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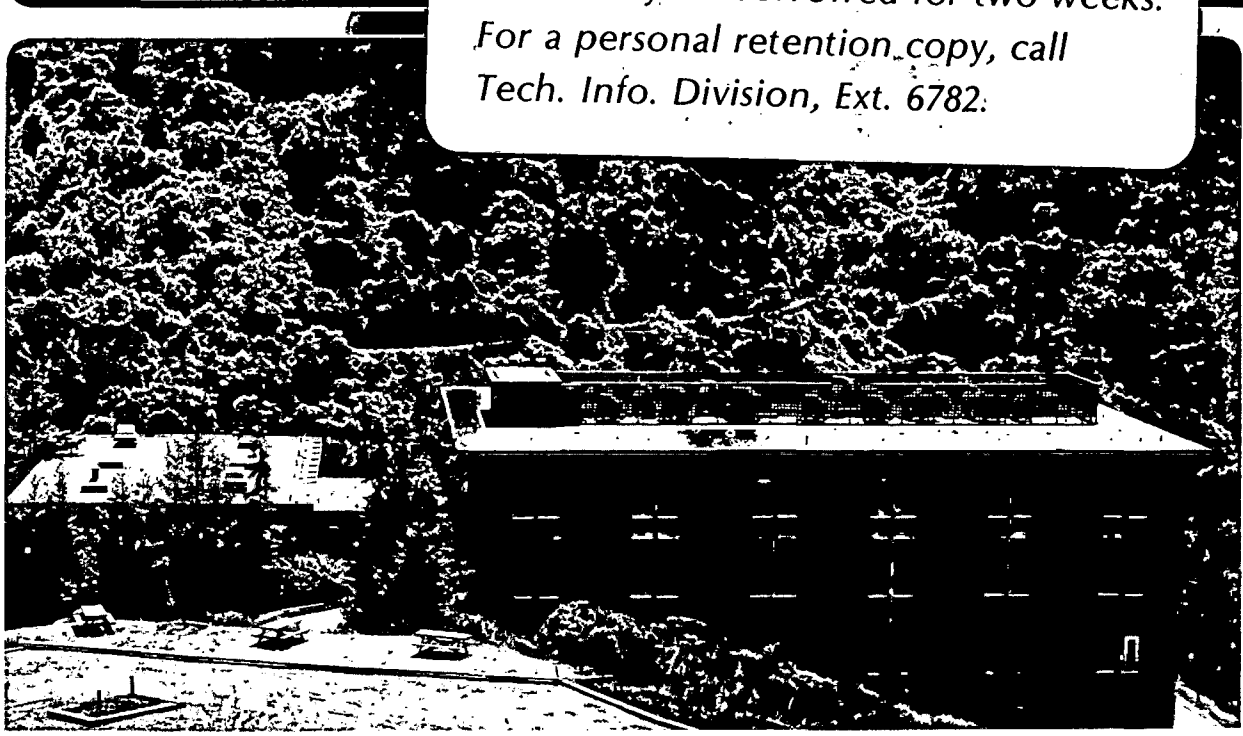

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THE ELASTIC CONTRIBUTION TO THE THERMODYNAMICS OF PHASE TRANSFORMATIONS IN SOLIDS†

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Phase transformations in real solids usually involve the formation of elements of new phase which differ in size or shape from the typical structural element of the parent. The associated elastic energy affects the thermodynamics of the transformation and strongly influences the nature and morphology of the product phase. Many of the consequences of elastic strain can be predicted or understood on the basis of models which treat the parent and product phases as linear elastic bodies. The linear elastic theory is reviewed in this paper. It is shown that the theory may be derived from a simple starting point: the strong harmonic model of a solid solution. From this starting point it is possible to develop both the microscopic and macroscopic formulations of the theory. The known results of the theory are extracted and recent extensions are presented and discussed.

Phase transformations in real solids usually involve the formation or reconfiguration of elements which differ in size or shape from the typical structural component of the parent phase. The phase transformation has the effect of introducing volumetric defects into the parent which are internally distorted themselves and cause distortions of the matrix in which they lie. The associated elastic strain influences the energetics of the phase transformation, the morphology of the product, and sometimes even the crystal structure and composition of the product phase.

The pioneering work of Eshelby (1) showed that many of the consequences of volumetric distortion could be understood or predicted from a linear elastic model in which both the defects and the matrix are taken to be linear elastic bodies whose mismatch is quantified in terms of the elastic strain necessary to achieve the volume, shape and orientation of one through the continuous deformation of the other. Eshelby specifically obtained an

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analytic solution for the elastic strain and elastic energy associated with a coherent ellipsoidal defect in an elastically isotropic body, and generalized the result in two directions which are directly pertinent to the theory of phase transformations: the elastic energy of a solid solution, modelled as a distribution of misfitting spheres in an isotropic matrix, and the elastic energy of a particle of new phase, modelled as an isolated ellipsoidal elastic inclusion. Eshelby's results emphasize the unity of these two problems in the context of the elastic theory.

The elastic model of a solid solution has, in fact, an independent history which traces back at least to Zener's (2) hypothesis that strain-induced elastic interactions are responsible for the ordering of carbon in Fe-C martensites, and to the Friedel (3) treatment of the isotropic solution of elastic atoms which anticipates the Eshelby result. A more detailed atomistic treatment was provided by the "lattice statics" model of Matsubara (4) and Kanzaki (5), who modified the lattice dynamics of Born and Huang (6) to compute the static equilibrium lattice displacements about a point defect. These results were generalized to distributions of point defects by Krivoglaz and Tichonova (7) and by Khachaturyan (8). Khachaturyan (9) subsequently developed the model into a microscopic elastic theory of the solid solution. Elements of the theory were re-derived in subsequent work by Cook and de Fontaine (10).

The fruitful application of the solid solution theory to phase transformations dates at least from the Cahn (11,12) theory of spinodal decomposition in cubic solids, which he developed from a semi-macroscopic perspective. The microscopic theory was used by Khachaturyan and Shatalov (13) to predict the structures of interstitial superlattices in tantalum, and has been used extensively in the theory of ordering reactions (14). An adaption of the microscopic theory was developed and used by Wen (15) and by Wen, Khachaturyan and Morris (16) to perform computer simulation studies of martensitic transformations and defect reconfiguration reactions in idealized elastic solids.

The Eshelby treatment of macroscopic inclusions was reformulated by Khachaturyan (17), who found a Fourier transform solution which permits the analysis of an arbitrary distribution of elastic inclusions in a body of uniform anisotropic elastic constants. Khachaturyan and Shatalov (18) generalized this result to treat interacting inclusions of different types, but still with the assumption of uniform elastic constants. Eshelby (1) had shown that it is possible to obtain the solution for an isolated ellipsoidal inclusion whose elastic moduli differ from those of the matrix. Lee, Barnett, and Aaronson (19) generalized this result to find an analytic solution for an ellipsoidal inclusion with mismatched elastic constants in an anisotropic matrix. The solution is, however, restricted to the case of an isolated particle.

The applications of the macroscopic elastic theory have been primarily to the theory of precipitate shapes and habits, the theory of metastable intermediate precipitate phases, and the theory of martensitic transformations. The wealth of useful applications is reviewed in a recent monograph by Khachaturyan (20).

The intent of this paper is to review the derivation of the linear elastic theory from a simple starting point: the strong harmonic model of a solid solution. From this starting point we develop both the microscopic and macroscopic models and show that virtually all relevant features of the elastic theory, including both alternate formulations and specific applications, are contained and can be extracted in a straightforward way. Since

the previous applications of the theory are found as special cases of the general model, the possibility of extending them in new directions is obvious and illustrated by examples drawn from recent work.

The Solid Solution

Theory

The solutions of interest here are those which may hypothetically be created by introducing solute species, modelled as elastic defects, onto the atom sites of a solvent host lattice. We are interested in computing the free energy of the solution for an arbitrary but specific distribution of the solute species. The theory will be written for a substitutional solution on a primitive solvent lattice. The generalization to intersitial solutions or non-primitive lattices is straightforward (9).

Assumptions and Kinematics

The Solution. The free energy of the solution will be referred to that of the solvent in a pure, undistorted state. The atom sites of the solution (labelled by the vectors $\underset{\sim}{x}$) can be brought into one-to-one correspondence with the lattice sites, $\underset{\sim}{r}$, of the reference state by the relations

$$\underset{\sim}{x}(\underset{\sim}{r}) = \underset{\sim}{r} + \underset{\sim}{u}(\underset{\sim}{r}), \tag{1}$$

where the vector function $\underset{\sim}{u}(\underset{\sim}{r})$ gives the displacement of the atom site from its reference position. The chemical state of the $(\nu + 1)$ component solid solution is then specified by the ν distribution functions, $c_p(\underset{\sim}{r})$, $p=1,\ldots,\nu$. The function $c_p(\underset{\sim}{r})$ has the value 1 if there is a solute of type p at the atom site referenced to $\underset{\sim}{r}$, and is zero otherwise. The average of $c_p(\underset{\sim}{r})$ over the lattice is the mean concentration, $\bar{c}_p$.

The Solute. In the elastic model of a solid solution one attempts to separate the chemical effect of the solute from its influence as an elastic defect in distorting the solvent lattice. The elastic defect is related to the geometric mismatch between the relaxed structures of the solute and the solvent and is defined in the model by the linear elastic strain, ε°_{ij}, whose negative is the strain required to deform the solute until it fits without distortion in the host lattice.

The definition of ε°_{ij} requires a clear specification of the structure and orientation of the relaxed reference state to which the solute is referred. When the solute preferentially forms a crystal having the same crystal structure as the solvent, or when the solute is an element of new phase whose crystal structure and orientation are specified, then the appropriate reference state is obvious. But when the solute preferentially forms a crystal having an equilibrium structure different from that of the solvent the reference is not unique and should be chosen so as to minimize the free energy of solution. Since the elastic energy increases quadratically with the magnitude of the elastic strain, the free energy of solution will usually be minimized if the reference used to define ε°_{ij} is that stable or metastable state of the pth solute which is geometrically closest to the structure of the solvent. The solution may then be made through a quasi-chemical cycle involving a structural transformation of the solute (if necessary) from its equilibrium state to the metastable structure closest to that of the solvent followed by a small elastic distortion to establish a coincident lattice. The second step defines the elastic strain $\varepsilon^{\circ}_{ij}(p)$.

If the reference structure for the pth elastic defect is identical to that of the host crystal then the reference strain $\varepsilon^{\circ}_{ij}(p)$ is a simple dilation (homogeneous expansion or contraction) and each solute species is represented by only one elastic defect. If the reference structure differs from that of the host lattice, however, a single solute species may give rise to several distinct elastic defects, which differ in the orientation of the principal axes of the reference strain with respect to the axes of the host crystal.

The Strong Harmonic Approximation. The solution differs from its reference state (the pure solvent) through the addition of solute and the imposition of lattice displacements. It follows that the associated free energy change may be expressed as a functional of the functions, $\underset{\sim}{u}(\underset{\sim}{r})$ and $c_p(\underset{\sim}{r})$ $(p=1,\ldots,\nu)$. We shall assume that this functional is adequately represented by the harmonic series:

$$\begin{aligned}\Delta G[\underset{\sim}{u}(\underset{\sim}{r}),\{c_p(\underset{\sim}{r})\}] = G_o &+ \sum_{pr}\Phi(p)c_p(\underset{\sim}{r}) \\ &+ \frac{1}{2}\sum_{p}\sum_{\underset{\sim}{r},\underset{\sim}{r}'}\Phi^{pq}(\underset{\sim}{r}-\underset{\sim}{r}')c_p(\underset{\sim}{r})c_q(\underset{\sim}{r}') \\ &+ \sum_{p}\sum_{\underset{\sim}{r},\underset{\sim}{r}'}\Phi^{p}_{i}(\underset{\sim}{r}-\underset{\sim}{r}')c_p(\underset{\sim}{r})u_i(\underset{\sim}{r}') \\ &+ \frac{1}{2}\sum_{\underset{\sim}{r},\underset{\sim}{r}'}\Phi_{ij}(\underset{\sim}{r}-\underset{\sim}{r}')u_i(\underset{\sim}{r})u_j(\underset{\sim}{r}') \qquad (2)\end{aligned}$$

where the sums are taken over the reference lattice and the coefficients are independent of position. Higher order terms are neglected. A non-zero term linear in the displacement, $\underset{\sim}{u}$, would be incompatible with the mechanical equilibrium of the reference state and has hence been eliminated.

The strong harmonic approximation has two consequences which concern the elastic constants of the bulk solution. First, the dynamical matrix is assumed to be independent of composition, which implies that the elastic constants are unchanged by alloying. For the body of this paper we shall, in fact, make the stronger assumption that the difference between the elastic constants of the solute and solvent may be neglected. A brief treatment of the consequences of differences in the elastic moduli is given in the final section, where the solutions to macroscopic inclusion problems are extracted from the theory. Second, while a matrix of bulk elastic constants can be obtained by imposing a macroscopic deformation on the harmonic crystal, these will not be the full elastic constants of the reference state. In the important case of a primitive lattice the computed elastic constants will, in fact, have an incorrect symmetry, being related by the strong Cauchy conditions rather than the less restrictive Voigt relations (25). This problem is inherent to the harmonic treatment of lattice vibrations and arises from the failure of the model to include many-body, anharmonic, and thermal effects which influence the elastic rigidity of real crystals. To partly compensate for this shortcoming of the model we shall replace the computed bulk elastic constants by the true elastic constants of the reference crystal wherever they appear.

Macroscopic Homogeneity. While the solute species may be configured in an essentially arbitrary way, we shall assume that the solution is sensibly homogeneous when viewed on a scale large compared with the dimension of the solute or of the largest relevant solute cluster. The assumption of macroscopic homogeneity permits an important decomposition of the vector displacement, $\underset{\sim}{u}(\underset{\sim}{r})$, within a macroscopic sample of the solution. Neglecting rigid rotation and surface terms;

$$u_i(\underset{\sim}{r}) = \varepsilon_{ij} r_j + \upsilon_i(\underset{\sim}{r}) \tag{3}$$

where ε_{ij} is a uniform elastic strain defined by the boundary displacement of the body of the solution and $\upsilon_i(\underset{\sim}{r})$ is an internal displacement field which may be taken to vanish over the boundary (or set to satisfy a periodic boundary condition). The distribution function for the pth solute may also be written as a sum of its mean and its variation:

$$c_p(\underset{\sim}{r}) = \bar{c}_p + \Delta c_p(\underset{\sim}{r}) \tag{4}$$

Evaluation of the Free Energy through an Eshelby Cycle

The terms which contribute to the free energy of the solid solution may be evaluated through the use of an equivalent cycle to create the solid solution along lines suggested by Eshelby (1). The equivalent cycle involves the six hypothetical operations:

1. Taking the pure solvent crystal, isolate ν clusters of which the pth contains N_p solvent atoms, and cut each cluster out of the solvent lattice. If surface effects can be ignored, the free energy of the assembly is not changed.

2. Substitute solutes of the pth type for atoms of the pth cluster and let the transformed cluster relax to its stress-free state. The transmutation causes the free energy change

$$\Delta G_2 = \sum_p N_p \Delta\mu_p^c = N \sum_p \bar{c}_p \Delta\mu_p^c \tag{5}$$

where $\Delta\mu_p^c$ is the chemical energy difference per atom between the solvent and the pth solute in its reference state. The associated free expansion of the pth cluster involves no energy change since the cluster is stress-free.

3. Let surface tractions be applied to each cluster to restore it to the shape it had before the transmutation occurred. The required strain is $\varepsilon_{ij} = -\varepsilon_{ij}^{\circ}(p)$. Since each cluster is macroscopic, the deformation may be described by continuum elasticity. If we neglect the work done on the loading mechanisms (which is recovered in any case) the net free energy change is the total mechanical work done on the clusters, which defines the "elastic self-energy," Φ_{el}°, of the solution and is:

$$\Delta G_3 = \sum_p \Phi_{el}^{\circ}(p) = \frac{N}{2} \sum_p \bar{c}_p v \lambda_{ijk\ell} \varepsilon_{ij}^{\circ}(p) \varepsilon_{k\ell}^{\circ}(p) \tag{6}$$

where v is the volume per atom site and $\lambda_{ijk\ell}$ is the fourth-order tensor of elastic constants.

4. Let the clusters ($p=1,\ldots\nu$) be reintroduced into the solvent crystal. Since each cluster just fits into the space from which it was removed, there is no free energy change.

5. Now, let the solute be dispersed through the host lattice at constant shape to create the solute distribution appropriate to the solid solution. The free energy change is the chemical free energy of mixing. It has two contributions: (1) an energy change $\Delta\mu_p^s$ per atomic defect on dissolution, which is associated with the replacement of the homogeneous environment of the defect by an environment of host atoms (if the defect were an element of new phase with bulk properties this energy would be simply the

chemical contribution to the surface energy of the defect particle), (2) a configurational energy change due to the mutual chemical interaction of solute defects. To second order in the solute interaction the resulting free energy change is

$$\Delta G_5 = N \sum_p \Delta\mu_p^s \bar{c}_p + \frac{1}{2} \sum_{pq} \sum_{\underset{\sim}{r}\underset{\sim}{r}'} V_{pq}^{ch}(\underset{\sim}{r}-\underset{\sim}{r}') c_p(\underset{\sim}{r}) c_q(\underset{\sim}{r}') \tag{7}$$

6. Finally, let the distributed atoms relax, introducing an equilibrium elastic strain into the lattice. In this relaxation, each solute atom will function as a center of force which acts to displace the lattice about it. The lattice displacement is opposed by the elastic resistance of the lattice. The associated energy is

$$\Delta G_6 = \Phi'_{el} = -\sum_p \sum_{\underset{\sim}{r}\underset{\sim}{r}'} f_i^p(\underset{\sim}{r}-\underset{\sim}{r}') c_p(\underset{\sim}{r}) u_i(\underset{\sim}{r}') + \frac{1}{2} \sum_{\underset{\sim}{r}\underset{\sim}{r}'} A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}') u_i(\underset{\sim}{r}') u_j(\underset{\sim}{r}) \tag{8}$$

The symmetrical tensor $A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}')$ is the Born-von Karman tensor (dynamical matrix) of the host lattice, and the $f^p(\underset{\sim}{r}-\underset{\sim}{r}')$ are the "Kanzaki" forces which act from a solute atom of type p at location $\underset{\sim}{r}$ on an atom at site $\underset{\sim}{r}'$. Since the elastic relaxation is spontaneous, $\Phi'_{el}<0$; the physical effect of the elastic relaxation is to remove part of the elastic energy which was introduced when the solute species were deformed to fit properly into the host lattice.

The total free energy change is separable into chemical and elastic terms:

$$\Delta G = \Delta G_{chem} + \Delta\Phi_{el} \tag{9}$$

where

$$\Delta G_{chem} = N \sum_p \bar{c}_p \Delta\mu_p + \frac{1}{2} \sum_{pq} \sum_{\underset{\sim}{r}\underset{\sim}{r}'} v_{ch}^{pq}(\underset{\sim}{r}-\underset{\sim}{r}') c_p(\underset{\sim}{r}) c_q(\underset{\sim}{r}') \tag{10}$$

is the chemical free energy change, with $\Delta\mu_p$ the sum of $\Delta\mu_p^c$ and $\Delta\mu_p^s$ and

$$\Delta\Phi_{el} = N \sum_p \bar{c}_p \frac{v}{2} \lambda_{ijk\ell} \varepsilon_{ij}^{\circ}(p) \varepsilon_{k\ell}^{\circ}(p) - \sum_p \sum_{\underset{\sim}{r}\underset{\sim}{r}'} f_i^p(\underset{\sim}{r}-\underset{\sim}{r}') c_p(\underset{\sim}{r}') u_i(\underset{\sim}{r}) + \frac{1}{2} \sum_{\underset{\sim}{r}\underset{\sim}{r}'} A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}') u_i(\underset{\sim}{r}) u_j(\underset{\sim}{r}') \tag{11}$$

is the elastic contribution to the free energy. The terms appearing in these equations have the form required by the strong harmonic approximation (eq.2). The coefficients are, of course, restricted by the symmetry of the crystal in its solute- and deformation-free state and are further restricted by the requirement that $\Delta\Phi_{el}$ be invariant to rigid body displacements.

Evaluation of the Elastic Contribution to the Free Energy

The instantaneous displacement field, $\underset{\sim}{u}(\underset{\sim}{r})$, is the sum of a static and a dynamic displacement. The former is a consequence of the shift in the equilibrium lattice positions as the lattice is strained; the latter results from lattice vibrations. In the strong harmonic approximation lattice vibrations do not contribute to ΔG. The dynamical matrix, $\underset{\sim}{A}$, is unaffected by alloying, so the vibrational free energy is unchanged from its value in the reference state. The free energy change is hence due to the static equilibrium displacement field.

Using equations 3 and 4,

$$\Delta\Phi_{el} = \Phi^{\circ}_{el} - N\epsilon_{ij}\sum_p \Lambda_{ij}(p)\bar{c}_p + \frac{N}{2}\Lambda_{ij\ell m}\epsilon_{ij}\epsilon_{\ell m}$$

$$- \sum_p \sum_{\underset{\sim}{r}\underset{\sim}{r}'} f^p_i(\underset{\sim}{r}-\underset{\sim}{r}')\upsilon_i(\underset{\sim}{r}')\Delta c_p(\underset{\sim}{r})$$

$$+ \frac{1}{2}\sum_{\underset{\sim}{r}\underset{\sim}{r}'} A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}')\upsilon_i(\underset{\sim}{r})\upsilon_j(\underset{\sim}{r}') \tag{12}$$

where Φ°_{el} is the elastic self energy and is independent of the displacement. The tensors $\Lambda_{ij}(p)$ and $\Lambda_{ij\ell m}$ are given by the summations:

$$\Lambda_{ij}(p) = \frac{1}{2}\sum_{\underset{\sim}{r}} [f^p_i(\underset{\sim}{r})r_j + f^p_j(\underset{\sim}{r})r_i] \tag{13}$$

$$\Lambda_{ij\ell m} = \frac{1}{N}\sum_{\underset{\sim}{r},\underset{\sim}{r}'} A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}')r_\ell r'_m = -\frac{1}{2}\sum_{\underset{\sim}{r}} A_{ij}(\underset{\sim}{r})\underset{\sim}{r}_\ell \underset{\sim}{r}_m \tag{14}$$

<u>The Macroscopic Strain</u>. The net stress-free strain of the crystal on forming the solid solution can be found, along with the values of the tensors $\Lambda_{ij}(p)$ and $\Lambda_{ijk\ell}$, from the condition that the solution obey Hooke's Law in response to small imposed stresses. By the usual relations of elasticity, the macroscopic elastic stress is related to the homogeneous strain by

$$\sigma_{ij} = \frac{\partial}{\partial\epsilon_{ij}}\left(\frac{\Delta\Phi_{el}}{V}\right) = -\sum_p \frac{\Lambda_{ij}(p)}{v}\bar{c}_p + \frac{1}{v}\Lambda_{ijk\ell}\epsilon_{k\ell} \tag{15}$$

where V is the crystal volume.

Defining the tensor $\bar{\epsilon}_{ij}$ by the relation

$$\Lambda_{ijk\ell}\bar{\epsilon}_{k\ell} = \sum_p \Lambda_{ij}(p)\bar{c}_p \tag{16}$$

we have

$$\sigma_{ij} = \frac{1}{v}\Lambda_{ijk\ell}(\epsilon_{k\ell} - \bar{\epsilon}_{k\ell}) = \frac{1}{v}\Lambda_{ijk\ell}\epsilon^{el}_{k\ell} \tag{17}$$

where $\epsilon^{el}_{k\ell}$ is that part of the elastic strain due to the externally imposed stress σ_{ij}. In the stress-free state $\sigma_{ij}=0$ and $\epsilon^{el}_{k\ell}=0$; then from eq. 15:

$$\bar{\epsilon}_{ij} = \sum_p \frac{1}{v} S_{ijk\ell}\Lambda_{k\ell}(p)\bar{c}_p \tag{18}$$

where $S_{ijk\ell}$ is the elastic compliance tensor, the tensor inverse to $\lambda_{ijk\ell}$. Equation 18 shows that Vegard's Law is obeyed with respect to each of the solute species, as is expected since the model is second order. In the limit $\bar{c}_p=1$, $\bar{\epsilon}_{ij}=\epsilon^{\circ}_{ij}(p)$, and we are led to the simple result

$$\bar{\epsilon}_{ij} = \sum_p \epsilon^{\circ}_{ij}(p)\bar{c}_p. \tag{19}$$

The value of $\Lambda_{ij}(p)$ which is consistent with eq. 18 is

$$\frac{\Lambda_{ij}(p)}{v} = \sigma^{\circ}_{ij}(p) = \lambda_{ijk\ell}\epsilon^{\circ}_{ij}(p), \tag{20}$$

where $\sigma^{\circ}_{ij}(p)$, the "transformation stress", is a material constant.

In the absence of external stress the macroscopic strain is just the uniform relaxation strain, $\bar{\epsilon}_{ij}$. The associated elastic contribution to the free energy of the stress-free crystal is:

$$\Delta\phi_{el} = \frac{N}{2}\sum_{pq}(v\lambda_{ijk\ell}\epsilon^{\circ}_{ij}(p)\epsilon^{\circ}_{k\ell}(q))\bar{c}_p(\delta_{pq} - \bar{c}_q) + \text{terms in } \upsilon(r)). \tag{21}$$

External Stress. The computation of the Gibbs free energy in the presence of an external stress involves some subtlety because of the use of the stress-free solvent crystal as the reference state. The Gibbs free energy change is the sum of the elastic energy added to the body by the external stress and the change in the elastic potential of the loading mechanism. The change in the potential energy of the loading mechanism is the sum of the work done on the loading mechanism during the elastic deformation of the solution, and the virtual work done in creating the solution from the reference state under the applied stress, σ_{ij}. It follows that the total contribution of the external stress to the Gibbs free energy is

$$\Delta G_{ext} = V\sigma_{ij}(\varepsilon_{ij}^{el} + \bar{\varepsilon}_{ij}) = V\sigma_{ij}\varepsilon_{ij} , \tag{22}$$

where ε_{ij} is the total strain and V is the volume of the crystal.

The Internal Strain. The equilibrium local displacement field $\underset{\sim}{\upsilon}(\underset{\sim}{r})$ must provide a minimum of the elastic energy. A necessary condition is, from eq. 16:

$$\sum_{\underset{\sim}{r}'} A_{ij}(\underset{\sim}{r}-\underset{\sim}{r}')\upsilon_j(\underset{\sim}{r}') = \sum_{p\underset{\sim}{r}'} f_i^p(\underset{\sim}{r}'-\underset{\sim}{r})c_p(\underset{\sim}{r}') \tag{23}$$

Since the local displacement $\underset{\sim}{\upsilon}(\underset{\sim}{r})$ vanishes on the boundary of the body (by its definition), the Fourier transform of both sides of euqation 23 may be taken to give:

$$\hat{A}_{ij}(\underset{\sim}{k})\hat{\upsilon}_j(\underset{\sim}{k}) = \sum_p \hat{F}_i^p(\underset{\sim}{k})\Delta\hat{c}_p^*(\underset{\sim}{k}) \tag{24}$$

where the Fourier transform of the arbitrary tensor function, $\underset{\sim}{\psi}(\underset{\sim}{r})$, is

$$\hat{\underset{\sim}{\psi}}(\underset{\sim}{k}) = \sum_{\underset{\sim}{r}} \underset{\sim}{\psi}(\underset{\sim}{r})e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}} \tag{25}$$

and $\underset{\sim}{\psi}^*(k)$ is its complex conjugate. The solution of eq. 24 for the Fourier component $\hat{\upsilon}_i(\underset{\sim}{k})$ is

$$\hat{\upsilon}_i(\underset{\sim}{k}) = \hat{G}_{ij}(\underset{\sim}{k})\sum_p \hat{F}_j^p(\underset{\sim}{k})\Delta\hat{c}_p^*(\underset{\sim}{k}) \tag{26}$$

where $\hat{\underset{\sim}{G}}$ is a Green's function inverse to the dynamical matrix $\underset{\sim}{A}$.

If the solution (eq. 26) for the internal displacement field is used in equation 12 the last two terms on the right hand side of the equation sum to give, with equations 21 and 22,

$$\begin{aligned}\Delta\Phi_{el} &= V\sigma_{ij}\varepsilon_{ij} \\ &+ \frac{N}{2}\sum_{p,q}(v\lambda_{ijk\ell}\varepsilon_{ij}^{\circ}(p)\varepsilon_{k\ell}^{\circ}(q))\bar{c}_p(\delta_{pq} - \bar{c}_q) \\ &- \frac{1}{2N}\sum_{p,q}\sum_{\underset{\sim}{k}}[\hat{F}_i^p(\underset{\sim}{k})\hat{G}_{ij}(\underset{\sim}{k})\hat{F}_j^{*q}(\underset{\sim}{k})]\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}_q^*(\underset{\sim}{k}).\end{aligned} \tag{27}$$

This expression gives the total elastic contribution to the free energy of the solution.

Separation of Physically Distinct Contributions to the Elastic Energy

Physically, the elastic contribution to the free energy of the crystal can be divided into four parts: (1) the elastic self energy, which is a simple sum of one-particle elastic energies and is equal to the energy which would be observed if the particles did not interact, for example, if they were present in infinite dilution; (2) a configuration-independent pairwise interaction energy whose magnitude depends only on the type and the total concentration of the solute atoms present; this interaction is indirect and has its source in the elastic image forces which arise from relaxation of the unconstrained crystal boundary; (3) a configuration-dependent pairwise interaction energy which results from the direct elastic interaction of the defects; (4) the contribution of external forces. While equation 27 superficially appears to separate the elastic energy into physically distinct terms, it does not; parts of both the self energy and the "image force" contributions are buried in the third term on the right hand side. The identity

$$\frac{1}{N}\sum_{\underset{\sim}{k}}\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}^*_q(\underset{\sim}{k}) = N\bar{c}_p(\delta_{pq} - \bar{c}_q) \tag{28}$$

has the consequence that the average values

$$Q_{pq} = \langle\hat{F}^p_i(\underset{\sim}{k})\hat{G}_{ij}(\underset{\sim}{k})\hat{F}^{*q}_j(\underset{\sim}{k})\rangle = \frac{1}{N}\sum_{\underset{\sim}{k}}\hat{F}^p_i(\underset{\sim}{k})\hat{G}_{ij}(\underset{\sim}{k})\hat{F}^{*q}_j(\underset{\sim}{k}) \tag{29}$$

add configuration-independent terms to the elastic energy.

To complete the separation of physically distinct contributions to the elastic energy we define the potentials

$$\Phi^\circ_{pq} = (v\lambda_{ijk\ell}\varepsilon^\circ_{ij}(p)\varepsilon^\circ_{k\ell}(q) - Q_{pq}), \tag{30}$$

$$\hat{\Phi}_{pq}(\underset{\sim}{k}) = \begin{cases} [Q_{pq} - \hat{F}^p_i(\underset{\sim}{k})\hat{G}_{ij}(\underset{\sim}{k})\hat{F}^{*q}_j(\underset{\sim}{k})] & (\underset{\sim}{k}\neq 0) \\ 0 & (k=0) \end{cases} \tag{31}$$

With these definitions

$$\Delta\Phi_{el} = V\sigma_{ij}\varepsilon_{ij} + N\sum_{p,q}\Phi^\circ_{pq}\bar{c}_p(\delta_{pq} - \bar{c}_q)$$

$$+ \frac{1}{2N}\sum_{p,q}\sum_{\underset{\sim}{k}}\hat{\Phi}_{pq}(\underset{\sim}{k})\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}^*_q(\underset{\sim}{k}). \tag{32}$$

The first term on the right is the free energy change due to the external load, the second is that which depends <u>only</u> on the average defect concentration, and the third gives the specific contribution of the defect configuration.

Using equation 28, the elastic contribution to the free energy in the absence of external load can also be written:

$$\Delta\Phi_{el} = \frac{1}{2N}\sum_{p,q}\sum_{\underset{\sim}{k}}\hat{\Phi}'_{pq}(\underset{\sim}{k})\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}^*_q(\underset{\sim}{k}) \tag{33}$$

where

$$\hat{\Phi}'_{pq}(\underset{\sim}{k}) = \hat{\Phi}^\circ_{pq} + \hat{\Phi}_{pq}(\underset{\sim}{k}) \tag{34}$$

Equation 33 shows correctly, but deceptively, that the elastic energy of the solution is due to the non-uniformity of the concentration field. It is true that the elastic energy would be zero if all $\Delta\hat{c}_p(\underset{\sim}{k})$ were zero, i.e., if the crystal were composed of identical pseudo-atoms which averaged the properties of the various components. But no such crystal can be composed of discrete atoms, and equation 32 shows that a crystal made of discrete atoms has an elastic energy which is, in part, independent of the defect configuration.

The Real Space Form of the Elastic Free Energy

There are four equivalent ways of writing the elastic contribution to the free energy as a lattice sum in real space, each of which is useful because of its mathematical form or because of the manner in which it separates the different contributions to the energy. We exhibit two of these:

1. Taking the Fourier transform of the last term on the right in equation 32 gives

$$\Delta\Phi_{el} = V\sigma_{ij}\varepsilon_{ij} + \frac{N}{2}\sum_{p,q}\Phi_{pq}\bar{c}_p(\delta_{pq} - \bar{c}_q) + \frac{1}{2}\sum_{p,q}\sum_{\underset{\sim}{r}\underset{\sim}{r}'}\Phi_{pq}(\underset{\sim}{r}-\underset{\sim}{r}')\Delta c_p(\underset{\sim}{r})\Delta c_q(\underset{\sim}{r}') \tag{35}$$

where

$$\Phi_{pq}(\underset{\sim}{r}-\underset{\sim}{r}') = \frac{1}{N}\sum_{\underset{\sim}{k}}\Phi_{pq}(\underset{\sim}{k})e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}-\underset{\sim}{r}')} \tag{36}$$

This form of the real-space interaction preserves the separation of physically distinct contributions to the free energy. Only the last term is sensitive to the precise configuration of defects.

2. Using the identity

$$\varepsilon_{ij} = \varepsilon_{ij}^{el} + \bar{\varepsilon}_{ij} = \varepsilon_{ij}^{el} + \sum_p \varepsilon_{ij}^{\circ}(p)\bar{c}_p \tag{37}$$

the elastic free energy may be written as the conventional lattice sum:

$$\Delta\Phi_{el} = V\sigma_{ij}\varepsilon_{ij}^{el} + \sum_p\sum_{\underset{\sim}{r}}\mu_p^{\circ}c_p(\underset{\sim}{r}) + \frac{1}{2}\sum_{p,q}\sum_{\underset{\sim}{r},\underset{\sim}{r}'}\Phi_{pq}^{E}(\underset{\sim}{r}-\underset{\sim}{r}')c_p(\underset{\sim}{r})c_q(\underset{\sim}{r}') \tag{38}$$

The first term on the right in this equation is the free energy of elastic compression of the lattice and is unaffected by the solute content or distribution. The second term is linear in the solute content; the coefficient, μ_p°, is the elastic contribution to the atomic chemical potential of species p in the dilute solution limit:

$$\mu_p^{\circ}(\sigma_{ij}) = V\sigma_{ij}\varepsilon_{ij}^{\circ}(p) + \frac{1}{2}\Phi_{pp}^{\circ} \tag{39}$$

The third term is a sum of binary solute interactions; $\Phi_{pq}^{E}(r-r')$ is a binary interaction potential which gives the total interaction energy of a solute pair:

$$\Phi_{pq}^{E}(\underset{\sim}{r}-\underset{\sim}{r}') = \Phi_{pq}(\underset{\sim}{r}-\underset{\sim}{r}') + \frac{\Phi_{pq}^{\circ}}{N} \tag{40}$$

The Long-Wavelength Approximation

The evaluation of the elastic contribution to the free energy of an arbitrary distribution of substitutional defects is straightforward given the results of the previous sections, and can be carried out on a computer with no greater difficulty than is involved in the computation of the chemical energy of a multi-component solution having long range binary interactions. However, the computation does require specific forms for both the dynamical matrix, $\underset{\sim}{A}(\underset{\sim}{k})$, of the lattice and the defect forces, $F_i^p(\underset{\sim}{k})$. With appropriate additional assumptions these coefficients can be estimated or extracted from diffraction data, as has been done, for example, by Blanter and Khachaturyan (21). But the precise evaluation of the lattice forces requires a major excursion into the physics of bonding.

If, however, one is interested in the behavior of defects which are, in aggregate, large on the scale of the crystal lattice, or if one is prepared to accept approximations in the spirit of the Debye approximation in lattice dynamics, then it is possible to evaluate the interaction potential in terms of the macroscopic elastic constants. To accomplish this we determine the long-wavelength limit of the potential $\hat{\Phi}_{pq}(\underset{\sim}{k})$.

Consider first the force $\hat{F}_j^p(\underset{\sim}{k})$. In the limit of small $\underset{\sim}{k}$ (long-wavelength)

$$F_j^p(\underset{\sim}{k}) = \sum_{\underset{\sim}{r}} f_j^p(\underset{\sim}{r}) e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}} \approx \sum_{\underset{\sim}{r}} f_j^p(\underset{\sim}{r}) - ik_\ell \sum_{\underset{\sim}{r}} f_i^p(\underset{\sim}{r}) r_\ell \tag{41}$$

The first term on the right vanishes. The second may be simplified by adding and subtracting symmetrizing terms and evaluated as

$$\hat{F}_j^p(\underset{\sim}{k}) = -ik_\ell v\sigma^\circ_{j\ell}(p) \tag{42}$$

The Green's function, $\hat{G}_{ij}(\underset{\sim}{k})$ is the inverse of the dynamical matrix, $\hat{A}_{ij}(\underset{\sim}{k})$, whose long wavelength form is

$$\hat{A}_{ij}(\underset{\sim}{k}) = v\lambda_{ik\ell j}k_k k_\ell = |k|^2 v\lambda_{ik\ell j}e_k e_\ell = |k|^2 v\Omega^{-1}_{ij}(\underset{\sim}{e}) \tag{43}$$

where $\underset{\sim}{e}$ is a unit vector in the direction of $\underset{\sim}{k}$ and the equation defines the matrix Ω^{-1}_{ij}. It follows that

$$\hat{G}_{ij}(\underset{\sim}{k}) = \frac{1}{v|k|^2}\,\Omega_{ij}(\underset{\sim}{e}) \tag{44}$$

With these relations the average interaction, Q_{pq} (eq. 29) becomes:

$$Q_{pq} = \frac{v}{N}\sum_{\underset{\sim}{k}} e_i\sigma^\circ_{ij}(p)\Omega_{j\ell}(\underset{\sim}{e})\sigma^\circ_{\ell m}(q)e_m = \frac{v}{N}\sum_k B'_{pq}(\underset{\sim}{e}) \tag{45}$$

where the second equation defines the scalar $B'_{pq}(\underset{\sim}{e})$. And

$$\hat{\Phi}_{pq}(\underset{\sim}{k}) = \hat{\Phi}_{pq}(\underset{\sim}{e}) = Q_{pq} - B'_{pq}(\underset{\sim}{e}) \qquad (k\neq 0) \tag{46}$$

In the long-wavelength approximation the potential depends only on the macroscopic elastic constants and on the direction, $\underset{\sim}{e}$, of $\underset{\sim}{k}$. The potential was defined to vanish at $\underset{\sim}{k}=0$ in eq. 31.

The Elastic Contribution to The Free Energy of The Solid Solution

The derivation of the expression (eq. 38) for the elastic energy, $\Delta\Phi_{el}$, assumes a specific, though arbitrary, distribution of the elastic defects. In a typical solid solution the distribution of solutes is neither known nor fixed, so the thermodynamic contribution to the elastic energy is determined by a weighted average over a representative ensemble. If the solution has a given composition (c_p, $p=1,\ldots,\nu$) and temperature then the states of the solution differ through the specific choice of the distributions $c_p(\underset{\sim}{r})$, $p=1,\ldots\nu$. Since the volume of the solution is independent of the atom distribution the canonical ensemble may be used. The only parameter in the expression for the elastic energy which depends on the solute distribution is the Fourier coefficient, $\Delta c_p(\underset{\sim}{k})$; hence the elastic contribution to the Gibbs free energy of the solution is

$$\langle\Delta\Phi_{el}\rangle = V\sigma_{ij}\varepsilon_{ij} + \frac{N}{2}\sum_{p,q}\Phi^{\circ}_{pq}\bar{c}_p(\delta_{pq}-c_q)$$
$$+ \frac{1}{2N}\sum_{p,q}\sum_{\underset{\sim}{k}}\hat{\Phi}_{pq}(\underset{\sim}{k})\langle\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}^*_q(\underset{\sim}{k})\rangle \tag{47}$$

where $\langle\Delta\hat{c}_p(\underset{\sim}{k})\Delta\hat{c}^*_q(\underset{\sim}{k})\rangle$ is an average over the canonical ensemble.

Applications

The Random Solid Solution

If the solute distribution is random then, by equations 28, 46 and 47 the average of the potential $\hat{\Phi}_{pq}(\underset{\sim}{k})$ is zero. The elastic contribution to the free energy of a random solution is hence

$$\langle\Delta\Phi_{el}\rangle = V\sigma_{ij}\varepsilon_{ij} + \frac{N}{2}\sum_{p,q}\Phi^{\circ}_{pq}\bar{c}_p(\delta_{pq}-\bar{c}_q) \tag{48}$$

The elastic energy depends only on the configuration-independent terms.

The Binary Solution of Tetragonal Defects on a Cubic Lattice

Most of the solutions which are of practical interest in metallurgy have cubic structures. The solutes in these systems usually behave as spherical inclusions (the usual substitutional solute) or as tetragonal defects (such as carbon in BCC iron). Both solute types are included in the general case of tetragonal inclusions on a cubic lattice. We can easily find the relevant equations for a binary solution. Generalization to the multicomponent solution of tetragonal defects is straightforward.

Matrix Elastic Properties. A crystal of cubic symmetry has a maximum of three independent elastic constants, which are usually taken as the Voigt constants, c_{11}, c_{22} and c_{44}. Using the dimensionless forms

$$c_1 = \frac{c_{11}}{c_{44}},\ c_2 = \frac{c_{12}}{c_{44}},\ \Delta = c_1 - c_2 - 2,\ \Lambda = c_1 + 2c_2$$

the matrix of elastic constants is

$$\lambda_{ijk\ell} = c_{44}(\delta_{ik}\delta_{j\ell} + c_2\delta_{ij\ell k} + \Delta\delta_{ij}\delta_{jk}\delta_{k\ell}), \tag{49}$$

where the parameter Δ is the "anisotropy factor," which vanishes for an isotropic matrix. The coordinate axes are taken parallel to the cubic axes of the crystal. The Green's tensor, $\Omega(\underset{\sim}{e})$, which governs the elastic energy in the long-wavelength approximation is defined by the equation

$$\Omega^{-1}_{ij}(\underset{\sim}{e}) = \lambda_{ik\ell j} e_k e_\ell, \tag{50}$$

which can be inverted to give

$$\Omega_{ij}(\underset{\sim}{e}) = f_{ij}(\underset{\sim}{e}) d^{-1}(\underset{\sim}{e}) \tag{51}$$

where $f_{ij}(e)$ is the cofactor of the (ij) element of the matrix $c_{44}^{-1}\,\underset{\sim}{\Omega}^{-1}(\underset{\sim}{e})$ and $d(\underset{\sim}{e})$ is the determinant of this matrix.

<u>The Transformation Strain</u>. If the stress-free strain of the defect is tetragonal, with principal axes parallel to those of the matrix, the transformation strain can be written

$$\varepsilon^{\circ}_{ij} = \varepsilon(\delta_{ij} + \eta\delta_{i3}\delta_{j3}), \tag{52}$$

where η is the "tetragonality,"

$$\eta = (\varepsilon^{\circ}_{33} - \varepsilon^{\circ}_{11})/\varepsilon^{\circ}_{11}, \tag{53}$$

<u>The Elastic Energy</u>. The elastic self-energy of the tetragonal inclusion is

$$\tfrac{1}{2}\lambda_{ijk\ell}\varepsilon^{\circ}_{k\ell} = \tfrac{1}{2}c_{44}\varepsilon^2[3\Lambda + 2\Lambda\eta + c_1\eta^2] \tag{54}$$

The energy function, $B'(\underset{\sim}{e})$ (eq. 45), is

$$B'(\underset{\sim}{e}) = e_i\sigma^{\circ}_{ij}\Omega_{jk}\sigma^{\circ}_{k\ell}e_\ell = c_{44}\varepsilon^2 b(\underset{\sim}{e}) \tag{55}$$

where

$$b(\underset{\sim}{e}) = d^{-1}(\underset{\sim}{e})\{(\Lambda+c_2\eta)^2 f_1(\underset{\sim}{e}) + 2(\Delta+2)\eta(\Lambda+c_2\eta)f_2(\underset{\sim}{e}) + (\Delta+2)^2\eta^2 f_3(e)\}, \tag{56}$$

$$f_1(\underset{\sim}{e}) = e_i f_{ij} e_j = 1 + 2\Delta\Gamma_4(\underset{\sim}{e}) + 3\Delta^2\Gamma_6(\underset{\sim}{e})$$

$$f_2(\underset{\sim}{e}) = e_i f_{i3} e_3 = e_3^4 + \Delta(1-e_3^2)e_3^2 + \Delta^2\Gamma_6(\underset{\sim}{e})$$

$$f_3(\underset{\sim}{e}) = e_3 f_{33} e_3 = e_3^4 + c_1(1-e_3^2)e_3^2 + \Delta^2(c_1+c_2)\Gamma_6(\underset{\sim}{e}), \tag{57}$$

$$d(\underset{\sim}{e}) = c_1 + \Delta(c_1+c_2)\Gamma_4(\underset{\sim}{e}) + \Delta^2(\Lambda+1)\Gamma_6(\underset{\sim}{e}), \tag{58}$$

$$\Gamma_4(\underset{\sim}{e}) = e_1^2e_2^2 + e_1^2e_3^2 + e_2^2e_3^2$$

$$\Gamma_6(\underset{\sim}{e}) = e_1^2e_2^2e_3^2 \tag{59}$$

From equation 45,

$$Q = vc_{44}\varepsilon^2\langle b(\underset{\sim}{e})\rangle = c_{44}\varepsilon^2\left(\frac{v}{4\pi}\right)\oint b(\underset{\sim}{e})\,d\omega \tag{60}$$

It follows from equations 30, 46 and 47 that the elastic energy per unit volume of a solution of tetragonal defects on a cubic lattice is:

$$<\Delta\Phi_{el}> = V[\sigma_{ij}\varepsilon_{ij} + \frac{1}{2}c_{44}\varepsilon^2<\Delta\phi_{el}>] \tag{61}$$

where

$$<\Delta\phi_{el}> = [(3\Lambda+2\Lambda\eta-c_1\eta^2) - <b(\underset{\sim}{e})>]\ \bar{c}(1-\bar{c})$$

$$- \frac{1}{2N}\sum_{\underset{\sim}{k}}[b(\underset{\sim}{e})-<b(\underset{\sim}{e})>]\ <|\Delta c(\underset{\sim}{k})|^2>. \tag{62}$$

The configuration dependence of the elastic energy is given by the second term of eq. 62. If the solution is random this term vanishes since $<|\Delta c(k)|^2>$ is constant.

Spherical Defects on An Isotropic Lattice: The Eshelby Equations

If the defects are spherical (η=0) and the matrix is isotropic (Δ=0) then equation 56 simplifies to:

$$b(\underset{\sim}{e}) = c_1^{-1}\Lambda^2 = <b(\underset{\sim}{e})>. \tag{63}$$

It follows that the second term in equation 62 vanishes; the elastic free energy is independent of the configuration of the defects. The elastic contribution to the free energy is, in the absence of external stress:

$$<\Delta\Phi_{el}> = \frac{1}{2}Vc_{44}\varepsilon^2\Lambda[3-c_1^{-1}\Lambda] \tag{64}$$

For an isotropic solution

$$c_{44} = \mu,\ c_1 = 2(1-\nu)\ (1-2\nu)^{-1},\ c_2 = 2\nu(1-2\nu)^{-1}.$$

where μ is the shear modulus and ν is Poisson's ratio. Using this notation in equation 64 we have:

$$<\Delta\Phi_{el}> = 2\mu V(\frac{1+\nu}{1-\nu})\varepsilon^2\bar{c}(1-\bar{c}), \tag{65}$$

which is precisely the equation derived by Eshelby (1) from a specific analysis of the interaction of dilational defects in an isotropic matrix.

Spherical Defects on A Cubic Lattice: The Cahn Equation

If the defect is spherical (η=0) and the matrix cubic, as is usually assumed for substitutional solutions on a cubic lattice, then equation 56 gives:

$$b(\underset{\sim}{e}) = \Lambda^2 d^{-1}(\underset{\sim}{e})f_1(\underset{\sim}{e}) = \Lambda^2\xi(\underset{\sim}{e}). \tag{66}$$

and, in the absence of external stress,

$$<\Delta\Phi_{el}> = \frac{V}{2}(c_{11}+2c_{12})\varepsilon^2\{(3-\Lambda<\xi(\underset{\sim}{e})>)\bar{c}(1-\bar{c})$$

$$- \frac{\Lambda^2}{2N}\sum_{\underset{\sim}{k}}[\xi(\underset{\sim}{e})-<\xi(\underset{\sim}{e})>]\ <|\Delta\hat{c}(\underset{\sim}{k})|^2>\} \tag{67}$$

The elastic contribution to the free energy of a cubic binary solution of spherical defects was previously computed by Cahn (11). He approximated the geometric function in the elastic energy to obtain a relation which can be written, in the present notation:

$$\langle\Delta\Phi_{el}\rangle = \frac{V}{2}(c_{11} + 2c_{12})\varepsilon^2(\frac{1}{N})\sum_{\underset{\sim}{k}}\{3-\Lambda[c_1 - 2\Delta\Gamma_4(\underset{\sim}{e})]^{-1}\}\langle|\Delta c(k)|^2\rangle \quad (68)$$

Equation 68 follows from 67 if the inverse of equation 28 is used to gather the two bracketed terms. The result is:

$$\Delta\Phi_{el} = \frac{V}{2}(c_{11} + c_{12})\varepsilon^2(\frac{1}{N})\sum_{\underset{\sim}{k}}\{3-\Lambda\xi(\underset{\sim}{e})\}\langle|\Delta c(\underset{\sim}{k})|^2\rangle \quad (69)$$

which is identical to the Cahn equation under the approximation

$$\xi(\underset{\sim}{e}) \approx [c_1 - 2\Delta\Gamma_4(\underset{\sim}{e})]^{-1}. \quad (70)$$

The approximation is exact for the symmetry directions [100], [110] and [111].

Spinodal Decomposition in a Cubic Crystal

Spinodal decomposition results from the spontaneous growth of composition fluctuations to establish a quasi-periodic profile. The development of the theory of spinodal decomposition in elastic solids (11,12) has concentrated on the onset of decomposition in an initially random binary solution on a cubic lattice, so we shall exhibit the equations for that case.

Thermodynamic Criteria. If composition fluctuations are imposed on an initially random solid solution, the total free energy change is the sum of chemical and elastic contributions. In the long-wavelength limit (20):

$$\Delta G = \frac{V}{2N}\sum_{\underset{\sim}{k}}\{\frac{\partial^2}{\partial c^2}[\Delta G_o(c)] + mk^2 - c_{44}\varepsilon^2[b(\underset{\sim}{e}) - \langle b(\underset{\sim}{e})\rangle]\}\langle|\Delta c(k)|^2 \quad (72)$$

where $\Delta G_o(c)$ is the chemical free energy of a random solution of composition $\bar{c}$. If the coefficient is negative for any $\underset{\sim}{k}$ then the solution is unstable with respect to an increase in the amplitude of the corresponding composition wave. Letting $\underset{\sim}{n}$ be the direction for which $b(\underset{\sim}{e})$ takes on its maximum value, the relevant condition is

$$\frac{\partial^2}{\partial c^2}[\Delta G_o(c)] < c_{44}\varepsilon^2[b(\underset{\sim}{n}) - \langle b(\underset{\sim}{e})\rangle]. \quad (73)$$

When this inequality is satisfied the solution will spontaneously develop a periodic decomposition in the direction $\underset{\sim}{n}$ (which is degenerate by symmetry). Since $b(\underset{\sim}{n}) < \langle b(\underset{\sim}{e})\rangle$, decomposition commences when $\frac{\partial^2}{\partial c^2}[\Delta G_o(c)]$ is positive; spinodal decomposition precedes the "chemical" spinodal.

Equation 73 follows the Khachaturyan (9,20) development of the theory. The original presentation of the theory, by Cahn (11,12), sets a slightly different, though equivalent (10) criterion. Cahn's starting point was the Gibbs free energy of the relaxed, homogeneous crystal, $\Delta G(c)$. The vanishing of the second compositional derivative of this quantity defines the thermodynamic or "incoherent" spinodal. Since $\Delta G(c)$ includes the configuration-independent part of the elastic energy, then for a random solution

$$\frac{\partial^2\Delta G(c)}{\partial c^2} = \frac{\partial^2}{\partial c^2}[\Delta G_o(c)] - N\Phi^\circ_{pp} \quad (74)$$

If this equation is used in 72, and the result specialized to the case of a spherical solute, then

$$\Delta G = \frac{V}{2N}\sum_{\underset{\sim}{k}}\{\frac{\partial^2}{\partial c^2}[\Delta G(c)] + mk^2 + (c_{11} + 2c_{12})\varepsilon^2[3-\Lambda\xi(\underset{\sim}{e})]\}\langle|\Delta c(k)|^2\rangle, \quad (75)$$

which is the form derived by Cahn (11).

The last term in the bracket in eq. 75 is not the elastic energy of a composition wave; it contains configuration-independent elastic terms which cancel the similar terms embedded in $\Delta G(c)$. It may be given a physical meaning as the sum of the elastic energy of the spinodal wave (which is negative for the favored directions) and an elastic "virtual work" which maintains the coherence of the lattice during decomposition. The sum is positive, and has the consequence that the "coherent" spinodal limit, which is given by

$$-\frac{\partial^2}{\partial c^2}[\Delta G(c)] = (c_{11} + 2c_{12})\varepsilon^2[3-\Lambda\xi(\underset{\sim}{n})], \tag{76}$$

where $\underset{\sim}{n}$ is the most favored orientation, always lies inside the thermodynamic spinodal.

<u>The Preferred Orientation</u>. The preferred orientation, $\underset{\sim}{n}$, for the spinodal wave is, from equation 72, the direction which maximizes $b(\underset{\sim}{e})$, and hence minimizes the total elastic energy. The preferred direction has been found for the general case of a tetragonal solute in a cubic matrix by Wen, Kostlan, et al. (22). If $\underset{\sim}{n}$ is referred to the spherical coordinates (θ,ϕ), where θ is the polar angle from the teragonal axis, or [001] direction, and ϕ is the azimuthal angle measured from the [100] direction then: (1) if $\Delta\leqslant 0$, $\phi=0$ (if $\Delta=0$, ϕ is arbitrary) and

$$\cos^2\theta = \begin{cases} 1 + \frac{\eta_o}{\eta} & -\infty \leqslant \eta \leqslant -\eta_o \\ 0 & -\eta_o \leqslant \eta < 0 \\ 1 & 0 < \eta < \infty. \end{cases} \tag{77}$$

where $\eta_o = \frac{\Lambda}{(c_1+c_2)}$; (2) if $\Delta>0$, $\phi = \frac{\pi}{4}$ and

$$\cos^2\theta = \begin{cases} [\frac{\eta}{\eta 1} - 1]\ [(\frac{\Delta}{\Delta+4}) - \frac{\eta}{\eta_1}]^{-1} & -\infty < \eta < -\eta_1 \\ 0 & -\eta_1 < \eta < -\eta_2 \\ [1 + \frac{\eta}{\eta_2}]\ [3 + \eta]^{-1} & -\eta_2 < \eta < \eta_3 \\ 1 & \eta_3 < \eta < \infty \end{cases} \tag{78}$$

where $\eta_1=(\Delta+4)\Lambda[\Delta\Lambda+4(c_1+c_2)]^{-1}$, $\eta_2=\Delta\Lambda[\Delta\Lambda+4c_1]^{-1}$, and $\eta_3=\Delta\Lambda(2c_1)^{-1}$. In the special case of a spherical solute these equations give the familiar results $\underset{\sim}{n}$=[001] if $\Delta<0$ and $\underset{\sim}{n} = 1/\sqrt{3}$ [111] if $\Delta>0$.

<u>The Macroscopic Inclusion</u>

If the elastic inclusions are macroscopic (on the scale of the atomic structure) then it is reasonable to treat them by a continuum analysis in which the underlying atomic structure is never referred to at all. The original treatment of the macroscopic inclusion, by Eshelby (1), was a continuum theory of this type as were the subsequent analyses by Khachaturyan (17) and Khachaturyan and Shatalov (18). One of the objectives of the present work, however, is to emphasize the underlying unity of the elastic theory, so we shall obtain the elastic theory of macroscopic inclusions from the theory of atomic (or elementary particle) defects. That analysis will proceed directly to the Khachaturyan-Shatalov (18) equation, which is the most

general of the various formulations. The Eshelby (1) solution for the ellipsoidal inclusion can then be extracted. It can, moreover, easily be shown that the treatment of a thin-plate or isolated ellipsoidal inclusion does not require the assumption of uniform elastic constants which has been made in the body of this review. Dropping this assumption permits an alternative derivation of the Lee, Barnett, and Aaronson (19) solution for the isolated ellipsoidal inclusion with arbitrary elastic constants.

Theory

Assumptions and Kinematics.

The solid will be assumed to contain ν types of inclusions, which are coherent with the matrix and derivable from it through the stress-free transformation strains, $\varepsilon^{\circ}_{ij}(p), p=1,\ldots,\nu$. The inclusions are macroscopic in the sense that the long-wavelength approximation applies and the discrete lattice may be ignored. The elastic constants are assumed uniform unless otherwise specified. The distribution of the pth inclusion is given by the function $\theta_p(\underset{\sim}{r})$, which takes the value 1 when r is inside the inclusion and is zero otherwose. The domain over which $\theta_p(\underset{\sim}{r})$ is non-zero need not be simply-connected, since the function may describe a distribution of discrete particles of type p, but the domain is assumed to be composed of simply-connected volumes, each of which is large compared to the lattice spacing. With this understanding, $c_p(\underset{\sim}{r})=\theta_p(\underset{\sim}{r})$ and $\bar{c}_p=\bar{\theta}_p=V_p/V$, the volume fraction of the pth defect.

The Elastic Strain Field.

Uniform Elastic Constants. It follows from the results of the previous section that, given uniform elastic constants and no external stress,

$$\varepsilon_{ij}(\underset{\sim}{r}) = \bar{\varepsilon}_{ij} + \upsilon_{ij}(\underset{\sim}{r}) \tag{79}$$

where $\bar{\varepsilon}_{ij}$ is the stress-free expansion of the body:

$$\bar{\varepsilon}_{ij} = \frac{1}{V}\sum_p V_p \varepsilon^{\circ}_{ij}(p) \tag{80}$$

and $\upsilon_{ij}(\underset{\sim}{r})$ is the internal strain field:

$$\upsilon_{ij}(\underset{\sim}{r}) = \frac{1}{2}(\upsilon_{i,j} + \upsilon_{j,i}). \tag{81}$$

The internal displacement, $\underset{\sim}{\upsilon}(\underset{\sim}{r})$, satisfies the equation:

$$\lambda_{ij\ell m}k_j k_\ell \hat{\upsilon}_m(\underset{\sim}{k}) = -ik_j \sum_p \sigma^{\circ}_{ij}(p)\hat{\theta}_p(\underset{\sim}{k}) \tag{82}$$

which is obtained from equation 24 by replacing $\hat{A}_{im}(\underset{\sim}{k})$ and $\hat{F}^p_i(\underset{\sim}{k})$ by their long-wavelength forms. (Since $\underset{\sim}{r}$ now defines a continuum rather than a discrete lattice, the Fourier transforms are integral transforms.) The reverse Fourier transform of eq. 82 can be written

$$[-\sum_p \sigma^{\circ}_{ij}(p)\theta_p(\underset{\sim}{r}) + \lambda_{ij\ell m}\upsilon_{m,\ell}]_{,j} = \sigma_{ij,j} = 0, \tag{83}$$

which is Cauchy's First Law. The solution to equation 82 is:

$$\hat{\upsilon}_i(\underset{\sim}{k}) = -i|\underset{\sim}{k}|^{-2}\Omega_{im}k_\ell \sum_p \sigma^{\circ}_{m\ell}(p)\hat{\theta}_p(\underset{\sim}{k}), \tag{84}$$

from which

$$\hat{\upsilon}_{i,j}(\underset{\sim}{k}) = e_j \Omega_{im}(\underset{\sim}{e}) e_\ell \sum_p \sigma^\circ_{m\ell}(p) \hat{\theta}_p(\underset{\sim}{k}), \tag{85}$$

whose symmetric part is the internal strain $\hat{\upsilon}_{ij}(\underset{\sim}{k})$.

Inhomogeneous Elastic Constants. If the elastic constants of the inclusions differ from those of the matrix there is no simple general solution for the internal strain. A particular solution can, however, be found for the case in which the internal strain within each inclusion is constant ($\upsilon^\dagger_{ij}(p)$). In this case the internal stress field may be written

$$\sigma_{ij}(r) = \lambda_{ij\ell m} \upsilon_{m,\ell} - \sum_p \sigma^\circ_{ij}(p) \theta_p(\underset{\sim}{r}), \tag{86}$$

where the "effective transformation stress",

$$\bar{\sigma}^\circ_{ij}(p) = \sigma^\circ_{ij}(p) - \Delta\lambda^p_{ij\ell m} \upsilon^\dagger_{\ell m}(p), \tag{87}$$

where $\sigma^\circ_{ij}(p)$ is the transformation stress computed from the true elastic constants of the pth inclusion and $\Delta\lambda_{ij\ell m}$ is the difference between these and the elastic constants of the matrix. Using this notation the Fourier transform of Cauchy's First Law (83) regenerates eq. 82 with $\underset{\sim}{\sigma}^\circ$ replaced by $\bar{\underset{\sim}{\sigma}}^\circ$. The solution is

$$\hat{\upsilon}_{i,j}(\underset{\sim}{k}) = e_j \Omega_{im}(\underset{\sim}{e}) e_\ell \sum_p \bar{\sigma}^\circ_{m\ell}(p) \hat{\theta}_p(\underset{\sim}{k}) \tag{88}$$

This solution requires a constant $\upsilon^\dagger_{ij}(p)$, a result which has only been established for isolated inclusions having a thin-plate or ellipsoidal form. It is unlikely that non-trivial multi-particle examples exist, but eq. 88 may nonetheless be useful as a first approximation.

The Elastic Energy.

Uniform Elastic Constants. When the elastic constants are uniform the elastic energy of an arbitrary distribution of inclusions can be calculated from the continuum limit of the atomic model. In the long wavelength limit eq. 33 for the elastic energy of a stress-free defect solution can be written

$$\Delta\Phi_{el} = \frac{1}{2V} \sum_{p,q} \sum_{\underset{\sim}{k}}{}' B_{pq}(\underset{\sim}{e}) \hat{\theta}_p(\underset{\sim}{k}) \hat{\theta}_q(\underset{\sim}{k}), \tag{89}$$

where

$$B_{pq}(\underset{\sim}{e}) = \lambda_{ijk\ell} \varepsilon^\circ_{ij}(p) \varepsilon^\circ_{k\ell}(q) - e_i \sigma^\circ_{ij}(p) \Omega_{j\ell}(e) \sigma^\circ_{\ell m}(q) e_m \tag{90}$$

(the second term on the right is $B'_{pq}(\underset{\sim}{e})$, eq. 45 and we have replaced $\Delta c_p(\underset{\sim}{k})$ by $v^{-1}\theta_p(\underset{\sim}{k})$ and removed the k=0 term from the summation). The summation may now be replaced by an equivalent integral, giving

$$\Delta\Phi_{el} = \frac{1}{2(2\pi)^3} \sum_{p,q} \int d^3k B_{pq}(\underset{\sim}{e}) \hat{\theta}_p(\underset{\sim}{k}) \hat{\theta}_q(\underset{\sim}{k}) \tag{91}$$

where the integral is taken over the Brillouin zone of the crystal so as to exclude the singularity at the origin (i.e., its principal value is meant). Equation 91 is the Khachaturyan-Shatalov equation (18).

Since $B_{pq}(\underset{\sim}{e})$ is independent of the magnitude of $\underset{\sim}{k}$, the Khachaturyan-Shatalov equation can be rewritten in the convenient form:

$$\Delta\Phi_{el} = \frac{1}{2} \sum_{p,q} \oint \left(\frac{d\omega}{4\pi}\right) B_{pq}(\underset{\sim}{e}) H_{pq}(\underset{\sim}{e}) \tag{92}$$

where $d\omega$ is the element of solid angle, the integral is taken over the unit sphere, and

$$H_{pq}(\underset{\sim}{e}) = (\frac{1}{2\pi^2})\int_0^{k_{max}} \theta_p(k\underset{\sim}{e})\hat{\theta}^*_q(k\underset{\sim}{e})k^2dk. \tag{93}$$

Equation 92 expresses the elastic energy of an arbitrary distribution of inclusions as an integral whose kernal is the product of two terms, one of which, $B_{pq}(\underset{\sim}{e})$, is an energy which depends on the transformation strain and the elastic constants of the matrix while the other, $H_{pq}(\underset{\sim}{e})$, is a geometric factor which depends only on the distribution of inclusions. Using the definition, eq. 90, and the identity, analogous to 28

$$\int \frac{d^3k}{(2\pi)^3}\, \theta_p(\underset{\sim}{k})\theta^*_q(\underset{\sim}{k}) = \oint H_{pq}(\underset{\sim}{e})\frac{d\omega}{4\pi} = V[\bar{\theta}_p\delta_{pq}-\bar{\theta}_p\bar{\theta}_q], \tag{94}$$

where $\bar{\theta}_p$ is the volume fraction of p,

$$\Delta\Phi_{el} = \frac{V}{2}\sum_{p,q}\sigma^\circ_{ij}(p)\varepsilon^\circ_{ij}(q)[\bar{\theta}_p\delta_{pq}-\bar{\theta}_p\bar{\theta}_q] - \frac{1}{2}\sum_{p,q}\int B'_{pq}(\underset{\sim}{e})H_{pq}(\underset{\sim}{e})\frac{d\omega}{4\pi}. \tag{95}$$

The second term on the right gives the relaxation energy $\Delta\phi'_{el}$ due to the internal strain field. The relaxation term may be re-phased in the usual continuum form

$$\Delta\Phi'_{el} = \frac{1}{2}\int\frac{d^3k}{(2\pi)^3}[\sigma_{ij}(\underset{\sim}{k})\upsilon^*_{ij}(\underset{\sim}{k})] = \frac{1}{2}\int dv[\sigma_{ij}(\underset{\sim}{r})\upsilon_{ij}(\underset{\sim}{r})] \tag{96}$$

<u>Inhomogeneous Elastic Constants.</u> For simplicity we shall assume that the volume fraction of inclusions is negligible, so that the homogeneous strain, $\bar{\varepsilon}_{ij}$, may be ignored, and that the body is stress-free. The strain is assume equal to the constant $\upsilon_{ij}(p)$ within inclusion p. Substituting the Fourier transforms of the internal stress (eq. 86) and strain fields (eq. 88) into eq. 96 gives the relaxation energy in the form

$$\Delta\Phi'_{el} = \frac{1}{2}\sum_{p,q}\oint\frac{d\omega}{4\pi}[e_i\bar{\sigma}^\circ_{ij}(p)\Omega_{j\ell}(\underset{\sim}{e})\bar{\sigma}^\circ_{\ell m}(q)e_m]H_{pq}(\underset{\sim}{e}). \tag{97}$$

Adding the self-energy terms we obtain an equation of the form of the Khachaturyan-Shatalov equation with

$$B_{pq}(\underset{\sim}{e}) = \lambda^p_{ijk\ell}\varepsilon^\circ_{ij}(p)\varepsilon^\circ_{k\ell}(q)\delta_{pq}-e_i\bar{\sigma}^\circ_{ij}(p)\Omega_{j\ell}(e)\bar{\sigma}^\circ_{\ell m}(q)e_m \tag{98}$$

<u>The Preferred Inclusion Shape and Habit: the thin-plate inclusion.</u>

Consider an isolated inclusion which is small compared with the body in which it is embedded. Then the elastic energy is, in the stress-free case:

$$\Delta\Phi_{el} = \frac{1}{2}\oint\frac{d\omega}{4\pi}\, B(\underset{\sim}{e})H(\underset{\sim}{e}). \tag{99}$$

<u>The Preferred Shape.</u> It is easy to show that the elastic energy is minimized if the precipitate has the form of a thin plate with a definite crystallographic habit. Let $\underset{\sim}{n}$ be the direction for which $B(\underset{\sim}{e})$ is minimum. Then $B(\underset{\sim}{e}) \geqslant B(\underset{\sim}{n})$ and, in the stress-free case,

$$\Delta\Phi_{el} \geqslant \frac{1}{2}\, B(\underset{\sim}{n})\oint\frac{d\omega}{4\pi}\, H(\underset{\sim}{e}) = \frac{1}{2}\, V_p B(\underset{\sim}{n}) \tag{100}$$

The equality holds for an arbitrarily thin plate whose normal is $\underset{\sim}{n}$.

The elastic energy is always minimum for a thin plate perpendicular to $\underset{\sim}{n}$ but may, in some cases, reach the same minimum for other geometries. If $\tilde{B}(\underset{\sim}{e})$ is isotropic, as it is for a simple dilation in an isotropic body, then $\Delta\Phi_{el}$ is independent of shape. If $B(\underset{\sim}{e})$ is isotropic in a plane, as it is for hexagonal symmetry, and has a minimum value for $\underset{\sim}{e}$ lying in that plane, then

the energy is also minimized by a thin rod shape (20).

The preferred physical shape of the inclusion is determined by the balance between the elastic energy, which is a volume term and usually prefers a thin-plate shape, and the surface energy, which prefers a spherical or faceted shape. In the limit of large inclusion size the volume terms dominate and a plate-like morphology is expected. The small-particle case is discussed by Khachaturyan (20); the common progression of precipitate shape from sphere to cube to thin plate during coarsening is easily interpreted.

The Internal Strain. The internal strain field can be found from the inverse Fourier transform of $\hat{\upsilon}_{i,j}(\underset{\sim}{k})$, (eq. 85). In the thin-plate limit the shape factor, $\hat{\theta}_p(\underset{\sim}{k})$, is negligible for the $\underset{\sim}{k}$ outside a thin rod in the direction, $\underset{\sim}{n}$, normal to the plate. Hence

$$\upsilon_{i,j}(\underset{\sim}{r}) \cong n_j \Omega_{im}(\underset{\sim}{n}) \sigma^{\circ}_{m\ell} n_{\ell} \theta_p(\underset{\sim}{r}). \tag{101}$$

Two important results follow from eq. 101: (1) the strain is constant inside the thin-plate inclusion; (2) the constant displacement gradient inside the particle has a dyadic form,

$$\upsilon_{i,j} = n_j \ell_i(\underset{\sim}{n}). \tag{102}$$

Equation 102 has the consequence that the strain within the inclusion is an "invariant plane strain": The sum of a simple expansion or contraction along the normal, $\underset{\sim}{n}$, of the inclusion and a constant shear in the plane of the particle. The result is that a perfect crystallographic match is established between the inclusion and the matrix in the plane of the interface, which is hence an invariant plane of the total strain, $\varepsilon^{\circ}_{ij} + \varepsilon_{ij}$, describing the geometric change from the matrix to the constrained inclusion.

An Invariant Plane Transformation Strain. If the transformation strain, $\underset{\sim}{\varepsilon}^{\circ}$, is itself an invariant plane strain, it can be written as the symmetric part of a dyad:

$$\varepsilon^{\circ}_{ij} = \frac{1}{2}(\ell_i n_j + \ell_j n_i) \tag{103}$$

If the inclusion is a thin plate in a stress-free body, and the habit is $\underset{\sim}{n}$ or $\underset{\sim}{\ell}$ then the elastic energy, $\Delta\Phi_{el}$, is identically zero (by eq. 99). This result establishes the basic assumption of the "phenomenological theory" of martensite particle or inclusion habits; since $\Delta\Phi_{el} \geq 0$ the preferred habit is a vector of the dyad (the directions $\underset{\sim}{n}$ and $\underset{\sim}{\ell}$ are degenerate). But it should be noted that the derivation is for a thin plate. A particle of finite thickness will have a finite elastic energy, and could have a different preferred habit.

The Influence of External Stress. An external stress adds the contribution

$$\Delta G(\underset{\sim}{\sigma}) = V\sigma_{ij}\varepsilon^{el}_{ij} + V_p\sigma_{ij}\varepsilon^{\circ}_{ij} \tag{104}$$

to the free energy. Since $\Delta G(\underset{\sim}{\sigma})$ is independent of inclusion geometry, it will not change the preferred shape or habit of the particle. However, if the transformation strain is non-spherical then the transformation may generate several distinct crystallographic variants of the inclusion phase. In this case a non-spherical stress will remove the degeneracy of the variants and promote the formation of that (or those) which provide the least value of the factor $\sigma_{ij}\varepsilon^{\circ}_{ij}$. This phenomenon is well known from research on stress-induced martensites, and was described by Eshelby (1).

The influence of external stress is more complicated when the transformation strain $\underset{\sim}{\varepsilon}^{\circ}$ is itself a variable, as it is when the inclusion is a composite particle or ordered phase whose stress-free strain varies with the state of order or the configuration of the internal constituents. Then the external stress may change the habit as well as the energy of the particle. If the particle forms in the stress field and if the various states of the particle are freely convertible, the internal constitution and habit should be chosen to establish a least value of

$$\Delta\Phi_{el} - V\sigma_{ij}\varepsilon^{el}_{ij} = V_p[\sigma_{ij}\varepsilon^{\circ}_{ij} + \frac{1}{2}\varepsilon^{\circ}_{ij}\phi'_{ijk\ell}(\underset{\sim}{n})\varepsilon^{\circ}_{k\ell}] \tag{105}$$

where

$$\phi'_{ijk\ell}(\underset{\sim}{n}) = \lambda_{ijrs}n_r\Omega_{st}(\underset{\sim}{n})n_u\lambda_{tuk\ell}. \tag{106}$$

It follows from eq. 105, for example, that the internal state and possibly the habit of twinned martensite plates may change with the applied stress at the time of their formation.

Finite Thickness. It is not possible for an inclusion of finite size to reach the true thin-plate limit since the surface-to-volume ratio of such an inclusion would be arbitrarily large and incompatible with a finite surface tension. If the particle is finite in thickness but thin then the method of Khachaturyan and Hairapetyan (23) can be used to write the elastic energy as the sum of a volume term and an edge energy which formally resembles the energy of a dislocation loop. Given cubic symmetry and a large value of the aspect ratio, (diameter divided by thickness):

$$\Delta\Phi_{el} = V_p\{\frac{1}{2}B(\underset{\sim}{n}) + \frac{\beta\ell n\kappa}{\pi\kappa}\} \tag{107}$$

where

$$\beta_{ij} = \left(\frac{\partial^2 B(\underset{\sim}{e})}{\partial e_i \partial e_j}\right)_{\underset{\sim}{e}=\underset{\sim}{n}} = \beta\delta_{ij}, \tag{108}$$

Inhomogeneous Elastic Constants. Since the relaxation strain is constant within the thin-plate precipitate, the effect of a modulus mismatch in the inclusion may be found analytically. The solution is, in fact, trivial. Since the relaxation strain is confined to the inclusion the strain energy and the habit plane in the stress-free case can be found by substituting the correct elastic constants for the inclusion into equations 100 and 101.

The Ellipsoidal Inclusion.

The ellipsoidal inclusion is an important special case because of its constant internal strain and its flexible geometry, which permits its use to approximate various inclusion shapes from rods to flat plates. The present treatment of the ellipsoidal inclusion will be confined to the demonstration that the internal strain is constant in its interior, which has two corollaries: (1) the equations proposed by Eshelby (1) apply when the matrix is isotropic (i.e., the Khachaturyan (17) and Eshelby (1) solutions to the inclusion problem are consistent), and (2) the strain field and elastic energy associated with the ellipsoidal inclusion can be found analytically when the elastic constants of the matrix and inclusion differ (as was shown by Lee, Barnett, and Aaronson (19) through a different approach).

The Internal Strain. The internal strain within an ellipsoidal inclusion can be proved to be constant and evaluated from the following general theorem: If $\hat{F}(\underset{\sim}{e})$ is a function of $\underset{\sim}{e} = \underset{\sim}{k}/|\underset{\sim}{k}|$, and $\underset{\sim}{r}_o$ is any point within the

ellipsoid, then the Fourier transform

$$F(\underset{\sim}{r}_o) = \int \hat{F}(\underset{\sim}{e})\theta(\underset{\sim}{k})e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}_o}\frac{d^3k}{(2\pi)^3} \tag{109}$$

is a constant given by an integral over the unit sphere:

$$F(\underset{\sim}{r}_o) = \langle\tilde{F}\rangle = \oint\frac{d\omega}{4\pi}\tilde{F}(\underset{\sim}{e}'). \tag{110}$$

The function $\tilde{F}(\underset{\sim}{e}')$ in the integral is obtained from $F(\underset{\sim}{e})$ by the transformation

$$e_i = (\frac{e_i'}{a_i})g^{-\frac{1}{2}} \tag{111}$$

where a_i is the length of the ith principal axis of the ellipsoid, $R=(a_1a_2a_3)^{\frac{1}{3}}$ and

$$e_i' = \frac{k_i'}{k'}, \tag{112}$$

where $\underset{\sim}{k}'$ is a vector with components a_ik_i/R, $k'=|\underset{\sim}{k}'|$, and

$$g = [(\frac{e_1'}{a_1}) + (\frac{e_2'}{a_2}) + (\frac{e_3'}{a_3})]^{\frac{1}{2}}. \tag{113}$$

It follows via the inverse Fourier transform of eq. 85 that the internal strain within an ellipsoidal inclusion is a constant, $\varepsilon_{ij}^{\dagger}$:

$$\varepsilon_{ij}^{\dagger} = M_{ijk\ell}\varepsilon_{k\ell}^{o} \tag{114}$$

where the fourth-order tensor

$$M_{ijk\ell} = \int(\frac{d\omega}{4\pi g})\tilde{\Omega}_{ir}(\underset{\sim}{e}')\lambda_{rsk\ell}(\frac{e_s'}{a_s})(\frac{e_j'}{a_j}) \tag{115}$$

<u>Isotropic Media.</u> When the matrix is isotropic

$$\Omega_{ij}(\underset{\sim}{e}) = \frac{1}{\mu}[\delta_{ij} - \frac{e_ie_j}{2(1-\nu)}], \tag{116}$$

$$\sigma_{ij}^{o} = 2\mu[\varepsilon_{ij}^{o} + \delta_{ij}(\frac{\nu}{1-2\nu})\varepsilon_{ii}^{o}]. \tag{117}$$

Using these relations in eq. 114, the non-zero components of the matrix $M_{ijk\ell}$ are:

$$\begin{aligned} M_{IIII} &= (1-\nu)^{-1}[(2-\nu)\langle\tilde{e}_I^2\rangle - \langle\tilde{e}_I^4\rangle] \\ M_{IIJJ} &= (1-\nu)^{-1}[\nu\langle\tilde{e}_I^2\rangle - \langle\tilde{e}_I^2e_J^2\rangle] \\ M_{IJIJ} &= [2(1-\nu)]^{-1}[(1-\nu)(\langle\tilde{e}_I^2\rangle + \langle\tilde{e}_J^2\rangle) - 2\langle\tilde{e}_I^2e_J^2\rangle] \end{aligned} \tag{118}$$

where

$$\begin{aligned} \langle\tilde{e}_I^2\rangle &= \oint(4\pi g)^{-1}(\frac{e_I'}{a_I})^2d\omega \\ \langle e_I^2\tilde{e}_J^2\rangle &= \oint(4\pi g^2)^{-1}(\frac{e_I'}{a_I})^2(\frac{e_J'}{a_J})^2d\omega. \end{aligned} \tag{119}$$

and the e_I' are the component of the vector to the surface of the unit sphere. The elements M_{IJKL} may be shown to be identical to those found by Eshelby (1).

<u>Inhomogeneous Elastic Constants.</u> Since the internal strain is constant within an isolated ellipsoidal inclusion, the overall strain field and the

elastic energy associated with an ellipsoidal inclusion with a modulus mismatch may be readily found. It follows from eqs. 88 and 113 that the constant strain within the inhomogeneous inclusion is

$$\varepsilon^{\dagger}_{ij} = S_{ijk\ell}\bar{\sigma}^{\circ}_{k\ell} \tag{120}$$

where $S_{ijk\ell}$ depends on the elastic constants of the matrix only. Inserting the value of $\bar{\sigma}^{\circ}_{ij}$ from eq. 96 gives a linear equation for $\varepsilon^{\dagger}_{ij}$:

$$\varepsilon^{\dagger}_{ij} = S_{ijk\ell}[\lambda_{k\ell mn}\varepsilon^{\circ}_{mn} - \Delta\lambda_{k\ell mn}\varepsilon^{\dagger}_{mn}] \tag{121}$$

where the $\lambda_{k\ell mn}$ are the elastic constants of the matrix. The solution to this equation sets the value of $\bar{\varepsilon}^{\circ}_{ij}$, and permits the calculation of the strain field from eq. 97 and the determination of the elastic energy via eq. 107.

The existence of an analytic solution for inhomogeneous ellipsoidal inclusion was previously demonstrated by Lee, Barnett, and Aaronson (19) from the Eshelby (1) formulation of the problem in real space.

Applications

A variety of applications of the macroscopic elastic theory is presented and discussed in ref. 20. These principally concern the shapes, habits, internal state, or distribution of precipitates and martensite particles, and often closely predict the results of experimental work. As examples of the applications we will briefly discuss the shape, habit, and internal strain of tetragonal precipitates in cubic crystals, a case which includes a great many of the important intermediate hardening precipitates.

The Thin-Plate Tetragonal Inclusion in a Cubic Matrix.

Since the internal strain within a thin-plate inclusion is constant and confined to the inclusion, the internal strain and energy of the inclusion can and should be computed from the tetragonal elastic constants of the inclusion. But since these are rarely known most applications of the theory have assumed them to be equal to the elastic constants of the cubic matrix.

The Preferred Habit. If we neglect anisotropy in the surface energy then the preferred habit of a tetragonal inclusion is the plane perpendicular to the vector, $\underset{\sim}{n}$, which maximizes

$$B'(\underset{\sim}{e}) = e_i\sigma^{\circ}_{ij}\Omega_{j\ell}\sigma^{\circ}_{\ell m}e_m \tag{122}$$

If we neglect the difference between the elastic constants of the precipitate and matrix then $\underset{\sim}{n}$ can be found analytically, as was shown by Wen, Kostlan, et al. (21). The solution was given in eqs. 77 and 78. Under these approximations the habit of the tetragonal inclusion is identical to the preferred habit of a spinodal wave in a cubic lattice containing tetragonal defects. In particular, the predicted habit is of type (h0k) if the anisotropy factor, $\Delta>0$, and is (hhk) when $\Delta<0$. When the inclusion is cubic we have the familiar results: n=[001] for $\Delta<0$ and $1/\sqrt{3}$ [111] for $\Delta>0$. When the tetragonality, η, is positive, n=[001], i.e., the tetragonal axis is perpendicular to the habit plane (excepting a small range of η near zero in the $\Delta>0$ case).

The theory gives an accurate prediction of the habit planes of a variety of precipitate phases, including the (102) habit of Fe_4C in α-Fe, the (227) habit of V_2H in vanadium, the (001) habit of GP zones in several systems (20), the (001) habit of γ' and γ'' $Ni_3(Ti,Al,Nb,Ta)$ precipitates in Fe- and Ni-based superalloys, and the (102) habit of Ni_3V in superalloys (24). It misses the

(001) habit of $Fe_{16}N_2$ in α-iron but this habit is predicted if the finite thickness of the $Fe_{16}N_2$ precipitate is taken into account (25).

The theory also fails to predict the (103) habit common for oxides and carbides of the BCC refractory metals Nb, Mo, and V. Since these metals have positive anisotropy, the type of the habit is wrong; a (hhk) habit is predicted. This discrepancy is under investigation, but may have a simple explanation. Examination of the Nb_2O case (20) shows that (103) is the habit the precipitate would take if the (h0k) type were required. If the oxygen addition changes the sign of the anistropy, Δ, then use of the elastic constants of the precipitate would yield a preferred habit near (103).

The Internal Strain. The strain inside the thin-plate inclusion can be computed from eq. 101 if the stress-free strain and the elastic constants are known. A good match between the computed and measured internal strains had been obtained for GP zones (20), $Fe_{16}N_2$ in α-iron (25) and $VH_{0.45}$ in vanadium (20), where in all cases the matrix elastic constants were used. No counter-examples are known to us.

The elastic theory requires that a coherent thin-plate precipitate have a perfect crystallographic match with the matrix in the plane of the precipitate, i.e., that the habit plane be an invariant plane of the internal displacement. This result has the consequence that the internal strain may change the apparent symmetry of the precipitate phase. A coherent thin-plate cubic precipitate with a (001) habit in a cubic matrix will appear to be tetragonal in diffraction experiments; the tetragonality results from the concentration of the strain in the direction perpendicular to the habit, and has been observed experimentally, for example in GP zones in Al-Cu (26) and in Cu-Ni-Fe (27). A coherent tetragonal precipitate with a non-symmetrical habit may undergo more complex changes in apparent symmetry; the unusual crystallography of the nearly tetragonal $VH_{0.45}$ precipitate in a (227) habit in vanadium (28) is largely explained by the elastic theory (20).

The Finite Tetragonal Inclusion.

If a tetragonal precipitate is formed by a discrete nucleation process in a cubic crystal then finite interfacial tension will prevent the precipitate from achieving a limiting thin-plate morphology until it has coarsened to a large size. The result may be a shift in the preferred habit of the precipitate and a systematic change in its aspect ratio during coarsening. These effects have been studied in some detail for the particular case of $Fe_{16}N_2$ in α-iron (25,29).

The Preferred Habit. If the interfacial tension is assumed to be isotropic then the preferred habit is determined by the elastic energy. From eq. 95, $\underset{\sim}{n}$ should maximize the function

$$\Delta\Phi'_{el} = \oint B'(\underset{\sim}{e})H(\underset{\sim}{e})\frac{d\omega}{4\pi}; \tag{123}$$

where $B'(\underset{\sim}{e})$ is given by 121. If the shape of the particle has circular symmetry about $\underset{\sim}{n}$, as do, for example, the disc, lens, and spheroid, then the geometric factor

$$H(\underset{\sim}{e}) = H_{\kappa}(\alpha), \tag{124}$$

where the aspect ratio, $\kappa=2R/d$, is the ratio of particle diameter to thickness and $\alpha=\cos^{-1}(\underset{\sim}{e}\cdot\underset{\sim}{n})$ is the polar angle of $\underset{\sim}{e}$ with respect to $\underset{\sim}{n}$. Assuming cubic symmetry and letting β be the azimuthal angle about $\underset{\sim}{n}$:

$$\Delta\Phi'_{el} = \Delta\Phi'(\underset{\sim}{n},\kappa,\eta)$$
$$= (\frac{V}{4\pi})c_{44}\varepsilon_0^2 \oint b(\eta,\underset{\sim}{e})H_\kappa(\alpha)\sin\alpha d\alpha d\beta \qquad (125)$$

where $b(\eta,\underset{\sim}{e})$ is given by eq. 56. It follows that for a given particle shape the preferred habit depends only on the tetragonality, η, of the transformation strain and on the aspect ratio, κ.

Equation 125 was used to determine the preferred habit of $Fe_{16}N_2$ in α-iron as a function of aspect ratio, assuming a disc shape and the elastic constants of α-iron. The habit is always of type (hOK); however, the angle θ, between the preferred normal, $\underset{\sim}{n}$, and the tetragonal axis, [001], changes continuously from θ=22.5° (a habit near (102)) as $\kappa\to\infty$ to θ=0 (the (001) habit) when κ is small. The experimental results (30) show that $Fe_{16}N_2$ precipitates form as discrete particles of measurable thickness and have the (001) habit.

A similar shift in particle habit with aspect ratio was found by Mayo and Tsakalakos (31) for the hexagonal $MgZn_2$ precipitate from solution in Al.

The Change of Aspect Ratio on Coarsening. The aspect ratio of a small tetragonal precipitate should be determined by a balance between its elastic energy, which is minimized for large κ, and its interfacial tension, which increases as κ becomes larger. Using the approximation for the elastic energy given in eq. 107, the shape-dependent part of the free energy is

$$\Delta G' = \frac{V_p \beta \ln\kappa}{\pi\kappa} + \gamma S, \qquad (126)$$

where γ is the interfacial tension (assumed isotropic) and S is the surface area. For a thin disc of given radius this expression is minimized when

$$\frac{\kappa^2}{R(\ln\kappa-1)} = \frac{2\pi\gamma}{3\beta} \qquad (127)$$

which gives the preferred aspect ratio as a function of the particle radius, the surface tension, and the elastic factor, β, which is determined by the elastic constants and the particle habit.

Equation 126 predicts that the aspect ratio will increase with the particle radius, R, so that the left-hand side of the equation remains constant. This relation has been tested (29) against the coarsening data for $Fe_{16}N_2$ (28). While the data sets do not reproduce one another, each is well fit by equation 126. The interfacial tension of $Fe_{16}N_2$ can be estimated from the equation and the data after evaluating β. The results range from 6-29 ergs/cm^2 for $Fe_{16}N_2$.

Conclusions

There is no question that the linear elastic theory oversimplifies the physics of solutions, precipitates and inclusions. On the other hand, it offers the advantage of including a substantial part of the relevant physics in a unified model which is mathematically tractable, which offers sound qualitative interpretations of a variety of important reactions in the solid state, and which often yields surprisingly accurate numerical results. For those reasons the linear elastic theory warrants study and continued development as an integral part of the theory of phase transformations in solids.

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