

where  $\beta$  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

$$C_{44} = \tilde{C}_{44} + \frac{W_v}{C_v} \left( \frac{dC_{44}}{dT} \right)_v \quad (11)$$

$$C_s = \tilde{C}_s + \frac{W_v}{C_v} \left( \frac{dC_s}{dT} \right)_v \quad (12)$$

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:  $Z$ ,  $b$ ,  $\rho$ ,  $\epsilon_0$ , 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	$\beta$ , $10^{-4} \text{ deg}^{-1}$	$r_0$ , $10^{-8} \text{ cm}$	$W_v/TC_v$	$K^T$ , 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

Compound	$(\partial/\partial T)_V,$ $10^{-3}$ kb/deg			$(\partial/\partial P)_T$		
	$K^T$	$C_{44}$	$C_s$	$K^T$	$C_{44}$	$C_s$
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* [1970a, 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 *Hausühl* [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  $\epsilon_0$  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	$\bar{P}$	$\bar{\kappa}$	$\tilde{C}_s$	$\tilde{C}_{44}$
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