



THERMODYNAMIC CONSIDERATION OF THE TETRAGONAL LATTICE DISTORTION OF THE $L1_0$ ORDERED PHASE

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Abstract—In an attempt to understand the thermodynamic consequences of the tetragonal distortion accompanying the $L1_0$ ordering, we have conducted a theoretical investigation by treating the problem of a rigid lattice free energy model. The problem is treated as an elasticity problem and a generalized formulation is proposed in a form which can be directly utilized to study incoherent two phase equilibria. By use of the Static Concentration Wave (SCW) mean field model as a rigid lattice free energy model, the formulation is applied to the case of our interest. We show that the thermodynamic stability of the $L1_0$ phase may be significantly influenced by the tetragonal lattice distortion, depending on the magnitude of the associated strain energy relative to the competing positive entropic contribution in the free energy of the stress free $L1_0$ phase. In association with this, we suggest that the neglect of tetragonal distortion (i.e. the use of a rigid lattice free energy model) could be a source of serious errors particularly for alloys with lower $L1_0$ ordering transition temperatures (e.g. CuAu and InMg). A prototype phase diagram of the $\langle 001 \rangle_{f.c.c.}^*$ special point structures, calculated with the tetragonal distortion taken into account, has indeed displayed topological features which are fundamentally different from those of a rigid lattice phase diagram and, furthermore, has reproduced the main topological features of the AuCu–Au₃Cu and the InMg–In₃Mg sides of their respective phase diagrams.

1. INTRODUCTION

The crystal structure of the ordered $L1_0$ phase is schematically depicted in Fig. 1 along with that of the disordered f.c.c. phase. In terms of atomic configuration, the structure is characterized by alternating A and B atomic layers on successive (002) planes. It should be emphasized that in association with the characteristic alternate layering, the structure is homogeneously distorted from the f.c.c. along its tetragonal axis i.e. along the direction of layering. Numerous experimental studies have been conducted to show that the tetragonal lattice distortion of the $L1_0$ phase depends on the state of order of the atomic configuration. Among many others, an early X-ray investigation made by Roberts [1], in particular, presents this point. By correlating the tetragonality values with long range order parameters measured from the equiatomic CuAu alloys annealed at various temperatures, Roberts showed that the tetragonal

distortion of the $L1_0$ ordered structure is a thermodynamic quantity which can be directly related to the quadratic of the long range order parameter. A question immediately posed by such a link between the atomic configuration and the lattice geometry of the $L1_0$ phase is; what consequences may this lead to, either in the thermodynamics of the $L1_0$ ordering or in the alloy phase equilibria involving the $L1_0$ phase. For a better understanding of the $L1_0$ ordering transformation, it is essential to explore these questions. This is the main objective of the present investigation.

Theoretical understanding of the f.c.c. to $L1_0$ atomic ordering (or more generally, ordering in the f.c.c. lattice) has been a long standing problem. Most of the present theoretical perspectives of such transformations were put forward through various evaluation methods of the Ising model and of its extensions in terms of the range of atomic interaction. According to these models, the configuration-dependent part of the energy of an alloy is approximated by the sum of pairwise interatomic interactions, while atoms are assumed to sit on the lattice sites of a *non-deformable rigid lattice*. An initial effort to evaluate the rigid lattice Ising model in an application to the $\langle 001 \rangle^*$ special point ordering† in the f.c.c. lattice was made by Shockley in his calculation of a phase diagram of the prototype CuAu system by use of the Bragg–Williams mean field approximation [2]. It was shown

†A special point refers to a high-symmetry point in \mathbf{k} space, characterized by point group symmetries including intersecting symmetry elements. At special points, the Fourier transform of interatomic potential always has extrema by symmetry requirements alone. Special point ordering occurs when the wave vector of the concentration wave falls onto a special point at which the Fourier transform of interatomic potential becomes minimum.

that when the mean field approximation is used, the f.c.c. to $L1_0$ ordering on a rigid lattice is predicted to be thermodynamically of second order. Thus, regions of two phase (f.c.c. + $L1_0$) equilibrium were not present in his calculated phase diagram. Later, based on more elaborate calculations of the first order approximation [3], the Cluster Variation Method [4–7] and the Monte Carlo method [8, 9], the failure of the mean field approximation was explained to arise from its neglect of short range correlation effects.

A different view was put forward by Tachiki and Teramoto (T–T) [10] and later by Kajitani and Cook (K–C) [11] in their theoretical analyses of the $L1_0$ ordering transformation in the equiatomic CuAu system. By recovering the strong first order nature of the transformation through the incorporation of a tetragonal lattice distortion into the Bragg–Williams approximation to the rigid lattice Ising model, they suggested that the earlier failure of the mean field approximation should be ascribed to the limitation of the rigid lattice model itself, rather than to its neglect of short range order. For the past decade, with the advance in understanding of the fundamental properties of the Ising model, the problem of the rigidity of the model has attracted renewed attention in conjunction with theoretical calculations of incoherent order–disorder phase diagrams [12, 13]. In none of

these works, however, has due regard been given to the lattice distortion accompanying the f.c.c. to $L1_0$ ordering and little understanding has been acquired beyond that of T–T and K–C. We believe that the theoretical perspective proposed in the works of T–T and K–C is of major importance to the understanding of the f.c.c. to $L1_0$ ordering and that it should be developed further to explore questions which are beyond the realm of the thermodynamics of the rigid lattice.

Herein, we present our theoretical investigation of the thermodynamics of the $L1_0$ ordering and of the phase equilibria involving $L1_0$ phase. It is not easy to treat the problem of the rigidity of the Ising model. A complete approach to this problem necessarily involves the use of realistic interatomic potentials derived from first principle considerations. This is beyond the scope of the present work. Instead, we take an indirect approach following the manner of T–T and K–C. The approach concerns itself with the relaxation of non-physical forces associated with the condition of constant volume and crystal shape that is imposed on the thermodynamic potentials (Helmholtz free energy or grand potential) resulting from the various approximations to the rigid lattice Ising model. The advantage of this approach is such that one can treat the problem of lifting the rigidity purely as an elasticity problem and study its consequences independently without exploring more complicated fundamental questions. For the rigid lattice free energy, we use the mean field approximation in the Static Concentration Wave (SCW) method [14–17]. This is shown to provide an efficient framework which enables us to discuss qualitatively important thermodynamic characteristics of the $L1_0$ ordering system.

2. GENERAL FORMULATION OF INCOHERENT TWO PHASE EQUILIBRIUM

Consider a hypothetical two phase system of a binary alloy, where the atoms are configured on a rigid lattice to form two separate regions; one is a disordered phase with the solute concentration c_d and the other an ordered phase with the solute concentration c_o and the long range order parameter η (see Fig. 2). By “rigid lattice”, it is supposed that each phase is forced to remain strain free on the pure solvent lattice. The configurational free energy of each phase on the rigid lattice, that is, F_{rigid}^d for a disordered phase and F_{rigid}^o for an ordered phase, is given by a free energy model due to the rigid lattice Ising model. The resulting Helmholtz free energy may not be used to describe a phase in its stress free state particularly when the stress free crystal lattice is significantly different from that of the strain free rigid one. Given the Helmholtz free energy, the configurational free energy of a stress free phase can be attained through the relaxation of the non-physical forces which are responsible for the rigidity of the

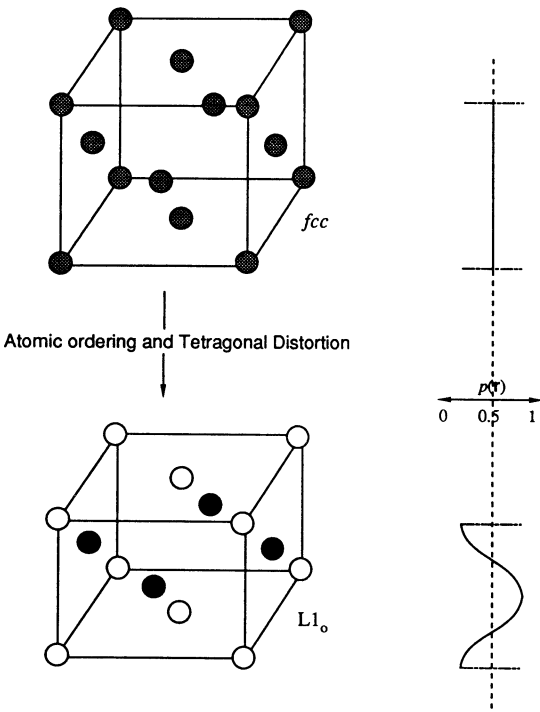


Fig. 1. Schematic diagram depicting the change in crystal structure due to ordering of the disordered f.c.c. to the fully ordered $L1_0$ phase in an equiatomic binary alloy. Notice tetragonal distortion as well as change in atomic configuration in the $L1_0$ ordered structure. A continuum (wave) description of the occupation probabilities $p(\mathbf{r})$ of the solute atoms is also presented for each crystal structure.

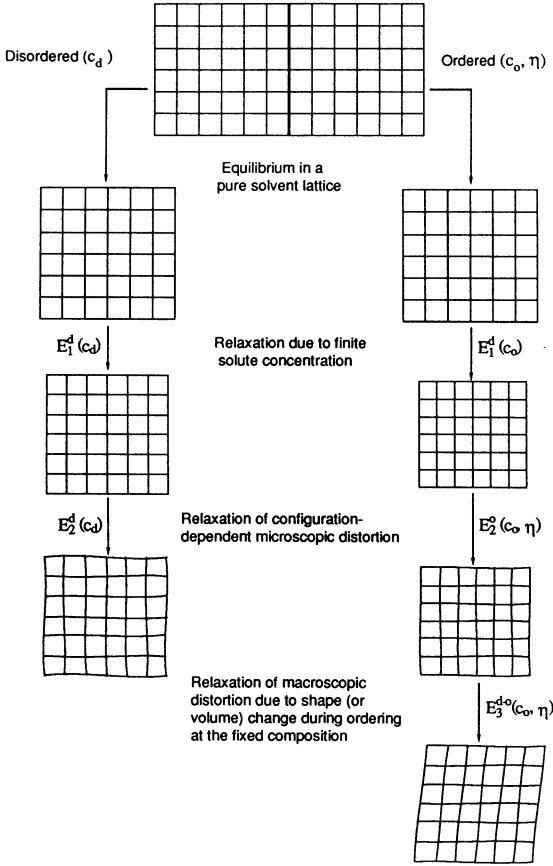


Fig. 2. Schematic diagram illustrating renormalization of rigid lattice free energies into stress free lattice equivalents.

strain free lattice. The process depicted in Fig. 2 may be formulated as

$$F^d(c_d)|_{\sigma^d=0} = F_{\text{rigid}}^d(c_d)|_{\epsilon=0} + \sum_i E_i^d(c_d) \quad (1)$$

$$F^o(c_o, \eta)|_{\sigma^o=0} = F_{\text{rigid}}^o(c_o, \eta)|_{\epsilon=0} + \sum_i E_i^o(c_o, \eta) \quad (2)$$

where $\epsilon = 0$ and $\sigma = 0$ denote the strain free solvent rigid lattice and the stress free crystal lattice of the phase in question, respectively and E_i represents the elastic energy relaxation due to a source i . For the ordered phase, the origins of elastic energy relaxation may consist of:

1. homogeneous lattice distortion due to finite solute concentration;
2. localized microscopic lattice distortion associated with a spatial distribution of atoms of different sizes;
3. macroscopic lattice distortion resulting from the difference between the stress free crystal lattice of the ordered phase and that of the disordered phase of the same solute concentration.

Relaxation of the elastic energy associated with the sources 1 and 2 may be properly described by the

microscopic elasticity theory developed by Khachaturyan [14, 20]

$$E_1 = -\frac{N}{2} \langle M(\mathbf{k}) \rangle c + \frac{N}{2} [-v_0 C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 + \langle M(\mathbf{k}) \rangle] c^2 \quad (3)$$

$$E_2 = \frac{1}{2N} \sum_{\mathbf{k}} [-M(\mathbf{k}) + \langle M(\mathbf{k}) \rangle] |\delta c(\mathbf{k})|^2 \quad (4)$$

where c , v_0 , N , C_{ijkl} and ϵ_{ij}^0 are, respectively, average solute concentration, volume of a solvent atom, total number of atoms, elastic constants and the stress free transformation strain accounting for the difference in the crystal lattice of the pure solvent and that of the pure solute. The strain ϵ_{ij}^0 is given by equation (5) when the composition dependence of the lattice constants is assumed to follow the Vegard's law. $M(\mathbf{k})$, $\langle M(\mathbf{k}) \rangle$ and $\delta c(\mathbf{k})$ are specified by equations (6), (7) and (8), respectively

$$\epsilon_{ij}^0 = \frac{da}{a dc} \delta_{ij} \quad (5)$$

$$M(\mathbf{k}) = F_i(\mathbf{k}) G_{ij}(\mathbf{k}) F_j^*(\mathbf{k}) \quad (6)$$

$$\langle M(\mathbf{k}) \rangle = \frac{1}{N} \sum_{\mathbf{k}} F_i(\mathbf{k}) G_{ij}(\mathbf{k}) F_j^*(\mathbf{k}) \quad (7)$$

$$\delta c(\mathbf{k}) = \sum_{\mathbf{r}} (c(\mathbf{r}) - c) e^{-i\mathbf{k}\cdot\mathbf{r}} \quad (8)$$

where $c(\mathbf{r})$, $F_i(\mathbf{k})$ and $G_{ij}(\mathbf{k})$ are solute concentration at lattice site \mathbf{r} , i th component of the Fourier transform of the Kanzaki force and the Born-von Karman tensor of the solvent lattice. Each of the latter two describes the force acting upon the solvent lattice by a solute atom and the stiffness of the solvent lattice against displacements, respectively.

The elastic strain associated with source 3 is macroscopic and depends on the degree of long range order of the ordered phase. When the average atomic configuration of the ordered phase can be represented by a single long range order parameter, the stress free transformation strain may be effectively described in a Taylor series expansion by equation (9)

$$\bar{\epsilon}_{ij} = \frac{1}{2} \frac{\partial^2 \bar{\epsilon}_{ij}}{\partial \eta^2} \Big|_{\eta=0} \eta^2. \quad (9)$$

In the expansion, the coefficient of the first order term is identically zero due to the strain invariance with respect to the translation of the disordered lattice and the contributions from the higher order terms are neglected. The change in elastic energy associated with the relaxation of the homogeneous strain $\bar{\epsilon}_{ij}$ is then given by

$$E_3 = -\frac{Nv}{2} C_{ijkl} \bar{\epsilon}_{ij} \bar{\epsilon}_{kl} \quad (10)$$

where v is the average atomic volume of a stress free disordered phase with the solute concentration c_o . Due to the relaxation represented by equation (3), the volume v now depends on the solute concentration and this needs to be taken into account in equation

(10). Assuming that the lattice parameters of a disordered phase vary according to Vegard's law, the average atomic volume v may be expressed by equation (11) for a lattice with cubic symmetry

$$v = \frac{1}{n} \left[a_{c=0} \left(1 + \frac{da}{a dc} c \right) \right]^3 \quad (11)$$

where n is the number of atoms in a unit cell of a disordered phase.

When the relaxations represented by equations (3), (4) and (10) are considered, the configurational free energy of each phase renormalized with respect to its stress free crystal lattice is determined from equations (1) and (2) to be

$$F_{\text{incoh}}^d(c_d) = F_{\text{rigid}}^d(c_d)|_{c=0} + E_1^d(c_d) + E_2^d(c_d) \quad (12)$$

$$F_{\text{incoh}}^o(c_o, \eta) = F_{\text{rigid}}^o(c_o, \eta)|_{c=0} + E_1^o(c_o, \eta) + E_2^o(c_o, \eta) + E_3^o(c_o, \eta). \quad (13)$$

The free energy with a form similar to equation (13) was suggested initially by Kajitani and Cook in their study on the nature of CuAu, CuPt and CuZn type ordering transitions in equiatomic alloys [11]. Since the treatment was concerned with single phase ordering transitions, their free energy expression did not include our first relaxation term. An incoherent equilibrium between an ordered and a disordered phase can now be determined by use of the free energies specified by equations (12) and (13). When a mean field approximation is used to estimate the configurational free energies $F_{\text{rigid}}^o|_{c=0}$, $F_{\text{rigid}}^d|_{c=0}$, the equilibrium conditions are given by the following:

at a temperature T ,

$$\left. \frac{\partial F_{\text{incoh}}^o}{\partial \eta} \right|_{T, c=c_o, \eta=\eta_e} = 0 \quad (14)$$

$$\left. \frac{\partial F_{\text{incoh}}^o}{\partial c} \right|_{T, c=c_o, \eta=\eta_e} = \left. \frac{\partial F_{\text{incoh}}^d}{\partial c} \right|_{T, c=c_d} = \mu \quad (15)$$

$$\frac{F_{\text{incoh}}^o|_{T, c=c_o, \eta=\eta_e} - F_{\text{incoh}}^d|_{T, c=c_d}}{c_o - c_d} = \mu \quad (16)$$

where η_e and μ are equilibrium long range order parameter and chemical potential respectively. For incoherent equilibrium between two different ordered phases, substitution of F_{incoh}^d in equations (14)–(16) with the free energy of the second ordered phase of the form of equation (13) will lead to the relevant equilibrium conditions.

3. FREE ENERGIES (f_{incoh}^*) OF $\langle 001 \rangle_{\text{f.c.c.}}^*$ SPECIAL POINT ORDERED STRUCTURES

The formulation advanced above is now specialized to derive the free energy expressions which will be used to study incoherent equilibria involving the $L1_0$ and/or $L1_2$ ordered phases.

3.1. Formulation of $F_{\text{rigid}}|_{c=0}$

From the mean field approximation to the rigid lattice Ising model, the free energy describing a strain free configurational state of an AB binary alloy is given by [17, 19]

$$F_{\text{rigid}} = \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} V(\mathbf{r}, \mathbf{r}') p(\mathbf{r}) p(\mathbf{r}') + kT \sum_{\mathbf{r}} \{ p(\mathbf{r}) \ln p(\mathbf{r}) + [1 - p(\mathbf{r})] \ln [1 - p(\mathbf{r})] \} \quad (17)$$

where $p(\mathbf{r})$ is the occupation probability of the lattice site \mathbf{r} by a solute atom and $V(\mathbf{r}, \mathbf{r}')$ is a pair-wise interaction energy between two solute atoms at lattice sites \mathbf{r} and \mathbf{r}' and is defined as $V(\mathbf{r}, \mathbf{r}') = V_{AA}(\mathbf{r}, \mathbf{r}') + V_{BB}(\mathbf{r}, \mathbf{r}') - 2V_{AB}(\mathbf{r}, \mathbf{r}')$. When the method of SCW [14, 17, 18] is used for the occupation probability $p(\mathbf{r})$, the following expressions are attained for the $L1_0$ and the $L1_2$ phase

$$F_{\text{rigid}}^{L1_0} = \frac{N}{2} [c^2 V(0) + c^2 \eta^2 V(\mathbf{k}^0)] + \frac{NkT}{2} \{ (c + c\eta) \ln(c + c\eta) + [1 - (c + c\eta)] \ln[1 - (c + c\eta)] + (c - c\eta) \ln(c - c\eta) + [1 - (c - c\eta)] \ln[1 - (c - c\eta)] \} \quad (18)$$

$$F_{\text{rigid}}^{L1_2} = \frac{N}{2} [c^2 V(0) + 3c^2 \eta^2 V(\mathbf{k}^0)] + \frac{NkT}{4} \{ (c + 3c\eta) \ln(c + 3c\eta) + [1 - (c + 3c\eta)] \ln[1 - (c + 3c\eta)] + 3(c - c\eta) \ln(c - c\eta) + 3[1 - (c - c\eta)] \ln[1 - (c - c\eta)] \} \quad (19)$$

where $V(\mathbf{k}^0) = \sum_{\mathbf{r}} V(\mathbf{r}) e^{-i\mathbf{k}^0 \cdot \mathbf{r}}$, $V(0) = \sum_{\mathbf{r}} V(\mathbf{r})$ and \mathbf{k}^0 is the wave vector of the $\langle 001 \rangle_{\text{f.c.c.}}^*$ special point ordering wave. In these free energy expressions, the concentration dependence of η is explicitly separated out into the form $c\eta$.

3.2. Formulation of $E_1 + E_2$

The sum of the elastic energy relaxation E_1 [equation (3)] and E_2 [equation (4)] can be reduced to equation (21) using the identity given by equation (20)

$$\frac{1}{N} \sum_{\mathbf{k}} |\delta c(\mathbf{k})|^2 \equiv Nc(1-c) \quad (20)$$

$$E_1 + E_2 = -\frac{N}{2} v_0 C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 - \frac{1}{2N} \sum_{\mathbf{k}} M(\mathbf{k}) |\delta c(\mathbf{k})|^2. \quad (21)$$

Taking the ensemble average of equation (21) and using the mean field approximation lead to

$$\langle E_1 + E_2 \rangle_E = -\frac{N}{2} v_0 C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 - \frac{1}{2N} \sum_{\mathbf{k}} M(\mathbf{k}) |\langle \delta c(\mathbf{k}) \rangle_E|^2 \quad (22)$$

where $\langle \rangle_E$ denotes an average over the Gibbs ensemble. Neglecting contributions other than from $\mathbf{k} = \mathbf{k}^0$ and using the identity of equation (23) yield equation (24)

$$|\langle \delta c(\mathbf{k}^0) \rangle_E|^2 \equiv (Nc\eta)^2 \quad (23)$$

$$\langle E_1 + E_2 \rangle_E = -\frac{N}{2} v_0 C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 - \frac{N}{2} c^2 \eta^2 F_i(\mathbf{k}^0) G_{ij}(\mathbf{k}^0) F_j^*(\mathbf{k}^0) \quad (24)$$

where \mathbf{k}^0 and η are defined as in equation (18) and (19). Since $F(\mathbf{k}^0) \equiv 0$ for the special point ordering wave \mathbf{k}^0 [21], equation (24) reduces to a simple form given by

$$\langle E_1 + E_2 \rangle_E = -\frac{N}{2} v_0 C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 \quad (25)$$

3.3. Formulation of $E_3(\eta)$

By use of the condition $\bar{\epsilon}_{ij}|_{\eta=1, c=c_{st}=0.5} = c_{st}^2 \beta_{ij} = \bar{\epsilon}_{ij}^0$, equations (9) can be rewritten for the L1₀ phase as

$$\bar{\epsilon}_{ij} = c_{st}^{-2} \bar{\epsilon}_{ij}^0 c^2 \eta^2 \quad (26)$$

where

$$\bar{\epsilon}_{11}^0 = \bar{\epsilon}_{22}^0 = \frac{a_{\text{ord}} - a_{\text{dis}}}{a_{\text{dis}}}, \quad \bar{\epsilon}_{33}^0 = \frac{c_{\text{ord}} - a_{\text{dis}}}{a_{\text{dis}}}$$

and

$$\bar{\epsilon}_{ij}^0 = 0 \quad \text{otherwise.}$$

a_{dis} , a_{ord} and c_{ord} are the lattice parameters of the disordered f.c.c. and of the perfectly ordered L1₀ phase of the equiatomic composition ($c_{\text{st}} = 0.5$). Substitution of equation (26) into equation (10) yields

$$E_3 = -\frac{Nv c_{st}^{-4}}{2} C_{ijkl} \bar{\epsilon}_{ij}^0 \bar{\epsilon}_{kl}^0 c^4 \eta^4 \quad (27)$$

where v is given by equation (11). It can be shown that equation (27) holds equally for the L1₂ phase when c_{st} and $\bar{\epsilon}_{ij}^0$ are properly replaced. Although the relative magnitude varies among different alloy systems, $\bar{\epsilon}_{ij}^0$ for the L1₂ ordering is, in general, negligibly small as compared with that for the L1₀ ordering (for example, it is $\sim 7.5 \times 10^{-4}$ for the CuAu₃ phase [22]). For this reason, $E_3(\eta) = 0$ will be assumed for the L1₂ phase.

3.4. Configuration free energies (f) in stress free states

The configurational free energies of the f.c.c. disordered, L1₀ and L1₂ ordered phases in their respective stress free state are now given by equations (28), (29) and (30), respectively, per a lattice point

$$f_{\text{f.c.c.}} = \frac{1}{2} c^2 V(0) + kT [c \ln c + (1-c) \ln(1-c)] - \frac{v_0}{2} C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 + \frac{\langle M(\mathbf{k}) \rangle}{2} (c^2 - c) \quad (28)$$

$$f_{\text{L1}_0} = \frac{1}{2} [c^2 V(0) + c^2 \eta^2 V(\mathbf{k}^0)] + \frac{kT}{2} \{ (c + c\eta) \ln(c + c\eta) + [1 - (c + c\eta)] \ln[1 - (c + c\eta)] + (c - c\eta) \ln(c - c\eta) + [1 - (c - c\eta)] \ln[1 - (c - c\eta)] \} - \frac{v_0}{2} C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2 - \frac{v c_{st}^{-4}}{2} C_{ijkl} \bar{\epsilon}_{ij}^0 \bar{\epsilon}_{kl}^0 c^4 \eta^4 \quad (29)$$

$$f_{\text{L1}_2} = \frac{1}{2} [c^2 V(0) + 3c^2 \eta^2 V(\mathbf{k}^0)] + \frac{kT}{4} \{ (c + 3c\eta) \ln(c + 3c\eta) + [1 - (c + 3c\eta)] \ln[1 - (c + 3c\eta)] + 3(c - c\eta) \ln(c - c\eta) + 3[1 - (c - c\eta)] \ln[1 - (c - c\eta)] \} - \frac{v_0}{2} C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 c^2. \quad (30)$$

4. RESULTS AND DISCUSSION

As we have seen from equations (28) to (30), by virtue of the special point symmetry, the relaxation term $\langle E_1 + E_2 \rangle_E$ is only a function of the solute concentration (quadratic in c assuming elastic constants are concentration-independent) and does not depend on the long range order of the ordered state. The new effect of the term is to reduce the $V(\mathbf{0})$ value which describes the resistance of a perturbed solution to the development of the concentration fluctuations of a long wavelength. This means that the addition of the term results in the increase in the decomposition tendency of an off-stoichiometric solution and, therefore, a wider two phase field in the equilibrium phase diagram. Since the relaxation term has little qualitative significance, we ignore it in the present study ($\langle E_1 \rangle$ term in equation (28) is ignored likewise). With the term $\langle E_1 + E_2 \rangle_E$ left out, we also neglect the concentration dependence of the atomic volume (v) of a disordered phase specified by equation (11) for physical consistency of the model. When the concentration dependence of the atomic volume and that of elastic constants are not taken into account, equation (27) can be recast into a simple form (per a lattice point) given by

$$e_3^{\text{L1}_0} = -16ec^4 \eta^4 \quad (31)$$

where e is a constant specified by equation (32) when the elastic stiffness tensor of the L1₀ phase is assumed to have the cubic anisotropy ($C_{11} = C_{1111} = C_{2222} = C_{3333}$ and $C_{12} = C_{1122} = C_{1133} = C_{2233}$)

$$e = v C_{11} \left\{ \left(1 + \frac{C_{12}}{C_{11}} \right) (\bar{\epsilon}_{11}^0)^2 + 2 \frac{C_{12}}{C_{11}} \bar{\epsilon}_{11}^0 \bar{\epsilon}_{33}^0 + \frac{1}{2} (\bar{\epsilon}_{33}^0)^2 \right\}. \quad (32)$$

By virtue of the simplification of equation (31), we can rewrite equations (28), (29) and (30) into a reduced form of equation (33) by use of the reduced parameters defined by equations (34a)–(34c)

$$f_i^* = \frac{f_i}{|V(\mathbf{k}^0)|} \quad (33)$$

$$\omega = \frac{V(\mathbf{0})}{|V(\mathbf{k}^0)|} \quad (34a)$$

$$\tau = \frac{kT}{|V(\mathbf{k}^0)|} \quad (34b)$$

$$\alpha = \frac{e}{|V(\mathbf{k}^0)|} \quad (34c)$$

where f_i denotes a free energy of a phase i , given by equations (28)–(30) with relaxation term $\langle E_1 + E_2 \rangle_E$ being omitted and e is given by equation (32). The results of calculations are now in order.

4.1. Long range order parameter of the stress free $L1_0$ phase

The temperature dependence of the equilibrium long range order parameter of the $L1_0$ phase can be determined numerically using equations (14) and (29). The results are plotted in Fig. 3 for the equiatomic alloy composition ($c = 0.5$) for three different α ($= e/|V(\mathbf{k}^0)|$) values. Curve A represents the case where the lattice of the $L1_0$ ordered phase is not relaxed from the strain free condition. The monotonic decrease of the long range order parameter with increasing temperature shows that the ordering transition is of the second order. When α exceeds a certain threshold value (to be discussed later), the long range order parameter curves (B and C) bifurcate into two branches above a certain temperature which defines the critical temperature of the second order transition for the $\alpha = 0$ case (curve

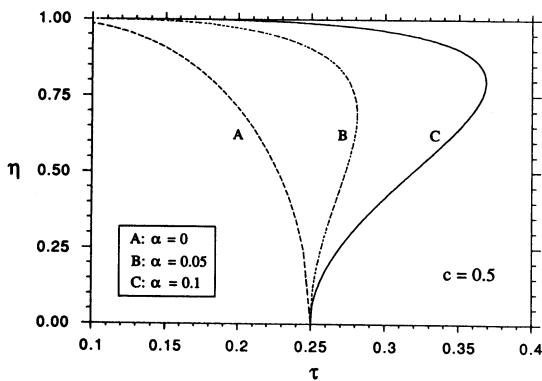


Fig. 3. Temperature (τ) dependence of the long range order parameter (η) for various α values. When the tetragonal distortion is suppressed ($\alpha = 0$), the $L1_0$ ordering transition is predicted to be thermodynamically of second order (A). As α increases, the ordering transition changes its character to weakly first order (B) and to strongly first order (C). This indicates that the problem of a rigid lattice model becomes increasingly serious as α value of an $L1_0$ ordering alloy becomes larger.

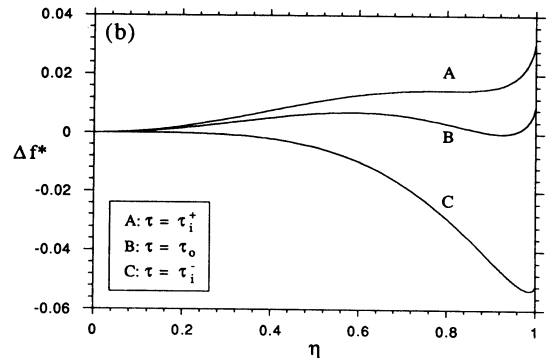
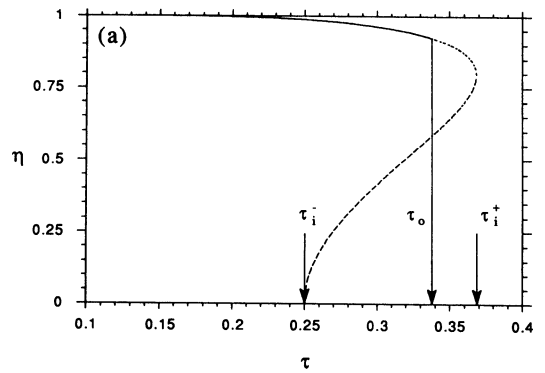


Fig. 4. (a) Temperature (τ) dependence of the long range order parameter (η) for $c = 0.5$ and $\alpha = 0.1$. (b) Associated free energy diagrams (Δf^* vs η) for three different characteristic temperatures.

A). This bifurcation indicates that the transition now has the first order nature. Three characteristic temperatures can then be defined [18, 23] and they are depicted for the $\alpha = 0.1$ case in Fig. 4(a). The nature of each characteristic temperature can be displayed expressly by means of the associated Δf^* vs η plot where Δf^* is defined to be $\Delta f^* = f_{L1_0}^* - f_{f.c.c.}^*$. This is shown in Fig. 4(b). For a given composition c , τ_i^- and τ_i^+ represent the limit of metastability of the disordered f.c.c. phase and of the ordered $L1_0$ phase, respectively and τ_0 is the temperature at which the free energies of the two phases become identical. Accordingly, when $\tau_0 < \tau < \tau_i^+$, the ordered $L1_0$ phase is metastable with respect to the disordered f.c.c. phase of the same composition and when $\tau_i^- < \tau < \tau_0$, the disordered f.c.c. phase is metastable with respect to the $L1_0$ phase.

The relative importance of the tetragonal lattice distortion in making the $L1_0$ ordering transition first order is strongly dependent on α . In fact, there exists a threshold value for the onset of the first order transition and it can be determined by analyzing the expansion of the change of free energy Δf^* [equation (35)] in terms of the long range order parameter

$$\Delta f^* = A_2 \eta^2 + A_4 \eta^4 + A_6 \eta^6 + \dots \quad (35)$$

where the coefficients A_2 , A_4 and A_6 are specified by equations (36a–c)

$$A_2 = \frac{\tau c^2}{2} \left[\frac{1}{c(1-c)} - \frac{1}{\tau} \right] \quad (36a)$$

$$A_4 = \frac{2\tau c^4}{4!} \left[\frac{1}{c^3} + \frac{1}{(1-c)^3} \right] - 16\alpha c^4 \quad (36b)$$

$$A_6 = \frac{4!\tau c^6}{6!} \left[\frac{1}{c^5} + \frac{1}{(1-c)^5} \right]. \quad (36c)$$

According to the expression, the first order transformation is only possible when the negative strain energy term accounting for the relaxation of the tetragonal distortion overrides the positive entropy term. In the mean field free energy model considered, the first order $L1_0$ ordering transition arises when the long range order parameter has branching solutions above τ_i^- . Applying these conditions to equation (36b) gives rise to the threshold value of α specified by equation (37)

$$\alpha_{\text{thresh}} = \frac{c(1-c)}{192} \left[\frac{1}{c^3} + \frac{1}{(1-c)^3} \right]. \quad (37)$$

For $c = 0.5$, the equation yields $\alpha_{\text{thresh}} = 0.0208\bar{3}$. From this analysis, it may be concluded that treating the tetragonal distortion in thermodynamic studies of the $L1_0$ ordering transition is increasingly important when the values of e and $|V(\mathbf{k}^0)|$ give a ratio which is above the threshold value.

The direct relationship between e and $|V(\mathbf{k}^0)|$ which came with the use of the reduced free energy provides us an important guide for assessing the relative effect of the tetragonal distortion on the thermodynamic nature of a $L1_0$ ordering transition among different alloy systems. Assuming e has a substantial magnitude, the effect may be significant for such a system whose transition temperature for the $L1_0$ ordering is relatively low since $|V(\mathbf{k}^0)|$ is expected to be smaller in such a case. Conversely, for an alloy with a high $L1_0$ ordering temperature, a large tetragonality alone may not bring about the first order nature of the transition. This is because the relative importance of the temperature dependent entropic contribution in competition with the strain energy term may vary among systems with different ordering transition temperatures. In this regard, binary alloys such as CuAu ($T_c = 385^\circ\text{C}$) and InMg ($T_c = 330^\circ\text{C}$) may be taken as the possible systems where the significant effect of the tetragonal distortion on the thermodynamics of the ordering is expected. We will give more detailed considerations on these systems in Section 4.2.

The criterion given above states that the mean field approximation is inadequate to treat such an $L1_0$ system with an α below the threshold value. This result, however, should not be taken as a suggestion that neglect of the tetragonal distortion may be justified when they are treated in terms of the higher order approximations. This is because the same magnitude of the strain energy term has a

more pronounced effect in the higher order approximations which produce systematically reduced entropy terms relative to the exaggerated mean field entropy.

4.2. Two phase (f.c.c. + $L1_0$) equilibrium

The qualitative nature of the phase equilibrium between the disordered f.c.c. and the $L1_0$ ordered phases has been studied by determining numerically the phase boundaries for various values of α and $\omega (= V(0)/|V(\mathbf{k}^0)|)$. Here, we do not allow the $L1_2$ phase to form in order to see the properties of the free energy given by equation (29) more clearly. The situation we are treating is not hypothetical but has reference to the cases of certain $L1_0$ ordering alloys e.g. NiPt alloy [24] where NiPt₃ $L1_2$ phase does not exist. Summary of the calculations is presented in Fig. 5(a) and (b).

Curve C in Fig. 5(a) represents a typical phase boundary predicted by the rigid lattice mean field model. In agreement with the curve A in Fig. 3, it separates the $L1_0$ phase from the f.c.c. phase by a line of the second order phase transitions. As shown by curves A and B in Fig. 5(a), phase diagrams with fundamentally different characteristics are predicted when the tetragonal distortion of the lattice is taken

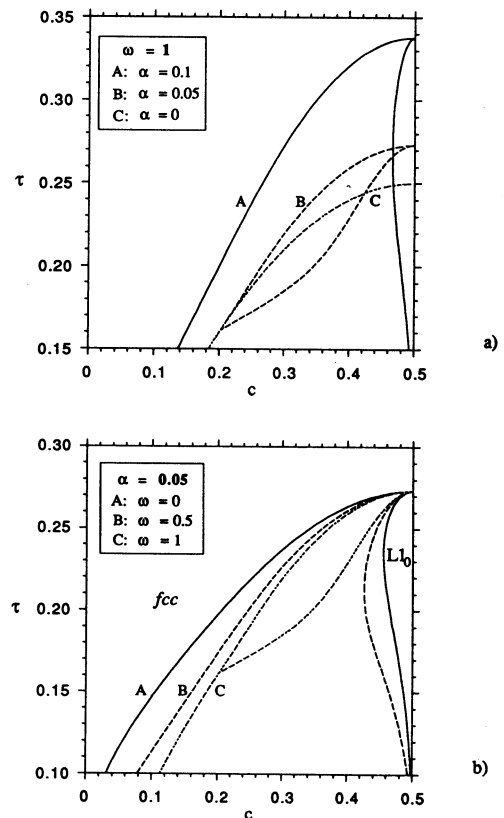


Fig. 5. Calculated phase diagrams for various α and ω values. No $L1_2$ phase is allowed in these phase diagrams. (a) $\omega = 1$. (b) $\alpha = 0.05$. From (a), notice that, consistent with the results shown in Fig. 3, phase diagram characteristics change drastically as α increases from $\alpha = 0$ (rigid state).

into account. A significant increase in the stability of the $L1_0$ ordered phase as well as the existence of a two phase field is noticeable, compared to the rigid lattice phase diagram. The relative width of the two phase field is found to be strongly dependent not only on α but also on ω which effectively measures the decomposition tendency of an undercooled off-stoichiometric f.c.c. disordered phase. This is shown in Fig. 5(b). The phase diagram attained with $\omega = 1$ and $\alpha = 0.05$ is instructive. It shows that, when the decomposition tendency is weak (ω is large), the two phase field boundaries merge into a second order transition line at a tricritical point (τ_B) where the coefficient of the harmonic term as well as that of the fourth order term vanishes, i.e. $A_2 = A_4 = 0$ in equation (35). Within the context of the free energy model used, in the composition range where the f.c.c. to $L1_0$ ordering is of second order, the homogeneous ordered phase may phase-separate into the two phase mixture of (f.c.c. + $L1_0$) by secondary decomposition. In principle, the phase diagram feature in question is not physically implausible. Nevertheless, in view of the intrinsic deficiency of the mean field approximation (i.e. neglect of the correlation effects), we presume that it may be rather an artifact due to the diminishing influence of the strain energy term in the solvent rich regions. It should be noted that the effect of the strain energy term is, however, still conspicuous in the solute rich regions ($c > 0.25$) where the two phase (f.c.c. + $L1_0$) equilibrium may be only physically meaningful if the $L1_2$ phase is allowed. For the ω values tested (up to $\omega = 4$), the existence of a two phase region has been always predicted for the composition range concerned.

4.3. Phase diagram of the $\langle 001 \rangle_{f.c.c.}^*$ special point ordered structures

Calculation of the phase diagram involving f.c.c., $L1_2$ and $L1_0$ phases was made using a model binary system with $\alpha = 0.05$ and $\omega [= V(\mathbf{0})/V(\mathbf{k}^0)] = 0.5$. The resulting phase diagram is shown in Fig. 6(b) together with the corresponding rigid lattice phase diagram [Fig. 6(a)]. Some topological features are quite distinct in the phase diagram of Fig. 6(b), compared to that of Fig. 6(a):

1. the disappearance of the two second order transitions (f.c.c. to $L1_2$ and f.c.c. to $L1_0$) at the equiatomic composition;
2. the appearance of the (f.c.c. + $L1_0$) two phase field;
3. the appearance of an invariant peritectoid reaction at an intermediate temperature.

These main features are unique to the mean-field free energy model considered and do not appear to depend on the particular choice of α and ω values.

In our earlier discussion, we proposed that the effect of a tetragonal lattice distortion would be

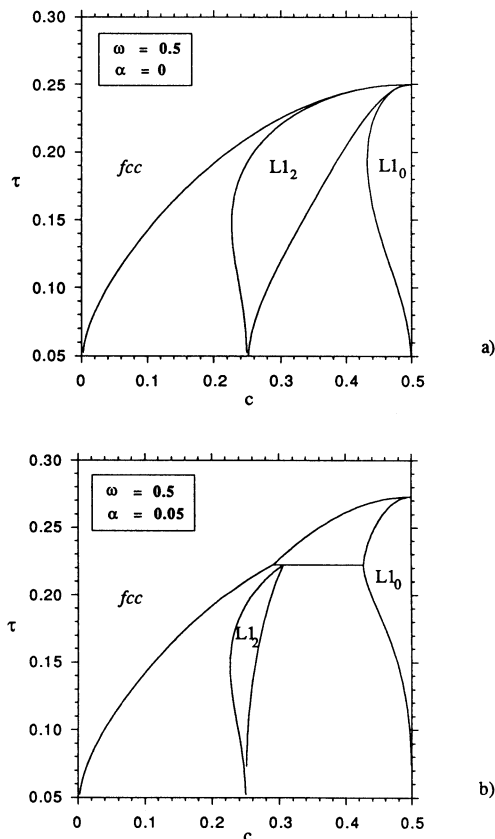


Fig. 6. Calculated phase diagrams of $\langle 001 \rangle^*$ special point ordered structures: (a) with no lattice relaxation and (b) with relaxation of configuration-dependent elastic energy contributions.

more pronounced in alloy systems which have relatively low f.c.c. to $L1_0$ ordering transition temperatures. In this regard, it is quite interesting that the calculated phase diagram displays some essential features of experimental phase diagrams of certain binary alloy systems such as CuAu and InMg alloys [25, 26]: a significant topological analogy between experimental phase diagrams and the calculated phase diagram is readily found in the AuCu– Au_3Cu (if the presence of CuAuII phase is neglected) and the InMg– In_3Mg side of the respective phase diagrams.

Due to the simplicity of the model used, however, care should be taken in evaluating such an agreement. This is because the tetragonal lattice distortion, in principle, can only explain the features directly related to the increase in the stability of the $L1_0$ phase. The absence of the congruent point at the stoichiometric $L1_2$ phase composition and the appearance of a peritectoid reaction are, in fact, inherited from the attributes of the mean field model. A more basic account of this feature may need to involve considerations of the nature of atomic interactions. With regard to this, some interesting results are found from previous investigations.

According to the CVM [7] and the Monte Carlo calculations [8, 9] of the phase diagrams for the rigid f.c.c. lattice Ising model with first (V_1) and second (V_2) nearest neighbor interaction, when V_2/V_1 is less than -0.25 , a phase diagram is predicted which has a topology identical to that of the rigid lattice mean field phase diagram [Fig. 6(a)]. In the case of CuAu alloys, analyses of the X-ray diffuse scattering data from disordered CuAu and CuAu₃ alloys have yielded $V_2/V_1|_{\text{CuAu}} = -0.4$ and $V_2/V_1|_{\text{CuAu}_3} \cong -0.53$ [27].† This suggests that the mean field type feature shown in Fig. 6(a) should be expected in the Au rich CuAu region when the rigid lattice Ising model is applied to calculate the phase diagram, if pairwise interaction and the composition independence of the interatomic pair potential are assumed. Although relevant experimental data are not available, the nature of atomic interactions is expected to be similar for the InMg alloys as well.

Based on this understanding, we have recalculated the phase diagram of Fig. 6(b) for the CuAu alloy. From the room temperature data of the lattice parameters [22] and of the elastic constants [28], the value of e [equation (32)] was determined to be $e/k = 91.4$ K where k is the Boltzman constant. The chemical pairwise interaction energy $V(\mathbf{k}^0)$ of the equiatomic CuAu alloy is not available in the literature and use was made of an estimated $V(\mathbf{k}^0)$ value [$V(\mathbf{k}^0)/k = -2361$ K] of the CuAu₃ alloy with the assumption that it does not change with composition: the estimation was made through $V(\mathbf{k}^0) = \sum_r V(\mathbf{r}) e^{-ik \cdot \mathbf{r}}$ by use of the real space interatomic potential values of up to the 8th coordination shell determined by Bessiere *et al.* from X-ray diffuse scattering of the disordered alloy quenched from $T = 573$ K [29]. The $V(0)/V(\mathbf{k}^0)$ ratio ($=3.375$) was determined by use of the V_i/V_1 (i : i th coordination shell) values of the equiatomic CuAu alloy due to Metcalfe and Leake [27]. The resulting phase diagram is presented in Fig. 7. In association with the assumption used, that is, $V(\mathbf{k}^0)$ independent of composition, the calculated diagram clearly suggests that the tetragonal distortion of the L1₀ ordered phase may be a contribution of substantial importance to engender the feature of interest in the CuAu phase diagram.

Within the framework of the mean field theory, the anharmonic fourth order term accounting for the relaxation of the tetragonal distortion may be regarded effectively as the internal energy correction due to the four body interaction of strength α which tries to form a Au or Cu single atomic layer. That is

$$\begin{aligned} \Delta U &= -\alpha \langle \delta p(\mathbf{r}_1) \delta p(\mathbf{r}_2) \delta p(\mathbf{r}_3) \delta p(\mathbf{r}_4) \rangle \\ &\approx -\alpha \langle \delta p(\mathbf{r}_1) \rangle \langle \delta p(\mathbf{r}_2) \rangle \langle \delta p(\mathbf{r}_3) \rangle \langle \delta p(\mathbf{r}_4) \rangle \\ &= -\alpha \eta^4. \end{aligned}$$

†The values were taken from the data for 800 K (CuAu) and for 573 K (CuAu₃).

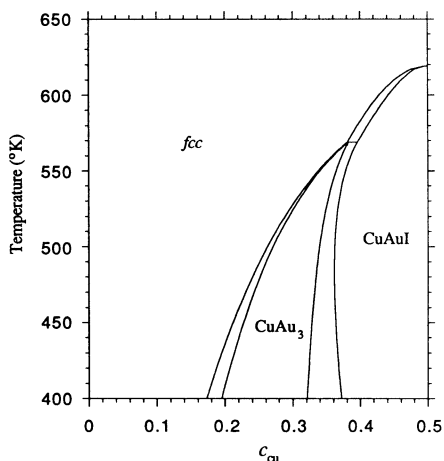


Fig. 7. The CuAu–CuAu₃ side of the CuAu phase diagram calculated by the mean field theory incorporating the tetragonal lattice distortion of the L1₀ phase.

This is, in fact, in interesting contrast to the prediction from a previous work. After Van Baal's initial work [4], Kikuchi and de Fontaine [5] have calculated the CuAu phase diagram in the CVM tetrahedron approximation to the first nearest neighbor Ising model by taking account of the tetrahedron CuCuCuAu and AuAuAuCu four body interactions. Many body interactions thus introduced have resulted in the features which show a good agreement with those of the experimental phase diagram including some quantitative aspects. It should be noted, however, that their calculated phase diagram is a rigid lattice diagram in view of the *rigid coherent* state of the L1₀ phase. Accordingly, the parameters used to fit their diagram to the experimental phase diagram may not be of much physical meaning.

Although our calculated phase diagram successfully reproduces the topological features of the Au-rich side of the CuAu phase diagram, it fails to reproduce quantitative aspects of the diagram. Except for the assumed composition independence of $V(\mathbf{k}^0)$, this is mainly due to an intrinsic deficiency of the mean field model, that is, the neglect of correlation effects. Calculation of a reliable phase diagram and thus a precise assessment of the role of the tetragonal lattice distortion should be then made by use of a free energy model which incorporates the correlation effects as well as the tetragonal lattice distortion. Within the framework of the SCW model, correlation effects can be effectively taken into account by the method developed by Badalyan and Khachatryan [30].

5. SUMMARY

A theoretical investigation was carried out to understand the effects of the tetragonal lattice distortion of the L1₀ phase on the thermodynamics of the L1₀ ordering and on the alloy phase equilibria involving

the $L1_0$ phase. In order to obtain a free energy model which will serve these purposes, we have treated the problem of rigidity of the Ising model. The treatment concerns itself purely with removal of the elastic energy contributions from a rigid lattice free energy which prevent the relaxation of the strain free rigid lattice into the stress free one. A generalized formulation was presented in a form which can be utilized directly to study incoherent two phase equilibria. By employing the SCW mean field model as rigid lattice free energy model, we have applied the formulation to the case of interest.

We have shown clearly that the thermodynamic stability of the $L1_0$ phase is influenced by the relaxation of the tetragonal distortion, through competition between the associated negative strain energy and the positive entropic contribution. In association with this, a criterion was established. It states that within the context of the mean field free energy model, the first order nature of the $L1_0$ ordering is recovered when $\alpha(=e/|V(\mathbf{k}^0)|)$ exceeds a threshold value ($=0.02083$). From this criterion, a conclusion was reached that the problem of a rigid lattice free energy model and thus of the neglect of the tetragonal distortion, could be more serious for alloy systems with lower $L1_0$ ordering transition temperatures (e.g. CuAu and InMg), given the same magnitude of the tetragonal distortion. By taking into account the tetragonal distortion, we have calculated a prototype phase diagram of the $\langle 001 \rangle^*$ special point ordered structures. The resulting phase diagram has displayed fundamentally different characteristics, as compared to the one due to a rigid lattice mean field model. In fact, the topological features of the calculated phase diagram appear to resemble those of the CuAu–CuAu₃ and the InMg–In₃Mg side of the respective experimental phase diagrams. Such an agreement clearly suggests an important role of the tetragonal distortion, as compared with that of many body interaction or equivalently of the composition-dependent interatomic potential which are proposed to explain the same features in the existing theoretical work. The conclusions obtained in this study are qualitative and, therefore, a precise assessment of the role of tetragonal distortion should be made by use of a free energy model which takes into account correlation effects. It is easily expected that the effects of the tetragonal distortion would be more pronounced in such a free energy model since it will produce a reduced entropy term relative to the exaggerated mean field entropy.

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