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Coherency strains in compositionally modulated systems and superlattices: spinodal decomposition and magnetoelasticity

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Systems with a coherently modulated composition are considered with regard to their elastic properties. The (stress-free) coherency strains are considered in a new frame where the "standard state" is redefined on the basis of the property under study. These strains are used in the study of the thermodynamics of spinodal decomposition in solids with a (generally) anisotropic distortion into a cubic matrix. Finally, the influence of these strains is considered in the study of magnetostrictive effects in such modulated systems or strained-layer superlattices.

1. Introduction

The theory of thermodynamics of inhomogeneous systems, although it had been treated by Gibbs in his foundations of the subject, has not been deeply studied nor, of course, applied and generalized in the degree that natural phenomena require. In particular, the theory of phase transformations of systems involving gradients of composition was the subject of the Cahn and Hilliard work [1] which, later [2–4], guided Cahn to develop the theory of spinodal decomposition by including in the work of Cahn and Hilliard [1] the elastic term due to "coherency strains".

This work prompted the development of a new theory of diffusion in the continuum [1, 5] as well as the microscopic [6] theory of elasticity and initiated the study of the thermodynamics of systems with a "dome" – the so-called miscibility gap – in their phase diagram. Envisaging the artificial production of materials resembling those that are the product of spinodal decomposition, Cook and Hilliard [7] were the pioneers of preparing and studying artificial composition-modulated thin films. After the advent of new instrumentation and preparation techniques, and because of the obvious technological interest of such systems of semiconductors, metals and semi-metallic materials, one clearly understands the importance of addressing questions concerning the thermodynamic metastability and/or the possibility of obtaining new properties from such exotic materials.

The possible significance of these strong strains in such artificially produced materials has been recently under intense study. For example, the possibility for coherency strain-induced piezoelectricity [8] or the onset of new and anisotropic properties from such "strained-layer superlattices" (SLS) [9] has been the subject of some recent work [e.g. 9–11]. However, it is not always taken into consideration that the periodically fluctuating strain of the SLS should be treated differently from that corresponding to a single interface [12] between two materials with a considerable lattice mismatch. The result is the approximation of an exact "effective" elastic modulus by the shear one.

The aim of this report is to contribute to the theory of the coherency strains in modulated systems as well as to proceed with possible applications. In Section 2, a theory of coherency strains will be given which is important for the development of the elasticity theory of the coherency-strain dependent part of the Helmholtz free energy. The spinodal decomposition mechanism will be discussed, in Section 3, in the light of this theory. Finally, magnetostriction will be studied, in Section 4, in accordance with the present development of elasticity in coherent modulations. In the Appendix the mechanism for linear homogeneous transformations, which are useful in studying elasticity in a manner such as that used here, will be given, together with a derivation of some results used in the main part of the report, in a form easily applicable in the study of other properties of compositionally modulated systems or SLS.

2. Coherency strains

Let us consider, in Fig. 1, two slabs of cubic materials A and B which are thick enough to be considered as semi-infinitely extending along the z direction; let them have lattice parameters a_1 and a_2, respectively. When their xy surfaces come together, the two lattices may be deformed in order to assume a coherent matching or, otherwise, the lattice mismatch could be taken up by the formation of a dislocation network. The present work is concerned with the former case, which results in the development of the so-called "coherency strains". In the "new" material the lattice spacing in the xy plane will have a value between a_1 and a_2 while the larger of them (a_1 in Fig. 1) will be expanded (and the shorter contracted) along the z direction. This coherency-strain related deformation will create a fluctuation of the interplanar spacing (along z) when such slabs are brought together periodically so that the new material will contain a periodically varying composition in the manner

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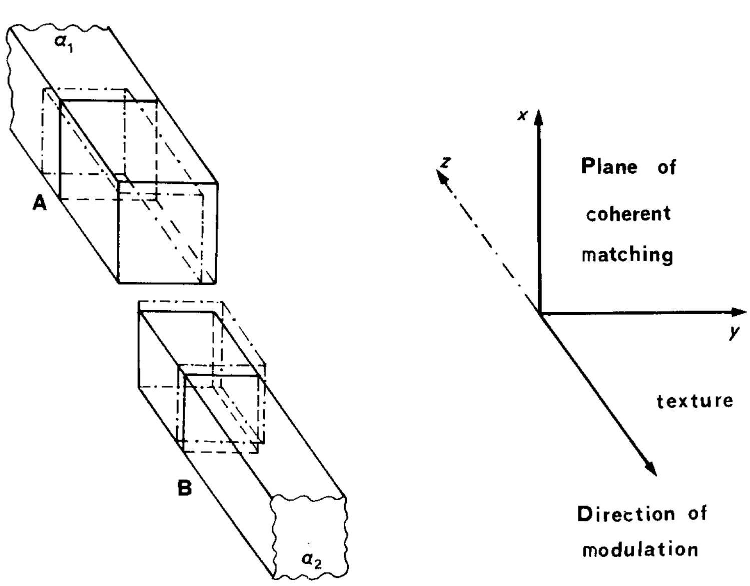

Figure 1 Two slabs (A, B) of cubic materials, having different lattice parameters, being deformed (dashed-dotted parts) in order to meet the requirement of coherence for fluctuation as shown.

A–B–A–. . . . It is important to distinguish between the different kinds of strain, for it is often a source of common confusion in the literature. The lattice mismatch can produce a local strain (ε^{inc}) without coherently matching the two lattices. When the latter occurs one has to consider the (stress-free) coherency strain (ε^*). In that case the total elastic strain (ε^{T}) is not simply the elastic one (ε^{E}) but has to incorporate the new strain. For example, for a coherent structure $\varepsilon^{\text{T}} = \varepsilon^{\text{E}} + \varepsilon^*$. We will now proceed with the derivation and discussion of the coherency strains in a superlattice formed by the periodic addition of A and B.

At first let us observe the initially obvious effect; material A will have suffered a deformation strain $\delta_1 = (a_0 - a_1)/a_1$ while B will take $\delta_2 = (a_0 - a_2)/a_2$, where a_0 is the *common* lattice spacing [8, 13] after the deformation as long as we have required coherence of the new lattice. Thus, in the xy plane there is no variation of the lattice spacing. We require that the molar (and total) volume remains the same and, hence, we have created lattice-spacing (interplanar) changes in the z direction – which is the direction of the periodic variation. The above-defined δ_1, δ_2 are planar strains while the strains in the modulation direction (z) will be given by $\delta_z = [d(z) - d_0]/d_0$, where the d variables will be defined below, and these strains will be *local* as opposed to the (constant) planar ones. Now about the meaning of d_0 and $d(z)$ we must clarify the following. It is important, before one defines the d variables, to have taken into consideration the physical property which will be under the influence of d and δ_z. Namely, it is of major significance to select the "standard" (or "reference") state according to the property which will be under investigation. For example, there is going to be a different influence of the standard state on the study of X-ray diffraction compared with, say, transport or magnetic properties. In particular, it is to be distinguished whether our "probe of measurement" is operating locally or by averaging out over the whole sample macroscopically. According to this thought we can proceed with the following definitions.

1. For strains relative to the average lattice spacing, d_0 is the *average* spacing over the entire thickness along the z direction (or, equivalently, over one modulation period).

2. The spacing d_0 can be that of a crystal with the same average composition as the local composition at point z; in other words, if $c(z)$ is the composition at point z, then d_0 is the lattice spacing of a homogeneous crystal with composition $c(z)$ while $d(z)$, in both 1 and 2 above, is the local lattice spacing at the interface at z. Of course, $d(z) \neq d_0(c(z))$.

The above two definitions of d_0 provide the definitions of the two standard states. For, when studying X-ray diffraction (or other properties by local-probe techniques, e.g. spin resonance) one must use Case 2 above, while Case 1 would be more appropriate for "bulk measurement" techniques.

We are now ready to proceed with the appropriate definition of the coherency strains. As expected, and shown in the Appendix, the linear compressibility of a cubic material, $1/(C_{11} + 2C_{12})$ where C_{ij} are the elastic constants, is independent of the direction. Therefore, we can use this to calculate the stresses due to deformation strains. One important point in the calculation of the stresses is that one must assume that, in the direction of the modulation, the deformation is stress-free and the stresses relax reversibly so that the work will take a minimal value. Thus, for Slab A we have $\varepsilon_x = \varepsilon_y = \delta_1$ and we seek ε_z under the requirement that the system be stress-free. We work in a transformed system (x', y', z') where

$$\sigma_{z'} \equiv 0 = C_{1'2'}\varepsilon_{x'} + C_{1'3'}\varepsilon_{y'} + C_{1'1'}\varepsilon_{z'}$$

We will see in the Appendix that we can have $C_{1'2'} = C_{1'3'}$ so that $C_{1'2'}(\varepsilon_{x'} + \varepsilon_{y'}) = -C_{1'1'}\varepsilon_{z'}$, or $2C_{1'2'}\varepsilon_{x'} = -C_{1'1'}\varepsilon_{z'}$ since $\varepsilon_{x'}$, $\varepsilon_{y'}$ do not depend on orientation and, therefore,

$$(C_{1'1'} + 2C_{1'2'})\,\delta_1 = C_{1'1'}(\delta_1 - \varepsilon_{z'})$$

Since the compressibility will be invariant under transformation we obtain, finally

$$\varepsilon_{z'} = \delta_1\left(1 - \frac{C_{11} + 2C_{12}}{C_{1'1'}}\right) \qquad (1)$$

It will be seen in the Appendix how one finds $C_{i'j'}$ which then gives the coherency strains through

Equation 1. Later, we will obtain (see Equations 4 below) these coherency strains for certain directions of cubic modulation. (The analysis appeared for the first time in Hilliard [5] but it was in some error. In other work by Hilliard [14, 15] parts of the above may also be found.)

Finally, we will relate coherency strains to the deformation tensors which describe these phenomena and will be used in applications in the following sections.

Let us assume $d_0(c_0)$ to be the average lattice spacing of the strain-free material of composition c_0. We may consider a variation of d around d_0 (of c_0) so that $d(c) = d_0[1 + \eta(c - c_0) + \ldots]$, where $\eta = (1/d_0)(\mathrm{d}d/\mathrm{d}c)_{c_0}$. Therefore $\delta_0 = [d(c) - d_0]/d_0 = \eta(c - c_0)$, in its general form. However, in the definition of δ_0 there is still room for some more manipulation. Indeed, one can use δ_0 in the form $\delta = \frac{1}{2}[(1 + \delta_0)^2 - 1]$, which is nothing but a first-order approximation. Let us now elucidate this point.

If x_i is the displacement of the material under stress and $\bar{x}_i$ denotes that of the unstressed solid, we will have $\Delta_{ij} \equiv \partial x_i/\partial \bar{x}_j$. We can now use the Langrangian strain parameter $\eta_{ij} = \frac{1}{2}(\Delta_{ki}\Delta_{kj} - \delta_{ij})$, where δ_{ij} is the Kronecker delta. This strain parameter, η_{ij} takes the following form in the case of orthonormal systems:

$$\eta_{11} = \tfrac{1}{2}(\Delta_{11}\Delta_{11} + \Delta_{21}\Delta_{21} + \Delta_{31}\Delta_{31} - \delta_{11}) \text{ etc.}$$

while $\Delta_{i \neq j} = 0$. Therefore

$$\begin{aligned} \eta_{11} &= \eta_{22} = \tfrac{1}{2}[(1 + \delta^{x,y})^2 - 1] \\ \eta_{33} &= \tfrac{1}{2}[(1 + \delta^{z})^2 - 1] \end{aligned} \tag{2}$$

As already mentioned above, these expressions merely represent a high-order approximation in strain.

Finally, we consider as an example an fcc solid modulated along [1 1 1], the usual case of fcc metals grown on to hexagonal substrates. Then $\delta^{1\bar{1}0}$ will be that for $\delta^{x,y}$ and $\delta^{111} \equiv \delta^{z}$. For the strain corresponding to the incoherent case we will have no internal stresses, and, therefore

$$\varepsilon^{\mathrm{inc}} = \delta_0 \cong \eta(c - c_0) = \frac{1}{a_0}\frac{\mathrm{d}a}{\mathrm{d}c}\bigg|_{c_0}(c - c_0) \tag{3}$$

For the strain corresponding to coherency, which is the case of interest to us, we will have

$$\varepsilon^* = \varepsilon^{\mathrm{inc}}\left(1 - \frac{C_{11} + 2C_{12}}{C_{1'1'}}\right)$$

after using Equations 1 and 3. Therefore, for cubic materials

$$\begin{aligned} \varepsilon^*[1\,0\,0] &= -2\varepsilon^{\mathrm{inc}}\frac{C_{12}}{C_{11}} \\ \varepsilon^*[1\,1\,0] &= -\varepsilon^{\mathrm{inc}}\frac{C_{11} + 3C_{12} - 2C_{44}}{C_{11} + C_{12} + 2C_{44}} \\ \varepsilon^*[1\,1\,1] &= -2\varepsilon^{\mathrm{inc}}\frac{C_{11} + 2C_{12} - 2C_{44}}{C_{11} + 2C_{12} + 4C_{44}} \end{aligned} \tag{4}$$

Since, for cubic systems, usually $(2C_{44} + C_{12} - C_{11}) > 0$, we can deduce from Equations 4 that the usual case will be

$$|\varepsilon^*[1\,0\,0]| > |\varepsilon^*[1\,1\,0]| > |\varepsilon^*[1\,1\,1]|$$

In Equations 4 one has the freedom of selecting, according to the problem under study, the following:

(a) The standard state; this will result in the corresponding δ values.

(b) The degree of the approximation (i.e. whether or not to use Equations 2; this will determine the final form of $\varepsilon^{\mathrm{inc}}$.

Also, referring to (a) above, one should look for the correct definition of the standard state within the framework of Section 2 together with Equations 2 and 3 of Flevaris *et al.* [13] for a_0.

3. Spinodal decomposition

In a general manner one has to distinguish between two types of phase-metastability: that which is infinitesimally small in degree and the one that is extremely short in extent but large in degree. The former is the case of a small composition fluctuation which extends over (macroscopically) large distances of a crystal. As shown by Gibbs [16], such a fluctuation will be stable when the increase of the concentration of one component would result in an increase of the corresponding chemical potential. This condition has been qualified to indicate such an instability by Cahn [2–4]; the boundary of this instability defines the miscibility gap for spinodal decomposition. He was the one who developed the theory of spinodal decomposition after the previous development of the new treatment for the thermodynamics of inhomogeneous systems by him and Hilliard [1, 17]. (For an excellent review on spinodal decomposition the reader should consult Hilliard [5].) Some important concepts are as follows.

Assume that the molar volume does not change with temperature and pressure. In addition, consider that all changes take place at a constant temperature while the average molar volume remains constant. This condition qualifies the use of the Helmholtz (rather than the Gibbs) free energy, F. Furthermore, in addition to the free energy of a homogeneous system one must now consider the following two contributions.

First, the increase of F due to the composition gradient that will be added when the concentration fluctuates. This contribution ought to be considered such as to introduce positive surface tensions and, also, not to depend on the "orientation" of the crystal. Second, and independent of the above "gradient-energy" contribution, there will be an elastic energy contribution due to stress-free changes of the molar volume with composition; this will occur along certain crystallographic directions where, consequently, the composition will fluctuate preferably. This second term, contrary to the first one, will introduce an anisotropy which will govern the kinetics of the early stages of spinodal decomposition. The latter contribution to F will be the subject of this section.

Approximate expressions for the coherency-strain elastic free energy were developed first by Cahn [2–4] for cubic solids with a composition fluctuation along [1 0 0] or [1 1 1]. Later, Hilliard [5] gave the general expression for cubic systems. However, all that work assumed isotropic deformation. Furthermore, attempts to extend the theory to lower-symmetry systems by Krivoglaz [18], Stubican and Schultz [19], Kittel [20, 21], Park *et al.* [22, 23] and Wu *et al.* [24] were not without errors.

More recently, the expression for the coherency-strain elastic free energy was derived for hexagonal-symmetry systems, and applied [25] to the study of Al–Mn–Zn. Also, a general expression for isotropic, cubic, hexagonal, tetragonal and orthorhombic systems has been developed [26, 27] and, also, applied recently [28] in the study of spinodal decomposition in the tetragonal system SnO_2–TiO_2. In this work [26–28] the deformation did not necessarily have to be isotropic while the entire theory could be treated in a quasi-discrete manner; among the rest, only the Cook and de Fontaine work [6] was not entirely in the continuum theory of elasticity.

As an application of the earlier work [26, 27], in the following we will give the coherency-strain dependent part of the free energy of cubic systems with anisotropic distortion, within the continuum theory of elasticity. From this it will become obvious how the elastic aeolotropy determines the anisotropic kinetics of spinodal decomposition.

Our objective is to calculate the elastic free energy density in terms of the coherency strains. To do this, following earlier work [26], we use again the relation $\varepsilon^{E}_{ij} = \varepsilon^{T}_{ij} - \varepsilon^{*}_{ij}$ and after applying the minimization condition we obtain the elastic free energy per unit volume in terms of ε^{*}_{ij} only (i.e. the coherency-strain energy) in the form

$$F_{\mathrm{el}} = \frac{1}{2}\int_{\mathrm{v}} C_{ijkl}\,(\varepsilon^{*}_{ij}\varepsilon^{*}_{kl} - 2u_{i,j}\varepsilon^{*}_{kl} + u_{i,j}u_{k,l})\,\mathrm{d}V$$

where V is the volume and u_{ij} the displacement gradients due to distortion while C_{ij} are the second-order elastic constants. From this expression for the coherency-strain elastic free energy one can get the following. First, by a minimization requirement, the appropriate [13] average lattice spacing as mentioned in Section 2. Second, the anisotropy of the energetics of the system. Third, by using the appropriate distortion tensor, the morphology of the system that underwent a composition transformation (or equivalently, prepared artificially to simulate decomposition deformation).

Let us now define the deformation tensor as

$$\tilde{\eta} = \begin{pmatrix} \eta_{11} & 0 & 0 \\ 0 & \eta_{22} & 0 \\ 0 & 0 & \eta_{33} \end{pmatrix}$$

Applying this distortion to the expression for F_{el}, we get for a cubic solid coherently modulated along [1 0 0]

$$F^{\mathrm{c}}_{\mathrm{el}}[1\,0\,0] = \frac{1}{2}\sum_{\substack{i,j=1\\ j=i+1}}^{3} [\eta^2_{ii}C_{11} + 2\eta_{ii}\eta_{jj}C_{12} - C^{-1}_{11}(\eta^2_{ii}C^2_{1i} - 2\eta_{ii}\eta_{jj}C_{1i}C_{1j})] \quad (5)$$

where i, j follow a cyclic permutation. Furthermore

$$\begin{aligned} F^{\mathrm{c}}_{\mathrm{el}}[1\,1\,0] = \frac{1}{2}\sum_{\substack{i,j=1\\ j=i+1}}^{3} (\eta^2_{ii}C_{11} + 2\eta_{ii}\eta_{jj}C_{12}) &- D_1\{[(\eta_1^2 + \eta_2^2)/2][C_{11}(C_{11} + C_{12}) \\ &+ C_{44}(C_{11} - C_{12})] + \eta_1\eta_2[C_{12}(C_{11} + C_{12}) \\ &+ C_{44}(C_{11} - C_{12})] + \eta_3 C_{12}[(\eta_1 + \eta_2)C_{11} \\ &+ (\eta_1 + \eta_2 + \eta_3)C_{12}]\} \end{aligned} \quad (6)$$

where $D_1^{-1} = C_{11} + C_{12} + 2C_{44}$. Similarly

$$F^{\mathrm{c}}_{\mathrm{el}}[1\,1\,1] = \tfrac{1}{2}(F_1\vartheta_{11} + 2F_2\vartheta_{12}) \quad (7)$$

or

$$\begin{aligned} F^{\mathrm{c}}_{\mathrm{el}}[1\,1\,1] = \tfrac{1}{2}[&(C_{11}\vartheta_{11} + 2C_{12}\vartheta_{12}) \\ &- D(T_1\vartheta_{11} + 2T_2\vartheta_{12})] \end{aligned} \quad (7a)$$

where $\vartheta_{11} = \Sigma^3_{i=1}\,\eta^2_{ii}$, $\vartheta_{12} = \Sigma^3_{i,j=1}\,\eta_{ii}\eta_{jj}$ (again with $j = i + 1$) and

$$D^{-1} = \tfrac{1}{27}(C_{11} + 2C_{12} + 4C_{44})(C_{11} - C_{12} + C_{44})^2,$$

$$F_1 = C_{11} - DT_1, \qquad F_2 = C_{12} - DT_2,$$

$$\begin{aligned} T_1 = \tfrac{1}{27}[&C_{11}(C^3_{11} + 2C^3_{12}) + 2C_{12}C_{44}(3C_{11} + 2C_{44}) \\ &+ 4C_{44}(C^3_{11} - C^3_{12}) + 3C^2_{11}(C^2_{44} - C^2_{12})] \end{aligned}$$

$$\begin{aligned} T_2 = \tfrac{1}{27}[&(C^3_{11} + 2C^3_{12})(C_{12} - C_{44}) \\ &+ 2C_{11}C_{12}C_{44}(3C_{11} + 2C_{44}) \\ &+ 3C_{11}C^2_{12}(C_{12} + C_{44}) - C^2_{11}C^2_{44}] \end{aligned}$$

$$T_1 + 2T_2 = \tfrac{1}{27}(C_{11} + 2C_{12})^2(C_{11} - C_{12} + C_{44})^2$$

The latter expression for $T_1 + 2T_2$ will be used later, for the case of isotropic distortion tensor, to yield the known Cahn–Hilliard relation, in Equations 15.

From these general expressions we can obtain simpler (and less general) ones for a tetragonal distortion in a cubic matrix, namely the case for which $\eta_{11} = \eta_{22} \neq \eta_{33}$ for both components or $\eta_{11} \neq \eta_{22} = \eta_{33}$ for one and $\eta_{11} = \eta_{33} \neq \eta_{22}$ for the other. This case was the subject of Khachaturyan's work [29]; he used a Green's function method which yields the same results with the present model [26–28].

If we assume $\eta_{11} = \eta_{22} \neq \eta_{33}$ Equations 7 give, for example,

$$F^{\mathrm{ct}}_{\mathrm{el}}[1\,1\,1] = \tfrac{1}{2}[(2\eta^2_{11} + \eta^2_{33})F_1 + 2(\eta^2_{11} + 2\eta_{11}\eta_{33})F_2] \quad (8)$$

If we require $(\partial F/\partial\eta_{33})_{\eta_{11},T,V} = 0$, Equation 8 gives

$$\eta_{33}[1\,1\,1] = -2\eta_{11}F_2/F_1 \quad (9)$$

and similarly for [1 0 0] and [1 1 0].

Two points must be stressed here. First, that which concerns Equation 8 with respect to a variation – as expected – of the stress-free strain. By applying the appropriate $\eta_{33}[1\,1\,1]$ from Equation 9, we obtain the "equilibrium" elastic free energy per unit volume in the form

$$F^{\mathrm{ct}}_{\mathrm{el,equ.}}[1\,1\,1] = \eta^2_{11}[F_1 + F_2 - (2F^2_2/F_1)]$$

Second, it must be noted that the requirement for equilibrium imposed on the free energy per unit volume can be extended. Indeed, if we consider the elastic free energy for one period of the modulation it would be possible to obtain a figure for the lattice spacing [13] as a function of the elastic constants, the period and its asymmetry in composition as mentioned above.

We must mention, finally, that the expressions for the coherency-strain elastic free energy given by Equations 5 to 3 reduce to those given by Cahn and Hilliard for the special case of isotropic distortion ($\eta_{11} = \eta_{22} = \eta_{33} = \eta$) which are

$$F_{\mathrm{el}}^{\mathrm{ci}}[h\,k\,l] = Y[h\,k\,l]\eta^2 \tag{10}$$

where

$$\begin{aligned} Y[1\,0\,0] &= C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}} \\ Y[1\,1\,0] &= \frac{C_{11} + 2C_{12}}{2}\left(3 - \frac{2(C_{11} + 2C_{12})}{C_{11} + C_{12} + 2C_{44}}\right) \\ Y[1\,1\,1] &= \frac{6C_{44}(C_{11} + 2C_{12})}{C_{11} + 2C_{12} + 4C_{44}} \end{aligned} \tag{11}$$

The growth rate of modulations (i.e. decomposition) is, in the case of isotropic distortion, maximum in the direction that minimizes Y. Our treatment above, as well as the alternative one given in the Appendix, yields this special "elastic modulus" Y which is very important in the work on modulated systems. One can use, in addition, the approximation defined by Equations 2 in order to have a higher approximation for the strains. We have already seen above the F_{el} to second order in the strains. The additional (to third order) contribution will be

$$(F_1 + F_2)\eta_{11}^3 + F_2\eta_{11}\eta_{33}(\eta_{33} - \eta_{11})$$

and to fourth order

$$\tfrac{1}{4}F_1\eta_{11}^4 + \tfrac{1}{4}F_2\eta_{11}^2(2\eta_{33}^2 + \eta_{11}^2)$$

which expressions, of course, would yield new expressions of the type of Equation 9.

4. Coherency-strain magnetostriction

In the foregoing two sections we have developed the theory of the coherency strains and, also, we have seen an application in studying the elasticity thermodynamics of cubic solids under anisotropic distortion. We will consider now the coherency-strain effects in the magnetism of modulated materials and SLS. Previous to this work there has been an application [8] of similar character but in piezoelectric properties. The following arguments are justified only when some prerequisites are satisfied. Namely, that the two materials have the same crystal structure and the lattice-spacing mismatch is within the acceptable limits for coherency and strong strain effects; the whole theory is applicable for modulation periods not as short as the atomic plane distances, where one should consider the microscopic theory and not the continuum theory of elasticity.

The tensor description of the magnetoelastic behaviour of crystalline materials is well known [30]. Also, it is known [31, 32] that, assuming a strain acting upon a magnetic solid, one can express the magnetoelastic energy by

$$F_{\text{m-el}} = -\lambda_{iklm}\sigma_{ik}M_lM_m \tag{12}$$

where there is no simple symmetry relation between the pairs ik and lm. Then the strains are related to relationships of the form

$$\begin{aligned} \varepsilon_{ii} &= S_1\sigma_{ii} + S_2(\sigma_{jj} + \sigma_{kk}) + \lambda_1 M_i^2 \\ \varepsilon_{ij} &= S_3\sigma_{ij} + \lambda_2 M_j M_i \quad \text{etc.} \end{aligned}$$

where i, j, k follow the cyclic permutation 1, 2, 3 with $k = j + 1 = i + 2$ and the S terms are functions of the C_{ij} variables. These expressions relate the elastic with the magnetoelastic energies of cubic materials. We will use the following formulation for the magnetoelastic coupling three-rank Q_{ijk} and four-rank Q_{ijkl} tensors:

$$\begin{pmatrix} 0 & 0 & 0 & Q_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & Q_{14} \end{pmatrix}$$

and

$$\begin{pmatrix} q_{11} & q_{12} & q_{12} & 0 & 0 & 0 \\ q_{12} & q_{11} & q_{12} & 0 & 0 & 0 \\ q_{12} & q_{12} & q_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{44} \end{pmatrix}$$

(Q_{ijk} is for m3m̄, 4̄3m, 432, 23,m3; it vanishes however for m3m, which class includes nickel. Also, Q_{ijkl} is for 4̄3m, 432 and m3m while for the 23,m3 it has $q_{13} \neq q_{12}$.)

We can now write the strain-field relations

$$\varepsilon_{ij} = Q_{ijk}H_k$$

or

$$\varepsilon_{ij} = Q_{ijk}H_k + Q_{ijkl}H_kH_l$$

Thus, if we consider the cases of 4̄3m, 432 or m3m we can have

$$\begin{aligned} \varepsilon_{11} &= Q_{11kl}H_kH_l \\ \varepsilon_{13} &= Q_{13kl}H_kH_l \quad \text{etc.} \end{aligned}$$

or

$$\varepsilon_{ij} = \varepsilon_{ji} = 2q_{44}H_iH_j \qquad (\text{for } i \neq j)$$

and

$$\varepsilon_{ii} = q_{12}(H_{i-1}^2 + H_{i+1}^2) + q_{11}H_i^2$$

where $i = 1, 2, 3$ in cyclic permutation. These relations show that $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ when $H_1 = H_2 = H_3$, as expected.

For magnetostrictive effects we therefore develop

$$\begin{aligned} \frac{\Delta l}{l} &= \sum_{\substack{i=1 \\ i \geqslant j}}^{3} \varepsilon_{ij}\beta_i\beta_j = \varepsilon_{11}\beta_1^2 + \varepsilon_{22}\beta_2^2 + \varepsilon_{33}\beta_3^2 \\ &\quad + \varepsilon_{12}\beta_1\beta_2 + \varepsilon_{23}\beta_2\beta_3 + \varepsilon_{31}\beta_3\beta_1 \\ &= [q_{12} + (q_{11} - q_{12})\beta_1^2]H_1^2 \\ &\quad + 2q_{44}\beta_1\beta_2H_1H_2 \\ &\quad + [q_{12} + (q_{11} - q_{12})\beta_2^2]H_2^2 + 2q_{44}\beta_2\beta_3H_2H_3 \\ &\quad + [q_{12} + (q_{11} - q_{12})\beta_3^2]H_3^2 \\ &\quad + 2q_{44}\beta_3\beta_1H_3H_1 \end{aligned}$$

or

$$\frac{\Delta l}{l} = \sum_{i=1}^{3} [q_{12} + (q_{11} - q_{12})\beta_i^2]H_i^2 + q_{44} \sum_{\substack{i,j=1 \\ i \neq j}}^{3} H_i H_j \beta_i \beta_j$$

where the direction cosines β_i define the direction of $\mathbf{\Delta l}$.

We need to know the dependence of the stress on the magnetic field, for we can write

$$\sigma_{ij} = 4C_{44}q_{44}H_iH_j = \sigma_{ji}$$

and

$$\begin{aligned}\sigma_{ii} = {} & C_{11}[q_{11}H_i^2 + q_{12}(H_{i+1}^2 + H_{i-1}^2)] \\ & + C_{12}[2q_{12}H_i^2 + (q_{11} + q_{12})(H_{i+1}^2 + H_{i-1}^2)]\end{aligned}$$

where $i = 1, 2, 3$ within a cyclic order. Thus, we have obtained above the relationships giving the stress and strain as a function of the magnetic field and the material properties. If we now work in the reverse way we can obtain the strain-induced internal magnetic field (i.e. we could study "morphic" effects).

Therefore, after we have obtained numerical values for F_1 and F_2, for a particular cubic solid (e.g. nickel), we can obtain the relation between δ^{111} and δ^{110} for modulation along $\langle 1\,1\,1 \rangle$, together with the so-developed coherency strains. Consequently, we can have the internal (planar) stresses due to those coherency strains. Finally, given the knowledge of the q values for that solid, we are now able to obtain the components of variation of the magnetic field induced in the solid by the lattice mismatch of the constituents and the coherency requirements.

As an example, let us see the effects of the coherency strains on the magnetic anisotropy of a textured material, with a $\langle 1\,1\,1 \rangle$ texture along the modulation direction. The relevant terms contributing to the mean free energy per unit volume will be those due to magnetoelastic, elastic, demagnetization, magnetic exchange and other anisotropic causes. In our case, we need only consider the first two since the rest will not depend on the anisotropy of the distortion tensor. Thus, we have $F_{\text{m-el}}$ as given by Equation 12 and $F_{\text{el}}[1\,1\,1]$ that given by Equations 7 and 7a or Equation 8. More analytically, we will have

$$F_{\text{m-el}} = -\lambda_1 \sum_{i=1}^{3} \sigma_{ii}M_i^2 - 2\lambda_2 \sum_{\substack{i=1 \\ j=i+1}}^{3} \sigma_{ij}M_iM_j \tag{13}$$

where $\lambda_1 = \lambda_{ii}$ $(i = 1, 2, 3)$ and $\lambda_2 = \lambda_{ij}$ $(j = i + 1)$. The equilibrium requirements will be $(\partial F_{\text{T}}/\partial\eta_{33})_{\eta_{11},\eta_{22},T,V} = 0$ for $F_{\text{T}} = F_{\text{m-el}} + F_{\text{el}}$. Thus

$$\eta_{33}F_1 + (\eta_{11} + \eta_{22})F_2 = \lambda_1 C_{11} M^2 \cos^2\theta_{\text{M}} \tag{14}$$

where θ_{M} is to be the angle between the modulation direction and the magnetization vector $\boldsymbol{M}$. Finally, by defining $F_{\text{m-el}}$ as in Equation 13 we obtained the condition for equilibrium of F_{T} with respect to the coherency strain η_{33}, (Equation 14), which will provide $\cos\theta_{\text{M}}$ in the angle-dependent, demagnetizing, exchange and other anisotropic terms of the total free energy per unit volume.

5. Summary and discussion

This report is concerned with the thermodynamics of compositionally modulated alloys and SLS. We have developed the theory of coherency strains in new ways; namely, by redefining various possible standard (or reference) states, as well as by examining the coherency requirement via the restriction of thermodynamic (stable or metastable) equilibrium. These conditions of equilibria provide us with relationships between the planar and the stress-free coherency strains. Thus, knowledge of the lattice parameters and the elastic constants of cubic solids allows us to calculate the appropriate coherency strains needed to study their influence on the elasticity thermodynamics.

Furthermore, we extended the theory of spinodal decomposition by developing new expressions concerning the coherency-strain elastic free energy of generally anisotropic distortion in a cubic matrix. These expressions may provide a useful tool in the study of phase transformations and the early stages of spinodal decomposition, by being easily applicable and considerably more general than those given by Cahn and Hilliard. One simple, though important, outcome of the present work is that, by using Equations 5 to 7 or 8, a known "aspect ratio" of the anisotropy of the distortion can provide immediately an estimate of its influence on the anisotropy of the elastic free energy. In addition, the easily applicable expressions given here for cubic systems under anisotropic distortions can be used in the treatments of various strain-induced properties of artificial composition-modulated systems or SLS instead of the rather approximate ones often used [9–12].

Finally, in Section 4 we presented a first attempt to include coherency strains in the magnetic properties. For some classes of cubic solids, we developed expressions by which one can proceed to examine the effect of the lattice mismatch between two materials on the magnetic behaviour of their alloy with a coherent modulation along a certain direction. Further work on the subject might reveal new important information. Also, by applying the requirement of equilibrium with respect to η_{33} we obtained the coherency strain effects on the magnetization direction. In addition, this work should be considered together with considering coherency-strain effects on the transport and optical properties. For example, in the case of "parallel-to-plane" isotropy ($\eta_{11} = \eta_{22} \neq \eta_{33}$, as also studied above) one can obtain a change in the "effective mass", upon applying the coherency-strain influences of the type

$$\Delta m_{\text{e}} = m_{\text{e}}[(1 + \eta_{11})^{-2}(1 + \eta_{33})^{-1} - 1]$$

By using a relation of the above form one can introduce the theory of coherency, as developed in this work, into the study of diffusion or other physical properties.

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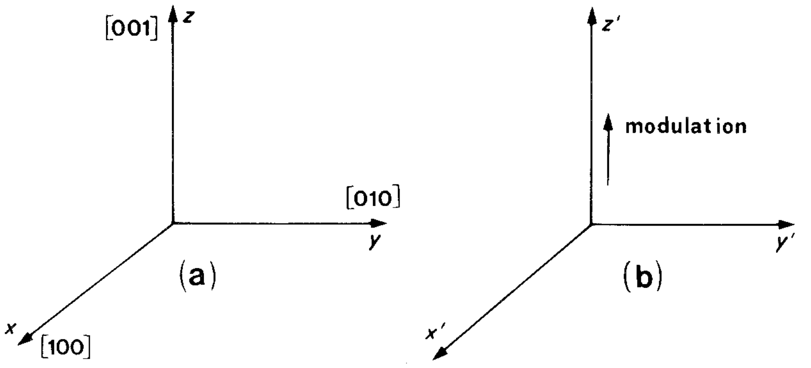

Figure A1 The two orthogonal systems for the transformation from (a) to (b) the system modulated along z'.

Appendix: Linear homogeneous transformations

It is often necessary, or simply useful, to transform to a new coordinate system; as an example consider a composition modulation z' and have the transformation from (a) to (b) in Fig. A1.

The following array will be helpful in understanding the transformation we will perform via the cosines (l, m, n) between the axes of (a) and (b):

$$\begin{array}{c|ccc} & x & y & z \\ \hline x' & l_1 & m_1 & n_1 \\ y' & l_2 & m_2 & n_2 \\ z' & l_3 & m_3 & n_3 \end{array}$$

For example, we will obtain

$$\begin{aligned} X_{x'} &= l_1 X_x + m_1 X_y + n_1 X_z, \ldots, \\ Z_{x'} &= l_1 Z_x + m_1 Z_y + n_1 Z_z, \ldots, \\ Y'_{x'} &= l_2 X_{x'} + m_2 Y_{x'} + n_2 Z_{x'}, \ldots, \\ X'_{x'} &= l_1^2 X_x + m_1^2 Y_y + n_1^2 Z_z + 2m_1 n_1 Y_z \\ &\quad + 2n_1 l_1 Z_x + 2l_1 m_1 X_y, \quad \text{etc.} \end{aligned}$$

The three stress components X_x, Y_y and Z_z correspond to normal tractions and X_y, Y_z and Z_x to tangential tractions. It is standard practice (and we mention it only for completeness) that the rotation of axes will give for the elastic constants

$$C'_{ijkl} = \frac{\partial x'_i}{\partial x_m}\frac{\partial x'_j}{\partial x_n}\frac{\partial x'_k}{\partial x_q}\frac{\partial x'_l}{\partial x_p} C_{mnqp}$$

where

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \qquad \sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

After applying these (known) properties we obtain for a cubic material the following relations between the initial and the transformed (primed indices) elastic constants:

$$\begin{aligned} C_{1'1'} &= C_{11} + 2(2C_{44} + C_{12} - C_{11})\phi_1 \\ C_{1'2'} &= C_{2'1'} = C_{12} + (C_{11} - C_{12})\omega_1 + 4C_{44}\xi_1 \\ C_{4'4'} &= C_{44}\varrho_2 + C_{11}\omega_2 + 2C_{12}\xi_2 \\ C_{1'4'} &= 0 \qquad C_{4'5'} = 0 \quad \text{etc.} \\ C_{1'6'} &= C_{11}(l_1^3 l_2 + m_1^3 m_2 + n_1^3 n_2) \\ &\quad + (2C_{44} + C_{12})[l_1^2(m_1 m_2 + n_1 n_2) \\ &\quad + m_1^2(l_1 l_2 + n_1 n_2) + n_1^2(l_1 l_2 + m_1 m_2)] \end{aligned}$$

where

$$\begin{aligned} \phi_1 &= l_1^2 m_1^2 + m_1^2 n_1^2 + n_1^2 l_1^2 \\ \omega_1 &= l_1^2 l_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2 \\ \xi_1 &= l_1 l_2 m_1 m_2 + m_1 m_2 n_1 n_2 + n_1 n_2 l_1 l_2 \\ \varrho_2 &= (m_2 n_3 + n_2 m_3)^2 + (l_2 n_3 + n_2 l_3)^2 \\ &\quad + (l_2 m_3 + m_2 l_3)^2 \\ \omega_2 &= l_2^2 l_3^2 + m_2^2 m_3^2 + n_2^2 n_3^2 \\ \xi_2 &= l_2 l_3 m_2 m_3 + m_2 m_3 n_2 n_3 + n_2 n_3 l_2 l_3 \quad \text{etc.} \end{aligned}$$

In addition $C_{2'2'} \simeq C_{3'3'} \simeq C_{1'1'}$ but with the corresponding ϕ values, while for $C_{5'5'}$ and $C_{6'6'}$ we replace $\varrho_2, \omega_2, \xi_2$ by $\varrho_3, \omega_3, \xi_3$ and $\varrho_1, \omega_1, \xi_1$, respectively. Also for $C_{1'3'}$, $C_{2'3'}$ we replace, in the expression for $C_{1'2'}$, ω_1, ξ_1 by ω_3, ξ_3 and ω_2, ξ_2, respectively.

We have therefore obtained the transformed C values as functions of the transformation cosines. In our case, for the modulation direction (z') being [1 1 1] (as in Fig. A1) we have

$$\begin{aligned} C_{1'1'} &= \tfrac{1}{3}(C_{11} + 2C_{12} + 4C_{44}) \\ C_{1'2'} &= \tfrac{1}{3}(C_{11} + 2C_{12} - 2C_{44}) \\ &= C_{2'1'} = C_{1'3'} = C_{3'1'} \\ C_{4'4'} &= \tfrac{1}{6}(C_{11} - C_{12} + 4C_{44}) \\ C_{5'5'} &= \tfrac{1}{3}(C_{11} - C_{12} + 4C_{44}) = C_{6'6'} \\ C_{2'2'} &= \tfrac{1}{2}(C_{11} + C_{12} + 2C_{44}) = C_{3'3'} \\ C_{2'3'} &= \tfrac{1}{6}(C_{11} + 5C_{12} - 2C_{44}) = C_{3'2'} \end{aligned} \tag{A1}$$

while $C_{1'6'} = C_{2'6'} = C_{1'4'} = C_{4'5'} = 0$ and the bulk compressibility $C_{1'1'} + 2C_{1'2'} = C_{11} + 2C_{12}$, invariant as would be expected. (The same result would have been obtained if (l_2, m_2, n_2), (l_3, m_3, n_3) were interchanged.)

Let us finally examine another "modulus". If we treat again the stresses of such a modulated system we see that

$$\begin{aligned} \sigma_{x'} &= C_{1'1'}\varepsilon_{x'} + C_{1'2'}\varepsilon_{y'} + C_{1'3'}\varepsilon_{z'} \\ \sigma_{y'} &= \sigma_{x'} \qquad \sigma_{z'} = 0 \end{aligned}$$

The latter expression yields $\varepsilon_{z'} = -2\varepsilon_{x'}C_{1'2'}/C_{1'1'}$ which, applied to the former one, gives

$$\sigma_{x'} = [C_{1'1'} + C_{1'2'} - (2C_{1'2'}^2/C_{1'1'})]\varepsilon_{x'} \tag{A2}$$

after we used the second one to obtain $\varepsilon_{x'} = \varepsilon_{y'}$. After substituting the new C values (Equations A1) into Equations (A2) we may obtain the new "elastic modulus" $Y[h\,k\,l]$ to fulfil the condition $\sigma_{i'} = Y[i']\varepsilon_{i'}$:

(a) [1 0 0]: $\sigma_{x'} = Y[1\,0\,0]\varepsilon_{x'}$, where $Y[1\,0\,0] = C_{11} + C_{12} - (2C_{12}^2/C_{11})$, since $C_{1'1'} = C_{11}$ and $C_{1'2'} = C_{12}$.

(b) [1 1 1]: the above $C_{1'1'}$, $C_{1'2'}$ and $C_{4'4'}$, substituted from Equations A1 into the expression $\sigma_{x'} = Y[1\ 1\ 1]\varepsilon_{x'}$, yield $Y[1\ 1\ 1] = 6C_{44}(C_{11} + 2C_{12})/(C_{11} + 2C_{12} + 4C_{44})$.

(c) Similarly, for other *h k l* one can now obtain the new *C* values and, therefore, the "new modulus" $Y[h\,k\,l]$ in an alternative way to what was used for the same purpose in Section 3. Also, expressions equivalent to Equations 4 can be directly obtained by substituting the appropriate $C_{i'j'}$ values in, for example, $\varepsilon^* = \varepsilon^{\text{inc}}[1 - (C_{11} + 2C_{12})/C_{1'1'}]$. One simply has to develop the expressions for this, equivalent to Equations A1.

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