



FORMATION OF AN ORDERED INTERMETALLIC PHASE FROM A DISORDERED SOLID SOLUTION—A STUDY USING FIRST-PRINCIPLES CALCULATIONS IN Al-Li ALLOYS

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Abstract—The formation of the ordered L1₂ phase in Al-Li binary solid solutions has been studied using *first-principles* electronic structure calculations in conjunction with the static concentration wave model. The effective multisite interactions have been determined by using Connolly–Williams prescription in the tetrahedron–octahedron (TO) cluster approximation for the f.c.c. lattice. The resulting Landau plots (free energy versus order parameter) have pointed out the temperatures below which instabilities with respect to ordering develops. Free energy–composition plots have been used for identifying the positions of the phase boundaries and of the critical spinodal. The results of this theoretical investigation have been presented in the form of a phase diagram in which different instability lines have been marked. Copyright © 1997 Acta Metallurgica Inc.

1. INTRODUCTION

Precipitation of an intermetallic compound from a dilute solid solution essentially requires rejection of solute atoms from the matrix, leading to local enrichment of solute concentration and ordering of solute atoms to produce the superlattice structure of the ordered intermetallic phase. The path through which a single phase solid solution decomposes to produce a second phase dispersion is governed by the consideration of instability of the system with respect to fluctuations in composition and in chemical and/or displacive ordering. The process of collection of solute atoms in a localized region for attaining local solute enrichment—known as *clustering*—may occur simultaneously or sequentially with *ordering* which involves the organization of solvent and solute atoms in a superlattice structure. The ordering and the clustering tendencies cannot co-exist if one considers only the first nearest neighbour interactions. This is why the possibility of concomitant ordering and clustering processes has not been examined until recently. The conditions for simultaneous or sequential operation of clustering and ordering have been identified [1–4] in terms of instabilities associated with the concentration fluctuations appropriate to the respective processes. The presence of such instabilities can be examined by free energy–composition plots and free energy–order parameter plots for different temperatures. The loci

of these instabilities, when superimposed on phase diagrams, mark different domains in the temperature concentration space where different mechanisms of phase reactions are possible from thermodynamic considerations.

An alloy system which is amenable to the thermodynamic analysis, as outlined above, should be such that the structure of the ordered intermetallic phase can be generated by replacement of atoms in the lattice of the parent disordered solid solution. In such situations free energy of the ordered phase can be expressed as a function of the order parameter, which in turn is related to the amplitude of the concentration wave associated with ordering. In order to examine the presence of clustering and ordering instabilities of the solid solution with concentration waves of appropriate wave vectors, the minimized value of the free energy is plotted against the solute concentration to find out the presence of inflection points. Depending on the values of the pair interaction parameters, the free energy–composition plots for the random as well as the ordered f.c.c. solid solutions exhibit the following four possibilities [3].

- (i) The disordered solid solution is metastable with respect to both ordering and clustering.
- (ii) The disordered solid solution is initially unstable with respect to ordering but metastable against clustering. The ordering of the solid solution to the optimum level can, subsequently, introduce a clustering instability in the ordered structure.
- (iii) The disordered solid solution is initially unstable with respect to clustering but metastable with

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respect to ordering. In this situation, clustering occurs first, which may make the solute-enriched regions unstable with respect to ordering.

- (iv) The disordered solid solutions are unstable with respect to both clustering and ordering.

Soffa and Laughlin [1, 2] have expounded these ideas in constructing the schematic free energy versus composition plots which illustrate different situations. They have plotted instability lines T_i^- , T_i^+ , T_{cs} , T_s and equilibrium phase boundaries (T_{eq} 's) defining the ordered, the disordered and the two-phase regions. While the presence of an instability can be determined by examining the sign of the second derivative of free energy with respect to an appropriate order parameter, the equilibrium phase boundaries are given by the principle of *common-tangents* on the free energy–concentration curves for the ordered and the disordered phases. The instability lines in the temperature (T)–concentration (c) plane are defined as follows:

T_i^- : the line below which the solid solution is unstable with respect to congruent ordering;

T_i^+ : the line above which the ordered solid solution becomes unstable with respect to spontaneous congruent disordering;

T_{cs} : the line below which spinodal clustering instability develops only after the system undergoes ordering to a certain extent;

T_s : the line below which the disordered phase becomes unstable with respect to clustering.

The relative positions of these instability lines as schematically illustrated in the phase diagram (see Fig. 1), identify the conditions under which different transformation sequences are possible from thermodynamic considerations.

2. PRECIPITATION OF δ' -(Al₃Li) IN DILUTE Al-Li ALLOYS

The precipitation of the metastable δ' -phase from dilute Al-Li alloys has been chosen in the present work, as in this system the interplay between the clustering and the ordering processes has been investigated theoretically [4–5]. First-principles calculations [6–8] for different superlattice structures in the system have yielded ground-state physical properties like formation energies, bulk moduli, equilibrium lattice parameters and cohesive energies, which show excellent agreement with the available experimental values. Metastable phase boundaries, particularly that between α (f.c.c.) and δ' -phase (Al₃Li-L1₂ structure), have also been obtained by using such calculations [6]. However, first-principles calculations have not yet been employed for examining the instabilities of the system with respect to clustering and ordering processes.

Experimental work in dilute Al-Li alloys has focused attention on the mechanism of the formation of the δ' -phase from the f.c.c. solid solution. Anomalous results from calorimetry experiments [9–12] and the presence of L1₂ superlattice reflections in as-quenched specimens [11–17] have suggested the

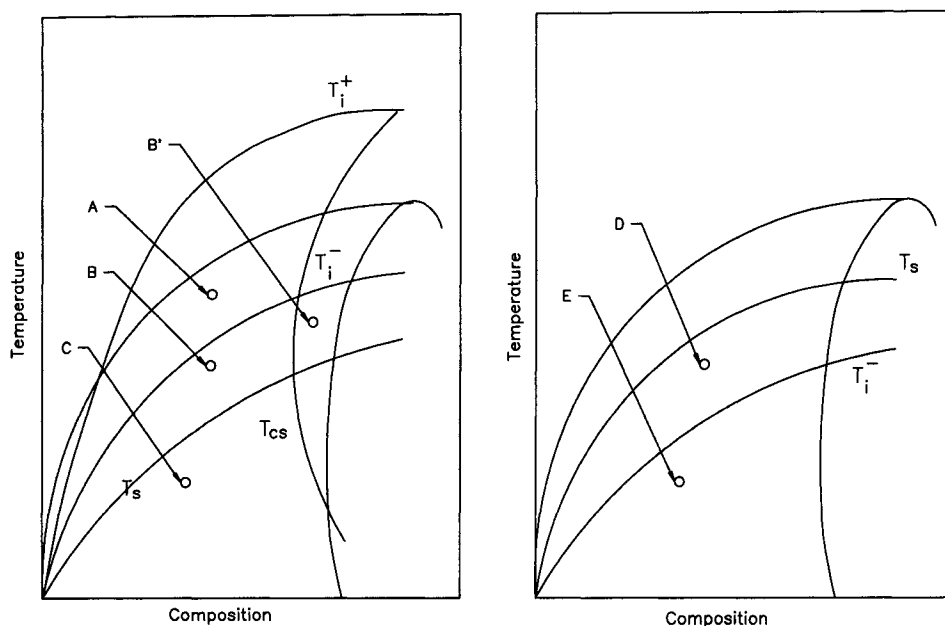


Fig. 1. The instability diagrams which schematically illustrate the relative positions of all the six instability lines (T_i^- , T_i^+ , T_{cs} , T_s and the two equilibrium phase boundaries). These lines segment the phase diagram into several domains in which different reaction mechanisms are operative. Domain A: $\alpha' \rightarrow \alpha + \beta$ (nucleation and growth). Domain B: $\alpha' \rightarrow$ spinodal ordering $\rightarrow \alpha + \beta$. Domain B': $\sigma' \rightarrow$ spinodal ordering \rightarrow spinodal clustering $\rightarrow \alpha + \beta$. Domains C and E: $\alpha' \rightarrow$ simultaneous ordering and clustering. Domain D: $\alpha' \rightarrow$ spinodal clustering \rightarrow spinodal ordering within solute enriched regions $\rightarrow \alpha + \beta$.

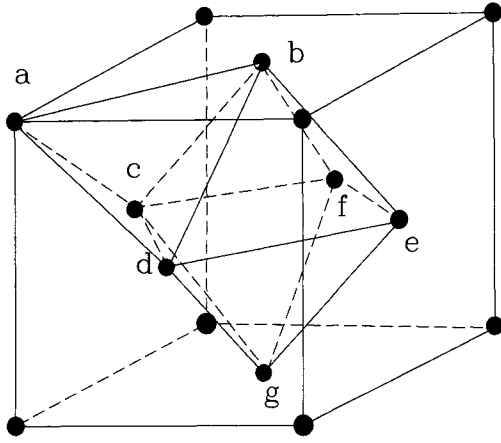


Fig. 2. Tetrahedron-Octahedron (TO) cluster approximation for the f.c.c. lattice. The tetrahedron ($abcd$) consists of only nearest neighbour pairs and the octahedron ($bcdefg$) consists of both nearest neighbour and next nearest neighbour pairs.

operation of the spinodal ordering process. In view of the success of the first-principles calculations in correctly determining ground state behaviour and metastable phase boundaries, we have made an attempt here to examine whether the free energy versus composition and the free energy versus order parameter plots, obtained by such calculations, can yield instabilities related to clustering and ordering processes.

3. METHOD OF CALCULATIONS

Studies on the decomposition behaviour of a given alloy system depend upon how accurately one can determine the free energy functions of the competing phases involved, namely, equilibrium as well as metastable. The ordering and clustering processes are governed by the interaction energies (or effective pair interactions (EPI), for nearest neighbour (NN) and higher coordination pairs and entropies associated with alloys having fluctuations in composition and in order parameter. These EPIs control the ground state energies of different ordered superstructures depending upon their sign and strength. Earlier, these interactions have been obtained either by fitting to experimental phase diagrams or from X-ray diffuse scattering intensities. However, in recent years, it has become possible to calculate these interactions from first principles. Furthermore, conventional mean field theory has been generalized to include *multisite or cluster-based* mean-field theory, which has greatly improved the level of approximation [18]. Here, we shall briefly describe the methodology of our *ab initio* calculations along with some specific results obtained on Al-Li system.

3.1. Cluster approximation

In the calculations based on cluster approximation, the given lattice is divided into small clusters, the vertices of which lie on the lattice sites (e.g. see Fig.

2). These clusters are distinguished by their different orientations in space, which is determined by the symmetry of the lattice. A particular configuration of the system is defined by assigning pseudospin variables, σ_p , to each of the lattice site p , which can take values $+1$ or -1 depending on whether the site p is occupied by $i = A$ or B , respectively, for a binary alloy. Hence, for a given cluster of γ lattice points, the γ -component vector $[\sigma_{p_1} \sigma_{p_2} \dots \sigma_{p_\gamma}]$ defines a configuration. The various microscopic as well as macroscopic properties of the lattice are determined by taking suitable averages over these clusters [19, 20]. Moreover, the state of order of the system is given in terms of cluster correlation functions, ξ_γ for the cluster γ , which are defined as

$$\xi_\gamma = \frac{1}{N_\gamma} \sum_{\{p_i\}} \sigma_{p_1} \sigma_{p_2} \dots \sigma_{p_\gamma}, \quad (1)$$

where the summation is over all possible configurations of the cluster γ and N_γ is the total number of γ -type clusters. The determination of effective pair/multisite interactions can be divided into two parts as discussed below.

(a) The determination of total energies using first-principle band structure calculations

The cluster approximation, used in the present investigation, considers the tetrahedron (T) and the octahedron (O) clusters, marked $abcd$ and $bcdefg$ respectively in Fig. 2. Both first and second near-neighbour interactions are included in this level of approximation (TO). The total electronic energies of all the possible ground state superstructures, under the first and the second nearest neighbour pair interactions, have been determined using the first principles electronic band structure method, namely the tight-binding linear muffin-tin orbital (TB-LMTO) method [21–23] in the so-called “atomic sphere approximation” (ASA) [24, 25]. We have used the Barth–Hedin exchange-correlation potential [26] within local density approximation (LDA). The total energies calculated for each ordered superstructure as a function of volume (V), have been minimized to get the equilibrium volume (V_0) and hence the equilibrium Wigner–Seitz radius (S_{av}). Other cohesive properties, such as bulk modulus (B), cohesive energy (E_{coh}) and energy of formation of the f.c.c.-based compound (E_{form}^{fcc}) have been obtained using the following relations.

$$B = V_0 \left(\frac{d^3 E_T}{dV^3} \right)$$

$$E_{coh} = E_T - \sum_i E_i^{atomic}$$

$$E_{form}(A_c B_{1-c}) = E_{coh}(A_c B_{1-c}) - [c E_{coh}^{fcc}(A) + (1-c) E_{coh}^{fcc}(B)]$$

where E_i^{atomic} is the atomic ground state energy of the i th constituent in the ordered compound, for which the minimized total energy is E_T . Table 1 shows a comparison between the calculated [7, 8] and the experimental values (within parenthesis) [27–29] of the cohesive properties, which shows a fairly good agreement.

(b) *Determination of effective pair interactions (EPI)*

We have used the Connolly–Williams method (CWM) [19, 20] for the calculation of EPIs. According to this prescription, the cohesive energy of a given superstructure (Ψ) is written as a rapidly convergent sum of pair and multisite interactions (J_γ) over the lattice, weighted by their corresponding cluster correlation functions (ξ_γ).

$$E_{\text{coh}}^\Psi(V) = \sum_{\gamma=0}^{\gamma_{\text{max}}} J_\gamma(V) \cdot \xi_\gamma^\Psi \quad (2)$$

where the summation is over all the subclusters (including the empty cluster) of the basic cluster (γ_{max}). For a *perfectly* ordered superstructures, the ξ_γ can be determined by inspection. Hence, one can determine the *volume dependent* effective cluster (multisite) interactions (ECIs) by inverting equation (2) to give

$$J_\gamma(V) = \sum_{\Psi} (\xi_\gamma^\Psi)^{-1} \cdot E_{\text{coh}}^\Psi(V) \quad (3)$$

where the summation is, now, over the various superstructures Ψ . Our calculated values of the EPIs (J_2) for the f.c.c.-based Al–Li alloys have been plotted in Fig. 3 as a function of the unit cell volume. These EPIs ($J_2^{(i)}$) for the i th coordination sphere are defined, in the Connolly–Williams method, as

$$J_2^{(i)} = \frac{1}{4} [W_{AA}^{(i)} + W_{BB}^{(i)} - 2W_{AB}^{(i)}]$$

where W_{jk} are the interaction potentials for the pairs of the type (jk). The values for the first and the second ($J_2^{(1)}$ and $J_2^{(2)}$) nearest neighbour interactions for the f.c.c. alloys, at an average equilibrium volume

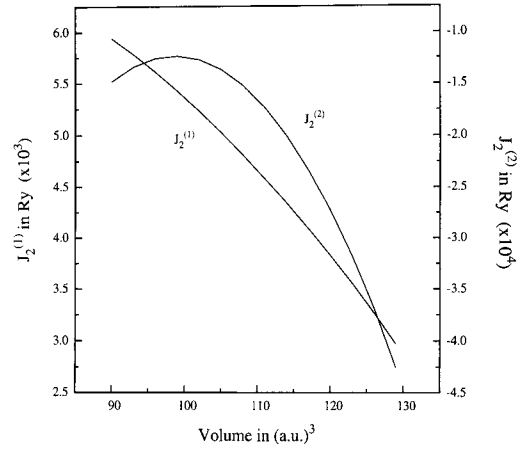


Fig. 3. The nearest neighbour and next nearest neighbour effective pair interactions ($J_2^{(1)}$ and $J_2^{(2)}$) for the Li–Al alloys, obtained using the TB-LMTO-CWM method, plotted as a function of volume.

of 107.0 (a.u.)³, are 4.882×10^{-3} and -1.463×10^{-4} Ry respectively.

3.2. *Free energy of the solid solutions with static concentration wave (SCW)*

We shall briefly describe the SCW model [5, 30, 31] and show how one can arrive at the free energy expression as a function of temperature (T), composition (c) and order parameter (η). In the SCW model, the probability, $n(\mathbf{R})$, of finding a solute atom at a lattice site \mathbf{R} is Fourier expanded as a sum of static concentration waves whose amplitudes, $Q(\mathbf{K})$, are the Fourier coefficients and whose wave vectors, \mathbf{K} , determine the superstructure periods.

$$n(\mathbf{R}) = c + \sum_{\mathbf{K}} Q(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{R}) \quad (4)$$

where c is the average concentration. The Fourier coefficients $Q(\mathbf{K})$ are expressed in terms of *normalized* (w.r.t. c) long range order parameter, η_n , via the following relation,

$$Q(\mathbf{K}) = \eta_n \cdot c \quad (5)$$

The internal energy is given as

$$E = \frac{N}{2} \sum_{\mathbf{K}} J(\mathbf{K}) \cdot Q(\mathbf{K}) Q^*(\mathbf{K})$$

where the asterisk (*) indicates the complex conjugate of the amplitude of the corresponding concentration wave, N is the total number of lattice sites and $J(\mathbf{K})$, the Fourier transforms of the pair interactions, are given by

$$J(\mathbf{K}) = N \sum_{\mathbf{R}} J(\mathbf{R}) \cdot \exp(i\mathbf{K} \cdot \mathbf{R}).$$

Table 1. Table of calculated ground state properties of f.c.c.-based superstructures of Al–Li alloys under the first and the second nearest neighbour pair interactions. Quantities within parentheses are the available experimental numbers

Structures	e/a	S_{av} (a.u.)	Bulk Mod. (GPa)	E_{coh} (kJ/mol)	E_{form} (kJ/mol)
f.c.c.-based					
Al (f.c.c.)	3.0	2.954 (2.99)	76.797 (76.3)	−405.798	0.0
Al ₃ Li (L1 ₂)	2.5	2.947 (2.95)	68.934 (66.0)	−366.150	−9.896
Al ₃ Li (DO ₂₂)	2.5	2.945	65.631	−365.453	−9.199
Al ₃ Li	2.33	2.947	68.622	−347.150	−7.410
AlLi (L1 ₀)	2.0	2.922	61.572	−318.191	−11.479
Al ₂ Li ₂	2.0	2.919	44.359	−318.021	−11.310
AlLi (L1 ₁)	2.0	2.952	44.378	−314.622	−7.911
AlLi ₂	1.66	2.946	34.960	−283.400	−9.717
AlLi ₃ (L1 ₂)	1.5	3.005	30.805	−261.589	−4.421
AlLi ₃ (DO ₂₂)	1.5	2.957	29.319	−265.579	−8.411
Li (f.c.c.)	1.0	3.107 (3.24)	19.033	−207.624	0.0

The configurational entropy in the Bragg–Williams approximation is given by

$$S = k_B \sum_{\phi}^{\Omega} N_{\phi} [n_{\phi} \ln n_{\phi} + (1 - n_{\phi}) \ln(1 - n_{\phi})]$$

where Ω is the total number of sublattices, n_{ϕ} and the N_{ϕ} are the occupation probability and the number of atoms on the ϕ th sublattice, respectively. The final expression for the configurational entropy, after substitution of equation (4), is

$$S = Nk_B [c \ln c + (1 - c) \ln(1 - c) - \frac{1}{2} (c - Q(\mathbf{K})) \ln(c - Q(\mathbf{K})) + \frac{1}{2} (c + Q(\mathbf{K})) \ln(c + Q(\mathbf{K}))]$$

where k_B is the Boltzmann constant. Hence, the Helmholtz free energy, F , given by

$$F = E - TS,$$

is obtained as a function of η , T and c on substitution of the normalizing relation (5). For example, the free energies of the disordered and the $L1_2$ ordered phases are respectively

$$\begin{aligned} F^{\text{dis}}(T, c) &= \frac{1}{2} J(000) \cdot c^2 \\ &\quad + k_B T \{c \ln c + (1 - c) \ln(1 - c)\} \\ F^{\text{ord}}(T, c, \eta_n) &= \frac{1}{2} (J(000) + 3J(\mathbf{K}) \cdot \eta_n^2) \cdot c^2 \\ &\quad + \frac{k_B T}{4} \{3c(1 - \eta_n) \ln c(1 - \eta_n) \\ &\quad + 3(1 - c(1 - \eta_n)) \ln(1 - c(1 - \eta_n)) \\ &\quad + (c(1 + 3\eta_n)) \ln(c(1 + 3\eta_n)) \\ &\quad + (1 - c(1 + 3\eta_n)) \ln(1 - c(1 + 3\eta_n))\} \end{aligned}$$

The normalized order parameter (η_n) is related to the standard order parameter (η), as $\eta_n = \eta/\eta_{\text{max}}$, where η_{max} is the maximum order parameter attainable at a given composition.

The free energy surface exhibits a curvature with respect to each of the \mathbf{K} -vectors in the first Brillouin zone. However, there will be a critical \mathbf{K} -vector, corresponding to the minimum principal curvature of the free energy surface which can be identified from the \mathbf{K} -space symmetry elements. These \mathbf{K} -vectors which terminate at the *special points* of the reciprocal lattice define the family of superstructures that can develop as a consequence of an instability reaction. The special points for the f.c.c. lattice (where symmetry elements intersect at a point) are $[000]^*$, $[100]^*$, $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]^*$ and $[1\frac{1}{2}0]^*$. These special points have been discussed in detail elsewhere [30–32]. The wave vector $[000]^*$ corresponds to the long wavelength concentration modulation in the disordered phase. The $L1_2$ structure is generated by the superposition of three $[100]^*$ concentration waves. The sequence of the calculations performed is indicated in the flow chart in Fig. 4.

4. RESULTS ON Al-Li ALLOYS

The $L1_2$ structure is generated by the superimposition of three (100) concentration waves. The special point (\mathbf{K}) for the $L1_2$ ordering is $[100]^*$. The Fourier transforms of the first and the second pair interactions have been calculated using the following matrix equation

$$\begin{bmatrix} J(\mathbf{K}) \\ J(000) \end{bmatrix} = \begin{bmatrix} -4.0 & 6.0 \\ 12.0 & 6.0 \end{bmatrix} \begin{bmatrix} J_2^{(1)} \\ J_2^{(2)} \end{bmatrix}$$

where the elements of the above two-dimensional matrix are the cell functions which gives the difference between the like and the unlike nearest neighbour pairs [3, 32]. The pair interactions, $J_2^{(i)}$, in the i th coordination sphere are taken as

$$J_2^{(i)} = [W_{AA}^{(i)} + W_{BB}^{(i)} - 2W_{AB}^{(i)}].$$

These effective pair interactions, in the reciprocal space, have been calculated for Al-Li alloys to give

$$\frac{J(000)}{k_B} = 36438.24 \text{ K} \text{ and } \frac{J(100)}{k_B} = -12884.48 \text{ K}.$$

The free energy expression for the $L1_2$ ordered phase has been minimized (using $J(000)$ and $J(100)$ as obtained above) w.r.t. order parameter η (by restricting the variation only up to η_{max}) at a given composition and temperature. The resulting F versus c plots obtained at different temperatures are shown in Fig. 5. Superimposed on these plots are the free energies of the disordered phase obtained as a function of composition at the same temperature. We have also generated the Landau plots, i.e. the free energy change due to ordering as a function of η at

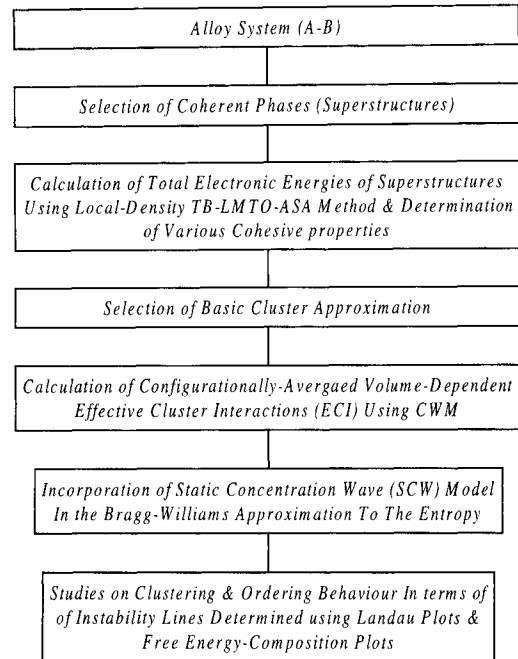


Fig. 4. A flow chart illustrating the scheme of the calculations.

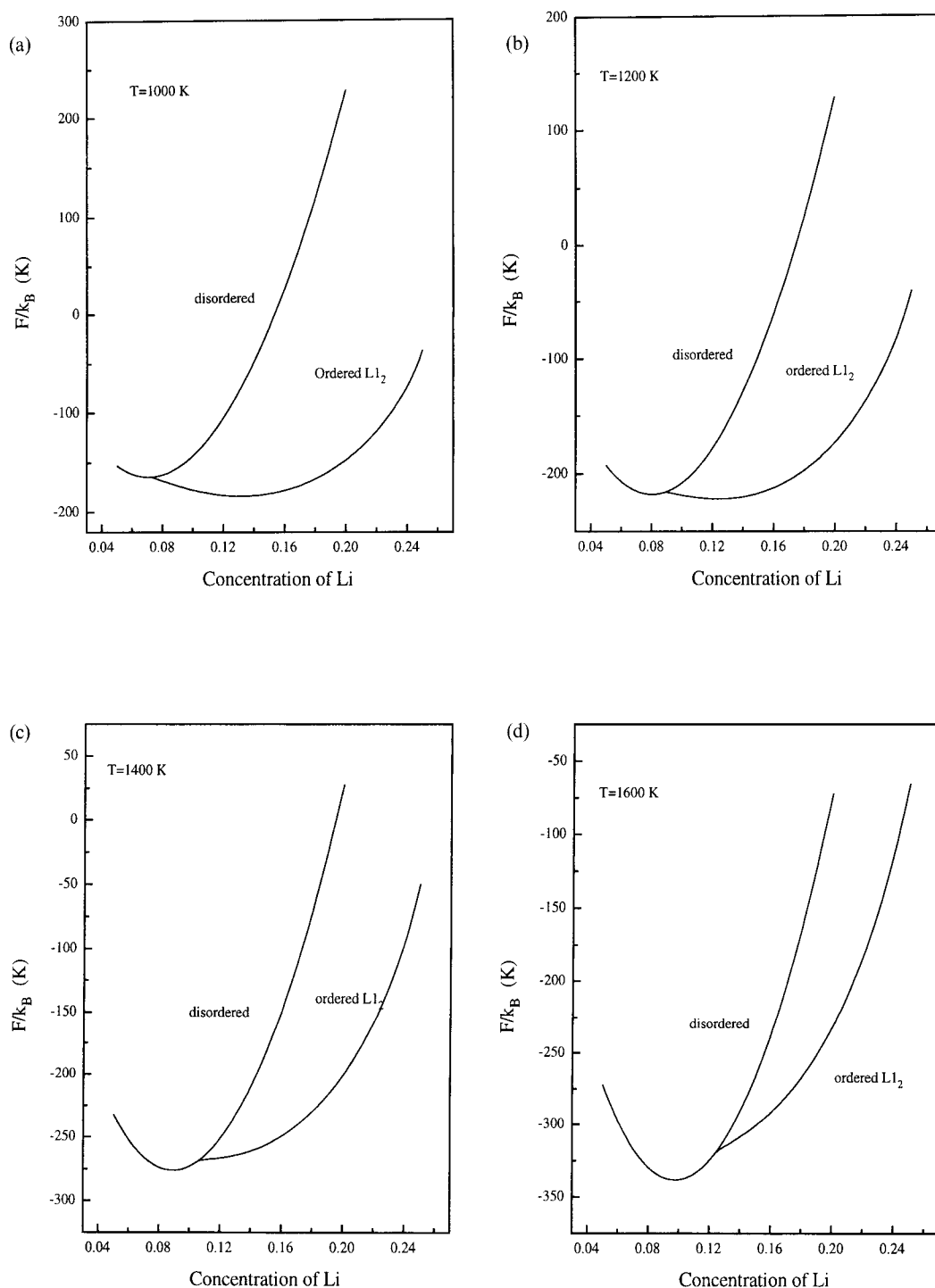


Fig. 5. The free energies of the ordered, δ' - Al_3Li and the disordered α phases plotted as a function of composition at a fixed temperature (a) at 1000 K; (b) at 1200 K; (c) at 1400 K and (d) at 1600 K, respectively. The free energies of the ordered phase were minimized with respect to order parameter, η , at fixed values of temperature and composition. A common-tangent method was used to determine the equilibrium phase boundaries between α and δ' phases.

a fixed composition. Our results have been given in Fig. 6.

It is possible to construct common tangents between the free energy-composition curves corresponding to the α - and the δ' -phases and the compositions marked by the points where the

common tangents touch the $F(c)$ curves indicate the metastable phase boundaries of the two phases. The Landau plots generated from the present first-principles analysis show the conditions at which the disordered solid solution develops instability with respect to $L1_2$ ordering. The temperature correspond-

ing to the onset of instability is defined as T_i^- which has been obtained from $F(\eta)$ plots.

Figure 7 illustrates the variation of equilibrium order parameter (η_{eq}) of the δ' -phase with respect to temperature at the stoichiometric composition. The results of the present theoretical analysis can be

summarized in Fig. 8 in which the metastable phase boundaries of α - and δ' -phases and the instability temperature, T_i^- , are plotted. These results are comparable with that obtained earlier by Garland and Sanchez [33] based on $J_2^{(1)}$ and $J_2^{(2)}$ values calibrated from experimental data.

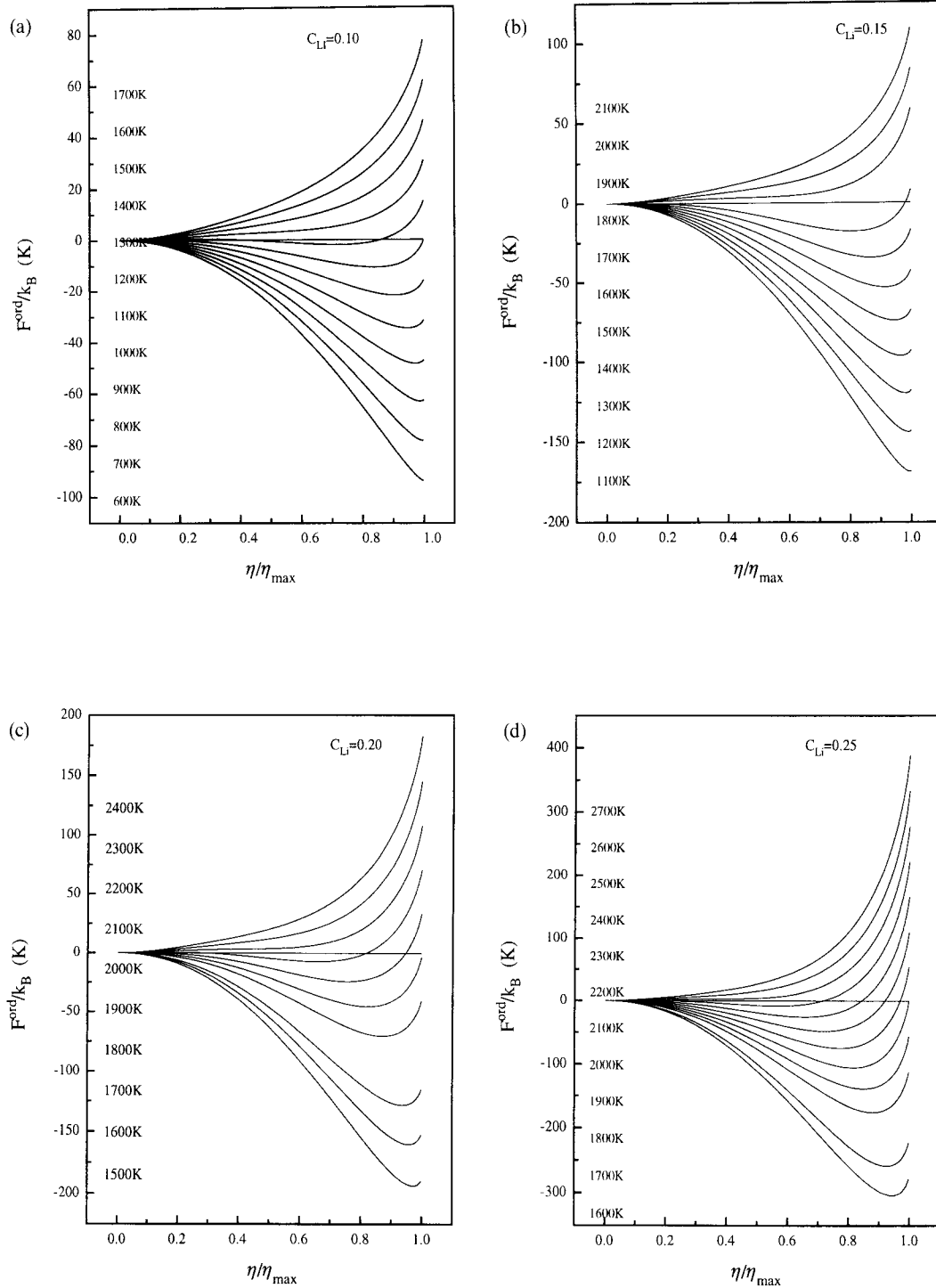


Fig. 6. The free energy (F) of ordering for the $L1_2$ phase plotted as a function of order parameter (η) at various temperatures and a fixed composition (the so-called Landau plots); (a) at 10 at% of Li; (b) at 15 at% of Li; (c) at 20 at% of Li; and (d) at 25 at% of Li, respectively. The instability line, T_i^- for ordering has been determined from these plots.

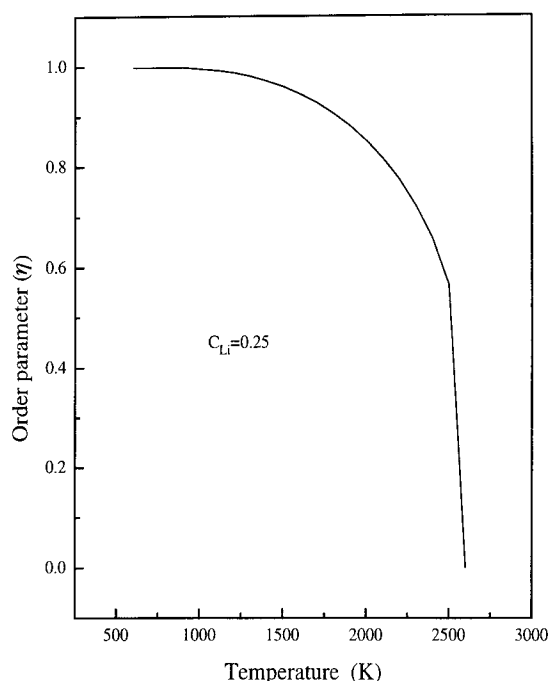


Fig. 7. The equilibrium order parameter (η_{eq}) for the Li_2 -structured Al_3Li at the stoichiometric composition, plotted as a function of temperature.

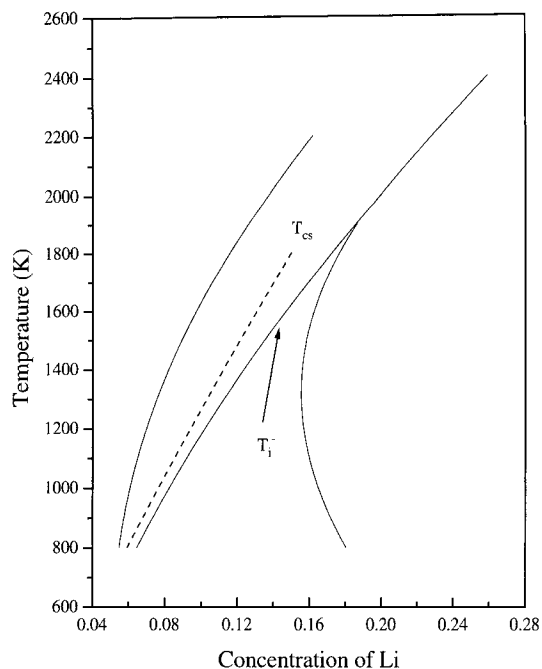


Fig. 8. A portion of the calculated phase diagram in which metastable phase boundaries of α - and δ' -phases have been determined using the common-tangent method. The ordering instability line T_i^- has been determined from the Landau plots as well as from its expression (see text). The clustering instability of the disordered phase T_s has been determined from its expression. The conditional spinodal line T_{cs} has been determined from the free energy versus composition curve for the δ' -phase.

In the SCW model, the ordering instability T_i^- and spinodal clustering instability T_s temperatures as a function of composition, are given as 30.

$$T_s = \frac{J(000)}{k_B} \cdot c(1-c) \text{ and } T_i^- = \frac{J(K)}{k_B} \cdot c(1-c).$$

These lines have also been plotted in Fig. 8. We have also plotted, in Fig. 8, the *conditional spinodal* line (T_{cs}), below which spinodal clustering instability develops after ordering has occurred to a certain extent. The T_{cs} instability line has been determined from the free energy versus composition curves for the ordered δ' -phase at different temperatures.

The present work demonstrates that first principles calculations can be used for predicting the path of a transformation sequence in a system in which the evolving phase is coherent with the parent phase. This approach is sensitive enough to reveal the thermodynamic tendencies which drive the transformation processes. In the hierarchy of the cluster approximations, the lowest level, i.e. point cluster (Bragg-Williams) approximation, has been used for the configurational entropy calculations, as the incorporation of higher level cluster approximation in the SCW model is quite involved.

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