predictions for phase transitions that have not yet been observed.

II.   TRANSITIONS AND ELASTIC CONSTANTS UNDER PRESSURE--THEORY

It follows from fundamental thermodynamic principles that
solids will transform to denser, more efficiently packed crystal
structures under increasing pressure. Attempts to make detailed
predictions of transition pressures based on a calculation of the
free energy difference between two phases have only been mar-
ginally successful, even when sophisticated models were applied
to very simple compounds [e.g., *Cohen and Gordon,* 1975]. It thus
does not appear that any successful quantitative theory of phase
transformations at high pressure based on thermodynamic equilib-
rium is available at the present time.

A.   Elastic and Thermodynamic Stability

The elastic stability criterion of *Born* [*Born,* 1940; *Misra,*
1940; *Born* and *Huang,* 1954, p. 129] states that for a lattice to
be mechanically stable, the Gibbs free energy must be a minimum
relative to any states reached by infinitesimal strains.   This
requires that the eigenvalues of the elastic constant matrix
should all be positive. For cubic crystals, these eigenvalues
coincide with the bulk modulus and the two shear moduli. We
shall refer to "shear moduli" in the following discussion, but it
is understood that for applications to crystals of general sym-
metry, the quantities of interest are the eigenvalues of the
elastic constant matrix. *Chang* and *Barsch* [1973] have made an
elaborate discussion of this point.
The Born stability criterion is a special case of the
general rule that the Gibbs free energy must be a minimum
relative to all possible small displacements of the atoms, which
requires that the frequencies of all the normal modes be positive.
Because there is so much more theoretical and experimental infor-
mation on the shear constants under pressure than there is for
the behavior of other normal modes, we will refer only to the
shear constants here, but most of this discussion can also be
applied to any mode of vibration.
There always exist reaction paths by which a crystal can be
continuously deformed from one crystal structure to another.
These reaction paths may be complicated, involving large
movements of some atoms, as in the case of reconstructive
transitions involving nucleation and growth or disproportionation.
Or, these paths may be fairly simple, involving relatively small
atomic displacements. In either case, the reaction paths (and
there may be several) between crystal structures can be defined
in terms of the lattice modes of either structure [*Musgrave,*
1970, p. 274]. The elastic constants are thus related to phase

transitions in two ways--through the Born stability criterion, and through the relationship of the elastic constants with the lattice modes which define the reaction coordinate leading from one crystal structure to another.

B. Behavior of Elastic Constants Under Pressure

Anderson [*Anderson*, 1970; *Anderson* and *Liebermann*, 1970; *Anderson* and *Demarest*, 1971] performed simple model calculations for four cubic lattices and showed that in these four cases one of the shear constants vanishes at high pressure. Some important conclusions of this work were that a shear elastic constant of a solid might decrease with pressure, perhaps after a temporary increase, and that the general trend of the less dense phases transforming to the more efficiently packed phases with increasing pressure could be predicted by the Born stability criterion.

Recently, more advanced techniques have been developed to extrapolate elastic constants to high pressure, and these techniques have been used to estimate the values of shear elastic constants at the phase transition. *Thomsen* [1970, 1971, 1972] used finite strain theory to predict that C_{44} for NaCl would vanish at the phase transition to the CsCl structure at 290 kbar. *Demarest* [1972a] used an improved lattice model, which included the next nearest neighbor (NNN) anion-anion interaction, to predict the value of C_{44} for seven alkali halides at the pressure of the polymorphic transition. In all cases, the transition took place before the predicted value of C_{44} reached zero. *Demarest* suggested an empirical modification of the Born criterion to predict a phase transition whenever C_{44}/K reached a critical value, α, with $\alpha \approx 0.15$ or 0.20. This modified Born criterion did a fairly good job of predicting all the known transitions occurring in the alkali-halides, including the case of NaCl, in which the new NNN calculation predicted that C_{44} would increase slowly with pressure.

C. Model Calculation of a Phase Change

In order to clarify the relationship between the modified Born criterion and the thermodynamic criterion for phase transformations, we recognize that the energy along the reaction path between the two phases can be expanded in a Taylor series in strain, whose leading coefficients are related to the elastic constants of the two phases [*Devonshire*, 1959]. Figure 1 shows that the NaCl - CsCl transformation can be accomplished by a compression in the (111) direction, which is equivalent to a combination of simple shears associated with the shear constant C_{44}. We used a Born model of the interatomic forces to calculate