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Thermodynamics of order in dilute fcc ternary alloys

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The present paper reports a thermodynamic study of fcc $L1_2$-ordered A_3B alloys under a small addition of a third element C. The derivation is based on a virial expansion of the cluster-variation method. A relation is established among the dimensionless energy parameter $J=(J_{AC}-J_{BC})/J_{AB}$ (J_{AB}, J_{AC}, and J_{BC} being, respectively, the effective pair interaction potential of pairs AB, AC, and BC), the substitutional-site preference of the C element, and the order-disorder transition temperature T_c. These two variables are interrelated through the parameter J which can be eliminated, thus leading to a direct relation between the site preference of the ternary element and the variation of T_c.

I. INTRODUCTION

Numerous metallic binary alloys show substitutional chemical ordering in their equilibrium phase diagrams. Since the structural state of the alloy is of primary importance for some of its physical properties, the addition of a third element can significantly influence the state of order, thus modifying some of the physical properties of the alloy. For example, the mechanical properties of Ni_3Al (γ') can be improved by a small addition of a third element, depending on where this element substitutes and on the composition of the initial binary alloy.[1]

Generalized mean field approximations such as Kikuchi's cluster variation method (CVM) can predict with good accuracy the order-disorder transition lines for ternary systems.[2] Input parameters are the effective pair interaction potentials, which can be experimentally deduced from diffuse scattering experiments for the three kinds of constituent-element pair.[3] These measurements are generally a difficult task, especially for ternary systems where a contrast variation method is required to access the pair potentials. In most practical cases, the system is ill-conditioned and only two pair correlation functions can be determined with reasonable accuracy.

The goal of the present work is twofold

(i) Extract as much information as possible on the effective pair interaction potentials from the sole characteristic features of the phase diagram, such as the variation of the order-disorder transition temperature upon adding a small amount of a third element,

(ii) Connect directly these characteristic features in bypassing the explicit use of the pair potentials. Such correlations between characteristics that could be measured independently should be very useful for alloy designing.

To discuss point (i), we refer to the recent studies by Enomoto *et al.*[4] and Wu *et al.*[5] based upon the cluster variation method in the tetrahedron approximation in $L1_2$ alloys for the calculation of the site occupation probability of the third element. Their results suggest that a single reduced energy parameter should be found which governs both the added element preference for a substitutional site and the variation of the order-disorder transition temperature T_c as a function of the concentration c of the added element. We shall demonstrate that this is indeed the case in using a viral expansion of the CVM tetrahedron approximation involving four independent sublattices (space group *Pmmm*). Subsequent algebraic derivation leads to a direct relation between the site preference and dT_c/dc [point (ii)]. Numerical examples of the master equation dT_c/dc versus site preference calculated for $L1_2$ ordered alloys are finally given.

II. FORMALISM

The method used here is the cluster variation method in the tetrahedron approximation (T-CVM); it is known to provide a consistent binary phase diagram.[6] The thermodynamical variables are the tetrahedron, pair, and point probabilities. The CVM free energy functional associated with a phase of symmetry *Pmmm* in the fcc lattice is[7]

$$\beta F=2\sum_i \beta E_i T_i+\sum_i 2T_i(\ln T_i-1)-\sum_i Y_i(\ln Y_i-1)+\tfrac{5}{4}\sum_i U_i(\ln U_i-1)\ , \tag{1}$$

where T_i, Y_i, and U_i are respectively the tetrahedron, pair, and point probabilities. E_i is the configurational energy of the ith configuration of the tetrahedron and β is the Boltzmann factor. The index i runs over all possible cluster configurations.

In the canonical ensemble (fixed concentrations), besides the normalization constraint there are two additional constraints on the tetrahedron probabilities:

$$\sum_i T_i=1\ ,\quad \tfrac{1}{4}\sum_i N_i^A T_i=C_A\ ,\quad \tfrac{1}{4}\sum_i N_i^C T_i=C_C\ , \tag{2}$$

where N_i^A (N_i^C) is the fraction of A (C) in the ith tetrahedron, and C_A (C_C) is the total concentration of A (C) in the alloy. For example, in the tetrahedron configuration $AABC$, $N_i^A=0.5$ and $N_i^C=0.25$.

Pair and point probabilities are partial sums of tetrahedron probabilities and can therefore be written as

$$Y_i = \sum_j N_{ij}^{Y} T_j \;, \tag{3a}$$

$$U_i = \sum_j N_{ij}^{U} T_j \;. \tag{3b}$$

The elements of matrices N_{ij}^{Y} and N_{ij}^{U} are positive integers, taking the value 0 or 1 whether the ith configuration of the subcluster Y and U is or is not embedded in the jth configuration of the tetrahedron. In the *Pmmm* phase, there are six matrices N^Y of dimension 9×81 and 4 matrices N^U of dimension 3×81; however, in higher symmetry phases, owing to sublattice degeneracies both the number of independent matrices and the dimensionality are reduced. For example, in the $A1$ phase, all the pairs belong to the same orbit, thus there is only one N^Y matrix of dimension 6×15.

The expression for the free energy βF (1) together with the constraints (2) form a Kuhn and Tucker set of equations[8] which can be solved using the standard Newton-Raphson iteration method. The three constraints require the introduction of three Lagrange multipliers λ_0, λ_A, and λ_C, respectively, for normalization and concentration constraints. From these definitions, λ_A and λ_C are equivalent to the chemical potentials A and C, and λ_0 represents the grand canonical free energy.

Then, minimizing the free energy (1) while keeping the constraints (2) is equivalent to minimizing the following expression:

$$\beta\mathcal{F} = \beta F + \beta\lambda_0 \left[1 - \sum_i T_i\right] + \beta\lambda_A \left[C_A - \sum_i N_i^{A} T_i\right] + \beta\lambda_C \left[C_C - \sum_i N_i^{C} T_i\right] . \tag{4}$$

In general, the basic cluster probability set does not form a basis as many configurations might be redundant and therefore cannot be chosen as variables for minimization purposes. This would be the case for a basic cluster whose point symmetry does not match the lattice symmetry, such as the double square in the square lattice; or the case of a multiheaded cluster such as the tetrahedron-octahedron in the fcc lattice. In the latter case, in addition to the normalization condition, constraints are involved to take into account the overlapping between the tetrahedron and the octahedron following regular shaped triangles. However, the tetrahedron cluster is a simplex and as long as we describe phases involving only one tetrahedron, the probabilities can be chosen as the independent variables.

The equilibrium state is defined by the set of T_i's fulfilling $\beta F/\partial T_i = 0$ under the constraints (2). Let **B** be the gradient of the free energy with respect to the T_i's; taking into account pair and point probabilities definitions (3a) and (3b), we finally obtain

$$B_i = 2\beta E_i + 2\ln T_i - \sum_j N_{ji}^{Y} \ln Y_j + \sum_j N_{ji}^{U} \ln U_j - (\beta\lambda_0 + N_i^{A}\beta\lambda_A + N_i^{C}\beta\lambda_C) = 0 \;. \tag{5}$$

As such, this equation is not suitable for numerical calculations in the vicinity of the binary edge AB of the phase diagram. Indeed, it contains diverging terms at $C_C = 0$ coming from the logarithms of vanishing probabilities and from the Lagrange multiplier λ_C. To overcome this difficulty we first observe that vanishing cluster probabilities decrease in the mean field limit $C_C \to 0$ as $C_C^{n_i}$, where n_i is the number of sites in the considered cluster occupied by C atoms. We therefore define new probability variables by

$$T_i = \tilde{T}_i c^{\alpha_i}, \quad Y_i = \tilde{Y}_i c^{\beta_i}, \quad U_i = \tilde{U}_i c^{\gamma_i} \tag{6}$$

where

$$\tilde{Y}_j = \sum_i N_{ji}^{Y} \tilde{T}_i = \sum_i \tilde{N}_{ji}^{Y} T_i \;, \quad \tilde{U}_j = \sum_i \tilde{N}_{ji}^{U} T_i \;,$$

α_i (β_i and γ_i) is the number of C atoms embedded in the ith configuration of the tetrahedron (of pairs and points), and c is a short notation for the concentration C_C.

Here, $\tilde{T}_i$, $\tilde{Y}_i$, $\tilde{U}_i$ take nonzero positive values, even on the binary side AB of the ternary system ABC. Since the number of C atoms in a tetrahedron is necessarily larger or equal to the number of C atoms in any of its embedded subcluster, we have the inequalities $\alpha_i - \beta_i \geq 0$ and $\alpha_i - \gamma_i \geq 0$ which ensure that the terms $\tilde{N}_{ji}$ never diverge as c approaches zero.

The equilibrium expression can now be rewritten in terms of the tilde variables as follows:

$$B_i = 2\beta E_i + 2\ln\tilde{T}_i - \sum_j N_{ji}^{Y} \ln\tilde{Y}_j + \sum_j N_{ij}^{U} \ln\tilde{U}_j - (\beta\lambda_0 + N_i^{A}\beta\lambda_A + N_i^{C}\beta\lambda_C) - \left[2\alpha_i - \sum_j \beta_j N_{ji}^{N} + \tfrac{5}{4}\sum_j \gamma_j N_{ji}^{Y}\right] \ln c = 0 \;. \tag{7}$$

At this stage, the only remaining diverging terms are λ_C and $\ln c$. But, as demonstrated in Appendix A, the prefactor of $\ln c$ in the expression (7) is equal to the factor of $\beta\lambda_C$ which, in turn, diverges like $-\ln c$ when approaching the binary edge. Thus, we can introduce a nondivergent chemical potential $\tilde{\lambda}_C$ defined by

$$\beta\tilde{\lambda}_C = \beta\lambda_C + \ln c \;, \tag{8}$$

which finally leads to the following equilibrium expression, equivalent to the previous one but with no divergence at the binary edge:

$$\tilde{B}_i = 2\beta E_i + 2\ln\tilde{T}_i - \sum_j N_{ji}^{Y} \ln\tilde{Y}_j + \sum_j N_{ji}^{U} \ln\tilde{U}_j - (\beta\lambda_0 + N_i^{A}\beta\lambda_A + N_i^{C}\beta\tilde{\lambda}_C) = 0 \;. \tag{9}$$

Being interested in the behavior of the thermodynamic quantities of the ternary ABC alloy near the binary edge AB, we can now expand the tilde variables in a Taylor series with respect to both the concentration c and the deviation Δa of the concentration of species A from its reference binary value. For example, the tetrahedron probabilities associated with $\alpha_i = 0$ (also denoted T_{i_0} for short in the following), are expanded as

$$\widetilde{T}_{i_0}=\widetilde{T}_{i_0}^{(0)}+\left[c\frac{\partial\widetilde{T}_{i_0}}{\partial c}+\Delta a\frac{\partial\widetilde{T}_{i_0}}{\partial\Delta a}\right]+\frac{1}{2}\left[c^2\frac{\partial^2\widetilde{T}_{i_0}}{\partial c^2}+2c\Delta a\frac{\partial^2\widetilde{T}_{i_0}}{\partial c\,\partial\Delta a}+\Delta a^2\frac{\partial^2\widetilde{T}_{i_0}}{\partial\Delta a^2}\right]$$

or using shorthand notation as

$$\widetilde{T}_{i_0}=\widetilde{T}_{i_0}^{(0)}+\mathbf{X}^T\widetilde{T}_{i_0}^{(1)}+\tfrac{1}{2}\mathbf{X}^T[\widetilde{T}_{i_0}^{(2)}]\mathbf{X}\ ,$$

where the vector $\mathbf{X}$ belongs to R^2 and has $(c,\ \Delta a)$ for components, and $\widetilde{T}_{i_0}^{(1)}$ accounts for the gradient of the probability set $\widetilde{T}_{i_0}$ with respect to these variables. The second-order terms are represented by the symmetric matrix of second derivatives $[\widetilde{T}_{i_0}^{(2)}]$. In the same way, the probabilities associated with the exponents $\alpha_i=1$ and $\alpha_i=2$ are respectively expanded as $(\widetilde{T}_{i_1}^{(0)}+\mathbf{x}^T\widetilde{T}_{i_1}^{(1)})$ and $\widetilde{T}_{i_2}^{(0)}$. The same expansion is carried out for the Lagrange multipliers too. Equations (9) are then solved, expanding in a cumulant series the logarithm function involving the various probabilities. Setting each term to zero in the expansion, three kinds of minimization subproblems appear.

(i) *The zeroth-order terms.* The zeroth-order terms correspond to $c=0$ and constitute a self-consistent system of nonlinear equations involving only cluster probabilities corresponding to configurations with no C atoms; that is to say, cluster variables associated with exponents α_i, β_i, and γ_i are equal to zero. At this stage the terms that are calculated are the zeroth-order of the probabilities $\widetilde{T}_i^{\alpha_i=0}$ and the two Lagrange multipliers $\beta\lambda_0$ and $\beta\lambda_A$ (i.e., $\widetilde{T}_{i_0}^{(0)}$; $\beta\lambda_0^{(0)}$; $\beta\lambda_A^{(0)}$).

(ii) *The first-order terms.* Having determined the binary system variables, the first-order terms have to be calculated. These terms split into two categories. The first group refers to all the tetrahedron configurations including one atom of C and also to the Lagrange multiplier $\beta\widetilde{\lambda}_C$ associated with the constraint equation: $1=\sum_{i/\alpha_i=1}N_i^C\widetilde{T}_i$. The tetrahedron variables (pairs and points) yielding the equality $\alpha_i=1$ ($\beta_i=1$ and $\gamma_i=1$) and the Lagrange multiplier $\beta\widetilde{\lambda}_C$ constitute a coherent system of nonlinear equations, just as the zero-order terms constituted a coherent system which was the binary alloy *AB*. Let us recall that the variables calculated are the zeroth-order term of the Taylor expansion of $\widetilde{T}_i^{\alpha_i=1}$ and $\beta\widetilde{\lambda}_C$.

The second group of variables determined at this stage deals with the first-order of the Taylor expansion of the probabilities associated with the exponent $\alpha_i=0$ ($\widetilde{\mathbf{T}}_{i_0}^{(1)}$) and of the Lagrange multipliers $\beta\lambda_0^{(1)}$ and $\beta\lambda_A^{(1)}$. These terms are the solution of a system of linear equations, the right-hand side of which involves the first group of variables.

(iii) *The upper order terms.* Let i_0 designate the order considered in the expansion; then every Lagrange multiplier has been determined up to order i_0-1, as well as the corresponding coefficients of the Taylor expansion of variables $\widetilde{T}_j^{\alpha_j}$, $\alpha_j<\alpha_{i_0}$. The next variables to determine, in a hierarchical order, are the zeroth order of tetrahedron configurations $\widetilde{T}_i^{\alpha_{i_0}}$ which involves solving a nonlinear system of equations, the first order of $\widetilde{T}_i^{\alpha_{i_0}-1}$, the second order of $\widetilde{T}_i^{\alpha_{i_0}-2}$ and so on, solving only a linear system of equations whose left-hand side remains the same. As described, the process can be pursued up to $i_0=4$, but higher-order terms can still be determined noticing that there is no more "zeroth" order to compute.

In this study we mainly focus our attention on the zeroth- and first-order terms. In the equilibrium phase diagram, the second- and higher-order terms are partly responsible for the orientation of the solubility lobe of the ordered phase as well as the orientation of the tie-lines of two-phase domains. However, their contribution makes the formalism unclear and may mask the physical meaning of equations in the problem we are considering.

In a first-neighbor pair-interaction (V) model Hamiltonian, a ternary alloy requires three effective pair interaction energies (J) defined as follows:

$$J_{ij}=\frac{V_{ii}+V_{jj}-2V_{ij}}{4}\quad\text{with } j>i\ . \tag{10}$$

As observed in the above section, $\beta\lambda_0$ and $\beta\lambda_A$ contribute to zero-order terms from factors $\beta\lambda_0^0$ and $\beta\lambda_A^0$ that depend only on J_{AB}, in contrast to all their higher-order terms, which depend on all three energy parameters. For example, the first-order terms correspond to cluster probabilities involving a unique C atom. Tetrahedra have four such configurations for which the energy contribution can be easily calculated as shown in the following table. It is convenient to introduce the notation $S=J_{AC}+J_{BC}$ and $D=J_{AC}-J_{BC}$:

*i*th configuration	Energy contribution E_i	
AAAC	$-3J_{AB}$	$-3S/2-3D/2$
AABC	$-2J_{AC}-J_{BC}-2J_{AB}$	$-3S/2-D/2-J_{AB}$
ABBC	$-J_{AC}-2J_{BC}-2J_{AB}$	$-3S/2+D/2-J_{AB}$
BBBC	$-3J_{BC}$	$-3S/2+3D/2$

It can easily be shown that the energy term E_i in the expression (9) is $4N_i^C$ for all tetrahedron configurations containing one unique C atom. Hence in the first-order expansion, the equilibrium relation becomes

$$B_i=2\beta E_i-12N\beta S+2\ln\widetilde{T}_i-\sum_j N_{ji}^{Y}\ln\widetilde{Y}_j+\tfrac{5}{4}\sum_j N_{ji}^{U}\ln\widetilde{U}_j-(\beta\lambda_0+N_i{}^A\beta\lambda_A+N_i^C\beta\widetilde{\lambda}_C)\ . \tag{11}$$

Relation (11) splits into two terms: the first one, $\beta\tilde{\lambda}_C + 12\beta S$, is constant when varying S, so that cluster probabilities $\tilde{T}_i^{\alpha_i=1}$ are unaffected by shifting S; the second term depends explicitly on D irrespective of the value of S. (This result doesn't depend on the CVM approximation and would have been obtained from a "perturbative" expansion of the density matrix.) Therefore, we obtain the important result that, at first order, *the thermodynamic state in the vicinity of the binary edge depends only on the energy parameter* $D = J_{AC} - J_{BC}$. This is easily understood since, indeed, D governs which site will be preferentially occupied by the C atom. Let us consider a simple example. Stating that the reference state of the binary alloy is $L1_2 A_3B$, we first assume that $J_{AC} = 1$ and $J_{BC} = -1$. Then, the tetrahedron with only one C atom and having the lowest energy is $AAAC$. The element C will thus occupy the sublattice defined by the B atoms. Conversely, if we now assume that $J_{AC} = -1$ and $J_{BC} = 1$, the tetrahedra with only one C atom and having the lowest energy are $AACB$, $ACAB$, $CAAB$: the C atom will occupy the sublattice defined by the A atoms. Note that, in both cases, the term $S = J_{AC} + J_{BC}$ is constant (and equal to zero in the chosen example).

We can thus define a dimensionless energy parameter which governs the state of order: $J = (J_{AC} - J_{BC})/J_{AB}$.

The other energy parameter S, associated with the clustering of C atoms, mainly governs the amplitude of the higher order terms and also controls the validity range of the virial expansion as discussed in Appendix B.

We have now to study the long-range order parameter, which describes how the C atoms distribute in the matrix, and to examine how it depends on J and on the reference state of the binary (AB) alloy.

III. APPLICATION

A. Addition of a ternary element C in an $L1_2$ ordered phase A_3B

The $L1_2$ structure consists of two different symmetry orbits, one being formed by the vertices of the unit cube (a), the other one by the face centers of the cube (b). The long-range order (LRO) parameter associated with the atomic species i is defined as the difference of the proportions a_i and b_i of element i between these two orbits: $\eta_i = a_i - b_i$ together with $\sum_i \eta_i = 0$. Since on a tetrahedron one point is a cube vertex and belongs to the first orbit and the other three belong to the second orbit, the LRO parameter associated with C, η_c is bounded by the inequalities $-4c/3 \leq \eta_c \leq 4c$. Thus, η_c tends toward zero when c approaches zero. Since we are interested in small c atomic fractions, we can expand η_c to first order: $\eta_c = c\,\partial\eta_c/\partial c = \dot{\eta}c$. The slope $\dot{\eta}$ indicates which of the two point orbits the C atoms will preferentially occupy. $\dot{\eta}$ depends only on three parameters: the dimensionless binary temperature kT/J_{AB}, the binary alloy concentration C_A, and the dimensionless ternary energy ratio J.

1. *The effect of J*

We have computed $\dot{\eta}$ versus J for several compositions of the binary alloy and several temperatures. All explored compositions belong to the $L1_2$ ordered domain of the phase diagram as computed by Kikuchi using the same thermodynamical approximation (Fig. 1). The results are given in Fig. 2. Three different behaviors of $\dot{\eta}$ are observed depending on J values.

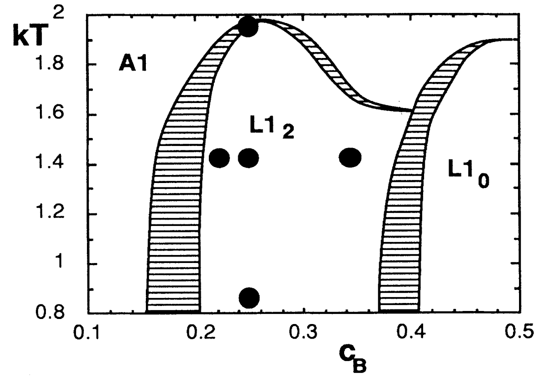

FIG. 1. Computed binary ordering phase diagram within the tetrahedron approximation.

(i) If $J > 1$, $\dot{\eta}$ is positive; C atoms occupy the vertices of the unit cube, irrespective of temperature and composition.

(ii) If $J < -1$, $\dot{\eta}$ is negative; C atoms occupy the face centers, irrespective of temperature and composition.

(iii) If $|J| \leq 1$, $\dot{\eta}$ varies rapidly with J and depends on temperature and composition.

These three behaviors correspond to the three kinds of occupation behavior proposed by Wu *et al.*[5] from a comparison of the energies for different alloy configurations in which C atoms occupy a or b sites. For the two first classes where $|J| \gg 1$, the order parameter is almost unaffected by the temperature and composition of the binary alloy (as long as long-range order exists, of course): the added element C substitutes exclusively on one kind of site. The site preference is essentially governed by a gain in the ordering energy. For ternary alloys belonging to the third class where $|J|$ is small, en-

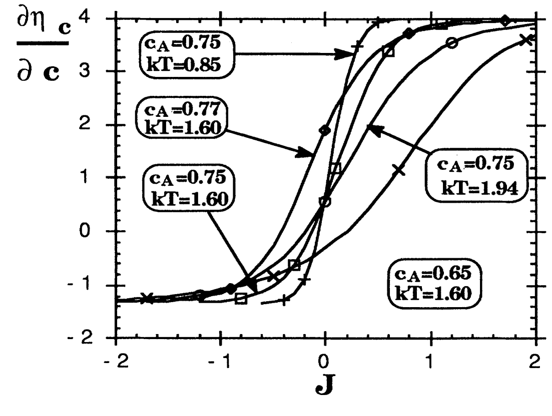

FIG. 2. $\dot{\eta}_c$ vs J for several values of temperature and reference binary-alloy composition both taken in the ordered domain of the binary phase diagram.

tropy factors are competitive with energy terms and a more careful analysis has to be performed.

2. *Effect of the temperature and the composition of the binary alloy for small $|J|$ values*

As shown on Fig. 2, the $\dot{\eta}$ curve is well approximated by a shifted Fermi function (SFF): $f(x)=1/[1+\exp(x)]$ or by a shifted hyperbolic tangent. By introducing another variable

$$Z(J)=\frac{1}{4}\ln\left[\frac{\frac{4}{3}+\dot{\eta}(J)}{4-\dot{\eta}(J)}\right],$$

which takes into account the boundary values of $\dot{\eta}$, we obtain almost straight lines (Fig. 3) which we defined as $Z(J)=(J-J_0)/\Delta J$. Therefore, J_0 is the center of symmetry of the function $\dot{\eta}(J)$ and ΔJ is the width. This simple form, which involves few parameters for the description of the slope of $\dot{\eta}(J)$, makes easier the description of both the influence of temperature and concentration on the occupation site preference. The values of J_0 and ΔJ are calculated by a least-squares fit of the function $Z(J)$ for each temperature and composition. J ranges from -2 to 3, this range being sufficient to reach the limiting values of $\dot{\eta}$.

As can be seen in Fig. 2, the temperature and the composition play an important part only when $|J|\leq 1$. This corresponds to the cases where the entropy contribution to the free energy has the same order of magnitude as the energy term. The temperature broadens the SFF as well as it is broadened when the composition deviates from the stoichiometry A_3B (Fig. 4). Both effects are related to the lowering of the binary-alloy long-range order due to either temperature or composition.

The center of symmetry J_0 is affected by the temperature as well as the concentration. In order to have a better understanding of the effects that the concentration may cause, let us study the case $kT=0$. Then, the order of the binary alloy is at its maximum and the SFF becomes a step function. Its width is zero and the position of the step depends only on the concentration (Fig. 5).

(i) $J_0=0$ when the composition is equal to the stoichiometric composition A_3B.

(ii) $J_0=1$ when the composition is understoichiometric $C_A<0.75$.

(iii) $J_0=-1$ when the composition is overstoichiometric $C_A>0.75$.

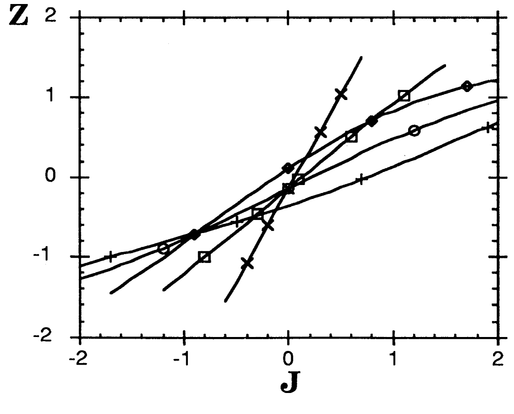

FIG. 3. Z vs J for the same cases as for Fig. 2.

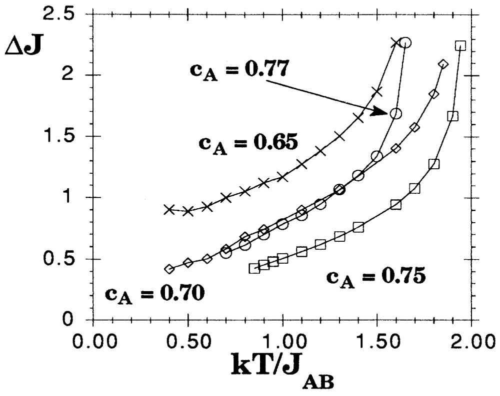

FIG. 4. Width ΔJ of the SSF vs temperature for several compositions of the reference binary alloy.

Thus, at low temperatures three behaviors can be distinguished according to the concentration values. When the temperature is raised and the concentration moves off stoichiometry, J_0 moves toward zero. As a matter of fact, ΔJ can be considered as an energy scale controlling the width of the distribution of the two sublattices' occupation by the ternary element. In that sense, the term $J_0/\Delta J$ is more meaningful than J_0 alone. Figure 6 shows $J_0/\Delta J$ as a function of the temperature for several values of the concentration C_A. When the temperature approaches T_c, the ratio tends toward zero, whatever the composition of the binary alloy.

B. Relation between the transition temperature and site preference

If it is assumed that the deficiency of A and/or B atoms in the γ' alloy is compensated by the ternary ele-

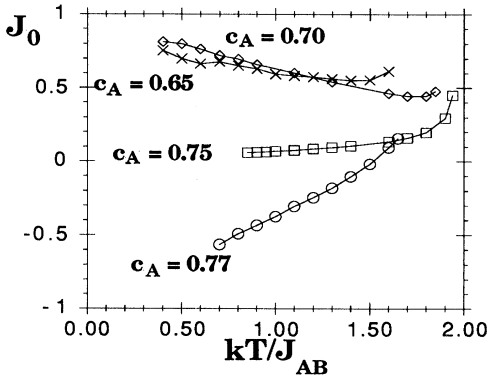

FIG. 5. Position of the center of symmetry of the SSF, J_0, vs temperature, for several compositions of the reference binary alloy.

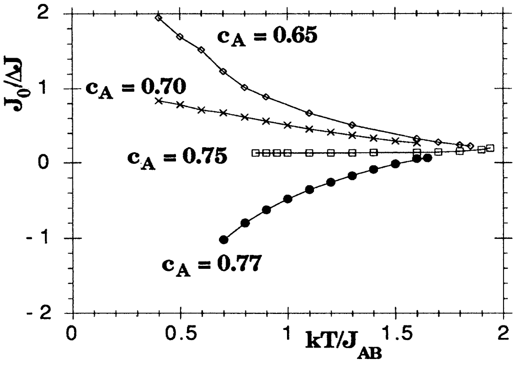

FIG. 6. Ratio $J_0/\Delta J$ vs temperature for several compositions of the reference binary alloy.

ment C in order to maintain the stoichiometry, the site preference of the ternary element is related to the γ' solubility lobe direction in the ternary phase diagram [9]. One can wonder if the site preference can be correlated to other features of the ternary phase diagram; hence, we try here to correlate the site preference to the evolution of the order-disorder transition temperature when adding a few percent of a ternary element to a binary alloy. We have then to consider a domain where two phases (an ordered phase $L1_2$ and a disordered phase $A1$) coexist in equilibrium. This domain is defined by both an upper and a lower transition temperature, these two limits being dependent on the ternary element concentration. The change of a transition temperature when adding a ternary element can be characterized by two derivatives with respect to the concentration of the added element C: $(T_c^{-1}\partial T_c/\partial c)_{L1_2}$ and $(T_c^{-1}\partial T_c/\partial c)_{A1}$. The equilibrium between the two phases implies that the (zeroth or first order of the) Lagrange multipliers in both phases are equal (since they are the grand-canonical free energy and the chemical potentials). The equality $\beta\tilde{\lambda}_{c_{L1_2}} + \ln c_{L1_2} = \beta\tilde{\lambda}_{c_{A1}} + \ln c_{A1}$ enables us to calculate the two partition coefficients:

$$\frac{c_{L1_2}}{c_{A1}} = K_{A_1}^{L1_2} = \frac{1}{K_{L1_2}^{A1}} = \exp(\beta\tilde{\lambda}_{c_{A1}} - \beta\tilde{\lambda}_{c_{L1_2}}) \; . \qquad (12)$$

It has been shown previously that the sum $\beta\tilde{\lambda}_c + 12\beta S$ is constant. Since the term $12\beta S$ is the same in both phases, the sum S does not appear in (12), which means that the following results depend strictly on the energy ratio J alone. Finally, it can be shown (Appendix C) that the two "logarithmic" derivatives of the temperature with respect to c can be explicitly calculated at the congruent point (binary alloy) from the following expression:

$$\left[\frac{1}{T_C}\frac{\partial T_c}{\partial c}\right]_{L1_2} = \frac{1-K_{L1_2}^{A1}}{S_{A1}-S_{L1_2}} , \quad \left[\frac{1}{T_c}\frac{\partial T_c}{\partial c}\right]_{A1} = \frac{K_{A1}^{L1_2}-1}{S_{A1}-S_{L1_2}} , \qquad (13)$$

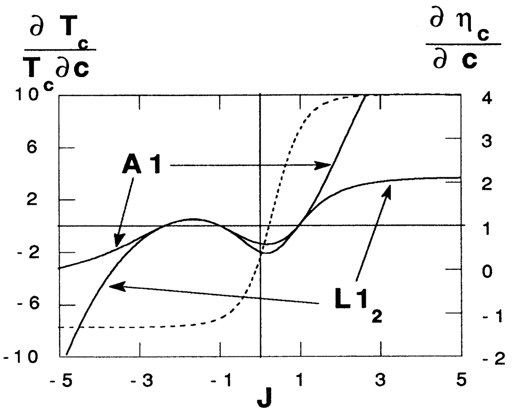

FIG. 7. Slopes of the phase boundaries $(T_c^{-1}\partial T_c/\partial c)_{L1_2}$, $T_c^{-1}(\partial T_c/\partial c)_{A1}$ and $\dot{\eta}_c$ vs the energy parameter J, for the binary congruent point.

where S_{A1} and S_{L1_2} are the entropies associated respectively with the phases $L1_2$ and A_1 at the binary congruent point. The temperature being fixed here, $K_{L1_2}^{A1}$ depends only on the energy ratio J; so do the derivatives $(T_c^{-1}\partial T_c/\partial c)$ and $\dot{\eta}$ which have been plotted as functions of J on Fig. 7. Choosing J as a curvilinear abscissa, we can map the graph $(T_c^{-1}\partial T_c/\partial c) = f(\dot{\eta})$ (Fig. 8) which correlates the change of the transition temperature upon adding a ternary element to $\dot{\eta}$. The relation between $(T_c^{-1}\partial T_c/\partial c)$ and $\dot{\eta}$ is not one valued: if $J=-1$ or $J=1$, the element C has exactly the same interaction properties as one of the elements of the binary alloy. This implies that the transition temperature remains unchanged or, equivalently, that both derivatives vanish. Large positive values of J can be achieved setting $J_{AC} \gg J_{BC}$. In such a case since the atoms C substitute preferentially on B sites, J_{A_3C} grows much larger than J_{A_3B} and the congruent temperature must necessarily increase. Reversing the argumentation for large negative values of J, we find that the congruent temperature must decrease. Therefore it is necessary that the curve at least intercept the $\dot{\eta}$ axis three times.

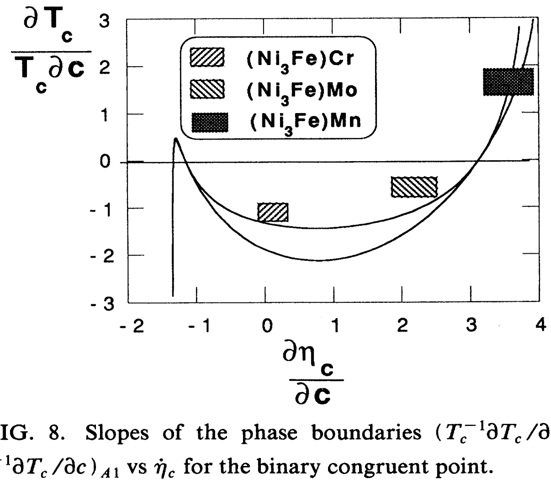

FIG. 8. Slopes of the phase boundaries $(T_c^{-1}\partial T_c/\partial c)_{L1_2}$, $(T_c^{-1}\partial T_c/\partial c)_{A1}$ vs $\dot{\eta}_c$ for the binary congruent point.

C. Experimental confirmation

Long-range order parameters and transition temperature can be measured using x-ray diffraction. However, measuring the two independent parameters that characterize an $L1_2$ phase in a ternary alloy requires the use of synchrotron radiation[10]. To our knowledge, both transition temperatures and long-range order parameters in a ternary alloy with a small amount of added element have been measured on only three alloys up to now: (Ni_3Fe)Cr, (Ni_3Fe)Mo and (Ni_3Fe)Mn.[10–12]. The results are shown on Fig. 8 together with the graph $(T_c^{-1}\partial T_c/\partial c)=f(\dot{\eta})$. The data provided by the diffraction experiments are represented using rectangles the size of which estimates the accuracy of measurements. The agreement seems quite correct, but these results have to be confirmed for other alloys.

IV. DISCUSSION

Two theoretical studies have been recently devoted to the substitutional behavior of a ternary addition in Ni-Al-X (γ') alloys[4] or in prototypic $L1_2$ compounds[5] using the Tetrahedron CVM.

Enomoto and Harada[4] studied eleven ternary additions, using phenomenological Lennard-Jones pair potentials. They classified the substitutional behavior of the eleven elements in three types corresponding to $J_{\text{Ni}X}-J_{\text{Al}X}\approx 0$ (preferential substitution on Ni sites); $J_{\text{Ni}X}\gg J_{\text{Al}X}$ (almost entire substitution on Al sites); J having intermediate values, for which the substitution is highly dependent on the bulk composition of γ'.

Our calculations give more general and accurate statements: given the effective pair interaction potentials, the bulk composition of γ', and temperature, any substitutional behavior may be precisely predicted. The influence of deviations from stoichiometry in the bulk γ' and of temperature can thus be readily seen. From our results, there is generally no preferential substitution on Ni sites when $J=0$. This tendency appears for clearly negative values of J, and the added element is entirely substituted for Ni sites when $J<-1$.

Enomoto and Harada have also investigated a relation between the substitutional behavior of Ni_3Al and the evolution of the order-disorder transformation temperature from metastable γ' to γ. They concluded that this temperature is raised by the addition of elements which are almost entirely substituted for Al sites and is decreased by the addition of the other elements. From this conclusion, one could suppose that any addition which is not essentially substituted on Al sites may be used as a means of decreasing the ordering energy of the alloy. However, our results show that it is necessary to have a closer look at such an addition. Figure 7 shows that the transformation temperature might remain almost unchanged for additions which are entirely substituted on Ni sites ($J<-1$). Recent studies[13,14] have related intrinsic brittleness of grain boundaries in $L1_2$ ordered alloys to the magnitude of the ordering tendency: Ni_3Al is brittle, Cu_3Au is ductile. The effect of alloying on the ductility of $L1_2$ compounds may thus be related to an evolution of the ordering energy. From this point of view, it is possible to improve the ductility of Ni_3Al by alloying with additions which cause the order-disorder transformation temperature to decrease. From our results, the elements which have a strong tendency to be substituted for Ni sites independently of the bulk composition of γ' are not suitable, as opposed to what would be suggested in the study of Enomoto and Harada. On the other hand, the ternary additions such that $J_{\text{Ni}X}\approx J_{\text{Al}X}$ would be good candidates to improve the ductility.

The site preference of ternary additions in an A_3B alloy with the $L1_2$ structure was also recently studied by Wu *et al.*,[5] by comparing the energies of different alloy configurations in which the addition substitutes on one sublattice or the other. Three types of occupation behavior have been recognized depending on the relative strength of the pair interactions of the alloy. These types of occupational behavior are in agreement with our results. The site occupation has been studied as a function of temperature and alloy composition and the model indicates that, under some conditions, the site preference can change with alloy composition and temperature. Our results are again in agreement with this conclusion and can be used to determine values of the different parameters for which such a behavior is predicted.

V. CONCLUSION

The mathematic scheme we followed consisted of a virial expansion of the tetrahedron cluster variation method framework. This expansion enabled us to calculate the thermodynamic quantities of a phase consisting of a small amount of ternary element C added to a binary AB alloy. We limited ourselves to the zero- and first-order terms of the expansion in order to fully understand what were the influences of each term. Considering a $L1_2$ phase as the reference state of the binary alloy, we have then shown that a single dimensionless parameter $J=(J_{AC}-J_{BC})/J_{AB}$ governs the behavior of both the site occupation $\dot{\eta}$ of the ternary element and the variation of the order-disorder transition temperature upon adding the ternary element $(T_c^{-1}\partial T_c/\partial c)$. The function $\dot{\eta}=f(J)$ can be considered as a shifted Fermi function whose center of symmetry and width depend on the precise reference state of the binary alloy. In agreement with the ground-state analysis of Wu *et al.*[4] we have found that at low temperature the behavior of the site preference $\dot{\eta}$ can be split into three categories. Basically, if $|J|>1$ the site preference is an intrinsic property of the three elements A, B, C and does not depend on the temperature nor on the binary alloy composition, whereas if $|J|\leq 1$ the lowering of the long-range order of the binary alloy (either due to the temperature or the binary alloy composition) influences the site preference $\dot{\eta}$. Considering then J as a curvilinear abscissa, we have found that the two accessible quantities $\dot{\eta}$ and $(T_c^{-1}\partial T_c/\partial c)$ were correlated, thus removing the explicit energy dependence. When comparing the relations found to the available experimental results, we find they are satisfied by the experimental data within the experimental accuracy.

The virial expansion presented in this study is not dependent on the tetrahedron cluster variation method and could be applied to other more accurate CVM's like the tetrahedron-octahedron CVM or to clusters involving long-range interactions which would be relevant when studying a phase stability upon adding a ternary element to a binary alloy. This method could also be applied to study the direction of extension of the γ-γ' phase boundaries. Finally, since the site preference of ternary additions may have some influence on the thermodynamic and kinetics of defects such as an antiphase boundary, further calculations are under way studying a possible relation between site preference and segregation of a ternary element at an antiphase boundary.

ACKNOWLEDGMENTS

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APPENDIX A

The purpose of the following calculations is to show that the factor of the term ln$c$ in the expression (7) is equal to N_i^C, thus allowing the divergent logarithm ln$c$ to be removed from expression (7) upon defining a nondivergent chemical potential of C.

The concentration constraint with respect to C [expression (2)] can also be expressed for any kind of tetrahedron subcluster.

$$\sum_i N_i^C T_i = \sum_i N_{y_i}^C Y_i = \sum_i N_{U_i}^C U_i = C_C \;, \tag{A1}$$

where $N_{y_i}^C$ ($N_{U_i}^C$) is the concentration of C in the ith pair (point). Since the clusters are considered nondegenerate, the concentration of C in a cluster is equal to the number of atoms C included in the subcluster. Thus, we have the following equalities:

$$4N_i^C = \alpha_i \;, \quad 2N_{Y_i}^C = \beta_i \;, \quad N_{U_i}^C = \gamma_i \;. \tag{A2}$$

Replacing the tetrahedron probabilities with the expressions (3a) and (3b) we obtain

$$\sum_i N_{Y_i}^C Y_i = \sum_i N_{Y_i}^C \sum_j N_{ij}^Y T_j = \sum_j \left[\sum_i N_{Y_i}^C N_{ij}^Y \right] T_j \;, \tag{A3a}$$

$$\sum_i N_{U_i}^C U_i = \sum_i N_{U_i}^C \sum_j N_{ij}^U T_j = \sum_j \left[\sum_i N_{U_i}^C N_{ij}^U \right] T_j \;. \tag{A3b}$$

Comparing (A1) with (A3) we have

$$\sum_i N_{Y_i}^C N_{ij}^Y = \sum_i N_{U_i}^C N_{ij}^U = N_j^C \;,$$

and thus, summing the contribution of the six pairs and four points we obtain

$$2\alpha_i - \sum_j N_{ji}^Y \beta_j + \tfrac{5}{4} \sum_j N_{ji}^U \gamma_j = 8N_i^C - 2 \sum_j N_{ji}^Y N_{Y_j}^C + \tfrac{5}{4} \sum_j N_{ji}^U N_{U_j}^C = N_i^C \;. \tag{A4}$$

The expression (A4) shows that the factor of ln$c$ in expression (7) is N_i^C, which is what we wanted to assert.

APPENDIX B

To define the validity range of the first-order expansion we developed, we may consider the variation of many physical quantities. Here, we choose to quantify the effect of the second-order expansion and of the energy parameter S upon the long-range order parameter η_c. At this level of approximation, η_c, which is now written

$$\eta_c = \left[\dot{\eta}_c + \frac{\partial \dot{\eta}_c}{\partial c} c + \frac{\partial \dot{\eta}_c}{\partial \Delta a} \Delta a \right] c \;,$$

depends explicitly on the following parameters: (i) the dimensionless energies: $\{\beta J_{AB},\ J = (J_{AC} - J_{BC})/J_{AB},\ \Sigma = (J_{AC} + J_{BC})/J_{AB}\}$; (ii) the binary reference concentration C_A; (iii) the expansion variables $(c, \Delta a)$.

It is not within the scope of this appendix to review the properties of η_c with respect to this set of parameters. To reduce the description of the problem, we first assign the parameters involved in points (ii) and (iii) by studying the $(A_3B)_{1-c}C_c$ compound (i.e., $\Delta a = -\frac{3}{4}c$). To precisely determine the validity range of the approximation, we introduce the variable

$$\alpha_c = \frac{\dfrac{\partial \dot{\eta}_c}{\partial_c} - \dfrac{3}{4} \dfrac{\partial \dot{\eta}_c}{\partial \Delta a}}{\dot{\eta}_c} c \;,$$

which measures the relative magnitude of the first neglected term in the Taylor series of $\dot{\eta}_c$.

In Figure 9, we have mapped, in the space parameter $x = J_{BC}/J_{AB}$; $y = J_{AC}/J_{AB}$, a typical contour plot of α_c at a medium temperature $\beta J_{AB} = 1.60$. The limiting values of x and y were chosen selecting materials that present an order-disorder transformation in a temperature domain [700 °C, 1500 °C]. We recall that, within the tetrahedron CVM framework, the critical temperature for ordering is of order $kT/J_{AB} = 2$ ($J_{AB} > 0$) while the critical temperature for demixing is of order 10 ($J_{AB} < 0$). It can be proven that α_c functionally behaves as

$$\frac{\exp(-3\Sigma) \dfrac{\partial \dot{\eta}_c}{\partial c}(J) - \dfrac{3}{4} \dfrac{\partial \dot{\eta}_c}{\partial \Delta a}(J)}{\dot{\eta}_c(J)} \;;$$

thus the constant-α_c regions corresponds to strips aligned in the direction of Σ (first diagonal) in Fig. 9. It must also be noticed that the variation of α_c with J (second diagonal) is much more marked than its variation with Σ, such that η_c is essentially governed by J. The corrective term α_c being a decreasing function of Σ within each strip, it takes its maximum value for negative values of

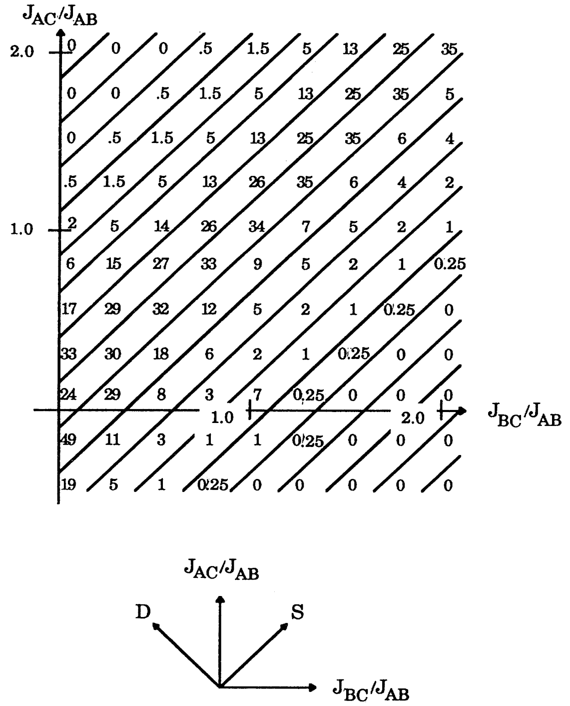

FIG. 9. Contour map of α_c (Appendix B) vs the dimensionless energy parameters J_{BC}/J_{AB} and J_{AC}/J_{AB}, at $kT=1.60$.

$J_{AC}+J_{BC}$ that correspond to C atoms clustering.

The effect of the ternary concentration c, on the validity range, can be roughly estimated from Fig. 9. For example, we may decide to neglect higher-order terms as long as the product $\alpha_c\ c$ is less than 20%. We see that for large values of J, corresponding to an asymptotical value of $\dot{\eta}_c$, the expansion is always meaningfull. For small value of J, the influence of the corrective term increases. In fact when J is close to J_0, $\dot{\eta}_c\ \alpha_c$ becomes the first nonzero term in the expansion series of η_c.

Varying the binary reference concentration would translate the strips along the J direction, while varying the reference temperature mostly affects the amplitude of the variation of α_c along J.

The effect of Σ might also be sensitive to the γ' solubility lobe direction and to the tie-line γ-γ' orientation. Up to a second-order expansion, one may expect to access such physical quantities, sketching for example the γ' solubility lobe through ellipses whose excentricity would depend on J and Σ. We did not try to do it here, as we were concerned that if the lobe intrudes too far into the Gibb's triangle, higher orders are required. Furthermore, as we work in the canonical space, such considerations would help only at the binary congruent temperature.

APPENDIX C

We obtain for the derivative of the free energy βF.

$$d\beta F = U\,d\beta + \beta\lambda_A dC_A + \beta\lambda_C dc \ , \tag{C1}$$

where U is the internal energy. As mentioned earlier, the Lagrange multiplier $\beta\lambda_0$ represents the grand-canonical free energy; that is, $\beta\lambda_0 = \beta F + C_A\beta\lambda_A + c\beta\lambda_C$. Taking the derivative of the previous expression for $\beta\lambda_0$ and replacing $d\beta F$ from (C1), we have:

$$d\beta\lambda_0 = U\,d\beta + C_A d\beta\lambda_A + c\,d\beta\lambda_C \ . \tag{C2}$$

Taking into account the fact that when c tends toward zero $\beta\lambda_C$ behaves as ln$c$, we can write

$$d\beta\lambda_0 = U\,d\beta + C_A d\beta\lambda_A + dc \ . \tag{C3}$$

The equilibrium between the two phases implies that the Lagrange multipliers in both phases are equal since they are the grand-canonical free energy and the chemical potentials. Furthermore, the concentration C_A at the congruent point is the same in both phases. Thus

$$\begin{aligned}(U_{A1}-U_{L1_2})d\beta &= dc_{L1_2} - dc_{A1} = (1-K^{A1}_{L1_2})dc_{L1_2} \\ &= (K^{L1_2}_{A1}-1)dc_{A1} \ . \end{aligned} \tag{C4}$$

Finally, using the equilibrium equality $\beta(U_{A1}-U_{L1_2}) = S_{A1}-S_{L1_2}$, we have

$$\begin{aligned}\left[\frac{1}{T_c}\frac{\partial T_c}{\partial c}\right]_{L1_2} &= \frac{1-K^{A1}_{L1_2}}{S_{A1}-S_{L1_2}} , \quad \left[\frac{\partial}{T_c}\frac{T_c}{\partial c}\right]_{A1} \\ &= \frac{K^{L1_2}_{A1}-1}{S_{A1}-S_{L1_2}} \ . \end{aligned} \tag{C5}$$

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[1] R. D. Rawling and A. Staton-Bevan, J. Mater. Sci. **10**, 505 (1975).

[2] R. Kikuchi, Acta Metall. **25**, 195 (1977).

[3] P. Cénédése, F. Bley, and S. Lefebvre, Acta Crystallogr. A **40**, 228 (1984).

[4] M. Enomoto and H. Harada, Metal Trans. **20A**, 649 (1989).

[5] Y. P. Wu, N. C. Tso, J. M. Sanchez, and J. K. Tien, Acta Metall. **37**, 2835 (1989).

[6] R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974).

[7] R. Kikuchi, Phys. Rev. **81**, 988 (1951).

[8] M. Minoux, in *Programmation mathématique, théorie et algorithmes* (Dunod, Paris, 1983).

[9] S. Ochiai, Y. Oya, and T. Suzuki, Acta Metall. **32**, 289 (1989).

[10] A. Marty, M. Bessière, F. Bley, Y. Calvayrac, and S. Lefebvre, Acta Metall. **38**, 345 (1990).

[11] H. Ferjani, F. Bley, and M. Fayard, Scr. Metall. **13**, 17 (1979).

[12] H. Ferjani, F. Bley, and Y. Calvayrac, J. Phys. (Paris) Colloq. **38**, C7-55 (1977).

[13] G. J. Ackland and V. Vitek, in *High Temperature Ordered Intermetallic Alloys III,* edited by C. T. Liu, A. I. Taub, N. S. Stoloff, and C. C. Koch, MRS Symposia Proceedings No. 133 (Materials Research Society, Pittsburgh, 1989), p. 105.

[14] A. Chiba, S. Hanada, and S. Watanabe, Mat. Trans. JIM **31**, 824 (1990).