

of the elastic constants from reference[42]. Then the \bar{P} , \bar{C}_{44} , and \bar{K} could be fit to the model. There are not parameters which will fit the elastic constants data of RbF, but the iterative procedure converged close enough so that the calculated thermal properties still have some validity.

4.2 The parameters

The parameters are given in Table 2. For purpose of comparison, Mayer's[54] values of the van der Waals constant C are given and the electronic polarizabilities determined by Tessman, *et al.*[55] are compared to the model values given by Y^2e^2/k .

A simple theory of the forces in alkali halides might expect Z to be related to the electronegativity difference, b_{+-} to be a constant, and the other parameters to be characteristic of the appropriate ion. Deviations from these relations might be due to an inherent defect in the potential function (2), the approximations made in treating thermal effects, perturbation of the ionic wavefunctions in a different way in different compounds, or errors in the input data.

The expected trend of ionicity with electronegativity is absent. Instead, Z seems to depend

mainly on the cation. In general the values are much closer to unity than might be expected from Pauling's[56] scale of ionicity.

The parameter b_{+-} varies widely, in a large part because it appears in the energy equation as a multiplier of the exponential term. While b_{+-} varies by almost 70 per cent for the different sets of input data in NaCl, the factors which enter into equations for \bar{P} , \bar{K} and $d\bar{K}/d \ln V$ vary by only 7 per cent. A large part of the variation of b_{+-} between compounds could be the result of experimental error.

The parameter ρ_- varies in general by about ± 0.015 among compounds with the same anion. ρ_+ is remarkably constant in the lithium and sodium halides in which the anion-anion forces are relatively strong in relation to the anion-cation forces.

The parameter C has a small effect relative to the exponential anion-anion term in the lithium-halides and NaF and its strong deviation here from what we might expect is not important. Except for KBr, KI and to a lesser extent NaI, the agreement with Mayer's[54] theory is rather good.

The anion polarizability, Y^2e^2/k has reasonable values for all compounds except LiF. The individual values of Y and k are not determined very

Table 2. Model parameters

Compound	Z	$b_{+-}(10^{-10} \text{ ergs})$	$\rho_-(\text{\AA})$	$\rho_+(\text{\AA})$	$C(10^{60} \text{ rthd vm}^6)$				Electronic polarizability $Y^2e^2/k (\text{\AA}^3)$	
					This paper	[54]	$-Y$	$k(10^6 \text{ dyn/cm})$	This paper	[55]
LiF*	0.803	97.6	0.108	0.064	-10.0	14.5	0.53	(-0.36)	-1.746	0.91
LiCl*	0.747	66.5	0.165	0.057	30.0	111.0	0.93	0.46	4.355	2.90
LiBr	0.816	57.7	0.190	0.062	139.0	185.0	2.48	3.17	4.509	4.14
LiI	0.808	70.2	0.204	0.064	247.0	378.0	2.13	1.46	7.191	6.23
NaF	0.906	72.4	0.123	0.096	-1.0	16.5	1.86	6.21	1.291	1.16
NaCl	0.900	33.0	0.193	0.097	105.0	117.0	2.67	4.70	3.509	3.26
NaBr	0.866	38.9	0.205	0.093	185.0	196.0	3.23	5.09	4.739	4.39
NaI	0.834	37.2	0.235	0.086	471.0	392.0	3.54	4.34	6.896	6.26
KF	0.952	78.7	0.132	0.122	18.0	18.6	26.06	776.0	2.017	2.01
KCl	0.966	70.0	0.175	0.131	100.0	131.0	3.85	8.06	4.252	4.17
KBr	0.936	96.3	0.175	0.127	111.0	206.0	3.73	5.79	5.555	5.29
KI	0.912	21.9	0.279	0.108	1056.0	400.0	3.16	2.79	3.579	7.39
RbF*	0.970	156.2	0.066	0.185	26.0	18.9	66.06	3958.0	2.544	2.57
RbCl	1.008	52.4	0.186	0.144	169.0	130.0	4.47	9.17	5.021	4.71
RbBr	1.008	37.6	0.211	0.148	298.0	215.0	3.46	4.28	6.439	5.92
RbI	0.992	35.7	0.239	0.145	601.0	428.0	3.37	2.90	9.085	8.09
NaCl (i)	0.893	51.3	0.175	0.098	61.0	117.0	2.75	4.99	3.491	3.26
NaCl (ii)	0.900	34.2	0.190	0.098	97.0	117.0	2.65	4.60	3.514	3.26
NaCl (iii)	0.892	30.5	0.194	0.097	101.0	117.0	2.74	5.03	3.451	3.26

*Thermal correction determined by method of Ref. [21].

†Inexact fit to elastic constants.

accurately due in part to the often large errors in ϵ_0 . They are sometimes strongly influenced by the values of the nearest neighbor force constants. The physically unreasonable values of the shell charge Y for RbF and KF is probably a result of neglecting the cation polarizability which is actually larger than the anion polarizability in these two compounds [55].

The general form of the interatomic potential function (2) is confirmed by the more-or-less reasonable values of the parameters. Experimental errors in the input data can account for much of the unexpected variation of the parameters among the different compounds, but the present model is clearly not sufficient for RbF and LiF.

4.3 The Cauchy failure

Also of interest in the evaluation of the model is the degree to which the model calculations fail to fit the third elastic constant, C_3 . The parameter of greatest theoretical interest is the Cauchy failure, $\Delta \equiv C_{12} - C_{44} - 2P$ which is equal to two-thirds of the calculated error in C_3 . It is well known that thermal effects contribute to the failure of the Cauchy relation in alkali halides. Because explicit thermal contributions have been calculated in the present paper, it is possible to isolate the portion of

the Cauchy failure due to multi-body or noncentral forces. This athermal Cauchy failure, $\bar{\Delta}$ is given in Table 3 as well as the dimensionless parameter $\bar{\Delta}/K$, and the pressure derivative $d\bar{\Delta}/dP$. There seems to be a general trend of $\bar{\Delta}/K$, increasing in the sequences Li-Na-K-Rb and F-Cl-Br-I. Trends in $d\bar{\Delta}/dP$ may be largely masked beneath errors in the experimental data and in the calculated thermal contributions. Only for LiF, LiCl and perhaps NaF could the calculation be improved by the use of the breathing shell model. For the other alkali halides, $\bar{\Delta}$ has the wrong sign for the breathing shell model, or is virtually zero.

5. COMPARISON WITH EXPERIMENT AT ZERO PRESSURE

Model calculations were performed on a grid of closely spaced volume-temperature points. By interpolating between tabulated values it was possible to determine the theoretical properties of the alkali halides at any desired pressure and temperature. Table 4 compares experimental and theoretical values of the Grüneisen parameter, γ_{th} , its isothermal volume derivative, $\partial \ln \gamma / \partial \ln V$, and the adiabatic Anderson-Grüneisen parameter, which is the dimensionless parameter related to the change of the adiabatic bulk modulus with temperature, $\delta_s = -1/(\beta B_s)(\partial B_s / \partial T)_p$. The theoretical calculations of Barsch and Achar [13] and of Roberts and Ruppel [12] are also tabulated. Both of these calculations involved a shell model whose parameters were assumed to be quadratic in pressure and were fitted to the elastic and dielectric constants and their first and second pressure derivatives, and were hence limited to calculations at zero pressure.

An error of about 10 per cent in γ_{th} can be attributed to experimental errors in the input data. In LiBr and LiI and, to a lesser extent NaF, the higher order anharmonic terms are probably responsible for the strong deviation of theory from experiment. The large error in γ_{th} calculated for KF, KBr, KI and RbI is unexplained by these factors. However the overall comparison with the calculations of other authors [3-11] is excellent.

Figure 1 compares theoretical values of the volume thermal expansion coefficient β of NaCl with experimental measurements of Meincke and Graham [57] and Leadbetter and Newsham [58] as a function of temperature at zero pressure. The results of the other alkali-halides are similar. At low temperatures there is good agreement between theoretical and experimental values of β (and hence γ_{th}). Above a certain critical temperature (about 200°K for NaCl), the values differ by an

Table 3. Athermal Cauchy failure $\bar{\Delta} = \bar{C}_{12} - \bar{C}_{44} - 2\bar{P}$ and its pressure derivative

	$\bar{\Delta}$ (kbar)	$\bar{\Delta}/K$	$d\bar{\Delta}/dP$
LiF*	-210.0	-0.32	-0.57
LiCl*	-55.8	-0.19	-0.75
LiBr	7.3	0.03	0.34
LiI	11.0	0.06	0.26
NaF	-48.9	-0.10	0.07
NaCl	-1.1	0.00	-0.13
NaBr	6.3	0.03	-0.23
NaI	14.1	0.09	-0.15
KF	20.6	0.07	0.43
KCl	5.1	0.03	0.15
KBr	-0.4	0.00	0.20
KI	7.0	0.06	-0.48
RbF	50.4	0.19	1.24
RbCl	14.6	0.09	0.18
RbBr	10.3	0.08	-0.04
RbI	11.1	0.11	-0.16
NaCl (i)	-5.4	0.02	-0.02
NaCl (ii)	-10.5	0.04	-0.26
NaCl (iii)	-2.7	0.01	-0.20

*Thermal contribution calculated by method of Ref. [21].