Theoretical Analysis of Solute-Lattice Coupling Parameters in the Microscopic Elasticity Theory and Application to Elastic Energy in β -Brass

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The microscopic theory of elasticity was reconsidered in detail in an ordered alloy system following the line of reasoning pursued by the present author. This has made it possible to express more clearly the physical meaning of solute-lattice energy and to describe solute-lattice coupling parameters (CP) $\Psi_i(n\gamma-n'\gamma')$ in terms of lattice CP (atomic force constants) $\Phi_{ij}(n\gamma-n'\gamma')$ and the stress-free strain η_{ji} either in Fourier space or in real space:

$$\Psi_i(\gamma; \gamma' / q) = (i/2)(a/2\pi)\eta_{ji}[\partial\Phi_{ij}(\gamma; \gamma' / q) / \partial q_i], \quad \text{in Fourier space,}$$

$$\Psi_i(n\gamma-n'\gamma') = -1/2\Phi_{ij}(n\gamma-n'\gamma')\eta_{ji}x_i(n\gamma-n'\gamma'), \quad \text{in real space,}$$

where $\Psi_i(\gamma; \gamma' / q)$ and $\Phi_{ij}(\gamma; \gamma' / q)$ are the Fourier representation of solute-lattice CP and lattice CP, respectively; the latter CP is identical to the element of the dynamical matrix of the system. In the Fourier space representation, the notation $2\pi q_i/a$ represents the allowed reciprocal point along the i direction in the first Brillouin zone. In the real space representation, $x_i(n\gamma-n'\gamma')$ indicates the inter-atomic distance along the i direction between the lattice points $x_i(n\gamma)$ and $x_i(n'\gamma')$, where $(n\gamma)$ indicates the γ^{th} lattice site in the n^{th} unit cell in the crystal.

As the result, all CP, i.e., solute, solute-lattice and lattice CP, which are usually treated as parameters in the microscopic theory of elasticity, are correctly described in terms of the force constants or the dynamical matrix and stress-free strains in the system. The estimation of elastic free energy associated with continuous ordering or continuous clustering is thus attributed to obtain experimentally the force constants or the dynamical matrix in the system.

Quantitative calculations of the elastic free energy in β -brass are made on the basis of the theoretical argument developed using the force constants. The contour maps of the elastic free energy in k -space are very much like to those estimated previously, using the experimentally obtained solute-lattice CP, in the sense that the significant anisotropy and the wave vector dependence of the elastic free energy appear in the contour maps in the first Brillouin zone. A deep valley of negative values with the minimum point at 0.03, 0, 0 is exhibited in the contour map of the elastic free energy along the $[100]^*$ direction in the $(001)^*$ plane. This result assures the spinodal decomposition with the wave vector of $\lambda=9$ nm exhibited experimentally in β -brass. In contrast, the prohibition of secondary ordering from the B2 to D0₃ phase in β -brass was consistently explained by the large positive value of elastic free energy at $1/2$ $1/2$ $1/2$ point in k -space.

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I. Introduction

The microscopic theory of elasticity is best known through its extensive use in the theory of lattice vibrations. The most fundamental and general scheme of the theory was developed by Born and his coworkers⁽¹⁾, who showed the influence of lattice vibrations on the thermodynamic properties of solids. Thus the relation between macroscopic elastic properties of crystals and microscopic atomic force constants have been subjects of considerable study. The theory was first applied by Matsubara⁽²⁾ to the problem of static displacements of atoms in crystals and greatly developed by Kanzaki⁽³⁾ who calculated the displacements about substitutional atoms and vacancies in Argon.

After the work accomplished on point defects in crystals⁽²⁾⁻⁽⁸⁾, the microscopic theory of elasticity was applied to solid solutions, first by Khachaturyan⁽⁹⁾ and later by

Cook and de Fontaine⁽¹⁰⁾. To calculate the elastic free energy of solid solutions and to estimate the equilibrium displacements of atoms as well, at least three parameters should be known beforehand, i.e. so called lattice coupling parameters (CP), solute CP and solute-lattice CP in the microscopic theory of elasticity, which are, respectively, the coefficients of the harmonic terms of atom displacements, the harmonic terms of concentration variations of atoms from the average concentration in the crystal and the cross terms between the atom displacements and the concentration variations. The lattice CP are identical to the well known atomic force constants in the theory of lattice vibration in crystal, and may be determined routinely by neutron diffraction experiments⁽¹¹⁾. Similarly, the solute-lattice CP have been determined experimentally from X-ray diffuse intensities with the help of neutron's experimental results⁽¹²⁾⁻⁽¹⁴⁾ or from the X-ray diffuse intensities themselves⁽¹⁵⁾⁽¹⁶⁾. However, they have never previously been the subject of theoretical study.

The solute CP, on the other hand, have been analyzed theoretically by Wu⁽¹⁷⁾ and indicated that they can be estimated analytically from the lattice CP.

The purpose of the present paper is, then, to obtain theoretically an analytical expression of the solute-lattice CP in terms of the lattice CP so that a quantitative calculation of the elastic free energy of a solid solution may be performed simply by using only one parameter. The second purpose of the present paper is to estimate the elastic free energy in the solid solution of β -brass using the present theoretical solute-lattice CP, in order to assure the present analysis by comparing the results with the previous one obtained using the experimentally determined solute-lattice CP and by confirming the consistency of the present predictions with those expected from the actual phase transitions in β -brass.

The microscopic formulation of elastic free energy in solid solution of an ordered phase is developed on the basis of the line of reasoning proposed in the present paper and an analytical expression of the solute-lattice CP are obtained in section II. In section III, the solute, solute-lattice and lattice CP are expressed in Fourier space (FS) and the elastic free energy is elucidated to be expressed solely as a function of lattice CP in FS (dynamical matrix). In section IV, the elastic free energy induced by the composition modulation in β -brass is estimated on the basis of the arguments developed in section III and compared with those obtained previously using the experimentally obtained solute-lattice CP. A brief discussion is given, in section V, on the solute-lattice CP obtained theoretically, and on the possible rearrangement of atom configuration in β -brass on the basis of the elastic free energy estimated.

II. Analytical Expression of Solute-Lattice Coupling Parameters

The microscopic formulation in this paper is made for an ordered alloy system which can readily be reduced to a disordered alloy system by ignoring the sublattices interpenetrating in the crystal. To simplify the mathematical treatment in the theory, we consider the ordered binary alloy composed of the solvent A and the solute B atoms and the crystal lattices are assumed to have simple Bravais lattices if they were in the disordered state. In the undistorted reference lattice, the atom position $x(n\gamma)$ which define the γ^{th} lattice site in the n^{th} unit cell in the crystal is expressed as

$$x(n\gamma) = n_1 a_1 + \gamma_1 b_1, \quad (1)$$

where each (γ) and (n) are the shorthand notation for the triplet numbers $\gamma_1, \gamma_2, \gamma_3$ and n_1, n_2, n_3 , respectively, in the undistorted reference lattice and a_1, a_2, a_3 are the unit cell translation vectors and b_1, b_2, b_3 are the atom translation vectors in the unit cell. Although we restrict our attention to Bravais lattices in the disordered state of the alloy system, we shall use non-primitive Cartesian lattice translation vectors for certain lattices since it is advantageous to do so because of symmetry considerations.

The following four operations are to be considered when formulating the microscopic theory of elasticity of an ordered alloy system:

Step 1: Consider blocks of pure solvent (A) and of pure solute (B) atoms which contain the same number of atoms as are contained in the binary ordered phase under consideration.

Step 2: Let a surface traction f_σ ($\sigma = A$ or B) be applied on each atom σ to attain the same average atomic size of an ordered phase. Consequently, the two blocks are deformed so as to have the same average lattice constant to that of the ordered phase.

Step 3: Make the ordered alloy, firstly by sticking two blocks together and then mixing solute and solvent atoms with under a constraint f_σ . This hypothetical ordered phase with the degree of order $\eta \ll 1$ is shown in Fig. 1(a).

The crystal lattice rearrangement in step 3 involves a change in binding energy (chemical energy) between atoms, but it does not yield any elastic energy because both atom species have the same size, although the system still involves self-interacting elastic energy posed by the surface traction f_σ .

Step 4: Remove the surface traction f_σ so that atoms may have their own sizes in the crystal and are allowed to move from their reference lattice points to the equilibrium one.

Figure 2 shows schematically the elastic energy $W_{\sigma\sigma'}$ generated by the relative displacement $u_i(n\gamma - n'\gamma')$ for a

Fig. 1 (a) Hypothetical binary alloy composed of solute B (shaded) and solvent A (open) atoms with the same size by the surface traction f_σ ($\sigma = A, B$). (b) Schematic drawing of atom displacements after releasing f_σ in solid solution to relax the strains exhibited by the difference of atom sizes between the solute and solvent atoms.

Fig. 2 Schematic drawing of the elastic free energy of a pair of atoms σ and σ' against the atom displacement $u_i(n\gamma - n'\gamma' / \sigma\sigma')$. The origin O refers to the lattice points of the ordered phase, while the point O' indicates the eigen displacement $w_i(n\gamma - n'\gamma' / \sigma\sigma')$.

pair of atoms σ and σ' ($\sigma, \sigma' = A$ or B) at $x(n\gamma)$ and $x(n'\gamma')$, respectively. The parameters $u_i(n\gamma - n'\gamma' / \sigma\sigma')$ are the Cartesian coordinates ($i=1, 2, 3$) of the relative displacements of the atoms defined in a vector form as follows:

$$u(n\gamma - n'\gamma') \equiv u(n\gamma) - u(n'\gamma') \quad (2)$$

The origin O in Fig. 2 indicates the lattice shown in Fig. 1(a) with each atom constrained by the surface traction f_σ . Therefore, the self-interaction elastic energy posed in step 3, which is commonly called the initial energy in the microscopic theory of elasticity, is given by the point $W^1_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$ on the elastic energy curve in Fig. 2.

The atom configuration corresponding to the minimum energy (vanishing elastic energy) O' in Fig. 2 defines a convenient standard state configuration: For the solute pairs (B-B pairs) at sites $(n\gamma)$ and $(n'\gamma')$, the standard configuration will be taken, as the first approximation, to be the configuration of sites $(n\gamma)$ and $(n'\gamma')$ on the pure solute lattice. This is also standing for the solvent pairs. For the solute-solvent pairs the standard state configuration is the $(n\gamma, n'\gamma')$ configuration of the equi-atomic lattice.⁽¹⁰⁾ Thus, it follows that the standard state configuration for the σ and σ' atoms can be determined uniquely by the atom species and that the atom pairs must undergo a relative displacement $w_i(n\gamma - n'\gamma' / \sigma\sigma')$ to reach their standard state configuration of no elastic energy from their positions on the average lattices of no displacement O' . Using the variation of solute concentration $\Delta c(n\gamma)$ defined as,

$$\Delta c(n\gamma) = \tau(n\gamma) - c(\gamma), \quad (3-a)$$

$$\tau(n\gamma) = \begin{cases} 1 & \text{if solute atom is located at } x(n\gamma) \\ 0 & \text{if not,} \end{cases} \quad (3-b)$$

$c(\gamma)$: average concentration of solute atoms on the γ^{th}

sublattice,

we can express the stress-free displacement $w_i(n\gamma - n'\gamma')$ as follows:

$$w_i(n\gamma - n'\gamma') = (1/2)[\varepsilon_{ij}(n\gamma) + \varepsilon_{ij}(n'\gamma')]x_j(n\gamma - n'\gamma'), \quad (4-a)$$

$$\varepsilon_{ij}(n\gamma) = \eta_{ij} \Delta c(n\gamma), \quad (4-b)$$

where $\varepsilon_{ij}(n\gamma)$ is the strain at the position $x(n\gamma)$ and concentration expansion tensor η_{ij} is defined as follows:

$$\eta_{ik} \equiv (1/a_i)(\partial a_k / \partial c), \quad (5)$$

where it is properly assumed that the coefficient η_{ik} does not depend on the average concentration $c(\gamma)$ on the sublattice but depends on the total average concentration c . Summation convention is applied to the repeated subscripts in the equation. It is evident from eqs. (4) and (5) that we have introduced Vegard's law which describes the linear variation of lattice constants with solute atom concentration. From the definition given above, $\varepsilon_{ij}(n\gamma)$ indicates stress-free strain of atoms, which depicts, in general, the stress-free strain associated with phase transformation.

The elastic energy exhibited for the pair of atoms after operating the step 4 is shown by the relaxed energy $W_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$ in Fig. 2. Using the stress-free displacement $w_i(n\gamma - n'\gamma' / \sigma\sigma')$, we can express the elastic energy as follows:

$$\begin{aligned} W_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma') = & -(1/2)\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma') \\ & \times [w_i(n\gamma - n'\gamma') - u_i(n\gamma - n'\gamma')] \\ & \times [w_j(n\gamma - n'\gamma') - u_j(n\gamma - n'\gamma')], \end{aligned} \quad (6)$$

where the symbol $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')$ is the force constant for the pair of atoms σ and σ' located at $x(n\gamma)$ and $x(n'\gamma')$, respectively, which is defined as the negative of the second derivative of the potential energy with respect to $u_i(n\gamma - n'\gamma')$ and $u_j(n\gamma - n'\gamma')$ at O' in Fig. 2. Substituting the stress-free displacements $w_i(n\gamma - n'\gamma' / \sigma\sigma')$ of eq. (4-a) into eq. (6), we can express the elastic free energy $W_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$ by the sum of the three energy terms, i.e. the initial energy $W^1_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$, the relaxation energy $W^{\text{SL}}_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$ and the lattice energy $W^{\text{L}}_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma')$.

The expression of the initial energy for the particular pair of atoms is given as follows:

$$\begin{aligned} W^1_{\sigma\sigma'}(n\gamma - n'\gamma' / \sigma\sigma') = & \psi(n\gamma - n'\gamma' / \sigma\sigma') \\ & \times [\Delta c(n\gamma)\Delta c(n'\gamma') + \Delta c(n\gamma)\Delta c(n\gamma)], \end{aligned} \quad (7-a)$$

$$\begin{aligned} \psi(n\gamma - n'\gamma' / \sigma\sigma') = & -(1/4)\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma') \\ & \times \eta_{ik}\eta_{jl}x_k(n\gamma - n'\gamma')x_l(n\gamma - n'\gamma'), \end{aligned} \quad (7-b)$$

where the symbol $\psi(n\gamma - n'\gamma' / \sigma\sigma')$ is called the solute CP by Cook and de Fontaine⁽¹⁰⁾, because it indicates the energy coefficient of the harmonic terms in the solute concentration variation $\Delta c(n\gamma)\Delta c(n'\gamma')$. It is to be noted that a similar analytical expression of the solute CP to eq. (7-b) was first derived by Wu⁽¹⁷⁾ under the assumption

that the force constant $\psi(n\gamma - n'\gamma' / \sigma\sigma')$ does not depend on atom species.

Operation by step 4 yields two different kinds of energies in the system; One is the relaxation energy caused by the initial set-up force (so called initial force) expressed by $-\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma') \times [-w_j(n\gamma - n'\gamma')]$. With this force, the pair of atoms σ and σ' located at $x(n\gamma)$ and $x(n'\gamma')$, respectively, makes a relative displacement $u_i(n\gamma - n'\gamma')$ in order to relax the strain generated by each atom which functions as a center of force acting to displace the lattice around it. Hence, the first relaxation energy $W_{\sigma\sigma'}^{\text{SL}}(n\gamma - n'\gamma')$, which is often called the solute-lattice coupling energy in the microscopic elasticity theory, can be represented by the cross terms with respect to $w_i(n\gamma - n'\gamma')$ and $u_i(n\gamma - n'\gamma')$ or $w_j(n\gamma - n'\gamma')$ and $u_i(n\gamma - n'\gamma')$ in eq. (6). Substituting $w_j(n\gamma - n'\gamma')$ of eq. (4-a) into eq. (6), we obtain the expression of solute-lattice coupling energy as follows:

$$W_{\sigma\sigma'}^{\text{SL}}(n\gamma - n'\gamma') = 2\Psi_i(n\gamma - n'\gamma' / \sigma\sigma') \times [\Delta c(n\gamma)u_i(n'\gamma') + \Delta c(n\gamma)u_i(n\gamma)], \quad (8-a)$$

$$\Psi_i(n\gamma - n'\gamma' / \sigma\sigma') = -1/2\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma') \times \eta_{j1}x_1(n\gamma - n'\gamma'), \quad (8-b)$$

where the negative sign occurs because $W_{\sigma\sigma'}^{\text{SL}}(n\gamma - n'\gamma')$ is the relaxation energy in the system while the displacement of atoms $u_i(n\gamma - n'\gamma')$ is assumed to take place under the constant force $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')w_j(n\gamma - n'\gamma')$. Thus, it is proved for the first time that the parameter $\Psi_i(n\gamma - n'\gamma' / \sigma\sigma')$, which is called the solute-lattice CP in the phenomenological theory of elasticity, can be expressed in terms of the force constant $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')$ and the concentration expansion coefficient η_{j1} .

The second energy term to be considered in the operation in step 4 is the one to be stored in the crystal due to the elastic resistance of the lattice to oppose the atomic displacement for relaxation. At the initial state of the system in step 4, no driving force for this second energy is born in the crystal. The force is yielded only by the atomic displacement and is described as $-\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')u_j(n\gamma - n'\gamma')$ in distinction from the initial force $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')w_j(n\gamma - n'\gamma')$. Therefore, this elastic energy which is well known as the lattice energy $W_{\sigma\sigma'}^{\text{L}}(n\gamma - n'\gamma')$ can be expressed as follows⁽¹⁾:

$$W_{\sigma\sigma'}^{\text{L}}(n\gamma - n'\gamma') = \Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')[u_i(n\gamma)u_j(n'\gamma') - u_i(n\gamma)u_j(n\gamma)]. \quad (9)$$

Summing up the above three energies for all the pairs in the crystal with a positive sign for the stored one, we have the total elastic free energy of the crystal:

$$\begin{aligned} W &= W^1 + W^{\text{SL}} + W^{\text{L}} \\ &= (1/2)\sum_{n\gamma}\sum_{n'\gamma'}\sum_{\sigma}\sum_{\sigma'}[\Psi(n\gamma - n'\gamma' / \sigma\sigma')\Delta c(n\gamma) \\ &\quad \times \Delta c(n'\gamma') + 2\Psi_i(n\gamma - n'\gamma' / \sigma\sigma')\Delta c(n\gamma)u_i(n'\gamma') \\ &\quad + \Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')u_i(n\gamma)u_j(n'\gamma')], \end{aligned} \quad (10)$$

with the supplementary definitions,

$$\Psi(n\gamma - n\gamma / \sigma\sigma) = \sum_{n'\gamma'}\sum_{\sigma'}\Psi(n\gamma - n'\gamma' / \sigma\sigma'), \quad (n\gamma \neq n'\gamma') \quad (11-a)$$

$$\Psi_i(n\gamma - n\gamma / \sigma\sigma) = \sum_{n'\gamma'}\sum_{\sigma'}\Psi_i(n\gamma - n'\gamma' / \sigma\sigma') = 0, \quad (n\gamma \neq n'\gamma') \quad (11-b)$$

$$\Phi_{ij}(n\gamma - n\gamma / \sigma\sigma) = \sum_{n'\gamma'}\sum_{\sigma'}\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma'), \quad (n\gamma \neq n'\gamma') \quad (11-c)$$

where the symmetry relation $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma') = \Phi_{ij}(n'\gamma' - n\gamma / \sigma'\sigma)$ is used to derive the eq. (10).

It is an exact conclusion in this section that once the force constants (elements of dynamical matrix) $\Phi_{ij}(n\gamma - n'\gamma' / \sigma\sigma')$ are to be obtained, the elastic free energy can readily be evaluated using the CP estimated thereby in the analytical way.

III. Fourier Representation of Elastic Free Energy

In the above discussion, the CP for the pair of atoms are considered to depend on the atom species σ and σ' of the pair. However, in the harmonic approximation of the elastic free energy, the CP are assumed to be independent of the atom species, and then they have the constant values of the hypothetical average crystal. Therefore, the symbol σ and σ' in the CP are, unless otherwise noted, to be omitted hereafter in the harmonic system.

On the other hand, in order to simplify the expression of the elastic free energy, we consider a series of systems stacked in three dimensions, each system having a volume V . That is, the cyclic boundary condition of Born-Von Karman is introduced for Fourier Transformation (FT) of the elastic free energy terms. For example, the solute-lattice CP in Fourier space are represented as follows:

$$\begin{aligned} \Psi_i(\gamma; \gamma' / q) &= (m_\gamma m_{\gamma'})^{-1/2} N^{-1} \sum_n \sum_{n'} \Psi_i(n\gamma - n'\gamma') \\ &\quad \times \exp[i\mathbf{k}(q) \cdot \mathbf{x}(n\gamma - n'\gamma')], \end{aligned} \quad (12)$$

where m_γ is the mass of an atom on the γ^{th} sublattice. The summation symbol n stands for N unit cells contained in the volume V . The wave vector $\mathbf{k}(q)$ is given by

$$\mathbf{k}(q) = 2\pi q_i \mathbf{a}_i^*, \quad (13-a)$$

where $\mathbf{a}_i^*$ are the translation vectors of the reciprocal lattice. The symbol (q) in eq. (13-a) is a shorthand notation for the triplet numbers q_1, q_2, q_3 defined by

$$q_1 = m_1 / L \quad (m_1: \text{integer in } 1 \sim L), \quad (13-b)$$

where L is the length of the domain D along the 1 direction under consideration. Substituting $\Psi_i(n\gamma - n'\gamma')$ of eqs. (8-b) and (11-b) into eq. (12), we obtain the following expression:

$$\Psi_i(\gamma; \gamma' / q) = (i/2)(a/2\pi)\eta_{j1}[\partial\Phi_{ij}(\gamma; \gamma' / q)\partial q_1], \quad (14)$$

where $\Phi_{ij}(\gamma; \gamma' / q)$ is the element of the lattice dynamical matrix which can be defined in a similar manner to the solute-lattice CP in FS of eq. (12). Because $\Phi_{ij}(\gamma; \gamma' / q)$ is a real number in Bravais lattices⁽¹⁾, the FT of solute-lattice CP's, $\Psi_i(\gamma; \gamma' / q)$, is a pure imaginary one as indicated

by $i/2$ in eq. (14).

The solute CP in FS was argued by Wu⁽¹⁷⁾ in the analysis of the initial energy of a disordered solid solution of metal alloys. The results can readily be extended to the case of the ordered phase as follows:

$$H(\gamma; \gamma'/q) = \sum_{\gamma'} Y(\gamma; \gamma'/0) + Y(\gamma; \gamma'/q), \quad (15-a)$$

$$H(\gamma; \gamma'/q) = Y(\gamma; \gamma'/q), \quad (\gamma \neq \gamma'), \quad (15-b)$$

$$Y(\gamma; \gamma'/q) = (1/4)(a/2\pi)^2 \eta_{ik} \eta_{jl} [\partial^2 \Phi_{ij}(\gamma; \gamma'/q) / \partial q_i \partial q_k], \quad (15-c)$$

where it is implicitly assumed in $Y(\gamma; \gamma'/q)$ that the initial term of the Fourier coefficients, $\Psi(n\gamma - n'\gamma')$, is equal to zero irrespective of the definition of eq. (8). in Ref. (17). Instead of our case of the ordered phase taken in this paper, Wu has argued on the system of a disordered solid solution in metal alloys and indicated $Y(0) = \sum_{\gamma'} Y(\gamma; \gamma'/0)$ of solid solution to be equal to $\Omega \eta_{ik} \eta_{jl} C_{ijkl}/2$ by using the elastic constant C_{ijkl} .

The FT of the total elastic free energy W of eq. (10), with the help of the expressions of solute CP in FS of eqs. (15) and solute-lattice CP in FS of eq. (14), gives the following simple expression under the mechanical equilibrium condition⁽⁹⁾⁽¹⁰⁾,

$$W = (N/2) \sum_{\gamma} \sum_{\gamma'} \sum_q Q(\gamma; \gamma'/q) Z(\gamma; \gamma'/q) Q^*(\gamma'/q), \quad (16-a)$$

$$Z(\gamma; \gamma'/q) = H(\gamma; \gamma'/q) - \Psi_i(\gamma; \gamma'/q) \Phi_{ij}^{-1}(\gamma; \gamma'/q) \times \Psi_j^*(\gamma; \gamma'/q), \quad (16-b)$$

where $Q(\gamma/q)$ is the FT of concentration variation $\Delta c(n\gamma)$ and the term $\Phi_{ij}^{-1}(\gamma; \gamma'/q)$ is the element of the inverse dynamical matrix. The following mechanical equilibrium condition was posed to derive the above representation of elastic free energy of the crystal.

$$-\Psi_i(\gamma; \gamma'/q) Q(\gamma'/q) = \Phi_{ij}(\gamma; \gamma'/q) U_j^*(\gamma'/q), \quad (17)$$

where $U_j^*(\gamma'/q)$ is the conjugate complex of the FT of displacement parameter $u(n\gamma')$. Hence, in Fourier space, the elastic free energy in an ordered phase, eqs. (16-a) and (16-b), and the equilibrium position of atoms, eq. (17), can be estimated by knowing only one parameter i.e. the elements of dynamical matrix $\Phi_{ij}(\gamma; \gamma'/q)$.

IV. Elastic Free Energy in β -Brass

The Cu-Zn system in near stoichiometric compositions has an ordered B2 structure below the order-disorder phase transition temperature at about 727 K. This ordered phase makes spinodal decomposition⁽¹⁸⁾, by aging, which was theoretically interpreted by the relaxation of the elastic strain in redistributing the atoms on the sublattices in β -brass⁽¹⁹⁾. In order to assure the present analysis of the solute-lattice CP of the elastic free energy, quantitative estimation of the elastic free energy is made in the β -phase with 38.9 at% Zn composition, which was shown experimentally to exhibit the spinodal decomposition⁽¹⁸⁾, on the basis of the above arguments. And it was checked whether the present theory could consistently predict the

occurrence of spinodal decomposition in the β -brass or not. In particular, the results will be compared with the calculations obtained previously by the present author using the experimental values of the solute-lattice CP.

In the case of the phase decomposition (lattice redistribution) in the solid solution of metal alloys, it is only significant to take into account the configurational energy which is defined as the difference between the energy of a given atomic (or defect) configuration and the energy of a random distribution of atomic species. The total elastic free energy are rewritten as the configurationally dependent part and independent one⁽⁹⁾⁽¹⁰⁾:

$$W = \sum_{\gamma} \sum_{\gamma'} [W_0(\gamma; \gamma') + W_{\text{conf}}(\gamma; \gamma')], \quad (18-a)$$

$$W_0(\gamma; \gamma') = (N/2) m_{\gamma} c(\gamma) [1 - c(\gamma) \delta_{\gamma\gamma'}] \langle Z(\gamma; \gamma') \rangle, \quad (18-b)$$

$$W_{\text{conf}}(\gamma; \gamma') = (N/2) \sum_q Q(\gamma/q) E_c(\gamma; \gamma'/q) Q^*(\gamma'/q), \quad (18-c)$$

$$E_c(\gamma; \gamma'/q) = Z(\gamma; \gamma'/q) - \langle Z(\gamma; \gamma') \rangle, \quad (18-d)$$

where $W_0(\gamma, \gamma')$ is the elastic free energy of the random distribution of atoms and $W_{\text{conf}}(\gamma, \gamma')$ is the configurationally dependent part of the elastic free energy (CEE). The parameter $\delta_{\gamma\gamma'}$ is the kronecker's delta and the symbol $\langle Z(\gamma, \gamma') \rangle$ in eq. (18-b) indicates the average value of $Z(\gamma; \gamma'/q)$ taken over the allowed (q) points in the first Brillouin zone of β -brass. The CEE $W_{\text{conf}}(\gamma, \gamma')$ of eq. (18-c) exhibits the simple form of functional composed of mutually independent term, i.e. so called CEE modulus $E_c(\gamma; \gamma'/q)$ and the amplitude square of the concentration variation waves, $Q(\gamma/q) Q^*(\gamma'/q)$. Hence, we are only necessary to focus on the CEE modulus $E_c(\gamma; \gamma'/q)$ to examine the phase stability against the lattice redistribution.

The theoretical values of solute-lattice CP in β -brass are estimated by eq. (8-b), using the lattice CP which are obtained from the neutron diffraction experiments in the β -brass with 47 at%–49 at% Zn composition⁽²⁰⁾. In Table 1 are listed such theoretical values along with those obtained experimentally by using the X-ray diffraction method⁽¹⁵⁾⁽¹⁶⁾, where the notation $\hat{\alpha}_i^x$ etc. are used to designate the CP after the expressions represented in Appendix I. In comparison, the theoretical values of the solute-lattice CP are considerably different from the experimental ones, which is clearly due to the lack of precise analysis of the diffuse intensities in X-ray diffraction method⁽¹⁵⁾ and a mere nearest neighbor assumption in the analysis⁽¹⁶⁾. However, the CP in FS are in good agreement each other at the extreme limit of long wavelength $k(q) = 0$. For example, along the $[100]^*$ direction, the solute-lattice CP in FS, $\Psi_1(q) = \sum_{\gamma} \sum_{\gamma'} \Psi_1(\gamma; \gamma'/q)$, at $(q) = \Delta, 0, 0$ is given by

$$\begin{aligned} \Psi_1(q) &= 4\pi i \Delta [4\hat{\alpha}_1^x + \hat{\alpha}_2^x(\alpha) + \hat{\alpha}_2^x(\beta) + 4\{\hat{\alpha}_3^x(\alpha) + \hat{\alpha}_3^x(\beta)\} \\ &\quad + 12\hat{\alpha}_4^x + 8\hat{\alpha}_5^x] \\ &= 4\pi i \Delta \times 102.23 \times 10^{-10} \text{ N (theory)} \\ &\quad 103.57 \times 10^{-10} \text{ N (experiment).} \end{aligned} \quad (19)$$

This result is rather important because the value of $\Psi_i(q)$

Fig. 3 Contour maps of CEE. moduli in unit of 10^{-21} J/atom, (a) $E_c(\alpha; \alpha/q)$, (b) $E_c(\alpha; \beta/q)$, (c) $E_c(\beta; \beta/q)$ in $(001)^*$ plane, and (d) $E_c(\alpha; \alpha/q)$, (e) $E_c(\alpha; \beta/q)$, (f) $E_c(\beta; \beta/q)$ in $(011)^*$ plane, respectively. Strong anisotropy and wavelength dependence of CEE are exhibited in a fashion similar to those estimated in Ref. (19), while, the present results are more consistent with the experimental ones.

spinodal decomposition in β -brass.

Because the eigenvectors $Q(\pm)$ are composed of two basic waves $Q(\alpha/q)$ and $Q(\beta/q)$, the growth or decay of

the waves along $Q(\pm)$ signifies the concurrent growth or decay of the waves in the α and β sublattice. It is evident that one of the eigenvalues is always in the region $Q(\alpha/$

Fig. 4 Typical basket-weave structure with the wave length of about 30 Å after the heat treatment at 325 K for 5d (120 h), indicating spinodal decomposition in the β -brass with composition of Cu-38.9 at%Zn.

Fig. 5 Schematic drawing of the CEE moduli surface around the origin of the amplitude space $Q(\alpha/q)-Q(\beta/q)$. The eigen vectors, $Q(+)$ and $Q(-)$, of the CEE moduli indicate the most rapidly decaying and growing concentration variation waves.

$q)Q(\beta/q) > 0$ and the other is always in the region $Q(\alpha/q)Q(\beta/q) < 0$. It signifies that there are two pairs of concentration waves with the same wave vector $k(q)$ in the α and β sublattice, and that one pair has the amplitude with the same sign (acoustic mode) and the other has a different sign (optical mode) of the amplitude. The example of an acoustic mode of concentration variation is shown in Fig. 8 under the assumption of continuous model of concentration variation. Simple rule is established⁽¹⁹⁾, that the mode of the eigen wave can be determined solely by the sign of the cross term $E_c(\alpha; \beta/q)$. That is, when it is negative, the eigenwave $Q(+)$ should be optical and the eigenwave $Q(-)$ should be acoustic and vice versa for the positive value of $E_c(\alpha; \beta/q)$. In that sense, similarity of cross terms, $E_c(\alpha; \beta/q)$, in the present calculation to the previous one is important. In fact, they have all negative values along $[100]^*$ direction

Fig. 6 (a) View of the contours of the eigenvalue $e(-)$ in $(001)^*$ plane and (b) in the $(011)^*$ plane, respectively, in units of 10^{-21} J/atom. The minimum point (q) appears at 0.03, 0, 0, which is consistent with the occurrence of spinodal decomposition in β -brass.

as shown in the contour maps of Fig. 3(b) in this paper and Fig. 3(b) in Ref. (19). Therefore, the acoustic mode should stand for the spinodal decomposition in the β -brass as shown in Fig. 8, where the amplitude ratio $Q(\beta/q)/Q(\alpha/q)$ which is identical to the direction of $Q(-)$ can be estimated as -0.999 for the present alloy. This value of the amplitude ratio indicates that the spinodal decomposition occurs on the β -sublattice and almost nothing on the α -sublattice, which is consistent with the previous prediction of the phase decomposition in β -brass with the degree of order $\eta=1$.

V. Discussion

The theoretical analysis of the solute-lattice CP was made in the phenomenological theory of elasticity. It is elucidated that the solute-lattice CP in FS can be ex-

Fig. 7 Eigenvalues $e(-)$ of the CEE moduli along the $[100]^*$ direction in k -space. (a) The present calculations exhibit the minimum value at $(q)=0.3, 0, 0$, (b) the previous results in Ref. (19) reveal no minimum value in the vicinity of the origin.

Fig. 8 Acoustic mode of long wavelength concentration variation as expected in β -brass. The two waves on the α and β sublattice have the same wavelength with the same phase angle.

pressed in terms of the first derivatives of the dynamical matrix elements with respect to the wave vector $k(q)$ in reciprocal space (k -space). As the result, the elastic free energy is proved to be expressed solely as a function of the dynamical matrix elements, i.e. by using the first (solute-lattice CP in FS) and the second (solute CP in FS) derivatives of the dynamical matrix elements and the dynamical matrix elements themselves (lattice CP in FS).

Gragg⁽²²⁾ has proposed a experimental method to determine both the lattice and the solute-lattice CP's simultaneously from X-ray diffraction experiments of diffuse intensity. The other two different methods to obtain the solute-lattice CP have been proposed by Wu and Cohen⁽¹³⁾ and have been tested via computer simulation. One of the methods which uses a linear least-squares analysis of phonon spectra which can be obtained from inelastic neutron scattering and analysis of X-ray diffuse intensity is proved to be more stable and reliable due to the simplicity of the analysis than the other one. To the author's knowledge, the accepted experimental procedure is most widely used in a Cu-20.9%Be alloy for determining solute-lattice CP required for the investigation of local atomic structure and static strains in the as-quenched state. Koo, Cohen and Shapiro⁽¹⁴⁾ examined a

single crystal of Cu-10.9 at% Be to investigate the origin of weak striated strain contrast (commonly referred to as tweed) in TEM observation. Elastic energy modulus $Z(q)$ in solid solution, which is identical to $\Sigma_\gamma \Sigma_{\gamma'} Z(\gamma; \gamma'/q)$ in eq. (16-b), have been estimated using the solute-lattice CP obtained by themselves. However, negative values of elastic energy moduli appeared in a region around the 100 reciprocal point. This is unrealistic, as pointed out by themselves. Thus, even a precise analysis of X-ray diffuse intensities would still involve errors, to some extent, in estimating solute-lattice CP. Therefore, that the solute-lattice CP can be evaluated analytically using the known values of force constants gives us considerable advantages.

Cook and de Fontaine has developed the microscopic elasticity theory in the system of solid solution⁽¹⁰⁾, where they have obtained the invariant relation between CP's:

$$\begin{aligned} \Psi(n\gamma - n'\gamma') = & \Psi_i(n\gamma - n'\gamma') \eta_{ij} x_j (n\gamma - n'\gamma') \\ & + (1/4) \Phi_{ij}(n\gamma - n'\gamma') \eta_{ik} \eta_{jl} x_k (n\gamma - n'\gamma') \\ & \times x_l (n\gamma - n'\gamma'). \quad (n\gamma \neq n'\gamma') \quad (20) \end{aligned}$$

The above relation can be obtained in the present paper by replacing $u_i(n\gamma - n'\gamma' / \sigma\sigma') = w_i(n\gamma - n'\gamma' / \sigma\sigma')$ in eq. (10), substituting eqs. (4-a) and (4-b) into eq. (10) and putting the energy of each atom pair equal to zero. Using the values of $\Psi_i(n\gamma - n'\gamma')$ and $\Phi_{ij}(n\gamma - n'\gamma')$ obtained from the neutron and X-ray scattering experiments, Wu and Cohen⁽¹³⁾ have estimated the solute CP $\Psi(n\gamma - n'\gamma')$ in eq. (20).

On the other hand, Wu⁽¹⁷⁾ has made theoretical analysis and reached the different expression for the solute CP's.

$$\begin{aligned} \Psi(n\gamma - n'\gamma') = & -(1/4) \Phi_{ij}(n\gamma - n'\gamma') \eta_{ik} \eta_{jl} x_k (n\gamma - n'\gamma') \\ & \times x_l (n\gamma - n'\gamma'). \quad (n\gamma \neq n'\gamma') \quad (21) \end{aligned}$$

These two different expressions for the solute CP $\Psi(n\gamma - n'\gamma')$ in eqs. (20) and (21) can be proved to be the same by substituting our expressions of solute-lattice CP's $\Psi_i(n\gamma - n'\gamma')$ of eq. (8-b) obtained in this paper into eq. (20). Hence, this is another proof of the solute-lattice CP that can be expressed in the form of eq. (8-b) in this paper.

On decreasing the temperature, a non-stoichiometric β -brass should take place either two phase decomposition into a stoichiometric B2 phase and a pure Cu (Zn) phase or a secondary ordering into a $D0_3$ phase⁽¹⁹⁾. This secondary ordering could take place by the concentration wave with the wave vector $k(\zeta) = (2\pi/a)(1/2, 1/2, 1/2)$ in Fig. 6(b). However, due to the large values of the elastic free energy at $k(\zeta)$ as shown in Fig. 6(b), the occurrence of the secondary ordering is prohibited in the β -brass. In contrast to it, two phase separation by spinodal decomposition, which occurs by the concentration wave with the wave vector $k(q) \sim (000)$, can be stimulated by lowering the elastic free energy of solid solution: Near the origin in the reciprocal space, essential contribution to the elastic free energy comes from the large gradient parts of the dispersion curves in acoustic modes. Con-

sequently, it is clear in the sense of elastic free energy that spinodal decomposition, instead of a secondary ordering, should take place in the nonstoichiometric β -brass.

We have so far emphasized that the advantage of the theory in which all CP's can be evaluated from the force constants and stress-free strains. However, the theory presented here, of course, has its limitations. In particular, Vegard's law approximation in eq. (4-b) restricts the theory to particular systems, and the harmonic approximation requires the assumption that the CP's are independent of the local composition. These two conditions are, generally speaking, considerably strict for ordered metal alloys. For example, in case of order-disorder transition of CuPt alloy⁽²³⁾, the stress-free strains change rapidly in proportion to the square of the degree of order, η^2 , (break down of Vegard's law), and in the case of Cu-Zn system⁽²⁴⁾, Young's modulus is elucidated to vary with η^2 . In fact, Kajitani and Cook⁽²⁵⁾ were successful for interpreting temperature dependence of η in the order-disorder transition, by taking into account additional correction factor in the form proportional to η^4 in the free energy. In the present case, the situation is likely the above cases. Therefore, to keep the theory available, it should be restricted to the small amplitudes of the concentration waves.

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Appendix

Notation of lattice (Φ_{ij}), solute-lattice (Ψ_i) and solute (Ψ) CP's, S is a shorthand notation of $S(\text{IIJJ}) = 2C_{12}/(C_{12} + C_{44})$ and upper suffi2x γ indicates sublattice α or β .

$(n\gamma - n'\gamma')$	Φ_{ij}	Ψ_i	Ψ
$(1/2, 1/2, 1/2)$	$\begin{pmatrix} -\alpha_1 & -\gamma_1 & -\gamma_1 \\ -\gamma_1 & -\alpha_1 & -\gamma_1 \\ -\gamma_1 & -\gamma_1 & -\alpha_1 \end{pmatrix}$	$\begin{pmatrix} \hat{\alpha}_1^x \\ \hat{\alpha}_1^y \\ \hat{\alpha}_1^z \end{pmatrix} = na/4 \begin{pmatrix} \alpha_1 + 2\gamma_1 S \\ \alpha_1 + 2\gamma_1 S \\ \alpha_1 + 2\gamma_1 S \end{pmatrix}$	$\bar{\alpha}_1 = (3/4)\eta^2 a^2 [(1/4)a_1 + C_{12}/(C_{12} + C_{44})\gamma_1]$
(100)	$\begin{pmatrix} -\alpha_2^y & 0 & 0 \\ 0 & -\beta_2^y & 0 \\ 0 & 0 & -\beta_2^z \end{pmatrix}$	$\begin{pmatrix} \hat{\alpha}_2^x(\gamma) \\ \hat{\alpha}_2^y(\gamma) \\ \hat{\alpha}_2^z(\gamma) \end{pmatrix} = na/2 \begin{pmatrix} \alpha_1^y \\ 0 \\ 0 \end{pmatrix}$	$\bar{\alpha}_2 = (1/4)\eta^2 a^2 a_2^y$
(110)	$\begin{pmatrix} -\alpha_3^y & -\gamma_3^y & 0 \\ \gamma_3^y & -\alpha_3^y & 0 \\ 0 & 0 & -\beta_2^z \end{pmatrix}$	$\begin{pmatrix} \hat{\alpha}_3^x(\gamma) \\ \hat{\alpha}_3^y(\gamma) \\ \hat{\alpha}_3^z(\gamma) \end{pmatrix} = na/2 \begin{pmatrix} \alpha_3^y + \alpha_3^y S \\ \gamma_3^y S + \alpha_3^y \\ 0 \end{pmatrix}$	$\bar{\alpha}_3 = \eta^2 a^2 [(1/2)a_3^y + C_{12}/(C_{12} + C_{44})\gamma_3^y]$
$(3/2, 1/2, 1/2)$	$\begin{pmatrix} -\alpha_4 & -\gamma_4 & -\gamma_4 \\ -\gamma_4 & -\beta_4 & -\delta_4 \\ -\gamma_4 & -\delta_4 & -\beta_4 \end{pmatrix}$	$\begin{pmatrix} \hat{\alpha}_4^x \\ \hat{\alpha}_4^y \\ \hat{\alpha}_4^z \end{pmatrix} = na/4 \begin{pmatrix} 3\alpha_4 + 2\gamma_4 S \\ 3\gamma_4 S + \beta_4 + \delta_4 S \\ 3\gamma_4 S + \delta_4 S + \beta_4 \end{pmatrix}$	$\bar{\alpha}_4 = (1/16)\eta^2 a^2 [9\gamma_4 + 2\beta_4 + C_{12}/(C_{12} + C_{44})(6\gamma_4 + \delta_4)]$ ($\eta = \eta_{xx} = \eta_{yy} = \eta_{zz}$)