wavevector. Φ^R indicates that only the short range (non-Coulombic) terms in (2) are used. The C matrix has a similar definition with Φ^R replaced by the coulombic energy Φ^C.

The exact equations for calculating the components of the R matrix for the NaCl lattice as well as the elastic and dielectric constants are well known[33–35]. The pressure, $\tilde{P}$, can be obtained from the straightforward differentiation of (2). Kellermann[36] has described in detail the procedure for calculating the C matrix.

3. THERMAL EFFECTS

3.1 The quasi-harmonic approximation

In the harmonic approximation, the total energy of the crystal is given by

$$\Phi = \tilde{\Phi} + \sum_i h\nu_i(1/2 + 1/(e^{h\nu/kT} - 1)) \qquad (5)$$

where $\tilde{\Phi}$ is the energy of the static (nonvibrating) lattice given by (2) and the ν_i are the frequencies of vibration of the normal modes. In the quasi-harmonic approximation, the frequencies are assumed to be functions of volume but not of temperature, and interactions between phonons are neglected. The pressure is then given by

$$P = \tilde{P} + \frac{1}{V}\gamma_e E_{vib}$$

where

$$\gamma_e = \frac{\sum \gamma_i E_i}{E_{vib}}$$

$$E_{vib} = \sum_i E_i$$

$$E_i = h\nu_i(1/2 + 1/(e^{h\nu/KT} - 1)). \qquad (6)$$

The mode Grüneisen parameters $\gamma_i \equiv (\partial \ln \nu_i / \partial \ln V)$ were calculated directly from the eigenvectors of the normal modes and the volume derivative of the dynamical matrix by the application of first order perturbation theory[37, 9]. Except in the high temperature limit, γ_e differs from the thermal Grüneisen parameter, γ_{th} which is given by

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*The experimentally measured elastic constants discussed in this paper are the same as Thurston's[39] "effective elastic constants", or Wallace's[37, p. 21] "stress strain coefficients", while I have made the assumption that Wallace's "elastic constants", (Thurston's $\bar{C}_{i,km}$) are not affected by temperature. Conversion of shear constants from the former to the latter involves the addition of the pressure, P.

$$\gamma_{th} \equiv \frac{V\beta K_\tau}{C_v} = \sum_i \frac{\gamma_i C_{vi}}{\sum_i C_{vi}} \qquad (7)$$

β is the volume thermal expansion coefficient, K_τ is the isothermal bulk modulus, C_v is the heat capacity at constant volume, and C_{vi} is the mode contribution to the specific heat given by

$$C_{vi} = \frac{(h\nu_i/KT)^2 e^{h\nu_i/KT}}{(e^{h\nu_i/KT} - 1)^2}. \qquad (8)$$

The summations over the normal modes were approximated by a properly weighted[38] average over forty seven non-equivalent wavevectors in the irreducible one forty-eighth of the first Brillouin Zone.

The thermal contributions to the isothermal and adiabatic bulk moduli and their pressure derivatives were determined by numerical differentiation of the thermal pressure, evaluated at different volumes, with the conversion from the isothermal to the adiabatic bulk modulus being made by the relation

$$K_s = K_\tau + \frac{\gamma_{th}^2 T C_v}{V}. \qquad (9)$$

There is a quasi-harmonic contribution to the shear elastic constants which depends on the second derivative of the mode frequencies with respect to shear strain. Although this contribution is not strictly negligible, it would require a great deal of computation and has been neglected in the present study. There is still a thermal contribution arising from a second order volume change under shear strain, which has been taken into account.* The vibrational contribution is thus given by

$$C_{shear} = \tilde{C}_{shear} - \frac{\gamma_e E_{vib}}{V}. \qquad (10)$$

3.2 Higher-order thermal effects

In this paper higher-order thermal effects have been neglected. These include the effect of three and four phonon interaction, or, equivalently, the contribution to the energy of third and fourth order terms to the Taylor expansion of the energy in terms of the atomic displacements (and the corresponding contributions to the pressure and bulk modulus).

The equations for calculating this higher-order contribution from a lattice model are given in detail by Wallace[40]. Cowley[7] has carried out the calculation for NaCl and showed that the contribu-

tion is negligible below 200°K and significant above 500°K. In the high temperature limit its contribution is proportional to T^2, and in NaCl tends to counteract the quasi-harmonic thermal pressure. It has been shown[7, 23] that the neglect of this effect in NaCl causes unreasonably large calculated thermal expansion at high temperature leading to a negative calculated value of K_r at a temperature below the experimentally observed melting temperature. This effect has been noted in the present quasi-harmonic calculation for fourteen alkali halides, implying that the error due to the neglect of this term will generally be a calculated pressure which is too large.

4. FITTING THE MODEL PARAMETERS

4.1 The input data

The equilibrium condition, the elastic constants K_s and C_{44}, their pressure derivatives (dK_s/dP) and (dC_{44}/dP), and the low and high frequency dielectric constants. ϵ_0 and ϵ_∞, were used as input data.

The input data was assembled from a variety of sources. When a choice had to be made, it was generally made on the basis of apparent accuracy, completeness of the data analysis, and the tabulation within the paper of thermodynamic parameters necessary to the present calculation, such as temperature, lattice constant r_0, and K_r. For purely

numerical reasons, the experimental (dK_s/dP) and (dc_{44}/dP) were converted to volume derivatives using the isothermal bulk modulus cited in that reference. Due to the relatively large experimental uncertainty in the pressure derivatives this procedure is essentially equivalent to using the pressure derivatives directly as input. The input data is given in Table 1. For completeness, C_s and (dC_s/dP) are also tabulated, although they were not used for input. In order to provide an estimate of how experimental errors affect the model parameters, four sets of input data were provided for NaCl.

An iterative procedure was used to determine the parameters which provided a fit of the experimental input data to quantities calculated according to Sections 2 and 3. The inversion process could not be carried out for LiF and LiCl. The thermal effects calculated by the model were very strong, and the model may actually be unstable $(K_r < 0)$ for these compounds at room temperature without the inclusion of higher order anharmonic effects. It is possible that a different iterative procedure would have given results for LiCl, but the strong deviation of LiF from the Cauchy relation would have made a fit impossible by any means. For purpose of comparison, thermal corrections to the pressure and elastic constants were made according to (9) to (12) of Ref.[21] using the temperature derivatives

Table 1. Input data

Compound	T°K	r_0(Å)	Elastic constants (kbar)			Pressure derivatives				Dielectric constants		
			K_s	C_{44}	C_s^*	K_s'	C_{44}'	$C_{s'}^*$	Ref.	ϵ_∞	ϵ_0	Ref.
LiF	300	2·0132	696·4	636·8	330·7	5·14	1·38	3·62	[41]	1·92	9·0357	[50, 51]
LiCl	295	2·5698	316·8	246	133	5·42	1·70	3·70	[42, 43]	2·75	11·05	[50]
LiBr	295	2·7507	255·9	193	104	5·39	1·80	3·75	[42, 43]	3·16	12·1	[50]
LiI	295	3·0114	191·6	140·7	74·3	5·79	1·96	4·00	[44, 43]	3·80	11·03	[50]
NaF	300	2·3165	482·0	282·2	366·0	5·18	0·205	4·79	[41]	1·74	5·0721	[52, 51]
NaCl	295	2·8196	252·1	128·0	182·6	5·26	0·369	4·786	[22]	2·31	5·8948	[52, 51]
NaBr	295	2·9890	206·4	99	146	5·29	0·46	4·83	[42, 45]	2·62	6·3968	[50, 51]
NaI	298	3·2364	162·2	74·2	106·0	5·48	0·59	4·76	[18]	2·91	6·60	[50]
KF	295	2·6740	316·0	125	255	5·26	−0·43	5·25	[42, 45]	1·85	6·05	[50]
KCl	295	3·1462	181·5	63·01	167·6	5·34	−0·39	5·61	[46]	2·13	4·8147	[52, 51]
KBr	300	3·3006	148·63	50·8	144·95	5·381	−0·328	5·684	[47]	2·33	4·8749	[52, 51]
KI	298	3·5334	121·5	37·3	116·7	5·10	−0·227	5·86	[18]	2·69	4·94	[52, 53]
RbF	295	2·8260	277·2	92·5	206·5	5·57	−0·70	4·93	[42, 48]	1·93	5·91	[52, 50]
RbCl	298	3·2903	162·98	47·53	152·18	5·35	−0·605	5·86	[19]	2·19	4·81	[52, 53]
RbBr	298	3·4453	136·58	38·40	134·79	5·30	−0·554	6·06	[19]	2·33	4·64	[52, 53]
RbI	298	3·6709	110·94	27·90	109·77	5·41	−0·494	6·12	[19]	2·63	4·69	[52, 53]
NaCl (i)	300	2·82015	250·36	127·81	182·40	5·27	0·37	4·92	[49]	2·31	4·8948	[52, 51]
NaCl (ii)	295	2·8196	247·1	127·2	182·1	5·27	0·37	4·79	[46]	2·31	5·8948	[52, 51]
NaCl (iii)	195	2·8090	257·9	130·1	202·7	5·13	0·32	4·76	[46]	2·31	5·8948	[52, 51]

*Not used as input data.