

Strain-Assisted Epitaxial Growth of New Ordered Compounds

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Epitaxial growth of metastable phases is discussed. A linearized theory predicts new ordered compounds stabilized by the interaction of atomic size differences with epitaxial strain during growth.

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This Letter concerns the epitaxial growth of new metastable ordered compounds. Epitaxial growth provides an important path to the synthesis of chosen metastable heterostructures such as quantum wells and superlattices in which different materials are grown one upon another.¹ Unexpected new homogeneous epitaxial phases also have occasionally been grown. Cunningham and Flynn² report a new metastable hcp phase of Ir. For compounds, surprising stability of ordered epitaxial AgAu is described by Cook³ and of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by Kuan *et al.*⁴; the phase diagrams indicate that these systems are disordered in bulk equilibrium. In what follows I treat the energetics of epitaxial compounds. Predicted new ordered structures are stabilized by the interaction of epitaxial strain with size differences among the component atomic species. The topic may be of general interest for both scientific and technical applications in the selection of new materials.

The main result is simply stated. When two similar crystals A and B alloy (they may be compounds), any misfit free energy from size differences makes the disordered A_xB_{1-x} for $x \sim 0.5$ unstable against decomposition into two dilute solutions.⁵ But any lattice spacing of A_xB_{1-x} usually changes monotonically with x . When grown in atomic registry with a substrate lattice matched to $A_{0.5}B_{0.5}$, the dilute solutions are therefore strained. The epitaxial strain energy generally exceeds the misfit energy. Thus, the complete range of compositions is stabilized for the epitaxial system. Any compound AB with free energy less than the disordered alloy $A_{0.5}B_{0.5}$ (as usually will happen) then becomes the stable epitaxial phase even though it cannot form in the bulk. Once formed, the compound lacks interfacial strains which could drive nucleation of heterogeneities. It is therefore reasonable to suppose that diffusive decomposition would indeed occur in registry with the substrate, much as in coherent spinodal processes,⁵ and could thus be suppressed.

A stably growing film has a structure set by the variations of free energy F with concentration x in the competing phases. Diffusive decomposition into dilute phases, without nucleation barriers, requires $\partial^2 F / \partial x^2 < 0$ in the disordered phase. Several factors including thermal, atomic, and epitaxial misfit free energies must be included. They are treated in what fol-

lows.

To model the energetics consider a harmonic basic crystal with a force-constant matrix \mathbf{C} which derives from appropriately long-ranged forces.⁶ The potential energy is

$$U = \frac{1}{2} \mathbf{x} \cdot \mathbf{C} \cdot \mathbf{x}, \quad (1)$$

with \mathbf{x} the vector of atomic displacements. At issue is the free energy when atoms with differing sizes are organized in various ways on the basic lattice. A perturbation due to atomic size misfit is now introduced in general as a near-neighbor linearly coupled interaction

$$H' = \sum_i [E_i^\pm \pm \lambda \sum_j x_{ij}], \quad (2)$$

where i indexes the size-active species and j runs over the n near-neighbor bonds, with length changes x_{ij} , per i atom. In H' , the positive sign is taken for small i atoms; the constants E_i^\pm play no part in phase equilibrium and will be dropped henceforth. Discussion is limited to crystal types of which A and B differ by a pure volume expansion, with volumes $V(1 \mp \Delta)$ due to small atoms and large atoms, respectively; here, V is the volume of the basic lattice.

The volume change serves to determine λ . The summed bulk compressive energy $\beta(\delta V)^2/2V$ and $\langle H' \rangle = nN\lambda a \delta V/3V$ are minimized for $\delta V = V\Delta$ only if

$$\lambda = 3\beta\Omega\Delta/an, \quad (3)$$

with a the near-neighbor bond length of the basic lattice, β the bulk modulus, $\Omega = V/N$ the volume per i atom, and N the number present. A free-energy change

$$F_r = -\frac{1}{2}\beta V\Delta^2 \quad (4)$$

accompanies this volume relaxation of pure A or B .

The energy of epitaxial strain can be shown to take a similar form. Suppose that the stress in the growth plane is σ , due to a misfit strain ϵ , and that the resulting strain in the growth direction is ϵ' , with zero stress. For a cubic crystal, then,

$$\begin{aligned} \sigma &= c_{11}\epsilon + c_{12}\epsilon + c_{12}\epsilon', \\ 0 &= 2c_{12}\epsilon + c_{11}\epsilon', \end{aligned} \quad (5)$$

with the c_{ij} isothermal elastic constants.⁷ The free energy of epitaxial strain follows by elimination of ϵ' as

$$F_e = V \sum_i \frac{1}{2} \sigma_i \epsilon_i = V (c_{11} + c_{12} - 2c_{12}^2/c_{11}) \epsilon^2,$$

or

$$F_e = \frac{1}{3} \beta V \delta^2 (1 - c_{12}/c_{11}). \quad (6)$$

Here, use has been made of the relation $\beta = (c_{11} + 2c_{12})/3$, and $\delta = 3\epsilon$ is the volume mismatch from which the strains derive.⁷

Free-energy changes associated with detailed microscopic structure occur when atoms of A and B intermix to form alloys or compounds. Changes of lattice potential energy and vibrational free energy are both important.^{6,8} They can be treated exactly for the model described above.

First, the quadratic form for the potential, Eq. (1), can be diagonalized for certain normal coordinates x_i , with curvatures γ_i^2 ; and, in addition, the linear coupling, Eq. (2), can be projected on these coordinates with coefficients $\lambda \alpha_i$, say. The complete potential can thus be rearranged as

$$\begin{aligned} U' &= \sum_i \frac{1}{2} \gamma_i^2 x_i^2 + \lambda \sum_i \alpha_i x_i \\ &= \sum_i \frac{1}{2} \gamma_i^2 y_i^2 - \sum_i \lambda^2 \alpha_i^2 / 2\gamma_i^2, \end{aligned} \quad (7)$$

with $y_i = x_i + \lambda \alpha_i$. This shows that the size perturbation leaves the vibrational force-constant matrix unaltered, as is well known for linear coupling, for example in lattice statics applications.⁹ The atoms merely undergo static shifts, with a consequent energy lowering $\sum_i \lambda^2 \alpha_i^2 / 2\gamma_i^2$.

Second, the vibrational free energy is large and must be handled accurately. All phase transformations may be regarded as rearrangements of the atoms among the sites of the basic lattice. The microscopic complication is that the eigenfunctions and frequencies all change with the locations of the different masses. The exact vibrational Hamiltonian after static shifts is

$$H = - \sum_s (\hbar^2 / 2M_s) \nabla_s^2 + \frac{1}{2} \mathbf{y} \cdot \mathbf{C} \cdot \mathbf{y}, \quad (8)$$

in which the sum extends over all atoms s , mass M_s . The eigenfrequencies ω_j are given by the secular equation⁶

$$\| |C_{ss} / M_s^{1/2} M_s^{1/2} - \omega_j^2 \delta_{ss} | \| = 0, \quad (9)$$

and satisfy the well known sum rule⁶

$$\prod_j \omega_j^2 = \| |C| \| \prod_s M_s^{-3}. \quad (10)$$

Consequently, the vibrational free energy^{6,8} at high temperature,

$$\begin{aligned} F_v &= kT \sum_j \ln(\hbar \omega_j / kT) \\ &= (kT/2) \ln \| |C| \| \prod_s (\hbar / kT \sqrt{M_s})^6, \end{aligned} \quad (11)$$

is independent of configuration. It is an exact result that the vibrational free energy plays no role in high-temperature phase transformations for the present model system.

Atomic misfit in random $A_x B_{1-x}$ alloys causes a change of potential energy. This can be calculated from static mode shifts, as in Eq. (7), with appropriate random coefficients α_i . Its dependence on γ_i^{-2} reveals the important role of long-wave properties in this energy. In fact this is a famous problem that has been treated extensively.^{8,10,11} The potential energy of mixing is

$$F_m = 0.9\beta V \Delta^2 x(1-x). \quad (12)$$

Quoted values of the coefficient vary somewhat from case to case. In elastic strain models¹⁰ the value is about 0.8 whereas it is about 1.0 in detailed atomic models of mixed salts.¹¹ Equation (12) is adequate for the present purposes.

A global understanding of the phase relationships is now accessible. The left-hand side of Fig. 1 shows how the free energy of bulk $A_x B_{1-x}$ depends on the composition x according to Eqs. (4) and (12). The zero of energy corresponds to pure A or B at the volume V . Inclusion of terms in E^\pm [Eq. (2)] or M [Eq. (10) and (11)] would skew the curve but leave phase relationships unchanged. At $T=0$ (heavy curve) the dilute phases lie lowest.^{10,11} At sufficiently high temperature, added entropy of disorder can stabilize the mixed state near $x=0.5$ (faint curves). However, ordered phases AB (broken curve) which are marginally preferred over the disordered state at $T=0$ can never occur. They remain hidden under the dome of free energy versus x . Note that for clarity the ordered phase is drawn sharply curved as if departures

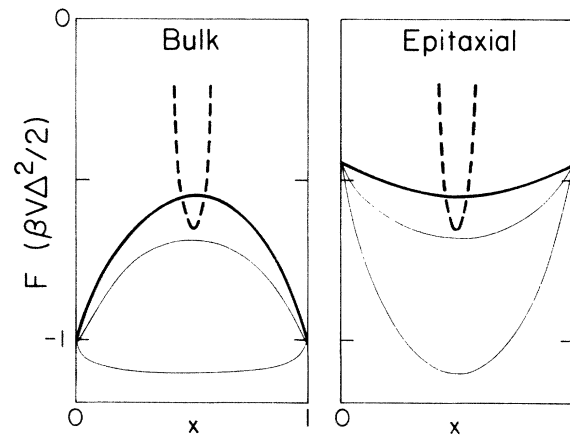


FIG. 1. Free energy as a function of composition x for bulk (left) and epitaxial (right) disordered $A_x B_{1-x}$ (thick curves) and ordered AB (broken lines). Faint lines include mixing entropy for $T \neq 0$.

from stoichiometry required large free energies. In real examples the broken lines may be flatter.

For epitaxial phases the picture is completely changed by the free energy of epitaxial strain. Equations (4) and (6) sum to an epitaxial relaxation energy

$$F_r' = -\frac{1}{2}\beta V\Delta^2(\beta/c_{11}) \quad (13)$$

for pure *A* or *B*. This is much less than the bulk value, Eq. (4), since typically $\beta/c_{11} \sim 0.4-0.5$. For a linear change of volume with *x*, $\delta = \Delta(2x-1)$, the corresponding concentration-dependent free energy from Eqs. (6) and (12) is

$$F_m' = -(1.1 - 2\beta/c_{11})\beta V\Delta^2x(1-x) \quad (14)$$

in place of Eq. (12). This is typically small and *negative* with $\partial^2 F/\partial x^2 > 0$ (right-hand panel of Fig. 1). The full range of epitaxial alloys is thus stable against diffusive decomposition. Furthermore, any ordered compound which has a free energy lower than the disordered alloy now becomes the stable epitaxial phase (broken line). The result holds for all compounds, not only for *x*=0.5. These conditions are sufficiently general that a directed search for new ordered compounds appears warranted.

As a well-controlled example consider mixed fcc alkali halides and, in particular, the ordered compound whose growth plane is sketched in Fig. 2. Large and small cations alternate among a common anion species (or vice versa); these planes are stacked by successive displacements of (*a*,0). The locations between dissimilar cations make the anions, mass *M*, unstable against a density-wave distortion in the pattern of the anion phonon, frequency ω_L , at the *L* point of the Brillouin-zone boundary, along (111). A brief calculation, with $\lambda = \beta a^2 \Delta$ for this case [cf. Eq. (3) with $\Omega = 2a^3$ and $n = 6$], yields for the energy change from

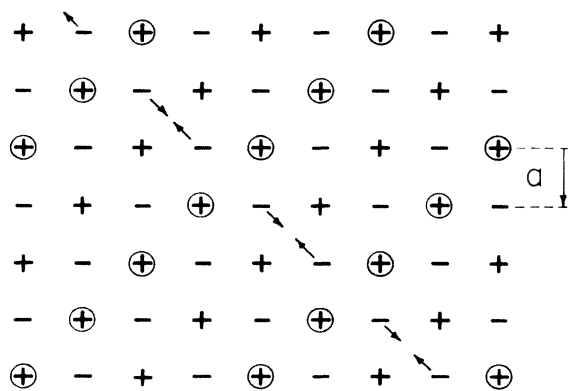


FIG. 2. Model ionic lattice including small and large (circled) cations. Growth planes are stacked with successive displacements (*a*,0). Arrows on one diagonal indicate in-plane anion phonon displacements at *L* (see text).

compound formation

$$F_c = -\frac{1}{2}\beta V\Delta^2(6\beta a/M\omega_L^2) \quad (15)$$

relative to the regular array (for additive size-dependent near-neighbor forces this is precisely the same energy zero used above for pure phases and alloys).

Table I gives experimental values of $J = \beta/c_{11}$ [Eq. (13)] and $K = 6\beta a/M\omega_L^2$ [Eq. (15)] for fcc alkali halides. Phonon frequencies were obtained from neutron data collected by Bilz and Kress,¹² bulk moduli from Tosi,¹³ and c_{ij} ratios from Simmons and Wang.¹⁴ For all basic lattices other than LiF the table shows that $K > J$. Size differences therefore lead to epitaxial ordered compounds which are more stable than the epitaxial dilute solutions, within the present linear stability analysis.

Systematic efforts to exploit size differences in the growth or ordered epitaxial compounds appear to be lacking. Other factors may be relevant to the observations for AgAu (Ref. 3) and $Al_xGa_{1-x}As$.⁴ For alkali halides, where size effects are clearly controlled, available data for *bulk* mixtures conform well¹¹ to Fig. 1. In several tens of phase diagrams, bulk ordered compounds do not form for even a single case of small misfit¹⁵; thermodynamic data, where available, fit Eq. (12) well.¹¹ In a few cases of *very large* misfit, reports of mixed bulk compounds have been supported, notably for LiF-CsF, LiF-RbF, and LiCl-CsCl (Ref. 15) (no structure data are given). This suggests that higher terms, beyond linear coupling, may also favor compound formation. No useful results for epitaxial rocksalt systems are yet available.

In summary, this Letter shows how the strain associated with atomic registry during epitaxial growth can interact with atomic size differences to stabilize new classes of ordered compounds. Such compounds in

TABLE I. Values of constants $J = \beta/c_{11}$ (upper) and $K = 6\beta a/M\omega_L^2$ (lower) calculated from data for fcc alkali halides (see text). With $K > J$ the epitaxial ordered compound is stable against size-induced decomposition into disordered epitaxial binaries for all lattices except LiF. Values of $M\omega_L^2$ generally differed little for anions and cations; the average is used in the table.

	Li	Na	K	Rb	Cs
F	0.586	0.497	0.484	0.480	0.415
	0.49	0.60	0.58	0.61	0.67
Cl	0.638	0.503	0.437	0.445	
	...	0.59	0.61	0.62	
Br	0.651	0.500	0.438	0.434	
	...	0.71	0.63	0.60	
I	0.660	0.531	0.447	0.430	
	...	0.70	0.61	0.56	

model materials like alkali halides would offer much of scientific interest including vibrational, excitonic, structural, and defect phenomena, particularly with broken site symmetry. For electronic materials induced ordering is, in addition, of significant technical interest through the opportunity it brings to increase carrier free paths, etc. Therefore, these possibilities appear to warrant detailed future exploration.

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Note added.—In a very interesting paper that appeared after this manuscript was submitted, Martins and Zunger¹⁶ treat structure and energetics of semiconductors. They recognize that strain can reduce the enthalpy of an epitaxial compound (in their case SiGe) below that of the pure components, and so tend to stabilize it. More precisely, both the stability and the existence of a barrier to diffusive decomposition depend on the composition dependence of the *free energy* in the several competing phases. These are the factors analyzed above in a model that isolates the relevant size effects. In a second recent development Jen, Cherng, and Stringfellow¹⁷ report ordered epitaxial phases of GaSb_xAs_{1-x} near $x = 0.5$. These may possibly be examples of the general behavior predicted here.

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