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Extrapolation of Elastic Properties to High Pressure in the Alkali Halides[1]

HAROLD H. DEMAREST, JR.[2]

Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York 10964

A central force model incorporating an electrostatic term, a Born-Mayer nearest-neighbor repulsion, and a Lennard-Jones 6–12 potential between anions is used to derive equations for the elastic constants. The measured elastic constants and pressure derivatives are used to evaluate the model parameters. The force between anions is stronger than the force experimentally determined for the isoelectronic inert gases and depends on the cation as well as the anion. The shear elastic constant C_{44} is predicted up to high pressure and is used to predict a phase transition in KF between 70 and 95 kb and in NaF between 300 and 450 kb.

The ability to extrapolate experimental data on the elastic properties of rocks and minerals from low temperatures and pressures to the high-pressure and high-temperature conditions of the mantle is of fundamental importance to anyone who wishes to discuss the composition of the earth's interior. Either finite strain theory [*Thomsen,* 1970, 1971] or lattice dynamical calculations can be used to make these extrapolations, as well as to gain insight into the zero-pressure elastic constants and their pressure derivatives.

Although much work has been done on lattice dynamics in recent years, zero pressure is assumed in many cases. This assumption makes direct application to high-pressure geophysics difficult. *Anderson and Liebermann* [1970] first showed how important lattice dynamical calculations could be to geophysics. In this and later papers [*Anderson,* 1970; *Anderson and Demarest,* 1971], it was shown that a simple lattice model employing only electrostatic and nearest-neighbor (NN) interactions can explain the variation of shear behavior between different simple cubic lattices and can be used to extrapolate the elastic constants to high pressure. *Sammis* [1970] showed that forces between next-nearest-neighbor (NNN) anions in the NaCl lattice play an important part in the pressure derivative of the shear elastic constant C_{44} and help explain its variation in different compounds having this structure. These forces are undoubtedly of great significance in most materials of geological importance, where oxygen-oxygen interactions can account for a large fraction of interatomic forces.

In the next two sections, a central force model with NNN interactions is proposed for the NaCl lattice, and the equations for the elastic constants are given. The arbitrary parameters are determined from the measured elastics constant data of 12 alkali halides. In the final section, the model is used to predict the elastic constants up to high pressure for these 12 compounds. The phase transition to the CsCl structure observed in many of these crystals at high pressure is discussed in terms of the macroscopic lattice instability that occurs when C_{44} is zero.

CENTRAL FORCE MODEL FOR NaCl LATTICE

The alkali halides with the NaCl lattice are among the simplest compounds from the standpoint of lattice dynamics. They are highly ionic, and, since all ions are on a center of symmetry, the polarizability of ions will have no effect on the elastic properties. Moreover, the deviation of these compounds from the Cauchy relation for central forces, $C_{12} - C_{44} = 2P$, is relatively small; thus it is indicated that the noncentral component of force from many-body interactions does not have a strong influence on the elastic constants. The central force next-nearest-

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[1] Lamont-Doherty Geological Observatory contribution 1757.

[2] Now at the Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024.

neighbor (NNN) model is therefore probably a fairly good approximation for the NaCl-type alkali halides, but it is probably not applicable to MgO, AgBr, or AgCl, whose elastic constants deviate widely from the Cauchy relation.

The energy per ion pair according to this model is given as

$$\Phi = \sum_{j=1}^{\infty} \pm \frac{Z^2e^2}{r_j} + \sum_{j=1}^{6} be^{-r_j/\rho} + \tfrac{1}{2} \sum_{j=1}^{12} \epsilon_0 \left[\left(\frac{r_m}{r_j}\right)^{12} - 2\left(\frac{r_m}{r_j}\right)^{6} \right] \tag{1}$$

The first term is the electrostatic energy summed over all ions in the lattice, Z being the effective ionicity and e the electronic charge. The second term, the nearest-neighbor overlap term, is summed over the six nearest neighbors and includes two arbitrary parameters: ρ, which controls the size of this potential well, and b, which controls its strength. The third term, a Lennard-Jones 6–12 potential, also has two arbitrary parameters: r_m, the separation at the potential minimum, and ϵ_0, the interaction energy at this separation.

The procedure for deriving equations for the pressure and the effective elastic constants from an energy equation like (1) is well known and straightforward. The following equations are derived in the appendix:

$$\begin{aligned}\tilde{P} = \frac{1}{2{r_0}^3} \Big\{ & -0.58252 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & + 2b \frac{r_0}{\rho} \left(\frac{r_0}{r}\right)^2 e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[48\left(\frac{r_m}{r'}\right)^{15} - 48\left(\frac{r_m}{r'}\right)^{9} \right] \Big\}\end{aligned} \tag{2}$$

$$\begin{aligned}\tilde{K} = \frac{1}{2{r_0}^3} \Big\{ & -0.77669 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & + \tfrac{2}{3} b \frac{r_0}{\rho} \left[2\left(\frac{r_0}{r}\right)^2 + \frac{r_0}{\rho}\frac{r_0}{r} \right] e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[240\left(\frac{r_m}{r'}\right)^{15} - 144\left(\frac{r_m}{r'}\right)^{9} \right] \Big\}\end{aligned} \tag{3}$$

$$\begin{aligned}\tilde{C}_{44} = \frac{1}{2{r_0}^3} \Big\{ & 1.27802 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & - 2b \frac{r_0}{\rho} \left(\frac{r_0}{r}\right)^2 e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[120\left(\frac{r_m}{r'}\right)^{15} - 48\left(\frac{r_m}{r'}\right)^{9} \right] \Big\}\end{aligned} \tag{4}$$

$$\begin{aligned}\tilde{C}_s = \frac{1}{2{r_0}^3} \Big\{ & -1.22153 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & + b \frac{r_0}{\rho} \left[\frac{r_0}{\rho}\frac{r_0}{r} - \left(\frac{r_0}{r}\right)^2 \right] e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[36\left(\frac{r_m}{r'}\right)^{15} \right] \Big\}\end{aligned} \tag{5}$$

$$\begin{aligned}\tilde{K}' = \frac{1}{6K{r_0}^3} \Big\{ & -3.1068 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & + \tfrac{2}{3} b \frac{r_0}{\rho} \left[4\left(\frac{r_0}{r}\right)^2 + 3\frac{r_0}{\rho}\frac{r_0}{r} + \left(\frac{r_0}{\rho}\right)^2 \right] e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[3600\left(\frac{r_m}{r'}\right)^{15} - 1296\left(\frac{r_m}{r'}\right)^{9} \right] \Big\}\end{aligned} \tag{6}$$

$$\begin{aligned}\tilde{C}_{44}' = \frac{1}{6K{r_0}^3} \Big\{ & 5.1121 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & - 2b \frac{r_0}{\rho} \left[2\left(\frac{r_0}{r}\right)^2 + \frac{r_0}{\rho}\frac{r_0}{r} \right] e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[1800\left(\frac{r_m}{r'}\right)^{15} - 432\left(\frac{r_m}{r'}\right)^{9} \right] \Big\}\end{aligned} \tag{7}$$

$$\begin{aligned}\tilde{C}_s' = \frac{1}{6K{r_0}^3} \Big\{ & 4.8861 \frac{Z^2e^2}{r_0} \left(\frac{r_0}{r}\right)^4 \\ & + b \frac{r_0}{\rho} \left[\left(\frac{r_0}{\rho}\right)^2 - 2\left(\frac{r_0}{r}\right)^2 \right] e^{-r/\rho} \\ & + (2)^{1/2} \epsilon_0 \left(\frac{r_0}{r_m}\right)^3 \left[540\left(\frac{r_m}{r'}\right)^{15} \right] \Big\}\end{aligned} \tag{8}$$

Here P is the pressure, K is the bulk modulus, and C_{44} and C_s, both equal to ½ $(C_{11} - C_{12})$, are the two shear moduli. The prime denotes the pressure derivatives, and the tilde indicates that these equations give the elastic constants of a static lattice in which thermal vibrations are absent. The thermal contributions to the elastic constants are relatively small and can be estimated. The thermal effect on the pressure and isothermal bulk modulus can be approximated by the Mie-Grüneisen equation of state and its volume derivative at constant temperature [*Tosi*, 1964]:

$$P = \tilde{P} + \frac{W_V}{C_V} \beta K^T \tag{9}$$

$$\begin{aligned}K^T = \tilde{K} + \frac{W_V}{C_V} \left(\frac{dK^T}{dT}\right)_V + V\left(\frac{K^T\beta}{C_V}\right)^2 \\ \cdot \left[TC_V - W_V - T\frac{W_V}{C_V}\left(\frac{dC_V}{dT}\right)_V \right]\end{aligned} \tag{10}$$

where β is the volume coefficient of thermal expansion. W_V and C_V, the vibrational energy and heat capacity, respectively, are estimated from the assumption of a Debye solid.

A consistent correction to the shear elastic constants gives

$$C_{44} = \tilde{C}_{44} + \frac{W_V}{C_V}\left(\frac{dC_{44}}{dT}\right)_V \qquad (11)$$

$$C_s = \tilde{C}_s + \frac{W_V}{C_V}\left(\frac{dC_s}{dT}\right)_V \qquad (12)$$

The variation of the thermal corrections to the elastic constants with volume will be ignored.

DETERMINING ARBITRARY PARAMETERS

Equations 2–5 and 9–12 allow the prediction of the elastic properties under any combination of pressure and temperature. There are five arbitrary parameters for the static lattice: Z, b, ρ, ϵ_0, and r_m, plus the measured values involved in the thermal corrections.

People working with this type of lattice model have often made unnecessary assumptions about the values of these parameters and then compared the resulting elastic constants and pressure derivatives with experimental results. *Sammis* [1970] assumed that the NaCl lattice had an ionicity of 100% and that the anion-anion interaction had the same Born-Mayer force constants as the anion-cation interaction. In a more sophisticated model, similar to the one described in this paper, *Sammis* [1971] assumed that the force constants for the anion-anion interaction were the same as those for the isoelectronic inert gases. *Weidner and Simmons* [1972] assumed that the anion-anion interaction was independent of the cation and a continuous function of the separation, although they made no assumption about the functional form of this function.

For many compounds, and particularly for the alkali halides, the experimentally measured pressure derivatives of the elastic constants are known to a much higher degree of certainty than the form of the interatomic potential and its parameters. When information on the pressure derivatives is available, it should be used to evaluate the parameters in the potential. This procedure allows the most accurate extrapolation of elastic properties to high pressure.

Because this model satisfies the Cauchy relation, there are only two independent elastic constants. The arbitrary parameters were determined by fitting the equations for the pressure, K and C_{44}, and their pressure derivatives (equations 2, 3, 4, 6, and 7). Thus five nonlinear equations in five unknowns had to be solved. In practice, four of the five parameters were linearized; thus the computer solutions were quicker to make, and each part of the Lennard-Jones potential was allowed to be either attractive or repulsive.

The room-temperature experimental data for

TABLE 1. Basic Data for the Alkali Halides at 295°K

Compound	β, 10^{-4} deg^{-1}	r_0, 10^{-8} cm	W_V/TC_V	K^T, kb	C_s, kb	C_{44}, kb
NaF	0.96	2.317	0.59	465	314	281
NaCl	1.19	2.820	0.70	240	182	126
NaBr	1.26	2.989	0.77	199	146	99
NaI	1.37	3.236	0.83	151	108	74
KF	1.02	2.674	0.70	305	255	125
KCl	1.11	3.146	0.76	175	168	63
KBr	1.16	3.300	0.82	148	143	50
KI	1.23	3.533	0.85	117	116	37
RbF	0.94	2.826	0.77	267	206	92.5
RbCl	1.03	3.291	0.82	156	151	46.5
RbBr	1.08	3.445	0.85	132	133	38
RbI	1.23	3.671	0.88	105	111	27.8

TABLE 2. Temperature and Pressure Derivatives of Elastic Constants for the Alkali Halides

	$(\partial/\partial T)_V$, 10^{-3} kb/deg			$(\partial/\partial P)_T$		
Compound	K^T	C_{44}	C_s	K^T	C_{44}	C_s
NaF	-23	-50	-117	5.25	0.205	4.79
NaCl	-14	-24	-64	5.38	0.37	4.79
NaBr	-20	-8	-53	5.44	0.46	4.83
NaI	-18	-4	-45	5.58	0.61	4.80
KF	-27	-39	-92	5.38	-0.43	5.25
KCl	-16	-21	-77	5.46	-0.392	5.61
KBr	-7	-18	-69	5.47	-0.328	5.68
KI	-4	-11	-58	5.56	-0.244	6.03
RbF	-27	-35	-97	5.69	-0.70	4.93
RbCl	-19	-20	-79	5.62	-0.56	5.88
RbBr	-15	-17	-67	5.59	-0.55	6.03
RbI	-13	-12	-55	5.60	-0.51	6.26

12 alkali halides were taken primarily from *Roberts and Smith* [1970*a*, *b*] and are more accurate in many cases than the values compiled by *Barsch and Chang* [1967]. Some of the data on the shear constants were taken from *Haussühl* [1960], who was also used by Roberts and Smith as a source of some of their data. The volume coefficient of thermal expansion, the thermal factor W_V/TC_V, the nearest-neighbor distance r_0, and the measured elastic constants are given in Table 1. Table 2 gives the pressure derivatives and the constant volume-temperature derivatives; Table 3 gives the derived $\tilde{C}_{ij}$.

One way to test this model is to compare the five model parameters with the values that we might expect from physical intuition. The model parameters are given in Table 4. The effective ionicity Z varies from 103% for RbI to 87% for NaF, decreasing as r_0 decreases. This range is what we should expect if an effective decrease of Z below unity results from a deformation of the ions from spherical symmetry.

The parameters for the Lennard-Jones NNN potential are plotted in Figures 1 and 2. The program for fitting the parameters permitted each part of the potential to be either attractive or repulsive. The expected result of an attractive $1/r^6$ force and repulsive $1/r^{12}$ force was obtained for all compounds except NaF, for which both forces were attractive, and RbF, for which both forces were repulsive. Since the NNN contribution in these two compounds is small enough to be influenced by errors in the elastic constants, this discrepancy is not serious. The general form of the Lennard-Jones potential for next-nearest neighbors is confirmed by the fact that both the equilibrium distance r_0 and the potential energy at this distance ϵ_0 increase with anion size for the sodium, potassium, and rubidium halides. The equilibrium distance r_m appears to be unaffected by the cation and is fairly close to the experimental

TABLE 3. Pressure and Elastic Constants of Static Lattice (All values in kilobars.)

Compound	$\tilde{P}$	$\tilde{K}$	$\tilde{C}_s$	$\tilde{C}_{44}$
NaF	-7.8	463	334	290
NaCl	-5.9	239	195	131
NaBr	-5.7	201	158	101
NaI	-5.0	153	119	77
KF	-6.4	307	274	133
KCl	-4.4	176	185	68
KBr	-4.1	148	160	54
KI	-3.6	117	131	40
RbF	-5.9	280	228	100
RbCl	-4.0	165	170	51
RbBr	-3.7	141	150	42
RbI	-3.5	113	125	31

TABLE 4. Model Parameters for the Alkali Halides

Compound	Z	b, 10^{-10} erg/bond	r_0, 10^{-8} cm	ρ, 10^{-8} cm	r_0/ρ	r_m, 10^{-8} cm	ε_0, 10^{-16} erg/bond
NaF	0.87	68.3	2.317	0.218	10.6	(2.99)	(311)
NaCl	0.91	29.8	2.820	0.293	9.6	3.89	442
NaBr	0.95	17.9	2.989	0.336	8.9	3.93	1073
NaI	0.97	13.0	3.236	0.379	8.5	4.22	1473
KF	0.92	84.8	2.674	0.251	10.7	3.16	457
KCl	0.95	59.4	3.146	0.306	10.3	3.78	1119
KBr	0.96	49.3	3.300	0.328	10.1	4.00	1388
KI	0.96	43.6	3.533	0.355	9.9	4.33	1674
RbF	0.94	194.0	2.826	0.245	11.5	(2.20)	(-6166)
RbCl	0.98	73.0	3.291	0.316	10.4	3.83	1973
RbBr	1.00	57.2	3.445	0.341	10.1	4.02	2269
RbI	1.03	41.4	3.671	0.379	9.7	4.31	2754

value for the isoelectronic inert gas for each anion (Figure 1). Although ϵ_0 increases as the anion size increases, as we expect, it varies with the cation, increasing in the sequence Na-K-Rb. It is as much as 10 times larger than the values for the inert gases (Figure 2). Thus, although the elastic constant data on the alkali halides support the idea of a Lennard-Jones-type of force between anions in which both attractive and repulsive terms are important, they indicate that the magnitude of these forces may be strongly dependent on the presence of a third body, the cation.

I therefore conclude that good accuracy cannot be expected from a simple force model of this type when the force constants are derived from data on the inert gases [*Sammis,* 1971] or from another compound [*Weidner and Simmons,* 1972; *Sammis,* 1970, 1971]. It is possible that a more sophisticated model (e.g., one that treats noncentral forces explicitly) will permit this type of assumption. Until such a model has been developed and tested, any model that is to be applied to complex materials with many important interactions (most oxides are of this type) will require a large amount of experimental data for evaluating the force constants if a high degree of accuracy is expected.

Table 5 lists the contributions of the five terms of the potential (coulombic, nearest neighbor, two NNN, and thermal) to the lattice energy, pressure, elastic constants, and pressure derivatives of NaCl, KCl, and RbCl. The NNN interactions have a small effect on C_s but a large effect on K and C_{44}. It is clear that the variation of C_{44}, and particularly of dC_{44}/dP, between compounds in the NaCl lattice can be explained by the Lennard-Jones anion-anion interaction, which increases in strength as the anions get closer together, owing to decreasing cation size (in the sequence Rb-K-Na), and as they get larger (in the sequence F-Cl-Br-I).

EXTRAPOLATION OF ELASTIC PROPERTIES TO HIGH PRESSURE

The equations for the elastic constants (2–5 and 9–12), together with the parameters evaluated in the previous section, can be used to predict the elastic properties at any pressure.

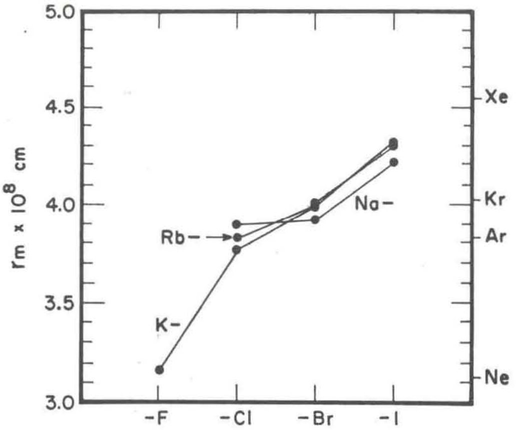

Fig. 1. Parameter in Lennard-Jones potential between anions in ten alkali halides.

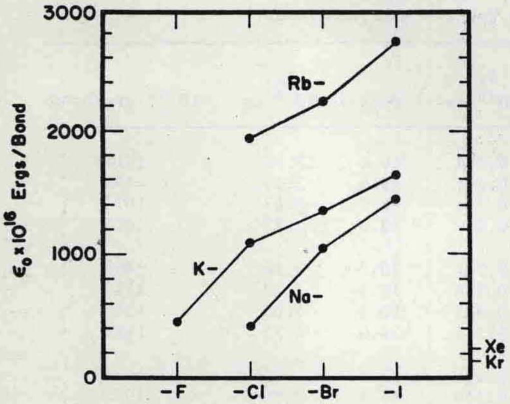

Fig. 2. Energy term in Lennard-Jones potential between anions in ten alkali halides.

These predictions fit the zero-pressure data for K, C_{44}, and their pressure derivatives, which were used to evaluate parameters.

The NNN model predicts almost the same bulk properties at high pressure as the simple nearest-neighbor model [*Anderson,* 1970]. The inclusion of NNN interactions affects the high-pressure bulk modulus much less strongly than the choice of a particular form for the nearest-neighbor repulsive energy (exponential or b/r^n). The effect of this choice has been discussed by *Anderson* [1970] and *Roberts and Smith* [1970*a*].

The shear elastic constant C_{44} in the NaCl lattice is of special interest because it decreases with pressure in the potassium and rubidium halides. Since a vanishing shear elastic constant is a sufficient condition for a phase transition [*Born,* 1940; *Misra,* 1940], it has been suggested that the phase transition from the NaCl to CsCl structure at high pressure may be associated with a macroscopic shear instability in which C_{44} decreases to zero [*Anderson and Demarest,* 1971; *Thomsen,* 1971]. C_{44} is plotted versus pressure for the sodium halides in Figure 3 and for the rubidium and potassium halides in Figure 4. Where a phase transition is well established at room temperature, C_{44} is plotted with a slightly thicker line up to the transition pressure. The value of C_{44} predicted by this theory is continued to higher pressure, but a narrower line is used. When a phase transition has not been well established, a narrow line is used. The data on the transitions

TABLE 5. Contributions of Various Terms to the Elastic Constants of NaCl, KCl, and RbCl

Parameter	Compound	Coulomb	NN	NNN (6)	NNN (12)	Thermal	Total
ϕ	NaCl	101	-10	4	-1	7	100%
	KCl	99	-10	4	0	8	100%
	RbCl	96	-12	6	-1	10	100%
P/K	NaCl	-0.36	0.35	-0.08	0.07	0.02	0
	KCl	-0.35	0.38	-0.09	0.03	0.02	0
	RbCl	-0.33	0.39	-0.12	0.03	0.02	0
K^T	NaCl	-0.49	1.37	-0.25	0.37	0.00	100%
	KCl	-0.47	1.57	-0.27	0.17	-0.01	100%
	RbCl	-0.44	1.64	-0.37	0.19	-0.02	100%
K'	NaCl	-0.65	4.95	-0.76	1.85		5.38
	KCl	-0.62	6.05	-0.83	0.86		5.46
	RbCl	-0.58	6.36	-1.12	0.97		5.62
C_{44}/K	NaCl	0.80	-0.35	-0.08	0.18	-0.02	0.53
	KCl	0.78	-0.37	-0.09	0.08	-0.03	0.36
	RbCl	0.74	-0.39	-0.12	0.09	-0.03	0.30
C_{44}'	NaCl	1.07	-1.37	-0.25	0.92		0.37
	KCl	1.03	-1.57	-0.27	0.42		-0.39
	RbCl	0.96	-1.62	-0.37	0.47		-0.56
C_s/K	NaCl	-0.84	1.53	0.00	0.05	-0.06	0.68
	KCl	-0.80	1.78	0.00	0.02	-0.10	0.90
	RbCl	-0.75	1.84	0.00	0.02	-0.12	0.99

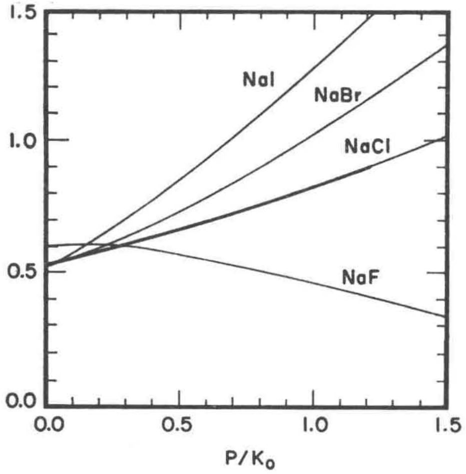

Fig. 3. Shear constant C_{44} versus pressure in sodium halides.

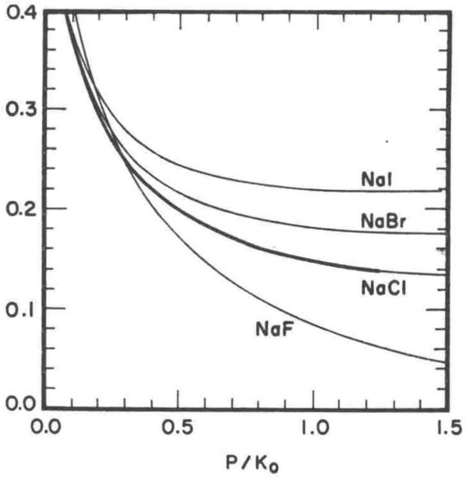

Fig. 5. C_{44}/K versus pressure in sodium halides.

have been taken from *Darnell and McCollum* [1970] and *Bassett et al.* [1968, 1969].

It is clear from Figures 3 and 4 that the low-pressure transitions in the rubidium halides, moderate-pressure transitions in the potassium halides, and relative stability of the sodium halides can be understood by looking at the relative pressures at which macroscopic instability occurs. It is also clear, however, that the actual phase transition invariably takes place at a much lower pressure than that predicted by the vanishing of C_{44}.

To predict the transition pressure more accurately without making a more detailed thermodynamic calculation, one can use an empirical rule that the transition occurs when C_{44} decreases to some critical fraction α of the bulk modulus K. C_{44}/K is plotted versus pressure for the sodium halides in Figure 5 and for the potassium and rubidium halides in Figure 6. As in Figures 3 and 4, well-established phase transitions are indicated by the change from a thick to a narrow line. The critical values of $\alpha = C_{44}/K$ at transition are given in Table 6. The value of α for NaCl is reasonable and tends to confirm my extrapolation of C_{44}.

It is possible to predict transition pressures in the other alkali halides by using Figures 5

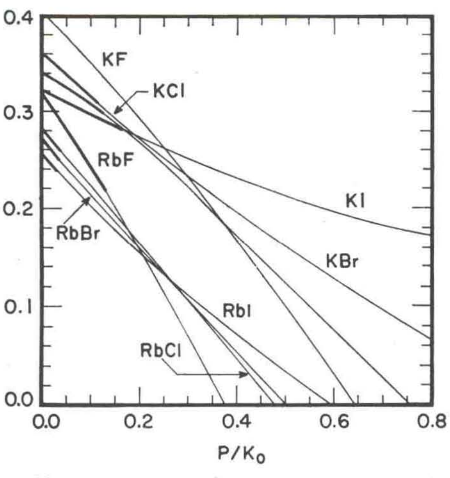

Fig. 4. Shear constant C_{44} versus pressure in potassium and rubidium halides.

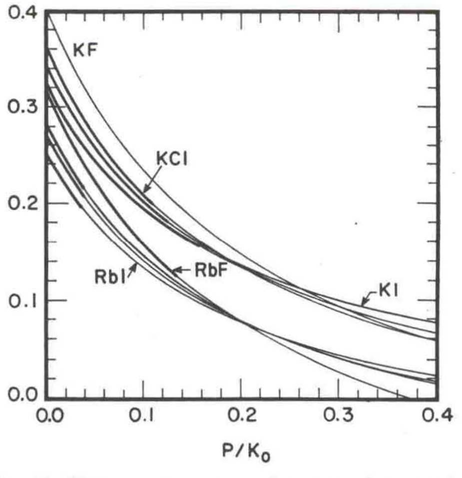

Fig. 6. C_{44}/K versus pressure in potassium and rubidium halides.

TABLE 6. $\alpha = C_{44}/K$ at the Phase Transition from NaCl to CsCl Structure for Some Alkali Halides

	F	Cl	Br	I
Rb	0.13	0.225	0.212	0.193
K		0.195	0.187	0.16
Na		0.14		

and 6. Figure 5 suggests that NaBr and NaI should never reach the critical point of instability and should therefore be stable to pressures greater than $P/K_0 = 1.25$ (250 and 190 kb, respectively). If the transition in RbF postulated by Darnell and McCollum is correct, the fluorides may have relatively low values of α. Taking this factor into account, I predict a transition in NaF between 300 and 450 kb and in KF between 70 and 95 kb. A transition must occur in KF before the macroscopic instability at 200 kb takes place.

The predictions of high-pressure shear constants and phase transitions that I have made in this section are based solely on data easily measured at low pressure. They provide estimates of the properties of these alkali halides at high pressure that should prove useful in the design of future high-pressure experiments.

APPENDIX

The procedures for deriving the equations for the effective elastic constants from a lattice model by the method of long waves [*Born*, 1926] is well known. For a diatomic centrosymmetric lattice such as NaCl, the equations are quite simple [*Blackman*, 1958; *Anderson and Liebermann*, 1970].

The general expression for lattice energy is given in (1) and for the unstrained lattice reduces to

$$\phi = Z^2e^2\frac{A_r}{r} + 6be^{-r/\rho} + 6\epsilon_0\left[\left(\frac{r_m}{r'}\right)^{12} - 2\left(\frac{r_m}{r'}\right)^{6}\right] \quad \text{(A1)}$$

where $r' = (2)^{1/2}r$ and where the summation of the electrostatic energy over all lattice points has been replaced by the Madelung constant for NaCl ($A_r = 1.74756$) and the other summations have been made. The pressure (equation 2) is obtained by straightforward differentiation of (A1), which yields

$$P = -(1/3V)r\,d\phi/dr \quad \text{(A2)}$$

where the volume per ion pair V is $2r^3$ for NaCl. The equations for the elastic constants are

$$C_s = \frac{1}{V}\sum\left[Q(x^4 - x^2y^2) + px^2\right] \quad \text{(A3)}$$

$$C_{44} = \frac{1}{V}\sum\left[Qx^2y^2 + px^2\right] \quad \text{(A4)}$$

$$K = \frac{1}{V}\sum\left(\tfrac{1}{3}Qx^4 + \tfrac{2}{3}Qx^2y^2 - \tfrac{1}{3}px^2\right) \quad \text{(A5)}$$

where

$$p = \frac{1}{r}\frac{\partial}{\partial r} \quad \text{(A6)}$$

and

$$Q = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\phi}{\partial r}\right) \quad \text{(A7)}$$

Here x and y are components of r, the interionic distance of the appropriate pair of ions in the summation. The summation is then broken into three parts corresponding to electrostatic, nearest-neighbor, and next-nearest-neighbor terms:

$$p = p^{\mathrm{E}} + p^{\mathrm{NN}} + p^{\mathrm{NNN}} \quad \text{(A8)}$$

$$Q = Q^{\mathrm{E}} + Q^{\mathrm{NN}} + Q^{\mathrm{NNN}} \quad \text{(A9)}$$

$$p^{\mathrm{NN}} = -(1/r^2)(r/\rho)be^{-r/\rho} \quad \text{(A10)}$$

$$Q^{\mathrm{NN}} = \frac{1}{r}\left(\frac{1}{r^2\rho} + \frac{1}{r\rho^2}\right)be^{-r/\rho} \quad \text{(A11)}$$

$$p^{\mathrm{NNN}} = -\tfrac{1}{2}\epsilon_0\frac{1}{r'^2}\left[12\left(\frac{r_m}{r'}\right)^{12} - 12\left(\frac{r_m}{r'}\right)^{6}\right] \quad \text{(A12)}$$

$$Q^{\mathrm{NNN}} = \tfrac{1}{2}\epsilon_0\frac{1}{r'^4}\left[168\left(\frac{r_m}{r'}\right)^{12} - 96\left(\frac{r_m}{r'}\right)^{6}\right] \quad \text{(A13)}$$

The NN and NNN contributions to the elastic constants are determined by a straightforward summation according to equations A3–A5 utilizing information on the crystal structure [e.g., *Anderson and Liebermann*, 1970; *Sammis*, 1970] and equations A11–A14. The electrostatic contributions involve lattice sums similar to the Madelung constant and were taken from *Cowly* [1962]. The results are equations 3–5.

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