

**PREDICTION OF HIGH PRESSURE PHASE TRANSITIONS
BY ELASTIC CONSTANT DATA**

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Abstract

The Born elastic stability criterion provides a useful method of predicting polymorphic transitions at high pressure. Elastic constants can be extrapolated to high pressure, and a phase transition must occur before any of the shear elastic constants vanish. Many pressure-induced transitions are related to a macroscopic shear of the crystal lattice, in which cases, the dimensionless ratio of the shear elastic constant to the bulk modulus C_T/K is related to the curvature of the free energy along the reaction coordinate leading from the low-pressure to the high-pressure phase, and this ratio is a crude indicator of the Gibbs free energy difference between the two phases.

¹ Present address

We calculate the free energy for a model lattice as it transforms continuously from the NaCl to the CsCl lattice at a number of pressures to demonstrate this connection between the shear elastic constant C_{44} and the pressure-induced phase change. We have measured the single crystal elastic constants of KCl from zero pressure to the phase transition at 20 kbar. These data show that the elastic constants vary linearly with pressure right up to the transition, when the shear constant C_{44} has decreased to the relatively low value of only 20.6% of the bulk modulus. In other alkali halides, we infer similar behavior of the ratio $\alpha = C_{44}/K$ at the transition from the extrapolation of low-pressure elastic constant data, and find similar behavior for other pressure-induced phase transitions with α usually in the range 0.15-0.20. This modification of the Born criterion can be used to predict phase transitions in several compounds when C_{44}/K decreases to a critical value.

I. INTRODUCTION

The experimental study of the polymorphism of solids under pressure is an important tool for learning more about solids and the earth's interior. A good theory to predict phase relations under pressure will be useful in helping to choose experiments that are most likely to yield useful results. Predictions could be applied to minerals or other solids of interest, which are either inaccessible to current experiments or for which results are not yet available.

A comprehensive theory based on a direct calculation of free energy differences is not available. The idea of using the extrapolation of data on the elastic constants at low pressures to predict transitions at high pressure by means of the Born criterion has been around for quite a while. In many cases, the Born criterion was used to predict a transition at the pressure at which a shear elastic constant reached zero; however, experimental evidence now shows that the transition takes place before this pressure.

In Section II of this paper, we show that the transition should take place when the shear constant reaches a critical fraction, α , of the bulk modulus. This new modification of the Born criterion makes possible improved predictions of the transition pressure in cases for which a shear elastic constant decreases under pressure, and also it permits good predictions when a shear constant increases very slowly with pressure.

In Section III, we present new experimental data on the elastic properties of KCl up to the phase transition at 20 kbar. This data is in excellent agreement with our theory.

In Section IV of this article, we gather together an assortment of data on elastic constants and phase transitions to try to test how well the modified Born criterion works, and we make some

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

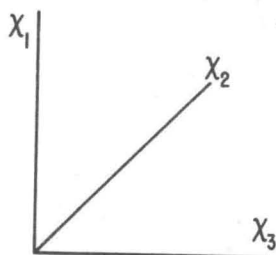
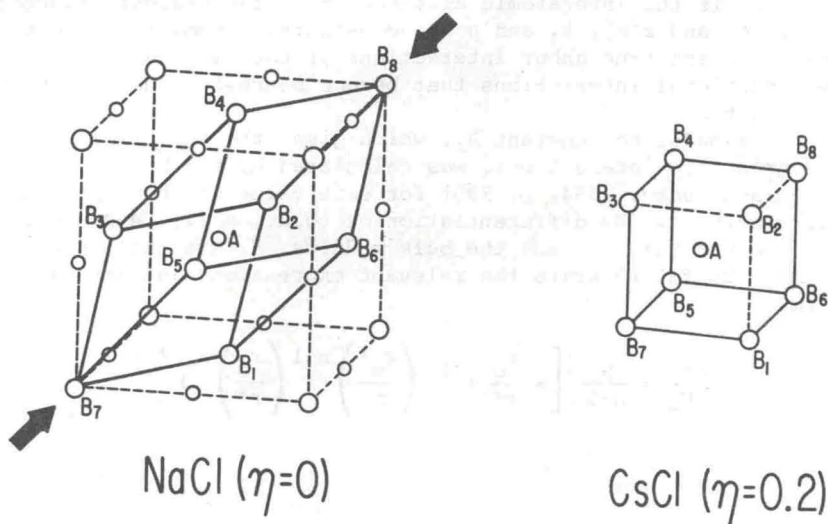
Anderson [Anderson, 1970; Anderson and Liebermann, 1970; Anderson and Demarest, 1971] performed simple model calculations for four cubic lattices and showed that in these four cases one of the shear constants vanishes at high pressure. Some important conclusions of this work were that a shear elastic 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, 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

the energy of the lattice as it is continuously transformed from the NaCl to the CsCl structure at a number of pressures, and the results demonstrate the connection between a relatively weak value of C_{44} and the thermodynamic stability of the CsCl lattice. Hyde and O'Keefe [1973] used a similar model to study some aspects of this transition, but they did not discuss C_{44} , and limited their calculation to zero pressure.



$$\eta_{ij} = \begin{bmatrix} 0 & -\eta & -\eta \\ -\eta & 0 & -\eta \\ -\eta & -\eta & 0 \end{bmatrix}$$

Fig. 1. Transformation from the NaCl to the CsCl lattice by a shear deformation.

In our model calculation, we ignored thermal effects and assumed that the energy of the lattice is given by the expression

$$F = \frac{z^2 e^2 A_r}{r} + \sum_{i=1}^8 \frac{b}{r_i^n} \quad (1)$$

where r_i is the interatomic distance, r is the nearest neighbor distance, and $z^2 e^2$, b , and n are constants. Summation is over the six nearest-neighbor interactions of the NaCl lattice and the two additional interactions that become nearest neighbors in the CsCl lattice.

The Madelung constant A_r , which gives the sum of all the electrostatic interactions, was calculated by the Ewald method [Born and Huang, 1954, p. 385] for each value of the reaction coordinate, η . By differentiation of equation (1), expressions for the pressure, P , and the bulk modulus, K , are obtained. It is most useful to write the relevant expressions in dimensionless form

$$\frac{F^*}{K V_0} = \frac{9}{n-1} \left[-\frac{r_0}{r^*} + \frac{1}{N} \left(\frac{r_0^*}{r_0} \right)^{n-1} \left(\frac{r_0}{r^*} \right)^n \right] \frac{A_r^*}{A_r} \quad (2)$$

$$\left(\frac{r_0^*}{r_0} \right)^{n-1} = \left(\frac{6 + 2 \left(\frac{r^*}{r_2^*} \right)^n}{6 + 2 \left(\frac{r}{r_2} \right)^n} \right) \frac{A_r}{A_r^*} \quad (3)$$

$$\frac{V_0^*}{V_0} = \left(\frac{r_0^*}{r_0} \right)^3 \frac{\beta^*}{\beta} \quad (4)$$

$$\frac{V^*}{V_0^*} = \left(\frac{r^*}{r_0} \right)^3 \left(\frac{r_0}{r_0^*} \right)^3 \quad (5)$$

$$\frac{K}{K_0} = \frac{1}{n-1} \left(\frac{V_0}{V} \right) \left[-4 \left(\frac{r_0}{r} \right) + (n+3) \left(\frac{r_0}{r} \right)^n \right] \quad (6)$$

where V is the volume and the subscript o refers to zero pressure. Quantities without an asterisk refer to the NaCl lattice, while quantities with an asterisk refer to the deformed lattice. For this deformation, the packing ratio, β is given by $\beta = 2 - 6\eta^2 - 4\eta^3$, and the next nearest neighbor distance, $r_2 = r(3-6\eta)/(3+6\eta^2)$, where η is the reaction coordinate or shear strain defined in Figure 1. We calculated the Gibbs free energy from

$$\frac{G^*}{K_o V_o} = \frac{F^*}{K_o V_o} + (P/K_o) \frac{V^*}{V_o} \quad (7)$$

at several reduced pressures for structures in the series NaCl \rightarrow CsCl. For the present calculation, we set the adjustable parameter $n = 11$. For each value of η and P/K_o , V^* was adjusted to obtain the minimum value for G^* .

The results are plotted in Figure 2 in the form $\Delta G/KV$. The vertical displacement of each curve is arbitrary. Symmetry requires that the slope of the free energy curve be zero at $\eta = 0$ and $\eta = 0.2$, while the curvature at $\eta = 0$ is related to the

elastic constants in the NaCl lattice $\left(\frac{1}{KV} \frac{\partial^2 \Delta G}{\partial \eta^2} = 6 \frac{C_{44}}{K} \right)$. This

curvature is extrapolated by a dashed line in Figure 1, and the dashed line is a good approximation to the solid curve up to $\eta \approx 0.1$. A large part of the free energy difference between the two phases can be accounted for by this extrapolation. For $P/K_o = 0$, $C_{44}/K = 0.40$, and there is a relatively large free energy difference. (C_{44}/K was calculated using equation (6) and equation A6 of Anderson and Demarest, 1971.) For $P/K_o = 0.2$, $C_{44}/K = 0.20$, and the free energy difference is quite small. At about $P/K_o = 0.3$ and $C_{44}/K = 0.06$, the free energies of the two phases are equal, and the phase transformation takes place. C_{44} does not vanish until a much higher pressure, $P/K_o \approx 0.48$.

Figure 2 shows that for this model, $C_{44}/K \approx 0.06$ at the transition. We expect that changes in the interatomic forces from this simple model to real crystals will affect both C_{44}/K and ΔG in a similar manner, preserving the result of a finite C_{44}/K at the transition.

There are at least two arguments which suggest that, for all transitions involving a finite displacement, C_t/K will not reach zero at the transition, where C_t is any shear constant.

1. There will always be a free energy barrier between the two stable phases at the transition. This corresponds to a hill on the curve of ΔG versus η (Figure 2). (If there were a valley, this would correspond to a more stable phase.) Since the extrapolation of ΔG based on C_t (the dashed line in Figure 1) will conform closely with the ΔG curve, at least initially, C_t will be

positive. We expect that the size of the energy barrier and hence the value of C_t/K at the transition will be similar for similar compounds undergoing the same transition.

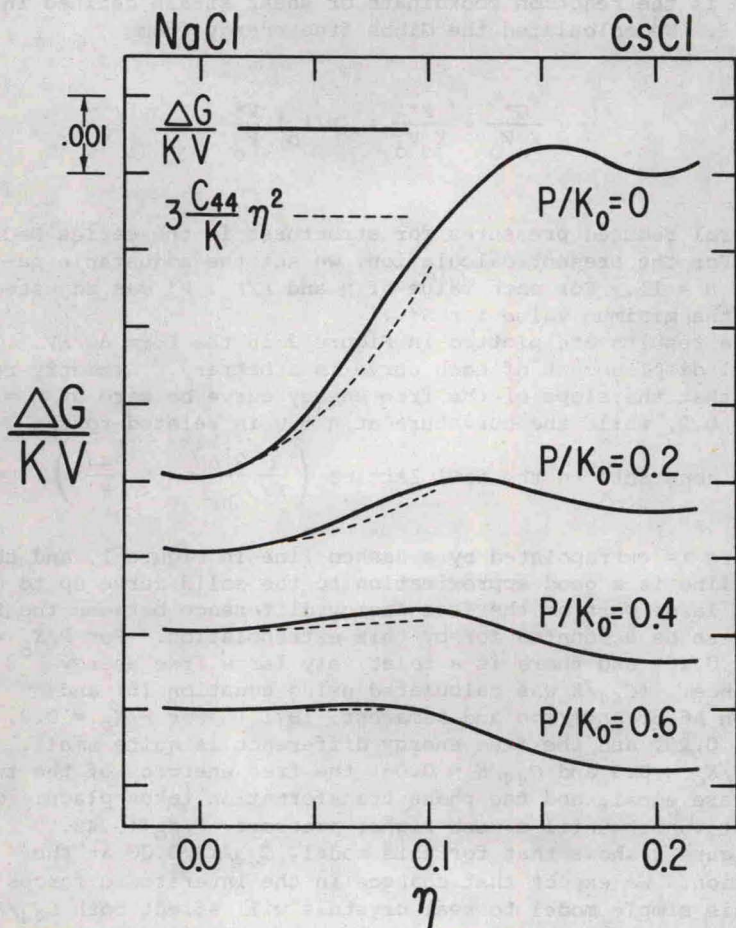


Fig. 2. Free energy change of a model crystal as it transforms from the NaCl to the CsCl structure.

2. If $C_t = 0$ at the transition, there are three stable phases all having the same free energy (the two phases in question, and a shear distortion of the low-pressure phase). This is in violation of the Gibbs phase rule, since we are not including temperature in our analysis.

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 \rightarrow 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

$$\alpha(P) = \alpha_0 (1 - 2P/K) \quad (8)$$

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

$$\alpha(P) = \alpha_0 \frac{1 + (K' - 2)P/K_0}{1 + K' P/K_0} \quad (9)$$

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

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

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

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

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

(P_{th} , K_{th} , etc.) approach negative infinity. While a negative value of the bulk modulus is forbidden by the Born stability criterion, it is possible that there will be a sudden decrease in the bulk modulus and some of the other elastic constants as an immediate precursor to a phase transition. This sort of precursor has been observed in calcite [Matsushima et al., 1975], but in most cases we expect that the phase transition will take place before this sort of thermal precursor can occur.

III. EXPERIMENTAL ELASTIC CONSTANTS OF KCl AT THE PHASE TRANSITION

We wanted to test our theories about the behavior of the elastic constants in the vicinity of a phase transition. KCl is an ideal candidate for this type of test since it has the well-studied NaCl structure and undergoes a phase transition to the CsCl structure at 19.3 kbar [Vaidya and Kennedy, 1971]. This is within the range of our experiment for the measurement of sound velocities under high hydrostatic pressures.

A. Experimental Technique

A technique similar to that described by Jayaraman and Maines [1971] was used to generate a hydrostatic environment. This involved a conventional piston cylinder device with a Teflon cell, which contains the sample and the pressure transmitting fluid (a 50/50 mixture of isoamylalcohol and isopentane). The sample was held in a special holder, and the wires from the transducer went out through alumina thermocouple tubing. Further details of the experimental method will be given in a forthcoming paper by Ota and Anderson.

Since we were unable to fit a manganin coil and our sample holder into the teflon cell at the same time and still allow enough room for the compression of the pressure fluid, we determined the pressure in the cell from the oil pressure driving the piston. The relationship between oil pressure and cell pressure was calibrated by placing a manganin coil and a Bismuth wire in the Teflon cell and by assuming that the resistance change in the manganin coil was linear up to the Bi I-II transition at 25.4 kbar. The effect of friction was about 5% of the total pressure.

A large KCl single crystal was purchased from the Harshaw Chemical Company, and from it were obtained two cubic samples, about 4 mm on a side, with faces oriented to within 0.6 degrees of the (100) and (110) directions. 20 Mhz P- or S- transducers were mounted to the samples with silver paint, and the travel times for P and S waves were measured by the method of pulse superposition, with a single transducer being used both to transmit and to receive the reflected pulse.

B. Results

The pulse repetition frequency was measured at zero pressure and as a function of pressure from 0 to 20 kbar for the two longitudinal and two shear waves described in Table 1. This provided enough information for the determination of the three independent elastic constants, with one redundant measurement for a check on our accuracy. Over the entire range, the consistency of our data was excellent.

TABLE 1. Velocities Used for Elastic Constant Determination

Mode	P	S	P	S
Propagation direction	(100)	(100)	(110)	(110)
Polarization direction	(100)	(010)	(110)	($\bar{1}\bar{1}0$)
ρv^2	C_{11}	C_{44}	$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	$\frac{1}{2}(C_{11} - C_{12})$

In Table 2, we compare our zero pressure elastic constants with those of other experimenters. The agreement with *Dobretsov* and *Peresada* [1969] is extremely good, while the agreement with the less recent work [*Lazarus*, 1949; *Haussuhl*, 1960; *Bartels* and *Schuele*, 1965; *Drabble* and *Strathen*, 1967] is only modestly good, with a two percent disagreement in the bulk modulus.

Our data for pulse repetition frequency as a function of pressure were converted to elastic constants as a function of pressure by *Cook's* method [1957]. In this analysis, we assumed $\beta = 110.4 \cdot 10^{-6} \text{ deg}^{-1}$, and $C_p = 12.23 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The normalized elastic constants $C(P)/C(0)$ are plotted in Figures 3 and 4 from zero to 20 kbar, and are tabulated in Table 3. Our results are remarkably linear. There is no indication of any strange behavior for either C_{44} or K in the neighborhood of the transition. The value of C_{44}/K at the transition is 0.205, a value in good agreement with the modified Born criterion.

There is no evidence of a slight decrease of a K at the transition, which might be expected if one of the normal mode frequencies were approaching zero at or very near to the transition pressure. We can calculate the mode Grüneisen parameter, γ_i , for the mode associated with any elastic modulus

C_i by the formula $\gamma_i = -\frac{1}{6} + \frac{1}{2} \frac{K_T}{C_i} \frac{dC_i}{dP}$ [*Schuele* and *Smith*, 1964].

According to our measurements γ_{44} decreases from -0.58 at zero pressure to -1.21 at 20 kbar. Apparently this decrease is not enough to cause a measurable effect on the thermal contribution to P or K .

TABLE 2. Comparison of Elastic Constants of KCl at Zero Pressure, kbar

	C_{11}	C_{12}	C_{44}	C_S	K_S
Present study	405.6	65.5	63.3	170.1	178.9
Dobretsov and Peresada [1969]	406.2	65.4	63.9	170.4	179.0
Drabble and Strathen [1967]	409.0	70.4	62.7	169.3	183.3
Bartels and Schuele [1965]	405.0	69.8	63.0	167.6	181.5
Hausuhl [1960]	407.8	69.0	63.3	169.4	181.9
Lazarus [1949]	409.5	70.6	63.0	169.4	183.6

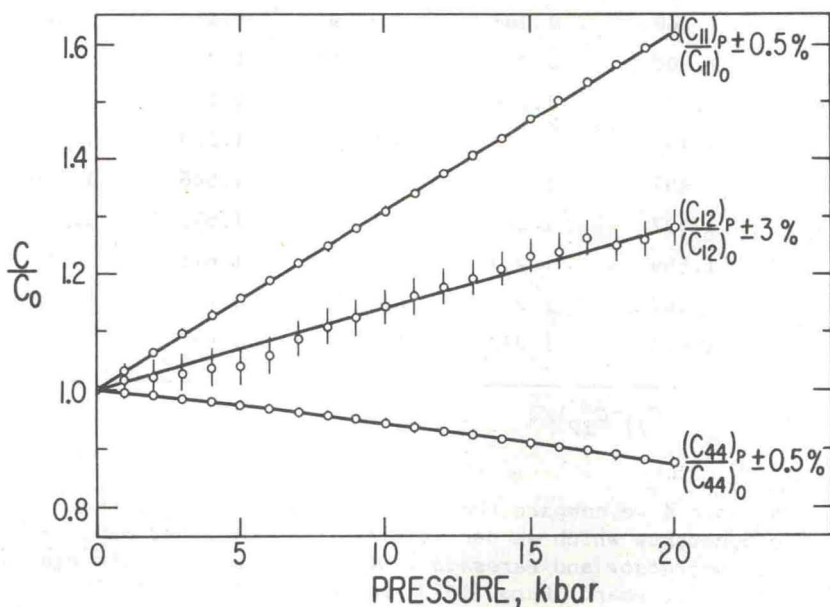


Fig. 3. Variation of elastic constants C/C_0 with pressure for KCl single crystal.

TABLE 3. Elastic Constants and Adiabatic Bulk Modulus of KCl Single-Crystal as a Function of Pressure

P, kbar	Elastic Constant				Bulk Modulus
	$C_{11}/C_{11}^{(0)}$	$C_{12}/C_{12}^{(0)}$	$C_{44}/C_{44}^{(0)}$	$C_s/C_s^{(0)}$ ^a	$K_s/K_s^{(0)}$
0	1.000	1.000	1.0000	1.000	1.000
1	1.031	1.014	0.9944	1.034	1.027
2	1.061	1.028	0.9889	1.067	1.053
3	1.094	1.035	0.9829	1.105	1.081
4	1.123	1.047	0.9771	1.138	1.106
5	1.151	1.049	0.9714	1.171	1.131
6	1.183	1.068	0.9651	1.205	1.158
7	1.216	1.094	0.9593	1.239	1.187
8	1.247	1.116	0.9530	1.272	1.214
9	1.276	1.129	0.9466	1.304	1.239
10	1.309	1.155	0.9398	1.338	1.267
11	1.337	1.169	0.9328	1.369	1.292
12	1.368	1.185	0.9259	1.403	1.319
13	1.400	1.207	0.9196	1.437	1.346
14	1.433	1.216	0.9127	1.475	1.375
15	1.465	1.234	0.9060	1.509	1.403
16	1.497	1.242	0.8991	1.546	1.430
17	1.527	1.263	0.8922	1.578	1.455
18	1.559	1.237	0.8853	1.621	1.483
19	1.587	1.255	0.8782	1.651	1.508
20	1.614	1.273	0.8712	1.680	1.532

$$a. C_s = (C_{11} - C_{12})/2$$

In Table 4 we compare the pressure derivatives of the elastic constants which we derive with those of other experimenters. *Dobretsov and Peresada* [1969] also measured the elastic constants to 20 kbar. *Wang* [1973] measured only C_{44} to 20 kbar. The other measurements were limited to lower pressures. Our pressure derivatives measure the average change from 0 to 20 kbar, while the others measure the average change at a much lower

pressure. We list the data of *Dobretsov* and *Peresada* in two ways: the average change over the whole pressure range, and the initial slope of their quadratic fit. Some of the discrepancies may arise because of the different range of pressures involved. While none of the pressure derivatives that we measure directly differ from the results of *Bartels* and *Schuele* by more than a few percent, these discrepancies combine to yield a 10% disagreement in dK_S/dP ; however, our dK_S/dP is in excellent agreement with that of *Dobretsov* and *Peresada*.

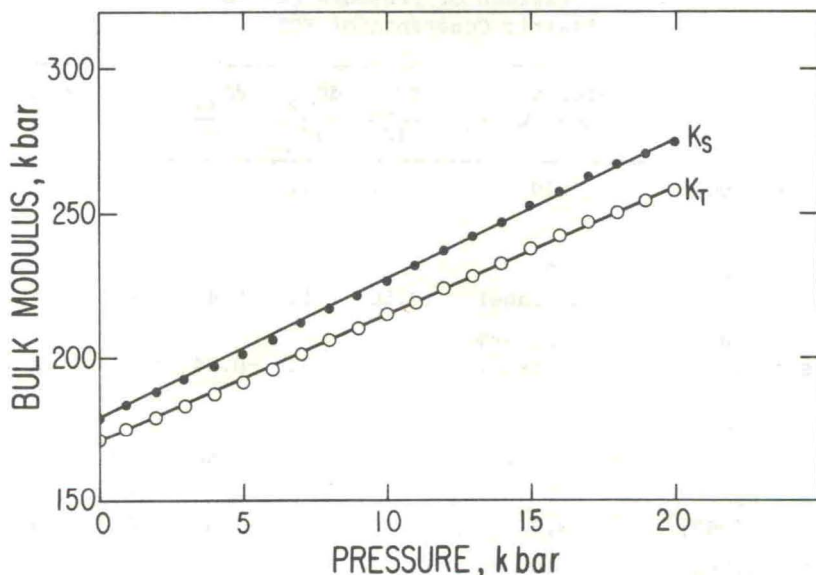


Fig. 4. Variation of adiabatic and isothermal bulk moduli, K_S , K_T , with pressure for KCl single crystal.

There is only a small amount of data from other compounds relating to the problem of the behavior of shear constants at a phase transition. *Reddy* and *Ruoff* [1965] showed that the elastic constants of RbBr are linear right up to the transition pressure at 4.5 kbar. Recent advances in the measurements of velocities in polycrystalline aggregates to pressure on the order of 100 kbar or more [*Voronov* and *Grigor'ev*, 1969; *Morris*, et al., 1976; *Frankel*, *Rich*, and *Homan*, unpublished] are able to provide useful information on the average sound velocities at high pressure. *Voronov* and *Grigor'ev* showed that the average shear velocity in AgCl decreased with pressure prior to the transition, which implies

that at least one of the single-crystal shear moduli (C_{44}) decreases toward the transition, but does not provide the much desired measurement of α . Frankel, et al., report sound velocities in polycrystalline NaCl to 27 GPa, just short of the transition, and they show a slight decrease of v_s leading up to the transition. Their data appear to be consistent with a model calculation [Demarest, 1972a] that predicted $C_{44}/K = 0.14$ at the transition.

TABLE 4. Comparison of Pressure Derivatives of Elastic Constants of KCl

	Pressure Range, kbar	$\frac{dC_{11}}{dP}$	$\frac{dC_{12}}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{dC_s}{dP}$	$\frac{dK_s}{dP}$
Present study	20	12.51	0.91	-0.41	5.80	4.78
Wang [1973]	20	-	-	-0.40	-	-
Dobretsov and Peresada [1969]	20 (average)	12.56	1.14	-0.43	5.14	4.81
Dobretsov and Peresada [1969]	linear term of quadratic fit	13.23	0.82	-0.34	5.80	5.12
Drabble and Strathen [1967]	0.004	13.00	1.56	-0.56	5.72	5.37
Bartels and Schuele [1965]	03.3	12.82	1.60	-0.39	5.61	5.34
Lazarus [1949]	10	12.21	1.09	-0.47	5.56	4.80

IV. EVALUATION, PREDICTIONS, AND CONCLUSIONS

The Born criterion for a phase transition has often been used to predict a transition at the pressure at which a shear constant vanishes. This is only the upper limit for a transition pressure, however, and any reasonably intelligent method of selecting a pressure somewhere between zero and the Born transition pressure would give more accurate predictions. On the basis of our earlier discussion, we believe that the best prediction of a phase transition which we can base on elastic constant data arises from the assumption that a transition will occur when C_t/K reaches a critical value α .

Table 5 displays some selected data relating to the value of α at a transition. We have grouped compounds with the same crystal structure together, and for each compound we either compute the "measured" value of α (usually by extrapolating the

elastic constants from low pressure), or we estimate a range of possible values for α and compute the transition pressure, again using extrapolations of the elastic constants. In all cases, the extrapolations were based on the measured pressure derivatives of the elastic constants. For the NaCl-type alkali-halides, we used a NNN lattice model extrapolation formula [Demarest, 1972a], while in all other cases we assumed that the elastic constants are linear with pressure. We conclude from earlier calculations [Demarest, 1972b] that this type of extrapolation is adequate for the present purposes up to reduced pressures of $P/K_0 \approx 0.5$.

TABLE 5. Evaluations of α and predictions of Phase Transition

Compound	Structure	Soft Shear Mode	Transition Pressure, kbar		α	
			Predicted	Experiment	Assumed	Measured
NaF	NaCl-CsCl	C_{44}		~300		0.14
NaCl				290		0.14
NaBr			>120		<0.20	
NaI			-		<0.20	
KF				17.3		0.26
KCl				19.3		0.20
KBr				17.4		0.19
KI				17.8		0.16
RbF				9.4		0.13
RbCl				5.2		0.22
RbBr				4.5		0.21
RbI				3.4		0.19
HgO	NaCl-CsCl	C_{44}	-		<0.26	
CaO			275-400		0.15-0.20	
SrO			1000-2200		0.15-0.20	
AgCl	NaCl-HgS	C_{44}		76		0.06
AgBr	NaCl-HgS			82		0.05
AgI	NaCl+tetragonal			97		-
Si	Diamond+white Sn	C_S^*		110		0.36
Ge				90		0.37
Diamond				-		-
CaF ₂	Fluorite+PbCl ₂	C_S		80		0.54
BaF ₂				20		0.36
CdS	Wurtzite+NaCl	C_{44}		25		0.18
ZnS	Wurtzite+Sphalerite	C_{66}		45		(0.29)
	+NaCl	C_{44}		117		0.18
TiO ₂	Rutile+Dist. Fluorite	C_S		50		0.16
SnO ₂			30-90		0.14-0.18	
GeO ₂			150-250		0.14-0.18	
SiO ₂	α Quartz+coesite	$\frac{1}{2}\lambda_2^*$		20		0.59
	α Quartz+stishovite	$\frac{1}{2}\lambda_2$		85		0.25
HgAl ₂ O ₄	Spinel*	C_S	300-700		0.15-0.20	
HgO·2.6Al ₂ O ₃	Spinel*		1000-2000		0.15-0.20	

$$*C_S = \frac{1}{2}(C_{11} - C_{12})$$

$$\lambda_2 = C_S + C_{44} - \sqrt{(C_S - C_{44})^2 + 4C_{14}^2}$$

Estimates of α for the NaCl→CsCl transition in the alkali-halides range from 0.13 (RbF) to 0.26 (KF). Most of the data seems to be centered in the range 0.15-0.20. The seven alkali halides for which no transition has been found will probably not transform to the CsCl structure. NaBr may transform above 120 kbar, but this is not clear since C_{44}/K never dips much below 0.20. MgO will probably not have a transformation of this type. SrO may transform to the CsCl structure at extreme pressures, and we think that CaO will probably transform between 270 and 400 kbar.

The silver halides transform to the cinnabar (HgS) structure with $\alpha \cong 0.05$. This transformation is not a pure shear, but it does involve a smaller shift of atom positions than does the NaCl-CsCl transition.

The metallic transitions in Si and Ge are among those which we do not expect to conform well with our theory, because of the change in electronic structure. Here $\alpha = 0.36$. There is no prediction of diamond going through this transition at high pressure. Our theory also fails to predict the high pressure transition in the fluorite structure.

The wurtzite → NaCl transition in CdS and ZnS is in perfect agreement with this theory ($\alpha = 0.18$). We neglect the complication of the sphalerite structure, which for ZnS is stable in an intermediate pressure range, depending upon the temperature and stoichiometry.

The transformation of rutile to distorted fluorite is in excellent agreement ($\alpha = 0.16$). We predict transitions in the range 30-90 kbar for SnO₂ and 150-250 kbar for GeO₂.

Our method fails to predict the α -quartz → Coesite transition. However even in this case, our method shows its usefulness. The Born criterion predicts a lattice instability at 180 kbar, while the modified Born criterion predicts the transition at 95-115 kbar. This is not too far from the transition to Stishovite at 85 kbar.

We have deliberately omitted from Table 5 elements or compounds for which all the shear moduli increase rapidly with pressure. We have selected an assortment of crystal structures for which there was sufficient readily available data to make a test of the modified Born criterion.

Table 5 confirms our theories concerning the interrelationship of pressure-induced phase changes and weak shear constants. Values of α tend to be similar for a particular transformation. In no case is α very small, and the smallest value here is 0.05. The modified Born criterion does not work when the transformation involves a change in the electronic structure of the compound, or when the transformation is in no way related to a shear (these cases were not included in the table). However, in many cases this method will permit good estimates of phase transition pressures with very little effort.

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