D. Modified Born Criterion for Phase Transitions

In all phase transitions involving a finite shift of the atoms, the phase transition will take place before any of the shear elastic constants reach zero. The expected critical ratio, $\alpha = C_t/K$, at the transition (where C_t refers to any shear constant with a relatively low value) will depend, to a large extent, on the relationship between the reaction coordinate connecting the low- and high-pressure phase and the shear strain. There are several possibilities.

1. The transformation may be a second order one involving a lowering of symmetry, in which case the shift of atoms at the transition is infinitesimal, and we expect $\alpha = 0$. An example of this is TeO_2 , which transforms continuously from a tetragonal to an orthorhombic structure above 9 kbar. Experiments by *Peercy* and *Fritz* [1974; *Fritz* and *Peercy*, 1975] and the theories of *P. Anderson* and *Blount* [1965] and *Boccara* [1968] confirm that in this case the shear elastic constant associated with this distortion does go to zero at the transition.

2. The transformation involves a macroscopic shear as in the case of the NaCl-CsCl structure transition. In general, we expect α to be larger when the macroscopic shear is larger, and we expect similar values of α for chemically similar compounds. When an empirical value of α is needed to predict a transition, we believe it is best to obtain α from experimental data on a similar compound having the same crystal structure.

3. The transformation primarily involves a macroscopic shear, but an additional distortion is involved (as in the case of the wurtzite → NaCl transition), or the transition can be represented by a transverse acoustic mode at the Brillouin zone boundary (a short-wavelength shear mode), as is the case for calcite [*Merrill*, 1975]. We still expect a relatively low value of C_t/K at the transition, but C_t/K will be a less sensitive measure of ΔG than in (2) above, because it is only approximately equal to the curvature of the free energy along the reaction coordinate. Thus, we expect larger values of α than in (2) above.

4. The transformation may involve optic modes. It may involve large atomic displacements (e.g., disproportionation), or a change of the electronic structure may be involved in addition to atomic displacements (graphite-diamond, or a Mott transition, for example). In these cases, we do not expect any particular value of C_t/K at the transition. Thus, the possibility always exists that a transformation will take place that could not be predicted by the modified Born criterion.

There may be some justification for making α a slowly varying function of pressure. *Anderson* [1975] pointed out that there will be a general tendency for the shear moduli to increase less quickly than the bulk modulus under pressure. This "mode spreading" is a direct result of the Cauchy relation for central forces. For average elastic moduli in the Voigt approximation, and assuming central forces, $C_t/K = 3/5 - 6/5\, P/K$. Since this average decrease of C_t/K will take place for all solids regardless of any phase relationships, it may be appropriate to exclude this effect from consideration. This may be done by making α pressure dependent by the equation

$$\alpha(P) = \alpha_o\ (1-2P/K) \tag{8}$$

If we assume $K' = dK/dP$ is constant, then

$$\alpha(P) = \alpha_o\ \frac{1+(K'-2)P/K_o}{1+K'\ P/K_o} \tag{9}$$

This change will in most cases be small compared to the uncertainty in α and in the extrapolated elastic constants, and, since we cannot show by experimental data whether it should be included, we shall neglect this effect.

E. Thermal Effects at a Transition

We have so far avoided an explicit treatment of thermal effects. The usual thermal contribution to the free energy and the elastic constants will not alter the qualitative feature of Figure 2. But if α is unusually small there may be an unusual thermal contribution to the free energy and its derivatives as a precursor to the phase transition.

In the quasiharmonic approximation, the thermal contribution to the Helmholtz free energy is given by

$$F_{th} = 1/2\ \sum_i h\nu_i + kT \sum_i \ln\ (1-e^{-h\nu_i/kT}) \tag{10}$$

where ν_i are the phonon (normal mode) frequencies, and

$$P_{th} = 1/V\ \sum \gamma_i h\nu_i\ [1/2 + 1/(e^{h\nu_i/kT} - 1)] \tag{11}$$

where $\gamma_i = \dfrac{-\partial \ln \nu_i}{\partial \ln V}$. When a lattice instability is approached, one of the ν_i's approaches zero, and F_{th} and its derivatives