

usual compliance matrix for crystals of either symmetry class 32 or 62.

APPENDIX C

Slope of phase boundary for coherent first-order transitions (assuming infinitesimal transformation strains) under conditions of nonhydrostatic stress. Let us assume that the solid-solid transition is characterized by a small reversible transformation strain $\Delta\epsilon_{ij}$, so that infinitesimal strain theory may be used. In this case the volume V never differs much from the volume V_0 in the reference state of stress and strain, so that the elastic work done by the applied stresses when the body undergoes a small virtual deformation $d\epsilon_{ij}$ is [Nye, 1957]

$$dW = V_0 \sigma_{ij} d\epsilon_{ij} \quad (C1)$$

where summation over repeated indices is understood.

We now define a thermodynamic potential function, which we shall prove has useful extremum properties at equilibrium under conditions of constant temperature and stress

$$G = U - TS - V_0 \sigma_{ij} \epsilon_{ij} + V_0 \langle P \rangle \quad (C2)$$

where the mean pressure $\langle P \rangle \equiv (-\sigma_{11} - \sigma_{22} - \sigma_{33})/3$. There are, in fact, many such functions that would serve our purpose, but (C2) has the virtue of reducing in the case of hydrostatic pressure to the conventional Gibbs free energy $G = U - TS + PV$.

The first and second laws of thermodynamics and (C1) can be combined to yield

$$dU \leq T dS + V_0 \sigma_{ij} d\epsilon_{ij} \quad (C3)$$

for any small spontaneous change in the entropy and state of strain of the elastic body, where the equality holds only when the body is in equilibrium. Differentiating (C2) and substituting (C3), we see

$$dG \leq -S dT - V_0 \epsilon_{ij} d\sigma_{ij} + V_0 d\langle P \rangle \quad (C4)$$

where the equality again implies equilibrium. Thus, at constant temperature and stress, G is a minimum at equilibrium, because any spontaneous change from a nonequilibrium state entails a decrease in G . Similarly, the chain of reasoning can be reversed to show that the first and second laws also imply the converse: whenever G is a minimum at constant temperature

and stress, the body is in elastic and thermal equilibrium.

Consider now a situation where n^a moles of the α phase are in equilibrium with n^b moles of the β phase. This can occur only if G of the composite system is unchanged by a transformation of an infinitesimal number of moles of material dn^b from the α to the β phase. That is, $dG = g^a dn^a + g^b dn^b = (g^b - g^a) dn^b = 0$, which requires that G per mole of α and β be equal: $g^a = g^b$. At a nearby point on the boundary at equilibrium $g^a + dg^a = g^b + dg^b$, which requires that $dg^a = dg^b$. Differentiation of (C2) yields

$$\begin{aligned} dg^a &= -s^a dT - v_0 \epsilon_{ij}^a d\sigma_{ij} + v_0 d\langle P \rangle \\ &= -s^b dT - v_0 \epsilon_{ij}^b d\sigma_{ij} + v_0 d\langle P \rangle = dg^b \end{aligned} \quad (C5)$$

where s^a and s^b are the entropies per mole of the α and β phases, v_0 is the volume per mole in some convenient reference state (say in the α phase), ϵ_{ij}^a is the strain in going from the reference state to the phase boundary, and ϵ_{ij}^b is greater than ϵ_{ij}^a by the strain $\Delta\epsilon_{ij}$ associated with the transition. Holding all components of the stress constant except σ_{kl} and eliminating the common term $v_0 d\langle P \rangle$ from both sides of (C5), we obtain the slope of the phase boundary in the $\sigma_{kl} - T$ plane

$$\begin{aligned} M_{kl} &\equiv -(\partial T_{\alpha-\beta} / \partial \sigma_{kl})_{\sigma \neq \sigma_{kl}} \\ &= v_0 \Delta\epsilon_{kl} / \Delta s \end{aligned} \quad (C6)$$

Thus, the increase of transition temperature with stress varies for the different components of stress proportionally to the corresponding component of the transformation strain.

Note that (C6) reduces to the standard Clapeyron equation 10 in the case of hydrostatic pressure (set $k = l$ and sum, with $d\sigma_{11} = d\sigma_{22} = d\sigma_{33} = -dP$). It is also closely analogous to the asymptotic relations derived for λ transitions. If the changes Δs and $\Delta\epsilon_{kl}$ are assumed to occur continuously in a very small interval of temperature or stress around the transition boundary, we see that an expression like (7) or (8) can be obtained by dividing both numerator and denominator of (C6) by either ΔT or $\Delta\sigma_{ij}$, respectively.

Since deriving equation C6 we have found it stated without proof and applied to the transi-

tion in the indium-thallium alloy system by *Burkart and Read* [1953], as well as a one-dimensional form of it used by *Flory* [1956] to deal with a reversible transition in protein fibers. A brief derivation is given by *Forsbergh* [1956, p. 357] with reference to the dependence of the Curie point on stress in ferroelectrics, which is valid, even though his statement that the generalization of the Gibbs free energy that he uses reduces to the standard one for hydrostatic pressure is incorrect (p. 346).

This treatment of coherent first-order transitions can be compared with other theories of nonhydrostatically stressed solids that have some features in common. *Verhoogen* [1951] presented a theory in which the chemical potential (G per mole) is uniform within a homogeneously stressed solid and the orientation of the phase boundary plays no role in thermodynamic equilibrium. These are two of the distinguishing characteristics of the above development, but his conclusion that it is sufficient to a first approximation to replace P in the hydrostatic equations by $\langle P \rangle \equiv (-\sigma_{11} - \sigma_{22} - \sigma_{33})/3$ in order to deal with a general stress is in agreement with our equations C5 and C6 only in the special case in which the transformation strain is isotropic (no shape change: $\Delta\epsilon_{kl} = \Delta v/3v_0$ for $k = l$, $\Delta\epsilon_{lk} = 0$ for $k \neq l$).

McLellan [1968] distinguished coherent and incoherent interfaces in his general treatment of phase equilibria, but he also appears to have limited his consideration to isotropic transformation strains. Thus our expression for equilibrium between coherent α and β single component phases related by an infinitesimal transformation strain $\Delta\epsilon_{kl}$, $g^\alpha = g^\beta$ can be rewritten

$$\begin{aligned} u^\alpha - Ts^\alpha + \langle P \rangle v_0^\alpha \\ = u^\beta - Ts^\beta + \langle P \rangle v_0^\alpha - v_0^\alpha \sigma_{ij} \Delta\epsilon_{ij} \\ = u^\beta - Ts^\beta + \langle P \rangle v_0^\beta - v_0^\alpha \sigma_{ij} \\ \cdot [\Delta\epsilon_{ij} - \delta_{ij}(\Delta\epsilon_{11} + \Delta\epsilon_{22} + \Delta\epsilon_{33})/3] \end{aligned} \quad (C7)$$

where the reference state of stress and strain is taken to be in the α phase right at the transition and δ_{ij} is 1 for $i = j$ and 0 for $i \neq j$, whereas *McLellan* [1968, his equation 40b] requires

$$\begin{aligned} u^\alpha - Ts^\alpha + \langle P \rangle v^\alpha \\ = u^\beta - Ts^\beta + \langle P \rangle v^\beta \end{aligned} \quad (C8)$$

In general, these two formulations of equilibrium are contradictory, but (C7) becomes identical to (C8) when $\Delta\epsilon_{ij}$ is isotropic.

Kumazawa [1963] recognized the importance of shape as a thermodynamic parameter, and his discussion of the effect of stress on twinning in calcite (p. 185) is similar to our procedure. However, he does not consider coherent polymorphic transitions in which a discontinuity in entropy occurs (latent heat) and thus does not derive nor use the nonhydrostatic analogy of the Clapeyron relation (C6).

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