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

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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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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

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

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:

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

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

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

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

$$\tilde{K}' = \frac{1}{6Kr_0^3}\left\{-3.1068\,\frac{Z^2e^2}{r_0}\left(\frac{r_0}{r}\right)^4 + \tfrac{2}{3}b\,\frac{r_0}{\rho}\left[4\left(\frac{r_0}{r}\right)^2 + 3\,\frac{r_0}{\rho}\frac{r_0}{r} + \left(\frac{r_0}{\rho}\right)^2\right]e^{-r/\rho} + (2)^{1/2}\epsilon_0\left(\frac{r_0}{r_m}\right)^3\left[3600\left(\frac{r_m}{r'}\right)^{15} - 1296\left(\frac{r_m}{r'}\right)^{9}\right]\right\} \quad (6)$$

$$\tilde{C}_{44}' = \frac{1}{6Kr_0^3}\left\{5.1121\,\frac{Z^2e^2}{r_0}\left(\frac{r_0}{r}\right)^4 - 2b\,\frac{r_0}{\rho}\left[2\left(\frac{r_0}{r}\right)^2 + \frac{r_0}{\rho}\frac{r_0}{r}\right]e^{-r/\rho} + (2)^{1/2}\epsilon_0\left(\frac{r_0}{r_m}\right)^3\left[1800\left(\frac{r_m}{r'}\right)^{15} - 432\left(\frac{r_m}{r'}\right)^{9}\right]\right\} \quad (7)$$

$$\tilde{C}_s' = \frac{1}{6Kr_0^3}\left\{4.8861\,\frac{Z^2e^2}{r_0}\left(\frac{r_0}{r}\right)^4 + b\,\frac{r_0}{\rho}\left[\left(\frac{r_0}{\rho}\right)^2 - 2\left(\frac{r_0}{r}\right)^2\right]e^{-r/\rho} + (2)^{1/2}\epsilon_0\left(\frac{r_0}{r_m}\right)^3\left[540\left(\frac{r_m}{r'}\right)^{15}\right]\right\} \quad (8)$$

Here P is the pressure, K is the bulk modulus, and C_{44} and C_s, both equal to $\frac{1}{2}(C_{11} - C_{12})$, 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]:

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

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