A differential cluster variation method for analysis of spinoidal decomposition in alloys

Zhi-Rong Liu\textsuperscript{1} and Huajian Gao\textsuperscript{1,2}

\textsuperscript{1} Max Planck Institute for Metals Research, D-70569 Stuttgart, Germany
\textsuperscript{2} Division of Mechanics and Computation, Department of Mechanical Engineering, Stanford University, Stanford, California 94305, USA

Abstract

A differential cluster variation method (DCVM) is proposed for analysis of spinoidal decomposition in alloys. In this method, lattice symmetry operations in the presence of an infinitesimal composition gradient are utilized to deduce the connection equations for the correlation functions and to reduce the number of independent variables in the cluster variation analysis. Application of the method is made to calculate the gradient energy coefficient in the Cahn-Hilliard free energy function and the fastest growing wavelength for spinodal decomposition in Al-Li alloys. It is shown that the gradient coefficient of congruently ordered Al-Li alloys is much larger than that of the disordered system. In such an alloy system, the calculated fastest growing wavelength is approximately 10 nm, which is an order of magnitude larger than the experimentally observed domain size. This may provide a theoretical explanation why spinodal decomposition after a congruent ordering is dominated by the antiphase boundaries.

PACS: 64.75.+g, 81.30.-t, 05.70.Ln, 64.60.Cn

Typeset using REVTEX
I. INTRODUCTION

Phase transformation is critically important to the development of new materials since it yields abundant microstructures in the micro/mesoscopic scales. In general, there are two kinds of kinetics for phase transformation, i.e., a nucleation process from an initial metastable state or a spinodal decomposition from an initial unstable state. In the latter case, the phase transformation is determined mainly by diffusion since there is no thermodynamic barrier.\(^1\)–\(^3\) Compared with that in a nucleation process, the domain size distribution width in a spinodal decomposition of binary systems is greatly compressed, which may produce rather interesting nanostructures.\(^4\) Spinodal decomposition has been commonly used to control grain structure in materials such as Alnico alloys and Al-Li alloys to enhance the properties of these materials.\(^5\)–\(^7\)

The mostly widely used continuum theory to describe spinodal decomposition was presented by Cahn and Hilliard.\(^8\),\(^9\) The free energy of a compositionally non-uniform alloy is expressed in the theory as a Ginzburg-Landau expression:

\[
F(\{c(r)\}) = \int [f_0(c) + \kappa(\nabla c)^2] d^3r, \tag{1}
\]

where \(f_0(c)\) is the local free energy density of the homogeneous system and \(\kappa\) is the gradient energy coefficient. In the initial stage of spinodal decomposition, the Cahn-Hilliard equation can be approximately linearized and analytically solved. When possible strain effect is ignored, one finds a fastest growing wavelength\(^10\)

\[
\lambda_m = 4\pi \left[ \frac{\kappa}{\partial^2 f_0(c)} \right]^{1/2}. \tag{2}
\]

It has been recognized that \(\lambda_m\) is an important quantity to characterize domain size distribution in the decomposition process, hence could be useful in the design and evaluation of new materials. The local free energy density \(f_0(c)\), which describes the equilibrium thermal properties of system, can be obtained from the highly accurate calculation-of-phase-diagram (CALPHAD) method or other theoretical methods such as cluster variation method (CVM).
and molecular dynamics (MD). However, the gradient energy coefficient $\kappa$, as a parameter related to the non-equilibrium kinetics, has seldom been directly calculated. Considering only the nearest-neighbor interactions, $\kappa$ of an AB binary alloy with simple cubic lattice was expressed under a point mean-field approximation (regular solution model) as:

$$\kappa = \frac{2}{3} h_{0.5}^M r_0^2,$$  \hspace{1cm} (3)

in which $h_{0.5}^M$ is the heat of mixing per unit volume at the composition $c = 0.5$ and $r_0$ is the nearest-neighbor distance. Recently, by using a supercell CVM approach, Asta and Hoyt calculated the gradient coefficient of Ag-Al alloys and revealed some behaviors of $\kappa$ that are different from the prediction of the regular solution model. As these authors pointed out, the values of $\kappa$ may have been influenced by the choice of parameters in their method because of the effects of higher order terms in the gradient expansion of free energy. In this paper, we present a differential cluster variation method (DCVM) to calculate the gradient energy coefficient. As will be shown, this method naturally avoids the influence of the higher order terms in free energy expansion.

In phase transformation, the decomposition process can be accompanied by an ordering process. Due to the long-range diffusion associated with decomposition and the short-range diffusion associated with ordering, a congruent ordering process frequently occurs prior to the decomposition process. For example, in Al-Li alloys, an important aerospace material, ordering and decomposition processes result in precipitates of an ordered $\delta'$ ($\mathrm{Al}_3\mathrm{Li}$) phase. If a congruent ordering process takes place first, spinodal decomposition does not occur from an initial disordered phase, but from a congruent ordered phase, in which case Eq.(3) is no longer applicable. It would be interesting to explore the influence of congruent ordering on the values of $\kappa$. By using the proposed DCVM method, we will calculate the gradient coefficient and the fastest growing wavelength of Al-Li alloys, and discuss implications on the actual decomposition process.
II. METHODS

Cluster variation method (CVM) is a highly efficient microscopic method to evaluate the configurational free energy and determine the order-disorder phase transformation. In an alloy system, the configurational free energy is determined by the probabilities of all possible configurations. The essence of CVM lies in using the probability of some small clusters to approximately evaluate the probability of the entire system in order to greatly decrease the number of independent variables. For example, in a point approximation, one needs only to determine the composition at every site such that the number of degrees of freedom of the system decreases from $2^N$ to $N$ where $N$ is the number of atoms in the system. For a homogeneous structure, clusters related by the symmetry operations of the lattice can be considered as identical, and the number of independent variables can be further reduced. For example, for the schematic system shown in Fig. 1 under the point approximation, the symmetry of the lattice has the following relations:

$$x_1 = x_3 = \cdots = x_{2i+1} = \cdots;$$
$$x_2 = x_4 = \cdots = x_{2i} = \cdots,$$

(4)

where $x_i$ denotes the point probability at site $i$. By using the above symmetry relations, the number of independent variables decreases from $N$ to $n$ ($n = 2$ in this case). In this way, the equilibrium properties of the system, including the local free energy density $f_0(c)$ in Eq. (1), can be easily determined.

When there are compositional fluctuations in the system, the free energy can be expanded upon the homogeneous state. In principle, the compositional fluctuations can be expressed in a sum of Fourier components and the free energy expansion of any Fourier component can be independently solved by the general $k$-space formalism of standard fluctuation theory. In this paper, however, we directly consider a composition gradient in the system (see Fig. 1) in order to evaluate the gradient coefficient $\kappa$ in Eq. (1). The introduction of the gradient will destroy the symmetry of the lattice (point group and translations), and Eq. (4) is no
longer valid. The number of independent variables would become much larger than that in the homogeneous case. One method to solve this problem is to enlarge the number of independent variables, i.e., to use a supercell, to include a non-uniform composition variance. In the work of Asta and Hoyt, 98 planes were used to calculate the gradient coefficient of Ag-Li alloys.\footnote{In fact, Eq. (1) is defined under the condition of small composition gradient $\nabla c$. If $\nabla c$ is too large, higher order terms in the free energy expansion may be important and cannot be simply ignored. To avoid the influence of higher order terms, one can examine the response of the system to an infinitesimal composition gradient. Such an analysis could bring a great advantage: clusters related by lattice symmetry operations under the uniform state can be related by some equations under an infinitesimal gradient variance, and one needs not to consider a supercell. We develop such a method in the following.}

Assume there are two kinds of infinitesimal variances applied upon the system: (1) an infinitesimal composition gradient $\nabla c = d g$ which keeps the composition at the origin as $c$ and (2) an infinitesimal uniform composition variance $d c$. In general, the variation of the correlation function of a cluster can be expanded as (we use the correlation function to effectively replace the probability function of the cluster in order to simplify the statement):

$$
\xi(c, d g, d c) = \xi(c) + \left( \frac{\partial \xi}{\partial g} \cdot d g + \frac{\partial \xi}{\partial c} \cdot d c \right) + \frac{1}{2} \left[ \frac{\partial^2 \xi}{\partial g \partial g} \cdot d g d g + 2 \frac{\partial^2 \xi}{\partial g \partial c} \cdot d g d c + \frac{\partial^2 \xi}{\partial c \partial c} (d c)^2 \right],
$$

(5)

where $\frac{\partial \xi}{\partial g}, \frac{\partial \xi}{\partial c}, \frac{\partial^2 \xi}{\partial g \partial g}, \ldots$ are expansion coefficients to be determined by minimizing the free energy. We have expanded $\xi$ only to second order terms because the gradient energy in Eq. (1) is related to the second order terms of the free energy. Now consider a translation operation (with a displacement vector $L$) which is a symmetry operation under the uniform case. When there is a gradient variance $d g$, the system after the translation is not identical to that before the translation. The composition of the system changed by $-L \cdot d g$ after translation. However, if one adds a uniform composition variance $L \cdot d g$ to it, the system will be identical to that before the translation. Therefore, for two clusters located at $r$ and
\( r+L \) which are related by the translation operation, the symmetry property gives

\[
\xi_{r+L}(c, dg, dc) = \xi_r(c, dg, dc + L \cdot dg).
\] (6)

By substituting Eq. (5) into the above equation, one obtains

\[
\xi_{r+L}(c) + \left( \frac{\partial \xi_{r+L}}{\partial t} \cdot dg + \frac{\partial \xi_{r+L}}{\partial c} \cdot dc \right) + \frac{1}{2} \left[ \frac{\partial^2 \xi_{r+L}}{\partial g^2} : dgdg + 2 \frac{\partial^2 \xi_{r+L}}{\partial g \partial c} \cdot dgdc + \frac{\partial^2 \xi_{r+L}}{\partial c^2} (dc)^2 \right] 
\]

\[
= \xi_r(c) + \left[ \frac{\partial \xi_r}{\partial g} \cdot dg + \frac{\partial \xi_r}{\partial c} (dc + L \cdot dg) \right] 
\]

\[
+ \frac{1}{2} \left[ \frac{\partial^2 \xi_r}{\partial g^2} : dgdg + 2 \frac{\partial^2 \xi_r}{\partial g \partial c} \cdot dg(dc + L \cdot dg) + \frac{\partial^2 \xi_r}{\partial c^2} (dc + L \cdot dg)^2 \right],
\] (7)

which gives the following connection equations for the expansion components:

\(
\xi_{r+L}(c) = \xi_r(c),
\) (8)

\[
\frac{\partial \xi_{r+L}}{\partial g} = \frac{\partial \xi_r}{\partial g} + \frac{\partial \xi_r}{\partial c} L,
\] (9)

\[
\frac{\partial \xi_{r+L}}{\partial c} = \frac{\partial \xi_r}{\partial c},
\] (10)

\[
\frac{\partial^2 \xi_{r+L}}{\partial g \partial g} = \frac{\partial^2 \xi_r}{\partial g^2} + 2 \frac{\partial^2 \xi_r}{\partial g \partial c} L + \frac{\partial^2 \xi_r}{\partial c^2} LL,
\] (11)

For a point group operation, similar equations can be given. Based on these equations, for a group of clusters related by the symmetry operations of the lattice, their correlation functions (or probability functions) can be expressed by that of a representative independent cluster even if there is an (infinitesimal) gradient variance.

To deduce the equations to solve the expansion coefficients, we expand the differential of the free energy as:

\[
\frac{\partial F(c, dg, dc)}{\partial \xi_i} = \frac{\partial F(c)}{\partial \xi_i} + \sum_j \frac{\partial^2 F(c)}{\partial \xi_i \partial \xi_j} d\xi_j + \frac{1}{2} \sum_{j,k} \frac{\partial^3 F(c)}{\partial \xi_i \partial \xi_j \partial \xi_k} d\xi_j d\xi_k
\]

\[
= \frac{\partial F(c)}{\partial \xi_i} + \sum_j \frac{\partial^2 F(c)}{\partial \xi_i \partial \xi_j} \left( \frac{\partial \xi_j}{\partial g} \cdot dg + \frac{\partial \xi_j}{\partial c} dc \right) + \frac{1}{2} \left[ \frac{\partial^2 \xi_i}{\partial g \partial g} : dgdg + 2 \frac{\partial^2 \xi_i}{\partial g \partial c} \cdot dgdc + \frac{\partial^2 \xi_i}{\partial c^2} (dc)^2 \right] 
\]

\[
+ \frac{1}{2} \sum_{j,k} \frac{\partial^3 F(c)}{\partial \xi_i \partial \xi_j \partial \xi_k} \left( \frac{\partial \xi_j}{\partial g} \cdot dg + \frac{\partial \xi_j}{\partial c} dc \right) \left( \frac{\partial \xi_k}{\partial g} \cdot dg + \frac{\partial \xi_k}{\partial c} dc \right).
\] (12)

For a non-point cluster, the minimization of the free energy gives...
\[
\frac{\partial F(c, dg, dc)}{\partial \xi_i} = 0. 
\]

(13)

For a point cluster, the free energy should be minimized under the composition constraint as

\[
\frac{\partial F(c, dg, dc)}{\partial \xi_i} = \mu_i, 
\]

(14)

where \(\mu_i\) is the chemical potential at site \(i\) which controls the composition in the system. It has a uniform value at different sites in a homogeneous system. When there is a gradient composition variance, \(\mu_i\) also varies with gradient. Combining Eqns. (12-14), the equations to determine the expansion coefficients, \(\frac{\partial \xi_i}{\partial g}, \frac{\partial \xi_i}{\partial c}, \frac{\partial^2 \xi_i}{\partial g \partial g}, \ldots\), can be easily obtained.

After solving the expansion coefficients, one can calculate the free energy of the system under any infinitesimal gradient and uniform variances as:

\[
F(c, dg, dc) = F(c) + \sum_i \frac{\partial F(c)}{\partial \xi_i} d\xi_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 F(c)}{\partial \xi_i \partial \xi_j} d\xi_id\xi_j 
\]

(15)

The gradient energy coefficient \(\kappa\) is then calculated according to Eq. (1). Since the free energy is expressed as an energy part and an entropy part in CVM, one can further calculate the contributions of the energy and the entropy to the gradient coefficient respectively. In the regular solution model, the entropy depends only on the point probability, hence it has no contribution to the gradient coefficient. When the correlations between different points are considered (such as CVM), as we will demonstrate next, the entropy will give contribution to the value of \(\kappa\). Eq. (15) can also be used to evaluate \(\frac{\partial^2 f_0(c)}{\partial c^2}\), a key quantity for evaluating the fastest growing wavelength [see Eq. (2)], since it is related to the second expansion term of the free energy under a uniform composition variance.

The method proposed here can be generalized to including higher order terms in the expansion of the free energy and other kinds of infinitesimal variance. This will not be pursued in this paper.
III. RESULTS AND DISCUSSIONS

Now we apply the above method to calculate the gradient energy coefficient along the (100) direction in the f.c.c. lattice.

To compare the new method with the regular solution approximation, we first consider an exemplary AB spinodal system with the nearest-neighbor interaction. The value of the nearest-neighbor effective pair interaction is arbitrarily chosen as $-100k_B$ ($k_B$ is the Boltzmann constant). The nearest neighbor pair is used as the basic cluster in CVM calculation for this case. This is a very “pure” spinodal system that experiences a decomposition into a mixture of A-rich and B-rich disordered phases at low temperatures. There is no other ordering or decomposition process in the system. The spinodal temperature at a composition $c = 0.5$ is determined as $T_c = 1090K$ in our calculation.

The calculation results of the gradient energy coefficient $\kappa$ as functions of temperature $T$ are shown in Fig. 2 for the uniform composition $c = 0.5$ (solid) and $c = 0.25$ (dashed). The result of the regular solution model is also plotted in Fig. 2 as the dotted line for comparison. For $c = 0.5$, the calculated $\kappa$ value is very close to the value predicted by the regular solution model at high temperatures ($T > 600K$). At low temperatures, the $\kappa$ value rapidly increases with decreasing temperature. When $c = 0.25$, the situation is similar, except that $\kappa$ is roughly 4% higher than the regular-solution-model value at high temperatures.

The values of $\kappa$ coming from energy and entropy contribution (denoted as $\kappa_E$ and $\kappa_S$) are calculated respectively and the results are plotted in Fig. 3. It can be seen that the entropy gives no important contribution to $\kappa$ at high temperatures, which is consistent with the prediction of the regular solution approximation. However, when the temperature is low enough ($T < 300K$), the entropy contributes an non-negligible negative value to the gradient coefficient $\kappa$. This result is comprehensible from the consideration that pair correlations involved in the CVM calculation is important at low temperatures.

In Fig. 4 the calculated values of $\kappa$ are plotted as a function of composition at temper-
atures $T = 500$ and $700 \, K$. Since the curves are symmetrical about $c = 0.5$, only the parts in the range $0 < c < 0.5$ are plotted. It can be seen that the $\kappa$ value at $c = 0.5$ is the closest to the regular solution approximation value. When the composition deviates from 0.5, $\kappa$ increases steadily. An increment of about 30% and 50% is obtained for $T = 500$ and $700 \, K$ respectively when the composition decreases to $c = 0$. Different from Ref. 11, no abnormal behavior is observed at $c = 0$ in Fig. 4.

From the above results, we see that the gradient coefficient $\kappa$ increases with decreasing temperature and composition (for $c < 0.5$). These characteristics are consistent with previous supercell CVM calculation results on Ag-Al alloys, where a similar spinodal decomposition process on disordered phase was considered. In comparison, our results are closer to the regular solution approximation values, while the previous supercell results for Ag-Al are about three to four times larger than the mean-field values.

Then we turn to a realistic system, Al-Li alloys, one of the best known examples for material ordering strengthening. In this system, ordering and decomposing processes coexist. Due to the difference in diffusion length scales, ordering process usually occurs much faster than the decomposing process. We first optimize the ordered parameter at every composition, i.e., use the conventional CVM process to determine the ordered state of the homogeneous system. Then we use the DCVM method to investigate the response of the system to a gradient variance. In other words, we calculate the gradient coefficient of the congruent ordered phase. The effective pair interaction parameters are taken from the study of Garland et al., where the nearest and second-nearest-neighbor effective pair interactions were chosen as $210 \, k_B$ and $-105 \, k_B$, respectively.

The calculated gradient energy coefficient $\kappa$, together with the contributions from energy and entropy parts ($\kappa_E$ and $\kappa_S$), are shown in Fig. 5 as functions of Li composition at $T = 500 K$. An extraordinary characteristic of the result is that the calculated $\kappa$ of Al-Li alloys here is about one order of magnitude larger than that in Ag-Al and Al-Zn alloys. This indicates that the congruent ordering greatly affects the gradient coefficient of the system. When a congruent ordering occurs in Al-Li alloys, the face-center sites of f.c.c.
lattice are mainly occupied by Al atoms, resulting in a very low local Li composition at these sites. This may be an important source of the large $\kappa$ in Al-Li alloys if one remembers that $\kappa$ increases for small composition in disordered phase (Fig. 4 and Ref. 11).

Fig. 5 also indicates that the entropy contribution to the gradient coefficient, $\kappa_S$, is positive in value. It even exceeds the contribution from the energy. This reveals a strong correlation effect between points at different sites for the congruent ordered phase.

By using the $\kappa$ value in Fig. 5, the fastest growing wavelength $\lambda_m$ is calculated according to Eq. (2) for various Li compositions. It appears that $\lambda_m$ is on the order of about 10 nm (Fig. 6). According to previous experiments and microscopic simulations, the modulation wavelength of Al-Li alloys in the early stage is about $1 \sim 2$ nm. The discrepancy between the current calculated $\lambda_m$ value and the experiments and the previous simulation results may be attributed to the existence of antiphase boundaries in the congruent ordered phase. When a spinodal decomposition occurs after a congruent ordering, the microscopic simulation reveals that the structural evolution in the decomposition process is dominantly governed by the antiphase boundaries produced in the congruent ordering process, e.g., the equilibrium disordered phase appears and grows at the antiphase boundaries. The antiphase boundaries play the role of nuclei for phase decomposition. Thus the modulation wavelength is determined by the distribution of antiphase boundaries. However, inside the spinodal region of the phase diagram, any fluctuation, no matter how small in degree, decreases the free energy and the system is unstable. So it is quite confusing why a spinodal decomposition does not occur inside the congruent ordered domains even if such process would be spontaneous. The calculation result of the fastest growing wavelength in Fig. 6 provides a key to answer this problem. For the spinodal decomposition process, there is a critical wavelength $\lambda_c = \lambda_m/\sqrt{2}$. Fourier components with modulation wavelength $\lambda < \lambda_c$ will decay while those with $\lambda > \lambda_c$ will grow. According to the results in Fig. 6, the critical wavelength $\lambda_c$ is larger than the size of congruent ordered domains observed in experiments and previous simulation. Therefore, the spinodal process is suppressed inside the congruent ordered domains. On the basis of this explanation, when a decomposition process occurs
after the congruent ordering, there is no essential difference for the systems inside and outside the spinodal region since the antiphase boundaries act as nuclei for decomposition. It also implies that an attempt to distinguish if the Al-Li alloys is spinodal or not after the congruent ordering is not important to the actual process.

It should be noted that the strain energy is not considered in the current calculation of the fastest growing wavelength $\lambda_m$. If the strain effect is involved, $\lambda_m$ is expected to be larger than the current values, which will not change the above conclusions.

Fig. 7 shows the gradient energy coefficient $\kappa$ of Al-Li alloys as functions of temperature when the Li composition is fixed as 15%. Different from the case of the disordered phase (Fig. 3), $\kappa$ of Al-Li alloys increases with increasing temperature. Only when the temperature is close to the stability limit of the ordered phase does the $\kappa$ value drop rapidly. Accordingly, the curve of the fastest growing wavelength exhibits a peak near the limiting temperature (see the inserted graphics in Fig. 7).

IV. SUMMARIES

In summary, a differential cluster variation method (DCVM) is developed this paper and used to calculate the gradient energy coefficient ($\kappa$) in the Cahn-Hilliard course-grained free energy for spinodal decomposition. The symmetry equations for clusters related by symmetry operations of a lattice are deduced under an infinitesimal composition gradient in the system. This treatment greatly reduces the number of independent variables in comparison with a supercell CVM analysis. The DCVM is an intrinsic method to determine different order terms in the gradient expansion of the free energy. The value of $\kappa$ of two systems with f.c.c. lattice are calculated by this new method. It is shown that the $\kappa$ values for the system with only the nearest-neighbor interaction are very close to the prediction of the point mean-field approximation (regular solution model) for most system states, while non-negligible differences exist at low temperatures and extreme compositions. For the Al-Li alloys where a congruent ordering occurs prior to the spinodal decomposition, $\kappa$ is
found to be much larger than the disordered system. The fastest growing wavelength is calculated to be approximately 10 nm at 500 \( K \), which is one order of magnitude larger than the experimentally observed domain size. This provides a theoretical explanation to the previous discovery that the spinodal decomposition after congruent ordering is dominated by the antiphase boundaries produced in the congruent ordering process.

ACKNOWLEDGMENT

This work was supported by a Max Planck Post-Doc Fellowship for ZL. The work is also supported by US National Science Foundation through Grant CMS-0085569. We thank Prof. Long-Qing Chen at the Pennsylvania State University for very helpful discussions.
REFERENCES

1. J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983), Vol. 8, p. 267.

2. K. Binder, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, Weinheim, 1991), Vol. 5, p. 405.

3. A. J. Bray, Adv. Phys. 43, 357 (1994).

4. S. Herminghaus, K. Jacobs, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elhaj, and S. Schlagowski, Science 282, 916 (1998).

5. B. Cullity, *Introduction to magnetic materials* (Addison-Wesley, Reading, MA, 1 edition, 1972).

6. J. M. Silcock, J. Inst. Metals 88, 357 (1959-60).

7. A. J. McAlister, Bull. Alloy Phase Diag. 3, 177 (1982).

8. J. W. Cahn, and J. E. Hilliard, J. Chem. Phys. 28, 258 (1958).

9. J. W. Cahn, and J. E. Hilliard, J. Chem. Phys. 31, 688 (1959).

10. J. W. Cahn, Acta Mater. 9, 795 (1961).

11. M. Asta and J. J. Hoyt, Acta Mater. 48, 1089 (2000).

12. A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).

13. R. Kikuchi, Phys. Rev. 81, 988 (1951).

14. R. Kikuchi, J. Chem. Phys. 60, 1071 (1974).

15. J. M. Sanchez and D. de Fontaine, Phys. Rev. B 21, 216 (1980).
16 H. E. Cook and D. de Fontaine, Acta Metall. 17, 915 (1969).

17 E. Nembach, Prog. Mater. Sci. 45, 275 (2000).

18 L. Q. Chen and A. G. Khachaturyan, Acta Metall. Mater. 39, 2533 (1991).

19 Z. R. Liu, B. L. Gu, H. Gui, and X. W. Zhang, Phys. Rev. B 59, 16 (1999).

20 J. S. Garland and J. M. Sanchez, in Kinetics of Ordering Transformations in Metals, edited by H. Chen and V. K. Vasudevan, p207 (TMS, Warrendale, PA, 1992).

21 J. Mainville, Y. S. Yang, K. R. Elder, M. Sutton, K. F. Ludwig, G. B. Stephenson, Phys. Rev. Lett. 78, 2787 (1997).

22 D. Z. Che, S. Spooner, and J. J. Hoyt, Acta Mater. 45, 1167 (1997).

23 R. Poduri and L. Q. Chen, Acta Mater. 46, 3915 (1998).

24 S. Banerjee, A. Arya, and G. P. Das, Acta Mater. 45, 601 (1997).
FIGURES

FIG. 1. Schematic graphics of a one-dimensional lattice with compositional gradient variance.

FIG. 2. The gradient energy coefficient $\kappa$ as function of temperature $T$ (in units of $K$) for a disordered f.c.c. binary system with the nearest-neighbor interaction $-100\ k_B$; $\kappa$ is measured in units of $k_B/a_0$ where $a_0$ is the lattice constant. The dotted line denotes the predicted value of the regular solution model.

FIG. 3. The energy part ($\kappa_E$) and the entropy part ($\kappa_S$) of the gradient coefficient as function of temperature (in units of $K$) for a disordered system with the nearest-neighbor interaction $-100\ k_B$. The composition is fixed as $c = 0.5$. $\kappa_E$ and $\kappa_S$ are measured in units of $k_B/a_0$ where $a_0$ is the f.c.c. lattice constant.

FIG. 4. The gradient energy coefficient $\kappa$ (in units of $k_B/a_0$) of a disordered f.c.c. binary system as function of composition $c$. The dotted line denotes the predicted value of the regular solution model.

FIG. 5. The gradient coefficient ($\kappa$) and its energy part ($\kappa_E$) and entropy part ($\kappa_S$) of the congruent ordered Al-Li alloys as function of Li composition when the temperature is fixed at $T = 500K$.

FIG. 6. The fastest growing wavelength $\lambda_m$ of the congruent ordered Al-Li alloys calculated according to Eq. (2). The temperature is fixed at $T = 500K$.

FIG. 7. The gradient coefficient of the congruent ordered Al-Li alloys as function of temperature when the Li composition is fixed at 15%. The inserted graphics is the corresponding fastest growing wavelength.
\[ C = C_0 + \alpha x \]
Gradient Coefficient (10^{-10} J/m)

Li composition

- $\kappa$
- $\kappa_E$
- $\kappa_S$
Gradient Coefficient ($10^{-10} \text{ J/m}$)

Temperature $T$ (K)

Inset: 

Wavelength $\lambda_m$ (nm)