TABLE 4. Model Parameters for the Alkali Halides

Compound	Z	$b,$ 10^{-10} erg/bond	$r_0,$ 10^{-8} cm	$\rho,$ 10^{-8} cm	r_0/ρ	$r_m,$ 10^{-8} cm	$\epsilon_0,$ 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, 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.
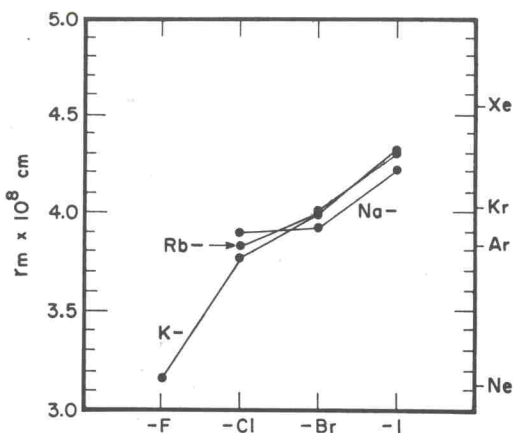

Fig. 1. Parameter in Lennard-Jones potential between anions in ten alkali halides.
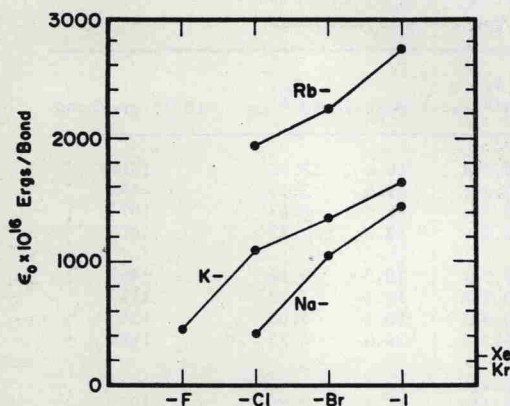
Fig. 2. Energy term in Lennard-Jones potential between anions in ten alkali halides.

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 [1970a].

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