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Thermodynamic aspects of chemically curved crystals

GYÖRGY SZABÓ
Central Research Institute for Physics, H-1525 Budapest, P.O. Box 49, Hungary

The thermodynamic stability of an elastic material with a constant concentration gradient is analysed in linear approximation within the framework of the Ginzburg–Landau theory including an external inhomogeneous field. The result suggests ways to produce stress-free, paraboloidically curved finite size crystals.

1. Introduction

The translation symmetry of crystals is closely related to the uniform distance determined by atomic forces between neighbouring atoms (or ions). A mechanically distorted crystal, however, represents an example of a state where the crystal symmetry is weakly broken. In this state the atoms are positioned along macroscopically curved surfaces and the "lattice constants" depend on position. A similar distorted state may be achieved by inhomogeneous temperature or chemical composition distribution. Large variation of the lattice constant is more easily achieved by composition changes than by non-uniform temperature distribution, therefore chemically curved crystals are studied in the present work.

It is known that in a linear approximation the curved crystal remains stress-free independent of its shape and size providing that the composition (or temperature) gradient is constant. In this case the "crystal planes" which are originally perpendicular to the gradient transform into paraboloids. This is the reason why curved crystals may be utilized to focus X- and neutron rays. Progress in this field has been reviewed by Caciuffo *et al.* [1]. Another interesting aspect of curved crystals is that in them the physical parameters vary uniformly along one direction. In general, the inhomogeneous composition is not stable thermodynamically although the resultant crystal is mechanically stable. With crystals of finite size, however, the curved state may be stabilized thermodynamically by the application of an external field or by a suitable choice of boundary conditions. Furthermore, the concentration variation adjusted at sufficiently high temperature may be frozen-in at room temperature because of low diffusivity. The above results are valid in linear approximation. The effect of non-linearity is considered as a restriction which limits the curvature and/or size of the curved crystal. Analysis of these limits goes beyond the scope of the present linear treatment.

Here, the Ginzburg–Landau formalism is utilized to investigate the equilibrium concentration variation in a finite elastic material. A similar model was used by Cahn [2, 3] to describe the spinodal decomposition in an elastic solid. This extended theory of spinodal decomposition could explain both the anisotropy of phase separation and the effect of an external (magnetic or elastic) field. Since that time the application of a homogeneous field has become a useful method for manufacturing alloys with desired properties. It is worth mentioning that the application of an inhomogeneous field as a promising method to produce controlled structural variations has already been proposed by Cahn [4].

Many features of the present model are well known from its other applications in solid/state physics. For example, in order to describe the α–α' phase transition in metal–hydrogen systems Horner and Wagner [5] developed a model which takes the effect of elastic interaction into account. Moreover, in magnetic systems, which are analogous to solid solutions, the phase transition is drastically changed by the elastic interaction (for a review see Bergman and Halperin [6]).

In these models an elastic lattice is combined with an Ising or Heisenberg type model. Generally the elastic degrees of freedom are eliminated by introducing two kinds of magnetic interaction. The first one is a short range interaction that can modify drastically the phase transition, while the second interaction is introduced to take into account the effect of free surface as detailed by Wegner [7]. Since these calculations tend to be complicated, the boundary conditions were chosen to be as simple as possible, e.g. a homogeneous strain, etc. The present paper might be considered as an extension of the previous work. Despite the simplifications, the results may be utilized for material design. The possibility of producing curved crystals from intercalation compounds and mixed superionic conductors will be discussed.

2. Formalism

The inhomogeneous composition of the elastic solid is described by $c(r)$, the variation of local concentration which satisfies the conservation law

$$\int_V c(r)\, \mathrm{d}^3 r = 0 \tag{1}$$

where we integrate over the finite volume of material.

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The components of strain resulting from this composition variation are

$$u_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right) \quad i, j = x, y, z \qquad (2)$$

where u_i is the ith component of the displacement vector u at point r.

The total free energy of our system may be separated into four contributions expressed in terms of $c(r)$ and u_{ij}

$$F = F_{\mathrm{e}} + F_{\mathrm{ch}} + F_{\mathrm{e\text{-}ch}} + F_{\mathrm{ext}} \qquad (3)$$

Adopting the summation convention for repeated indices, in linear approximation the elastic energy of an isotropic material is

$$F_{\mathrm{e}} = \int_V [\mu(u_{ij} - \tfrac{1}{3}u_{kk}\delta_{ij})^2 + \tfrac{1}{2}\kappa u_{kk}^2]\,\mathrm{d}^3 r \qquad (4)$$

where κ and μ are the moduli of compression and rigidity. The contribution of inhomogeneous composition is traditionally given as

$$F_{\mathrm{ch}} = \int_V \left[f(c) + \frac{\kappa}{2}\left(\frac{\partial c}{\partial r_k}\right)^2\right]\mathrm{d}^3 r \qquad (5)$$

where $f(c)$ is the free energy of a unit volume of material with homogeneous concentration c, and the gradient term describes the additional energy of inhomogeneities (such as domain walls). It is known from the theory of spinodal decomposition that the role of the gradient term is important for wavelengths of about 5 nm characteristic of the concentration fluctuations in binary alloys. On a macroscopic scale, however, this term is probably insignificant, therefore it is neglected henceforth.

Generally, $f(c)$ is expressed by its Taylor series

$$f(c) = f_0 + f_1 c + \tfrac{1}{2}f_2 c^2 + \cdots \qquad (6)$$

where the coefficients f_0 and f_1 are irrelevant from the viewpoint of minimalization due to the material conservation defined by Equation 1, and f_2 depends on temperature. In linear approximation the higher order terms are negligible.

The concentration variation is coupled linearly with the elastic distortion as

$$F_{\mathrm{e\text{-}ch}} = -\int_V gc(r)u_{kk}\,\mathrm{d}^3 r \qquad (7)$$

where $g = \alpha/\kappa$; is the relative change of volume caused by unit concentration variation. The fourth term in Equation 1 defined by

$$F_{\mathrm{ext}} = \int_V hzc(r)\,\mathrm{d}^3 r \qquad (8)$$

is introduced to take into account the effect of an external inhomogeneous field on the equilibrium state. On the one hand this contribution describes correctly the effect of gravitation that may be significantly enhanced by generating a centrifugal field. On the other hand, this term may be considered as a simplified description of other external effects such as mechanical bending.

The components of stress tensor are given by functional derivatives of free energy with respect to u_{ij}, thus

$$\sigma_{ij} = (-gc + \kappa u_{kk})\delta_{ij} + 2\mu(u_{ij} - \tfrac{1}{3}u_{kk}\delta_{ij}) \qquad (9)$$

The equations of mechanical equilibrium are

$$\frac{\partial \sigma_{ij}}{\partial r_j} = 0 \qquad (10)$$

These equations may be expressed in terms of the displacement vector by substituting Equations 2 and 9 into Equation 10

$$\left(\kappa + \frac{\mu}{3}\right)\frac{\partial^2 u_j}{\partial r_i \partial r_j} + \mu\frac{\partial^2 u_i}{\partial r_k^2} = gc \qquad (11)$$

For simplicity we assume a free surface, therefore on the surface

$$\sigma_{ij}n_j = 0 \qquad (12)$$

where n is the unit vector perpendicular to the surface. This equation gives a boundary condition for the solution of Equation 11.

It is worth mentioning that similar expressions are obtained for thermoelasticity in the textbook by Landau and Lifshitz [8].

3. Chemically curved state

First we briefly prove that in a linear approximation the linear variation of concentration results in a stress-free, curved state. For this purpose we assume that the concentration varies along the z axis as

$$c(r) = az \qquad (13)$$

It is easy to check that in this case Equation 11 has a cylindrically symmetrical solution

$$\begin{aligned} u_z(r) &= \frac{ga}{3\kappa}xz \\ u_y(r) &= \frac{ga}{3\kappa}yz \qquad (14) \\ u_z(r) &= \frac{ga}{6\kappa}(z^2 - x^2 - y^2) \end{aligned}$$

in which the translation and rotation are excluded at point $r = 0$. Simple mathematical manipulations give

$$u_{ij} = \frac{ga}{3\kappa}z\delta_{ij} \qquad (15)$$

and

$$\sigma_{ij} = 0 \qquad (16)$$

Since all the components of the stress tensor are zero in the whole material the boundary Condition 12 is trivially satisfied independent of the shape.

The geometrical properties of the chemically curved state are visualized in Fig. 1. This figure shows the distortion of a square cross-section at three different values of concentration gradient including the neutral state. The size variation of small squares is in agreement with the volumetric dilatation or contraction caused by the linear variation of concentration. At the same time, these small squares are weakly distorted, and the planes originally perpendicular to the z axis transform into paraboloids.

The middle plot of Fig. 1 suggests a simple picture: the z = constant planes close to the origin transform into spherical surfaces whose centre coincides with the point of the z axis where the extrapolated lattice

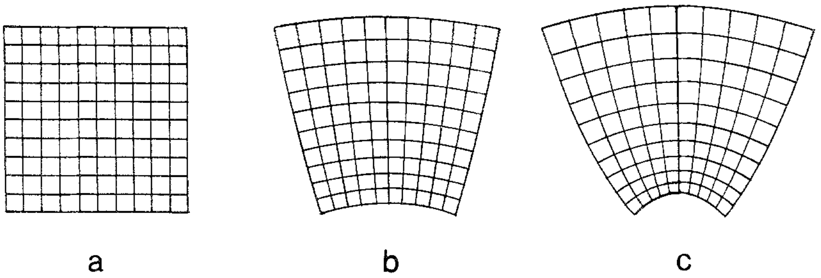

Figure 1 Cross-section of chemically curved states at different vertical concentration gradients. The relative changes of the "lattice constant" between the top and bottom are (a) 0, (b) 0.5 and (c) 1.

constant should vanish. If this is recognized one can easily estimate the curvature caused by a given concentration gradient. For example, 1% variation of the lattice constant between the top and bottom of a 1 mm thin slice of solid solution results in a spherically curved state with a radius of 10 cm.

The plot on the right-hand side of Fig. 1 shows clearly that both the horizontal and the vertical marker lines transform into parabolae intersecting each other perpendicularly as is characteristic of a parabolic coordinate system. A noticeable consequence of this behaviour is that this macroscopic distortion hardly changes the bond angles characteristic of crystal structures. On the other hand, this plot clarifies some drawbacks of this solution related to the increase of the displacement vector when increasing the size and concentration gradient. It is evident that the size and/or concentration gradient is/are limited by the validity of linear approximation which is not yet known.

The main conclusion of the above calculation is that stress-free (mechanically stable) crystals of linearly varying lattice constant may be produced by a constant gradient of either temperature or concentration. In the curved crystal the gradient of concentration (or temperature) induces particle (or energy) transport (see Equation 13) whose stabilization requires special boundary conditions. In contrast to energy transport, particle transport is generally prevented at room temperature so the linear concentration variation may be frozen-in for a long time despite the boundary conditions and the thermodynamic instability. For the preparation of such a state, however, the knowledge of thermodynamic stability is particularly important.

4. Thermodynamic stability

In order to analyse the thermodynamic stability in the stress-free case the total free energy has to be expressed in terms of the concentration gradient introduced by Equation 13. Substitution of Equation 14 into Equations 4 and 7 gives $F_e + F_{e-ch}$ in the following form

$$F_e + F_{e-ch} = -\int_V \frac{g^2}{2K}(az)^2 \, d^3r \qquad (17)$$

This quadratic contribution is negative in agreement with the well known fact that the elastic interaction assists the phase separation accompanied by volumetric change in solid solutions. At high temperatures the homogeneity is provided by the increasing role of entropy included in F_{ch}.

At $K = 0$ the total free energy may easily be minimized with respect to concentration gradient because the result becomes independent of size and shape. In the high temperature region ($f_2 > g^2/\kappa$) the equilibrium concentration gradient is

$$a_{eq} = \frac{h}{(f_2 - (g^2/\kappa))} \qquad (18)$$

In the absence of an external field ($h = 0$) this result suggests a homogeneous state above a critical temperature T_c defined by

$$f_2(T_c) = \frac{g^2}{\kappa} \qquad (19)$$

Despite the presence of an external field ($h \neq 0$) the chemical potential, which is the functional derivative of the total free energy with respect to the concentration, is constant therefore the mass transport is evidently zero in the bulk. It is well known that the time variation of concentration vanishes not only at zero but at constant current density too, corresponding to linear variation of concentration and chemical potential. By this means the required concentration variation may be stabilized with a suitable choice of boundary conditions providing constant mass transport through the bulk. A similar phenomenon may be observed in the temperature variation at constant heat current density.

According to Equation 18, in the vicinity of the critical temperature the external field can result in an arbitrary high concentration gradient which is obviously limited by the non-linear terms.

Below the critical temperature the total free energy is minimized at infinite concentration gradient. This result is usually interpreted as a tendency towards the complete phase separation which is the subject of spinodal decomposition. Within the framework of spinodal decomposition the time dependence of phase separation as well as the effect of finite K and nonlinearity are analysed in detail (for a review see, e.g., the paper by Langer [9]). Unfortunately, the effect of an inhomogeneous external field on the spinodal decomposition has not yet been analysed although it should permit controlled variation in concentrations below T_c.

5. Summary and conclusions

The theoretical possibility of the creation of chemically curved crystals with a uniform variation of "lattice constant" has been investigated within the framework of the Ginzburg–Landau formalism. The present description is restricted to a linear approximation, therefore, the results have a limited range of validity. Keeping these limits in mind, the present theory permits the manufacture of curved single crystals.

It is shown that a constant concentration gradient results in a stress-free paraboloidically curved state. In other words, the crystals are mechanically stable in spite of the linear variation of "lattice constant". In linear approximation this prediction is independent of the crystal size and shape. For simplicity the above statement is proved for an isotropic material, but it is easy to check that it remains valid in the more realistic case of cubic symmetry.

It is underlined that any deviation from the linear variation of concentration causes stresses. For example, a sinusoidal variation of concentration induces stress with the same periodicity in the bulk. The strength of this stress is proportional to the wavenumber of concentration variation, i.e. it vanishes when the wavelength tends to infinity. On the other hand, the condition of free surface (Equation 12) requires the addition of macroscopic modes which are the solution of the homogeneous version of Equation 11. These macroscopic modes depend on the shape except for those two which correspond to a constant and a linear variation in dilatation as discussed by Wegner [7]. In the light of these results it is not surprising that the stress disappears in a finite specimen since both the constant and the linear variation of concentration may be considered as a limit in which the wavelength goes to infinity. These fortunate circumstances made the present analysis simple.

In general, two thermodynamically stable states exist in solid solutions which are homogeneous or completely decomposed at equilibrium. At low temperatures, however, the thermodynamically non-stable composition distribution, e.g. linear, may be preserved for a long time due to the inefficient diffusion. The main difficulty is how to achieve the linear variation desired in our case.

Thermodynamics suggests two possibilities. In an open system a constant mass current density driven through the sample leads to a linear concentration variation in the bulk. This state may be achieved by a suitable choice of shape and boundary conditions. On the other hand, the application of an external field, such as mechanical bending or centrifugal force, can stabilize the linear concentration variation above a critical temperature. Below this critical temperature the homogeneous phase is no longer stable and the solid solution separates spontaneously into two phases with either nucleation or spinodal mechanism. In this temperature (and composition) region the effect of an external field with constant gradient is particularly interesting because it is a unique example for directional spinodal decomposition where the increase of long wavelength concentration fluctuation is preferred.

Beyond the linear approximation it is expected that the stress does not vanish completely in a chemically curved crystal. Instead, the stress probably has a minimum at small deviation from the linear concentration variation. The non-linear and size effects may influence the minimum value of stress, thus limiting the sample size and/or curvature. According to perturbation theory, the present results should be correct at sufficiently small concentration variation. A more precise determination of the limits is not possible since the mathematical description, which takes all the non-linear effects into consideration, is extremely complicated.

Chemical curvature is not only observed but consciously applied in some areas of solid state physics. For example, it is well known as a disadvantageous effect in thin layer technology. It is also observed in palladium membranes used as hydrogen filters. Recently, various techniques have been investigated in an attempt to produce monochromator crystals which may enhance the integrated intensity in a more controllable way than the conventional method of mechanical bending [1].

In principle any kind of solid solution or intercalation compound is suitable for preparing chemically curved crystals. Judging from the present analysis it needs a well controlled concentration distribution. The realization of this requirement, however, may be troublesome since any deviation from the linear composition distribution would lead to undesired stresses which may result in cracking and/or plastic deformation. It is worth mentioning that this effect is not so dangerous in those materials in which the diffusion can reduce the stresses. This is the reason why intercalation compounds and mixed superionic conductors which have no structural phase transition are proposed.

In an intercalation compound such as Na_xWO_3, the interstitial particle can reduce the compressive stress when it moves away from the compressed region. This stress relaxation mechanism is well known in metallurgy. In a mixed superionic conductor the substitution of the larger mobile ion by a smaller one decreases the compression. All the requirements including mechanical strength and high crystallographic symmetry may be fulfilled by mixed alkaline-earth halides of fluorite structure, such as $(Ba \cdot Sr)(F \cdot Cl)_2$ solid solutions. More recently the desired properties, except the cubic symmetry, have been observed by Lumbreras *et al.* [10] in mixed lead halides. Mixed alkali halides with NaCl structure might also be good candidates because sufficiently high ionic mobility is found in these materials (for a review see Johannesen and McKelvy [11]). In the above mentioned materials the high diffusivity permits the composition to be controlled by applying an inhomogeneous external field. The application of a centrifugal field may be another promising technique. Its effect on the concentration gradient was first observed by Anthony [12] in In–Au alloy. Recently, the centrifugally induced inhomogeneities were considered by Ogorelec [13] in non-stoichiometric superionic conductors. Unfortunately, in neither of these papers was the curvature investigated. It is evident that besides the methods suggested above there are other possibilities of preparing chemically curved crystals. With modifications, certain of the technologies developed for silicon processing seem to be applicable for producing curved crystals. For example, crystals might be grown both by the epitaxial methods and by the Czochralski technique if the melt (or vapour) composition were to be precisely controlled. It is to be hoped that in high technology increasingly sophisticated instruments will be fabricated for material design and that such instruments will increase the chance of preparing curved crystals.

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