

Fig. 3. Shear constant C_{44} 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 ther-

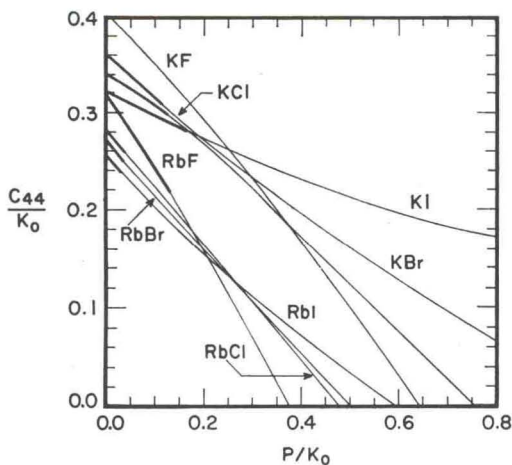


Fig. 4. Shear constant C_{44} versus pressure in potassium and rubidium halides.

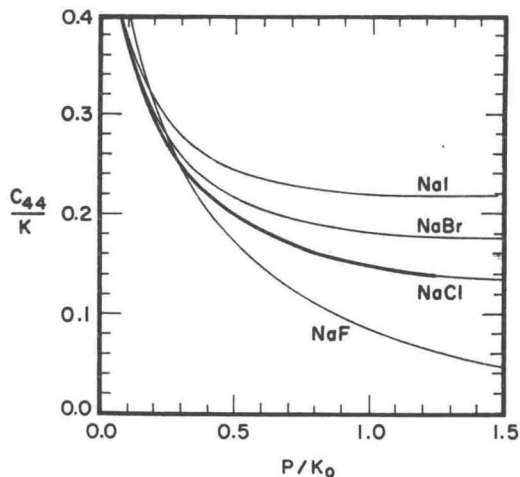


Fig. 5. C_{44}/K versus pressure in sodium halides.

modynamic 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

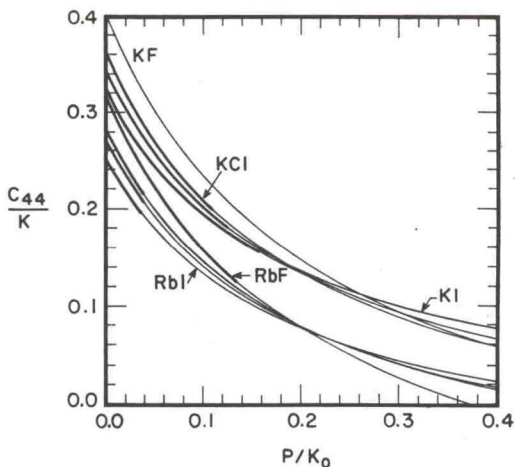


Fig. 6. C_{44}/K versus pressure in potassium and rubidium halides.

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

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

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

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

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

$$C_{11} = \frac{1}{V} \sum [Q(x^4 - x^2y^2) + px^2] \quad (\text{A3})$$

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

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

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:

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

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

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

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

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

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

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.