

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 marginally 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 equilibrium 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 symmetry, 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 information 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,  $\alpha$ , 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