational thermodynamics based on a generalized Bragg–Williams model incorporating first and second nearest-neighbor interactions. The formulation synthesizes and expands upon previous works and incorporates a strong pedagogical approach to elucidate the essential elements of the problem. The diffusional pathways governing microstructural development are predicted to be more complex, allowing for a multiplicity of decomposition mechanisms when second nearest-neighbor interactions are incorporated into the solution energetics, even in this mean field approximation. These higher order interactions markedly influence phase equilibria and phase stability. Ordering and clustering tendencies are not mutually exclusive but can occur synergistically, e.g. a conditional spinodal decomposition is predicted contingent on prior ordering of initially non-stoichiometric, disordered solid solutions. The role of second nearest-neighbor interactions on thermodynamic stability is discussed explicitly and compared to the classic treatments limited to first nearest-neighbor interactions only.

Keywords: generalized Bragg–Williams model; congruent ordering and precipitation; spinodal decomposition; ordering instability

1. Introduction

The coexistence of ordering and clustering effects/instabilities during decomposition of supersaturated solid solutions, involving precipitation of ordered phases, is well-established both theoretically and experimentally. It is also clear that the interplay of these tendencies can influence the morphology and scale of microstructures evolving during transformation from a single phase to a two-phase mixture. Prior to the 1970s, clustering and ordering were more or less considered as mutually exclusive homogeneous or continuous modes of coherent atomic rearrangement in a

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supersaturated solid solution and, in particular, concomitant spinodal decomposition and ordering instabilities were thought to be incompatible or unrelated behaviors. This simplistic view was ingrained in the field stemming from the textbook treatments of ordering and clustering which discussed the energetics and thermodynamic stability of binary alloys almost exclusively in terms of first nearest-neighbor (1st n-n) pairwise interaction energies and the sign of the so-called interchange energy, V, where:

$$V = 1/2\left(E_{\mathrm{AA}}^{(1)} + E_{\mathrm{BB}}^{(1)} - 2E_{\mathrm{AB}}^{(1)}\right) \tag{1}$$

and $E_{\mathrm{AA}}^{(1)}$, $E_{\mathrm{BB}}^{(1)}$ and $E_{\mathrm{AB}}^{(1)}$ are taken to be the effective strengths of 1st n-n atomic bonds or interactions within a so-called quasichemical description of the solution energetics. For V negative, $E_{\mathrm{AB}}^{(1)} > (E_{\mathrm{AA}}^{(1)} + E_{\mathrm{BB}}^{(1)})/2$, unlike pairs are favored and the system was classified as ordering. Clustering of like atoms is favored for $V > 0$, i.e. $E_{\mathrm{AB}}^{(1)} < (E_{\mathrm{AA}}^{(1)} + E_{\mathrm{BB}}^{(1)})/2$, and A–A and B–B bonds are preferred within the solid solution. However, extending the pairwise interaction description to allow for second nearest-neighbor (2nd n-n) interactions (and higher), the model becomes much richer since the 1st n-n and 2nd n-n interchange energies may be of opposite sign. This extended or so-called generalized Bragg–Williams model was employed by Ino [1] to elucidate the association of a miscibility gap with an ordering system ($\mathrm{A2} \rightarrow \mathrm{B2}$) consistent with the behavior reported in the Fe–Al system by Allen and Cahn [2]. The interchange energies are, thus, differentiated in terms of first and second nearest-neighbor (1st n-n and 2nd n-n interactions) as follows:

$$V = 1/2\left(E_{\mathrm{AA}}^{(1)} + E_{\mathrm{BB}}^{(1)} - 2E_{\mathrm{AB}}^{(1)}\right) \tag{2a}$$

$$U = 1/2\left(E_{\mathrm{AA}}^{(2)} + E_{\mathrm{BB}}^{(2)} - 2E_{\mathrm{AB}}^{(2)}\right), \tag{2b}$$

where V and U are the interchange energies and the superscripts refer to bond energies associated with first and second nearest-neighbor shells. This extended version of the quasichemical description allows for the coexistence and interplay between ordering and phase separating tendencies in the decomposition of metastable and unstable solid solutions.

In 1976, Kokorin and Chuistov [3] addressed the issue of the possibility of continuous isostructural or spinodal decomposition in conjunction with the formation of an ordered $\mathrm{A_3B}$ ($\mathrm{L1_2}$) phase within a supersaturated binary fcc solid solution, emphasizing the dependence of the free energy function on the long-range order parameter and the composition at a given temperature as well as the importance of incorporating second nearest-neighbor interactions in any quasichemical or generalized Bragg–Williams model if the description is to capture the complexity of possible thermodynamic instabilities and diffusional pathways during decomposition. Importantly, this case addresses the coexistence of ordering and clustering tendencies where the disorder $\rightarrow$ order transformation ($\mathrm{A1} \rightarrow \mathrm{L1_2}$) is thermodynamically first order under equilibrium conditions. The $\mathrm{A2} \rightarrow \mathrm{B2}$ disorder-to-order transformation treated by Ino [1] using the generalized Bragg–Williams approach is second/higher order. In the early 1980s, Rossiter and Lawrence [4] in a short paper also considered the coexistence of ordering and phase separation in binary fcc alloys with 2nd n-n interactions, essentially attempting to extend Ino's analysis to the cases of $L1_0$ and $L1_2$ ordering. These authors were on the right track for the A_3B ($L1_2$) case and, indeed, their analysis contained important results. However, they failed to elucidate significant features of their work, particularly showing that considerations of 1st n-n interactions only reproduce the simple ordering behavior described by Shockley [5,6] in his classic work and the vanishing of any miscibility gap or possible spinodal decomposition. Khachaturyan et al. [7] essentially employed a generalized Bragg–Williams and static concentration wave (SCW) description to describe phase equilibria and precipitation of the A_3B ($L1_2$) phase in the Al–Li system and discussed the possibility of spinodal decomposition of supersaturated, homogeneously ordered Al–Li solid solutions into a disordered and ordered phase similar to the behavior suggested by Datta and Soffa [8] in their studies of the age hardening Cu–Ti alloys. Soffa and Laughlin [9] used a graphical thermodynamic approach to analyze possible ordering and decomposition paths of supersaturated fcc solid solutions where the ordering reaction is first order under equilibrium conditions and free energy behavior as a function of the order parameter and composition similar to Kikorin and Chuistov [3]. Simmons and Laughlin [10] also used the approach of Khachaturyan's SCW methodology and analytically identified the instabilities cited by Soffa and Laughlin [9].

In this paper, the possible interactions of ordering and phase separation in decomposing binary fcc alloys will be elaborated, building upon and synthesizing previous analyses [3,4,7,11,12], emphasizing the important role of 2nd n-n pairwise interactions in broadening the diffusional pathways accessible to the system leading to the precipitation of an ordered phase. In 1966, Clapp [13] called attention to the need to include 2nd n-n interactions to describe the properties of ordered antiferromagnets decorating fcc lattices and Kikuchi and Sato [14] have expounded on the characteristics of superlattice formation in fcc compared to bcc systems. The analysis will be based on a generalized Bragg–Williams model with full appreciation of the limitations of the approach; namely, that the results can only be applicable quantitatively to the lower temperature regime of the system where local fluctuations or correlations in atomic configurations do not make a substantial contribution to the free energy of the solution. The presentation will embody a strong pedagogical flavor aimed at bringing a new generation of students, researchers and teachers into contact with the richness of the problem and its practical implications even within this first approximation. Also, it is hoped that the overview will catalyze an appreciation for more rigorous thermodynamic and kinetic analyses [15,16] in further elucidating these aspects of precipitation phenomena in alloys.

2. Generalized Bragg–Williams model: energetics and stability of fcc solid solutions exhibiting an ordered $L1_2$ phase

2.1. *General*

In referring to the Bragg–Williams model [17] applied to ordering in alloys throughout the literature, the fact that the original formulation of the problem made no explicit use of a detailed description of short-range forces acting within the solid solution is sometimes lost. The energetics of the solution were described simply in terms of an interchange energy, W, associated with moving A and B atoms originally in the 'right' positions to 'wrong' positions and that the energy for this exchange of positions is proportional to the degree of long-range order (η), defined in terms of the occupancies of appropriate sublattices. An expression for the equilibrium degree of order as a function of temperature was developed in terms of a simple kinetic equation describing the atomic transfer between sublattices, and the forward and back reactions were set equal at equilibrium. The ratio of rate constants (equilibrium constant) was set equal to a Boltzmann-like term $\exp(-W/k_BT)$, with $W = W_o\eta$ where W_o is the value of W in the perfectly ordered state ($\eta = 1$). When the solution thermodynamics are written in terms of AA, BB, and AB bond energies within the emerging superstructure resulting from preferential occupancies of α, β, γ, ... sublattices, the original Bragg–Williams model is found to be equivalent to the so-called quasichemical approach, assuming random mixing on the sublattices (regular solution). The assumptions of the Bragg–Williams theory of long-range order in alloys render the approach essentially equivalent to the Weiss molecular field theory, i.e. it is a mean field theory in the underlying physics even if the quasichemical description is employed to explicitly describe the energetics of the system. The assumption of random mixing on the sublattices and neglect of local correlations makes the model, in the language of the cluster variation method (CVM), a point cluster approximation [18,19]. The quasichemical approach of Bethe [20], emphasizing pairs of atoms, is a mean field approach in which the pairs are effectively immersed in a mean field. The Bragg–Williams model is often referred to as the zeroth approximation.

2.2. *Free energy model*

In the generalized Bragg–Williams model employed in these calculations and analyses, the free energy of mixing of solution relative to the pure components A and B can be written as

$$F_M = E_M - TS_M = E_1 + E_2 - k_BT \ln\omega, \tag{3}$$

where the heat of mixing term $E_M = E_1 + E_2$ is separated into two terms deriving from first and second nearest-neighbor interactions and the entropy of mixing term, $S_M = k_B \ln \omega$, is the ideal mixing (mean field approximation). Here, the vibrational component for the substitutional solid solution is neglected.

Figure 1 shows the α and β sublattices for the $A_3B/L1_2$ ordering. The atomic fractions of B atoms on the α and β can be written as

$$C_\alpha = C - 1/4\eta \tag{4a}$$

$$C_\beta = C + 3/4\eta, \tag{4b}$$

where C is the average composition and η is the Bragg–Williams LRO parameter defined by

$$\eta = (R - W)/(R + W), \tag{5}$$

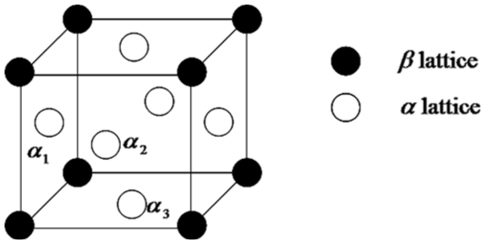

Figure 1. Conventional unit cell of the A_3B superstructure showing α and β sublattices (α_1, α_2 and α_3 are crystallographically equivalent).

with R being the total number of 'right' atoms and W the total number of 'wrong' atoms occupying the α and β sublattices. We, thus, write the heat of mixing term as

$$E_M = E_1 + E_2 = E_D + E_O, \tag{6}$$

where E_D is the heat of mixing of a disordered, random solid solution of A, and B atoms statistically occupying the sites of the fcc solid solution, and E_O is the change in free energy due to ordering with

$$E_1 = 6NV\{2C(1 - C) + 1/8\eta^2\} \tag{7a}$$

$$E_2 = 3NU\{2C(1 - C) - 3/8\eta^2\} \tag{7b}$$

$$E_D = NC(1 - C)\{12V + 6U\} \tag{7c}$$

$$E_O = N/16\eta^2\{12V - 18U\}, \tag{7d}$$

and V and U the interchange energies defined in Equations (2a) and (2b). For $\eta = 0$, one recovers the regular solution heat of mixing given by

$$E_M = E_D = NC(1 - C)\{12V + 6U\} = E_1 + E_2. \tag{8}$$

We have assumed V and U to be independent of temperature and $N = N_A + N_B$ is the total number of atoms of A and B, respectively. The entropic term is derived by assuming random mixing on the sublattices, i.e. the configurational entropy can be written as

$$S = k_B \ln \omega = k_B \ln \frac{\{3/4N\}!}{\{N_A^\alpha ! N_B^\alpha !\}} \frac{\{N/4\}!}{\{N_A^\beta !\}\{N_B^\beta !\}}, \tag{9}$$

with ω being the total number of possible arrangements corresponding to equivalent macrostates or distributions of A and B atoms on the sublattices; k_B is the familiar Boltzmann constant. The free energy of mixing functional is then written in terms of the concentration C and order parameter η as follows:

$$F_M = F(C, \eta) = NC(1 - C)\{12V + 6U\} + \frac{N}{16}\eta^2\{12V - 18U\} - TS_M \tag{10}$$

with the entropic term expanded as $-TS$ yielding:

$$-TS_{\mathrm{M}} = \frac{RT}{4}\left\{\begin{array}{l} 3\left(C-\frac{1}{4}\eta\right)\ln\left(C-\frac{1}{4}\eta\right)+3\left(1-C+\frac{1}{4}\eta\right)\ln\left(1-C+\frac{1}{4}\eta\right) \\ +\left(C+\frac{3}{4}\eta\right)\ln\left(C+\frac{3}{4}\eta\right)+\left(1-C-\frac{3}{4}\eta\right)\ln\left(1-C-\frac{3}{4}\eta\right) \end{array}\right\}. \tag{11}$$

Let us now briefly consider introducing the language of Khachaturyan's SCW approach within this more familiar Bragg–Williams/quasichemical formulation. The SCW method has been employed extensively by Khachaturyan and coworkers [7,21] and others [22] where the site occupancies and interchange energies are formulated in a $\boldsymbol{k}$-space (reciprocal space) representation through the use of the discrete Fourier transform. In this approach, the atomic arrangement in real space is described by the site occupation probability $n(\boldsymbol{r})$ given by

$$n(\boldsymbol{r}) = C + \sum_{\boldsymbol{k}} (\gamma\eta)\exp(i\boldsymbol{k}_0\cdot\boldsymbol{r}), \tag{12}$$

where γ is a parameter depending on the superstructure and the summation is over the so-called 'stars' of the structure. For the $\mathrm{L1_2}$ structure, $\boldsymbol{k}_0 = \mathbf{2\Pi}(\boldsymbol{a}_1^* + \boldsymbol{a}_2^* + \boldsymbol{a}_3^*)$ and γ is $1/4$; $\boldsymbol{r} = x\boldsymbol{a} + y\boldsymbol{b} + z\boldsymbol{c}$ is a real lattice vector specifying the atomic locations in the unit cell. For an emerging $\mathrm{L1_2}$ structure, we can write

$$n(\boldsymbol{r}) = C + \frac{\eta}{4}\left[e^{2\pi ix} + e^{2\pi iy} + e^{2\pi iz}\right]. \tag{13}$$

For any atomic arrangement, $n(\boldsymbol{r})$ can be written as

$$n(\boldsymbol{r}) = C + \sum_{\boldsymbol{k}} Q(\boldsymbol{k})\exp(i\boldsymbol{k}\cdot\boldsymbol{r}), \tag{14}$$

where $Q(\boldsymbol{k})$ is the amplitude of the Fourier component with wave vector $\boldsymbol{k}$ and C is the average composition as above. Here, the atomic arrangement is viewed as a superposition of concentration waves of wave vectors $\boldsymbol{k}$ of amplitude $Q(\boldsymbol{k})$ localized in the first Brillouin zone with x, y, z being atomic positions within the conventional fcc unit cell in real space. Furthermore, the interchange energies can be represented by a Fourier transform,

$$V(\boldsymbol{k}_0) = \sum_{\boldsymbol{r}} V(\boldsymbol{r})\ \exp(i\boldsymbol{k}_0\cdot\boldsymbol{r}), \tag{15}$$

where the summation is over first and second (or higher) nearest-neighbor shells. For the fcc-based solid solutions and the $\mathrm{L1_2}$ superstructure including first and second nearest-neighbor interactions:

$$V(\boldsymbol{k}_0) = -4V + 6U \tag{16a}$$

$$V(0) = 12V + 6U, \tag{16b}$$

where V and U are the first and second nearest-neighbor interchange energies defined above. Therefore, E_{D} and E_{O} can be written as

$$E_{\mathrm{D}} = NC(1-C)\{12V + 6U\} = NC(1-C)V(0) \tag{17}$$

$$E_{\mathrm{O}} = 3/16N\eta^2\{4V - 6U\} = -3/16N\eta^2\ V(\boldsymbol{k}_0), \tag{18}$$

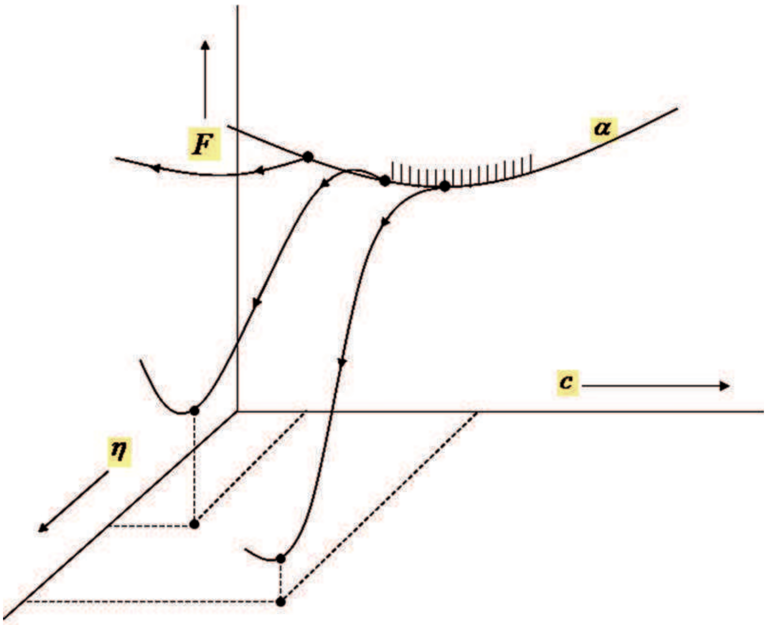

Figure 2. Schematic showing free energy curves in F–C–η space. Cross-hatching shows regions of thermodynamic instability with respect to ordering at constant composition.

incorporating the $\boldsymbol{k}$-space representation. The free energy functional can thus be written in this format as

$$F(C,\eta) = NC(1-C)V(0) - \frac{3}{16}N\eta^2 V(\boldsymbol{k}_0) + \text{Entropic Terms.} \tag{19}$$

Sometimes a normalization of the order parameter is used since the maximum degree of order possible in a homogeneously ordered state ($L1_2$) at composition C is $4C$. Writing $\eta' = \eta/\eta_{\max}$ with $\eta_{\max} = 4C$ allows the substitution $\eta = 4C\eta'$, leading to

$$F(C,\eta) = NC(1-C)V(0) - 3NC^2\eta'^2\ V(\boldsymbol{k}_0) + \text{Entropic Terms.} \tag{20}$$

Also, in calculations and plotting free energy vs. composition curves, it is sometimes convenient to drop linear terms in the composition noting that the relative free energies, common tangents and curvatures representing the solution energetics and stability are not changed; that is, we write

$$F(C,\eta) = -NC^2\ V(0) - 3NC^2\eta'^2\ V(\boldsymbol{k}_0) + \text{Entropic Terms} \tag{21}$$

without changing the essential thermodynamics.

Importantly, the solution free energy, $F(C,\eta)$, is a function of both composition and order parameter, and the graphical thermodynamics are contained in a F–C–η space as shown in Figure 2. In Figure 2, taken from Soffa and Laughlin [9], a Landau plot of the free energy versus order parameter at constant composition (for a first order $A1 \rightarrow L1_2$ ordering transition) is grafted onto the thermodynamic space delineating metastable and unstable states with respect to ordering. This leads to defining an ordering instability locus T_i^- where the free energy becomes monotonically decreased from $\eta = 0$ to $\eta = \eta^*$, an equilibrium state of order. The disordered state is unstable with respect to ordering and the system might be expected to order homogeneously or continuously (spinodal ordering) similar to the kinetic behavior for A2 → B2 ordering without the need for a classical nucleation step. The T_i^- instability locus is given by

$$T_i^- = C(1 - C)V(\boldsymbol{k}_0)/\boldsymbol{k}_\mathrm{B} \tag{22}$$

in this generalized Bragg–Williams (mean field) formulation.

An important step in the analysis of the possible interplay of ordering and clustering instabilities in the formation of an $\mathrm{L1_2}$ ordered phase within a supersaturated binary fcc solid solution is to delineate a path in the F–C–η space wherein, at each composition, an optimally ordered state obtains, $\eta = \eta_\mathrm{opt}$, that is, $F_\eta = 0$. Along this quasi-equilibrium curve, $F(C, \eta_\mathrm{opt})$, stability with respect to phase separation can be considered to be governed by $F_\mathrm{CC} = 0$ [1,3].

The preceding description of the configurational thermodynamics of a binary fcc solid solution with a tendency for $\mathrm{A1} \rightarrow \mathrm{L1_2}$ ordering will be used to analyze the thermodynamic stability of supersaturated solid solutions and the question of a so-called conditional spinodal phase separation contingent on prior ordering such as that described by Ino [1] for the A2 → B2 ordering system. Importantly, the role second nearest-neighbor interactions on the energetics and stability of fcc alloys within this approximation will be evaluated and emphasized.

3. Results

In this analysis of the energetics and stability of the fcc binary solid solutions, extensive use will be made of graphical thermodynamics based on computed free energy–composition ($F(C)$ versus C) curves derived from the generalized Bragg–Williams model with 1st and 2nd n-n interactions for the $\mathrm{A_3B}$ ($\mathrm{L1_2}$) ordering system. The role of second nearest-neighbor (2nd n-n) interactions, i.e. $U/|V| \neq 0$, will be a primary focus of the analysis. Figures 3a and b show computed F versus C curves for $U/|V| = 0$ (1st n-n interactions only) at $T/T_\mathrm{c} = 0.2$ and 0.4, respectively; T_c is the critical temperature for the stoichiometric composition $C = 0.25$ or $\mathrm{A_3B}$. The F versus C curves for the disordered and homogeneously ordered state are delineated and two-phase equilibria can be established by the common-tangent construction essentially reproducing the results of Shockley [5]. Figure 4 shows the optimum order parameter (η_opt) for the homogeneously ordered state as a function of composition for $U/|V| = 0$ and $T/T_\mathrm{c} = 0.4$ (recall that the maximum degree of order attainable for any composition is $\eta_\mathrm{max} = 4C$). The optimum order parameter η_opt at this temperature is $\eta_\mathrm{opt} = 4C$ for a broad range of composition as the free energy curve of the homogeneously ordered state approaches the intersection with the curve for the disordered solid solution. This intersection defines the locus T_o for the non-equilibrium states of the supersaturated solutions. To the right of this point of intersection, the disordered and ordered curves, a homogeneously ordered state of lower free energy than that of the disordered solid solution is available to the system.

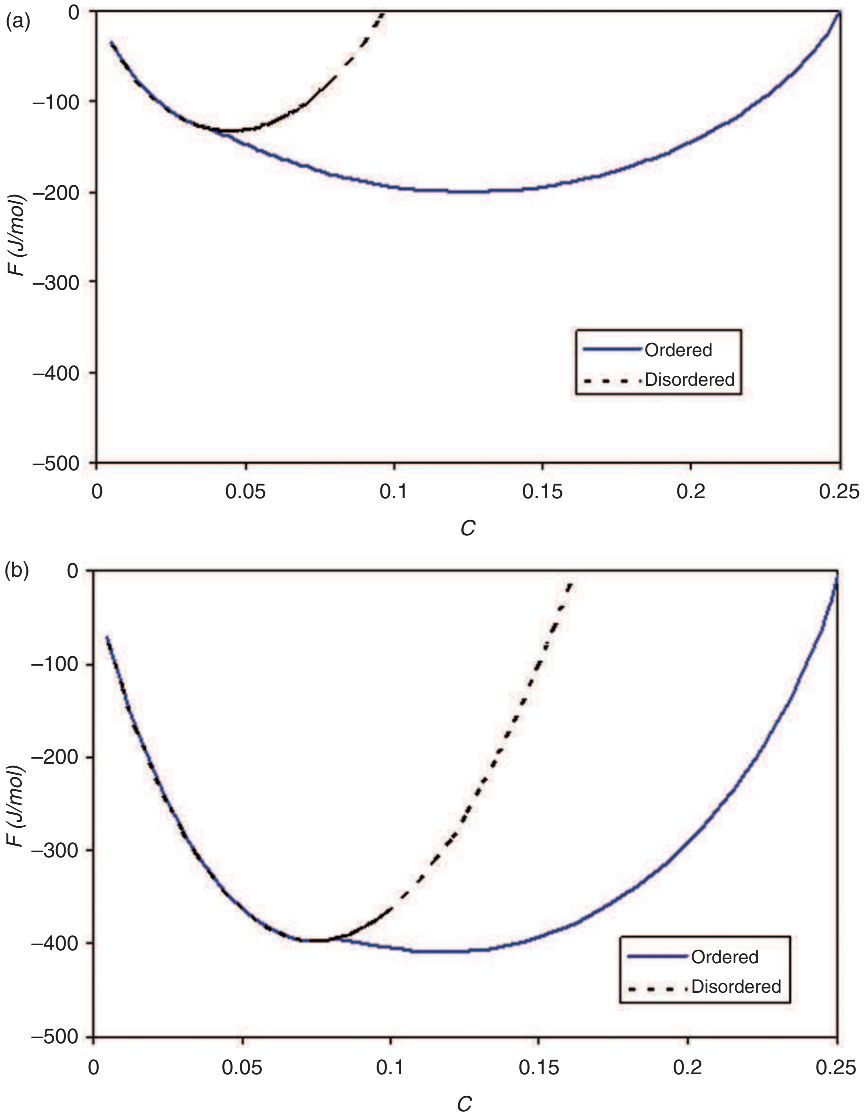

Figure 3. Free energy–composition curves when only 1st n-n interactions are included at (a) $T/T_c = 0.2$, and at (b) $T/T_c = 0.4$.

Notice that the order–disorder transition at the intersection clearly exhibits a first order character. The F versus C curves in Figures 5a and b exhibit a distinctly different behavior when 1st and 2nd n-n interactions are considered for $U/|V| = 0.4$ at $T/T_c = 0.2$ and 0.4, respectively. A broad composition range appears over which the F versus C curves for the homogeneously ordered states exhibit negative curvature, while the curvature of the disordered curve remains positive. As-quenched disordered supersaturated solid solutions are metastable with respect to

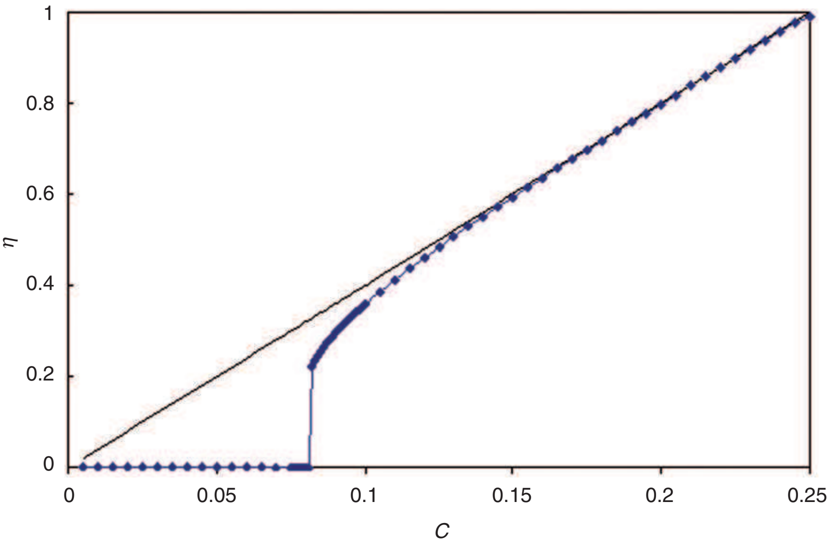

Figure 4. Optimum order parameter versus composition for 1st n-n interactions only when $T/T_c = 0.4$.

phase separation, and the formation of the A_3B precipitate phase requires a classical nucleation process. However, if the as-quenched disordered solution orders to the optimum ordered state allowed for a given composition, the possibility of a conditional thermodynamic instability with respect to phase separation/spinodal decomposition of the ordered state appears contingent on this prior ordering. When considering diffusional pathways and microstructural evolution in the decomposition of such supersaturated solid solutions involving an interplay between ordering and phase separation tendencies, the thermodynamic stability of the as-quenched disordered state with respect to ordering is relevant as discussed above. Khachaturyan et al. [7] and Soffa and Laughlin [9] addressed this transformation path in terms of continuous ordering and congruent ordering processes within the initially disordered solid solution at constant composition. Most relevant here is the ordering instability locus T_i^- defined earlier wherein the free energy of the system becomes monotonically decreasing to an ordered state η^* at constant composition (see Figure 2). In Figure 6, the optimum order parameter η_{opt} versus composition when 1st and 2nd n-n interactions is shown for $U/|V| = 0.4$ and $T/T_c = 0.4$.

In Figures 7a–c, the solvus boundaries for the two-phase region are shown when 1st and 2nd n-n interactions are taken into account compared to the original Shockley phase diagram with $U/|V| = 0$. Also included are the T_o and T_i^- loci and conditional spinodal temperature, T_{cs}, within the two-phase field. The temperature, T_{cs}, is an instability locus with respect to phase separation in the homogeneously ordered states as the stoichiometric composition is approached; that is, ordered states to the left of this line lie on the F versus C curve exhibiting negative curvature. Figures 8a and b are compiled summaries of the results for the case $U/|V| = 0.4$. Figures 9a and b represent a similar compilation of results for $U/|V| = 0$

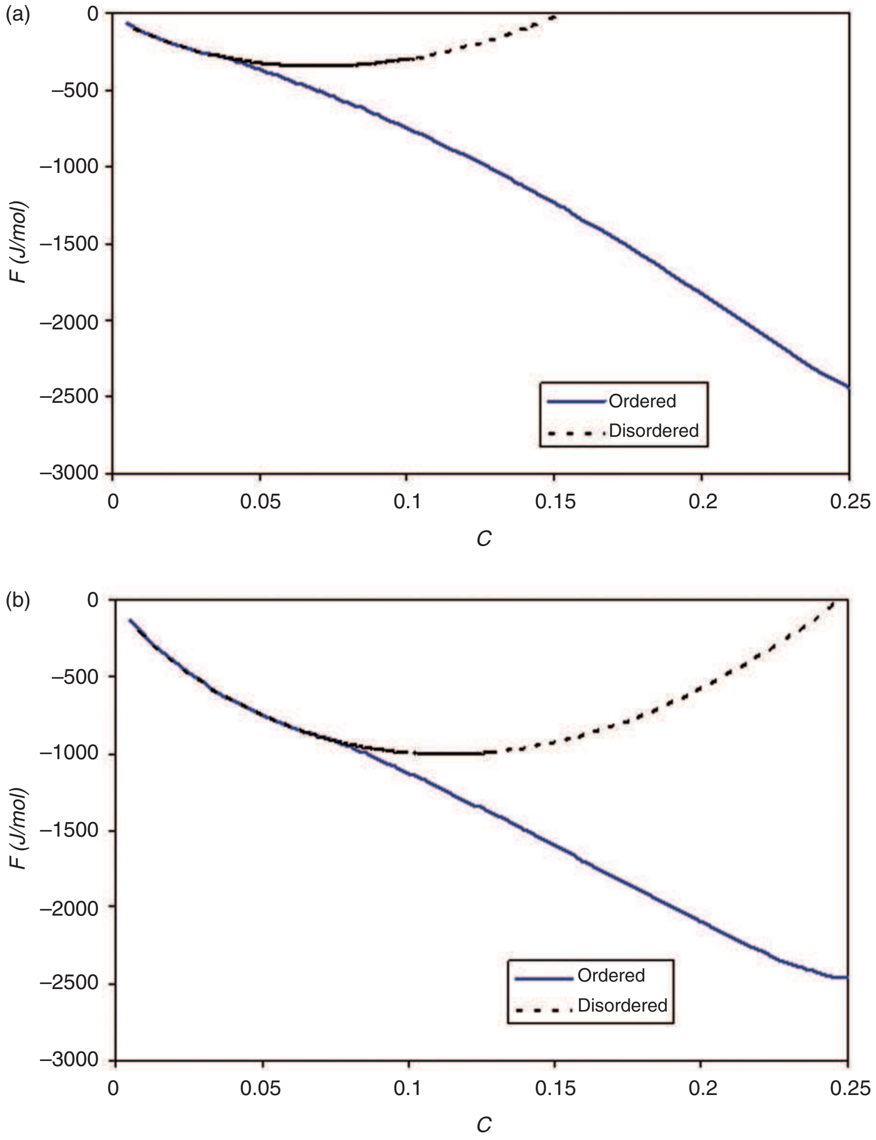

Figure 5. Free energy–composition curves when 1st and 2nd n-n interactions are considered ($U/|V| = 0.4$) at (a) $T/T_c = 0.2$, and at (b) $T/T_c = 0.4$.

for comparison. The importance of the higher order interactions in the energetics and stability of the solutions relevant to the precipitation of an ordered A_3B phase within a supersaturated fcc binary solid solution is striking and the potential decomposition paths leading to a two-phase mixture are more varied and complex compared to the $U/|V| = 0$ case. Indeed, in this generalized Bragg–Williams model, taking into account both 1st and 2nd n-n interactions, ordering and clustering

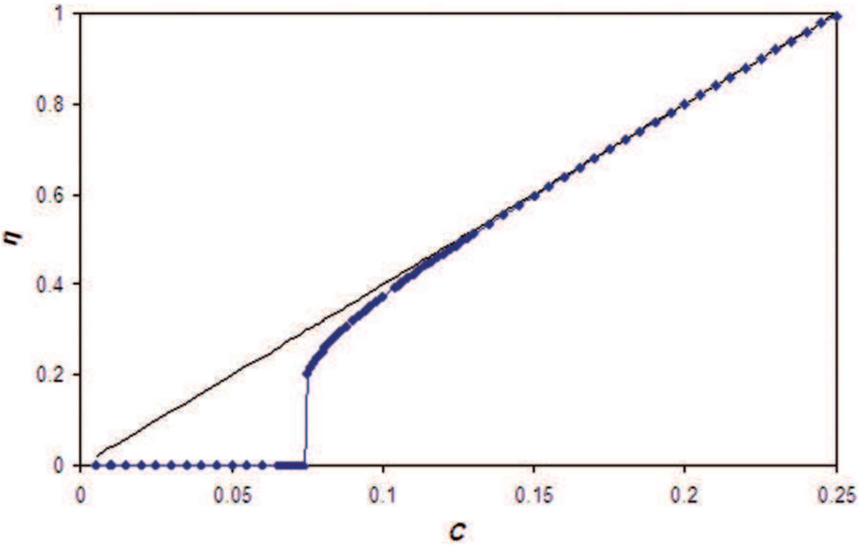

Figure 6. Optimum order parameter versus composition when 1st and 2nd n-n interactions are considered ($U/|V| = 0.4$) at $T/T_c = 0.4$.

tendencies are not mutually exclusive but can occur synergistically allowing, for example, a disordered supersaturated solid solution which is initially metastable with respect to the formation A_3B phase to spontaneously order and then undergo spinodal decomposition producing a disordered terminal solid solution in equilibrium with the ordered precipitate phase.

Note: The V and U values employed in these calculations correspond to a constant value of $V(0)$ of −400 meV (−3254.94 J/mol) similar to the approach to the solution energetics by M. Kompatscher in his doctoral thesis *Phase Separation in Ni-rich Ni–Ti*: *The Metastable States*, ETH, Zurich, 2001 and approximately relevant to the Ni–Ti system.

4. Discussion

From the foregoing thermodynamic analysis of fcc/$L1_2$ ordering and precipitation systems, it is evident that even within the generalized Bragg–Williams approximation, essential features of the behavior with respect to formation of an ordered precipitate within an initially disordered quenched alloy are lost when only 1st n-n interactions are considered in the solution energetics. Phase equilibria and the stability of the supersaturated state produced during heat treatment of alloys, such as Al–Li [23] and Ni–Ti [24], are predicted to be markedly different when 1st and 2nd n-n interactions are folded into the theoretical description, and these differences can be important in understanding the decomposition paths and microstructural evolution. The decomposition paths and subsequent microstructural development during aging of supersaturated fcc solid solutions are predicted to be more complex

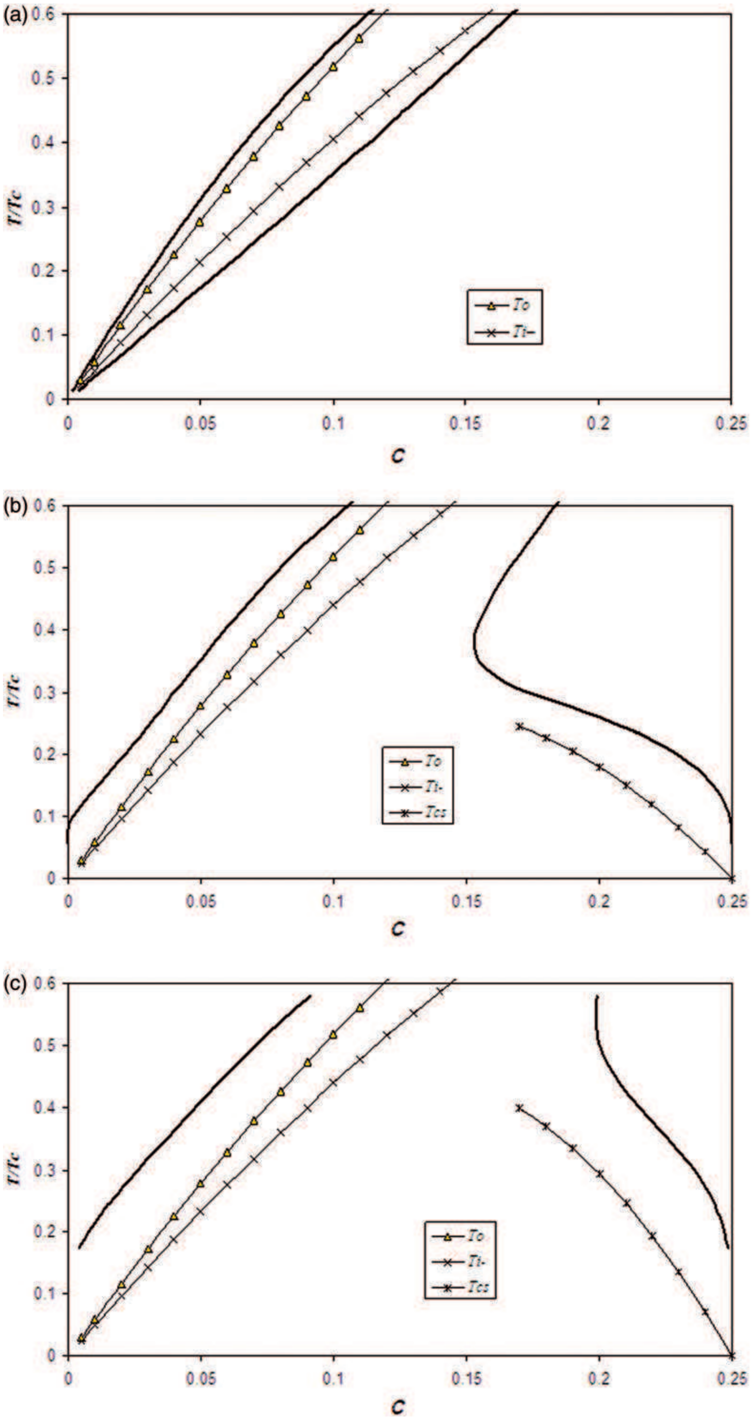

Figure 7. (a) Solvus boundaries and T_o and T_i^- loci when only 1st n-n interactions are considered. (b, c) Solvus boundaries and T_o and T_i^- loci when 1st and 2nd n-n interactions are considered for (b) $U/|V| = 0.2$, (c) $U/|V| = 0.4$, including conditional spinodal locus.

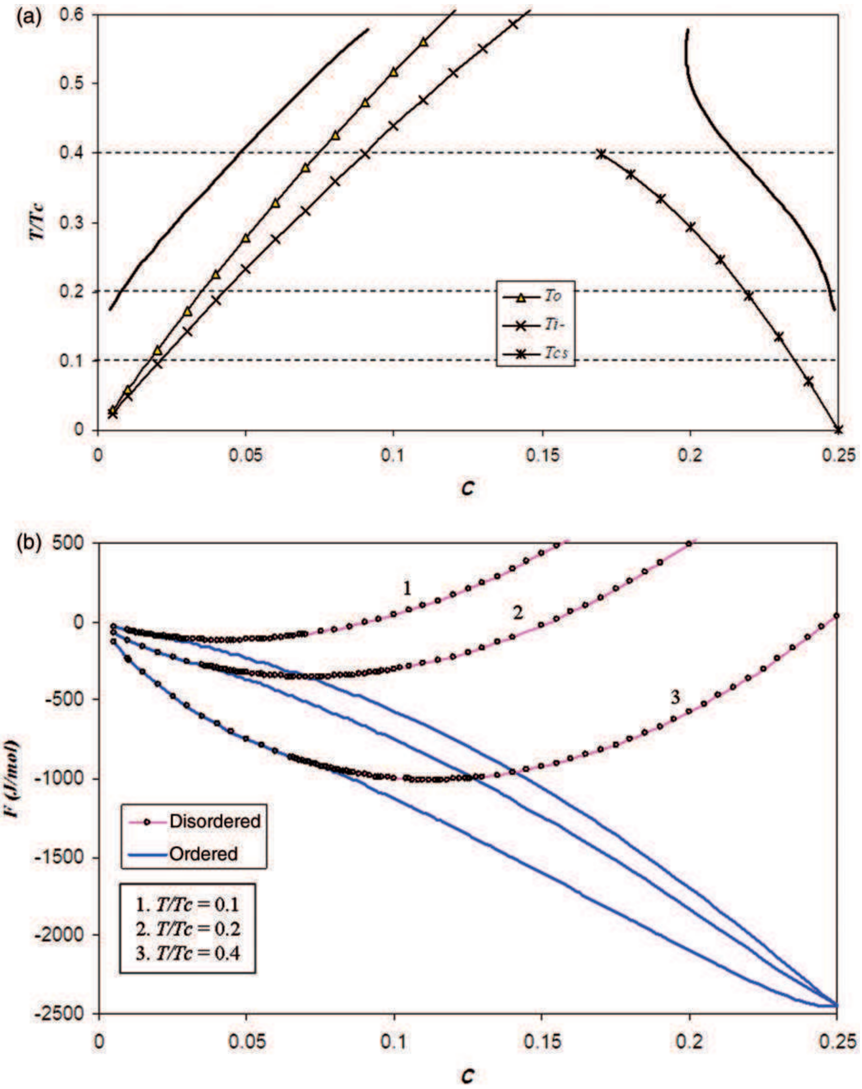

Figure 8. (a, b) Phase boundaries, instability loci and associated free energy versus composition curves at three T/T_c temperatures (indicated by dashed lines) for $U/|V| = 0.4$.

involving various interplays between ordering and phase separation as formulated above. New degrees of freedom thermodynamically and kinetically become available to the system leading to different reaction paths that, when understood, are amenable to exploitation in controlling the homogeneity and scale of the transformation products resulting from precipitation from solid solution. Spinodal decomposition as an alternative mechanism of phase separation to classical nucleation of the precipitating phase arises in the analysis of the topology of the F versus

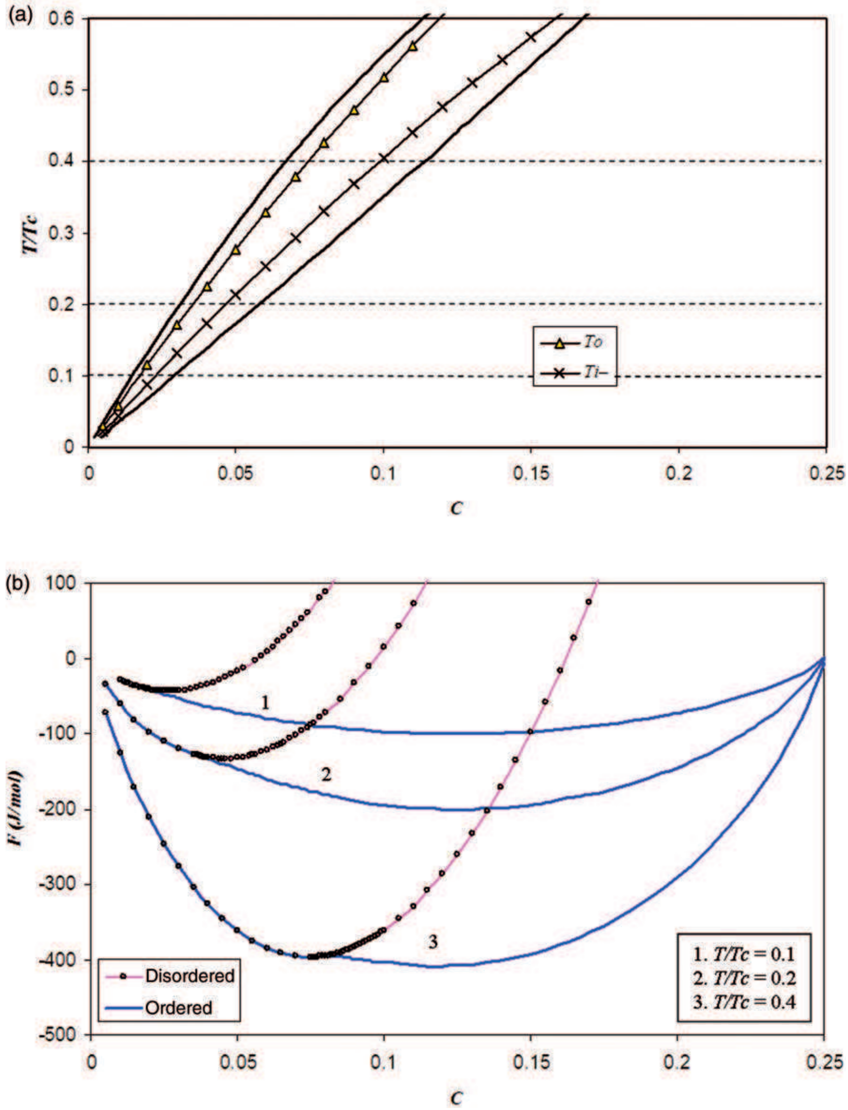

Figure 9. (a, b). Phase diagram and associated free energy versus composition curves at three T/T_c temperatures (indicated by dashed lines) when 2nd n-n interactions are excluded for comparison.

C diagrams. It is clear for the pairwise interactions explored in this analysis that binary fcc solid solutions with $V =$ negative (–) and $U = 0$, that is, an ordering system defined by 1st n-n interactions only, cannot undergo spinodal decomposition. However, incorporation of 2nd n-n interactions into this simple Bragg–Williams approach predicts possible spinodal paths (spinodal decomposition of homogeneously ordered solutions) involved in the formation of an equilibrium two-phase

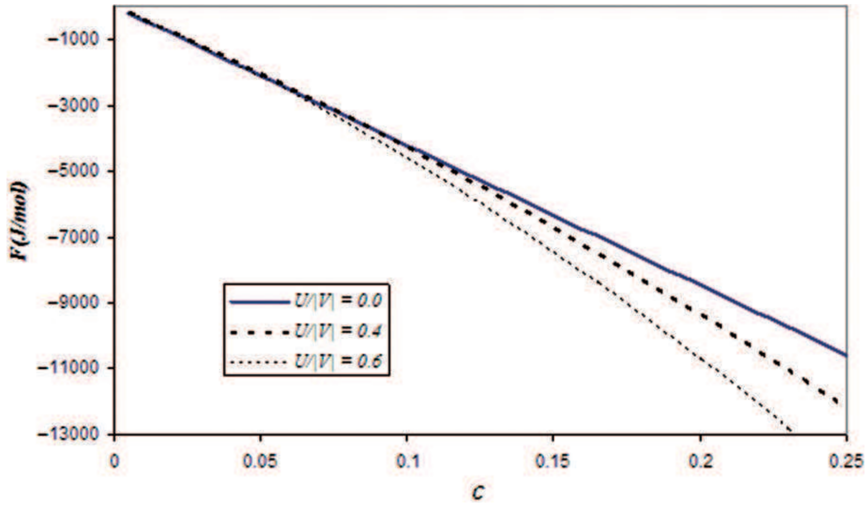

Figure 10. Free energy versus composition curves for the homogeneously ordered solutions at 0 K for different 2nd n-n interaction strengths.

mixture comprised of an ordered precipitate and a disordered matrix. Furthermore, this treatment based on the generalized Bragg–Williams model suggests that even in more rigorous approaches important thermodynamic and kinetic features of the system behavior will be lost if higher order pairwise interactions are not considered.

An interesting result of this analysis relates to the Third Law of Thermodynamics. At $T = 0$ K, the free energy $F = E$ of the solid solution is given by

$$F = N(12V + 6U)C - NC^2(12V + 6U) + 3/16N\eta^2(4V - 6U). \tag{23}$$

Taking $\eta = \eta_{\max} = 4C$, this becomes

$$F = N(12V + 6U)C - 24NUC^2. \tag{24}$$

This free energy function displays negative curvature, showing that the equilibrium state of the system is a two-phase mixture of pure A and A_3B, the relative proportions given by the lever rule at any composition to be consistent with the statement of the Third Law. If only 1st n-n interactions are taken into account, the free energy of $F = E$ of a homogeneously ordered solution (with positive entropy) is the same as that of the equilibrium two-phase mixture of pure A and fully ordered A_3B which has no entropy. However, this degeneracy is excluded by the Third Law which requires the entropy of the system go to zero, which is the case for the coexistence of pure A and the fully ordered phase. The off-stoichiometric, homogeneously ordered solution possesses a configurational entropy and is not allowed at 0 K. The curvature of the degenerate free energy functional is zero, it varies linearly with composition between $C = 0$ and $C = 0.25$. However, when the second nearest-neighbor interactions are included in the solution energetics, the homogeneously ordered states lie on a parabolic F versus C curve with negative curvature at 0 K, i.e. these non-equilibrium states are thermodynamically unstable with respect to decomposition into the equilibrium two-phase mixture (Figure 10). This further emphasizes the need to incorporate the higher order interactions even in the generalized Bragg–Williams model to capture essential thermodynamic properties of the fcc ordering and precipitation systems.

Finally, it should be mentioned that the decomposition of solutions incorporating interplay between ordering and phase separation may be influenced by APBs emerging in the homogeneously ordered states as well as by cooperative effects of the order parameter and composition along the free energy surface to produce non-classical nucleation modes of precipitate formation [21,22].

5. Summary

(1) In this paper, computational thermodynamics using a generalized Bragg–Williams model incorporating first and second nearest-neighbor pairwise interactions has been applied to analyze the energetics and stability of fcc binary ordering ($L1_2$)/precipitation systems focusing on the role of second nearest-neighbor interactions. In this approximation, it is evident that the system behavior is substantially different compared to when only first nearest-neighbor interactions are considered with respect to phase equilibria and thermodynamic stability.

(2) When second nearest-neighbor interactions are included in the solution energetics, ordering and clustering effects are not mutually exclusive; instabilities with respect to ordering and phase separation appear and these tendencies can manifest themselves concomitantly and/or synergistically allowing for a multiplicity of decomposition paths of supersaturated solutions.

(3) The limitations of this mean field so-called point approximation, in the parlance of modern cluster approaches, is well appreciated but it is suggested here that, to describe the behavior of the ordering ($L1_2$)/precipitation systems in any approach using first nearest-neighbor interactions only, a rich spectrum of thermodynamic and kinetic behavior is lost.

(4) The generalized Bragg–Williams model shows that a conditional spinodal decomposition of homogeneously ordered supersaturated fcc solutions to produce an equilibrium two-phase mixture comprised of a disordered terminal solid solution and a A_3B ($L1_2$) precipitate phase cannot occur unless higher order interactions are included in the solution energetics.

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