LATTICE MODEL CALCULATION OF HUGONIOT CURVES AND THE GRÜNEISEN PARAMETER AT HIGH PRESSURE FOR THE ALKALI HALIDES*

H. H. DEMAREST, JR.

University of California, Los Alamos Scientific Laboratory, Los Alamos, N.M. 87544, U.S.A.

and

Institute of Geophysics and Planetary Physics, and Department of Planetary and Space Science, UCLA, Los Angeles, Ca. 90024, U.S.A.†

Abstract—A seven parameter shell model of the interatomic forces in the NaCl lattice is used to make a detailed lattice dynamics calculation at arbitrary volume, for fourteen alkali halides. The calculated normal mode spectrum gives an explicit vibrational contribution to the pressure and the elastic constants in the quasiharmonic approximation. The seven parameters are chosen to fit low pressure ultrasonic data and the low and high frequency dielectric constants. Prediction of the Grüneisen parameter γ, $(\partial \ln \gamma / \partial \ln V)$, and $\delta_s = (-1/\beta B_s)(dB_s/dT)$ are in reasonable agreement with experiment. The calculated γ decreases monotonically with volume. Calculated Hugoniots are in good agreement with experiment for NaCl, NaBr and NaI, and in fair agreement for LiBr, LiI and NaF.

1. INTRODUCTION

Theoretical equations of state are of great importance to high pressure physics. They permit interpolation and extrapolation into regions in which experimental data is sparse or lacking. They help in planning future high pressure experiments and they are important in comparing static high pressure experiments with shock wave experiments, in which case the treatment of thermal effects at high pressure is particularly important.

Thermal effects in the equation of state can be treated to a high degree of accuracy through the Mie–Grüneisen equation of state, one form of which is

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

where P is the pressure, $\tilde{P}$ the pressure of the static non-vibrating lattice, E_{vib} is the vibrational energy, V the volume, and γ_e is one of the Grüneisen parameters. If the energy due to phonon–phonon interactions is neglected, then in the high temperature limit E_{vib} is a linear function of temperature at constant volume, and γ_e equals the thermodynamic

Grüneisen parameter and is a function of volume only. The treatment of thermal effects at high pressure thus depends mainly upon how γ varies with V. In the past, typical assumptions have been $\gamma = \gamma_0$, a constant, $\gamma/\gamma_0 = 1 - q(V_0 - V)/V_0$, or $\gamma = \gamma_0(V/V_0)^q$, where q is of the order of unity. There has been little justification for this type of assumption, and several authors[1, 2] have recently pointed out that there is a great deal of uncertainty about how γ varies with volume.

Many authors have shown that lattice-dynamics calculations, based on a simple atomic model and a summation over all modes of vibration can accurately predict the Grüneisen parameter at zero pressure as a function of temperature[3–11] and calculate its volume derivative[12, 13]. However, none of these authors have extended this type of calculation to the high pressure-high temperature regime. On the other hand, several authors have used an assumed interatomic energy function to predict the equation of state and elastic constants at high pressure[14-22], but with the exception of a preliminary report on the present work[23], they have not calculated the Grüneisen parameter consistent with this potential function, and their equations have usually been limited to a single isotherm.

In the present paper, an interatomic potential energy function is assumed and used to calculate not only the equation of state and elastic constants but also the Grüneisen parameter and other thermal

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properties at arbitrary volume and temperature. Thermal contributions to the pressure and elastic constants are calculated in the quasi-harmonic approximation. An important aspect of the present calculation is that while the form of the interatomic potential function is assumed, its arbitrary parameters and hence the strength of its individual terms are determined so that the model is in agreement with the elastic constants and their pressure derivatives at zero pressure. If a correct assumption has been made for the form of the interatomic potential, this fitting of parameters certainly gives the model the best chance of predicting equation of state, Hugoniot curves and various other thermodynamic properties of the alkali halides at high pressures.

An alternative approach to the determination of the equation of state at high pressure is finite strain theory, which has recently been extended by Thomsen[24–27] to include the high pressure-high temperature regime. It makes no assumptions about the nature of the interatomic forces and is thus applicable to a wider range of materials than the present lattice model calculation. However, it requires a great deal of experimental data as input, much of which is not presently available for most compounds, and it is apt to be inaccurate at low temperatures. Lattice theory and finite strain theory are thus presently complimentary to each other, with each one applicable to some compounds which are presently inaccessible to the other.

2. THE LATTICE MODEL

For the present calculation it was assumed that the potential energy per atom pair of the alkali halides, Φ_0 is given by

$$2N\Phi = \sum_{ij}^{\infty} \pm \frac{Z^2 e^2}{r_{ij}} + \sum_{ij}^{NN} b_{+-} e^{-r_{ij}/(\rho_+ + \rho_-)}$$
$$+ \sum_{ij}^{NNN} \left(\frac{C}{r_{ij}^6} + b_{--} e^{-r_{ij}/2\rho_-} \right). \quad (2)$$

The first summation over all lattice sites involves the electrostatic energy. The second summation over nearest neighbors (NN) involves the repulsive interaction between unlike ions arising from the Pauli exclusion principle and the kinetic energy of the electrons, and the third summation involves the van der Waals and repulsive interaction between next nearest neighbor (NNN) anions. The separation of the appropriate pairs of ions is r_{ij}, e is the electron charge, and Z, b_{+-}, b_{--}, ρ_+, ρ_- and C are assumed to be constants which vary from com-

pound to compound. This potential is similar to that used by several others in high pressure calculations[18, 19, 28–31]. Demarest[21, 23] and Sammis[20, 22] used alternatively a Lennard–Jones six–twelve potential between anions. Although it has not been shown whether the exponential or power law gives a better representation of the repulsive force between ions, it is probably more consistent for both the NN and NNN terms to be of the same form.

In addition the shell model formalism was used to permit the anion to be polarizable. In this formalism, the anion is assumed to consist of a spherical massless shell of charge Y through which short range forces with neighboring ions act, and a heavy ion core, bound to the shell with an isotropic spring of spring constant k. Both Y and k were assumed to be independent of volume.

A major defect of this model is that it has only central two-body forces, and therefore cannot be made to fit the three independent elastic constants of the cubic system exactly. Although several models have been developed such as the breathing shell model[32] which claim to solve this problem, they are only strictly applicable when $c_{12} - c_{44} - 2P < 0$, which is not the case for most of the alkali-halides, most notably RbF. Moreover, unlike the central force interactions assumed in the present study, it would be difficult to decide how many of these interactions should vary over a wide change in volume. Fortunately, for most alkali-halides the central force approximation is nearly correct and the present calculations will not be seriously in error.

The usual shell model equations [for example, 33], simplify to give the dynamical matrix D, whose eigenvalues are the squared circular frequencies ω^2

$$D = [\sqrt{m}]^{-1}(R + ZCZ - [R + ZCY]$$
$$\times [R + k + YCY]^{-1}[R + YCZ])[\sqrt{m}]^{-1} \quad (3)$$

where R and C are six by six matrices describing short range and coulombic interactions, Z and Y, are diagonal matrices giving the ionic and shell charges, and $[\sqrt{m}]$ is a diagonal matrix of the square root of the ionic masses. The R and C matrices are calculated by the summation

$$R\binom{\mu\nu}{\alpha\beta} = \frac{1}{N} \sum_{r(\mu,\nu)}^{N^2} \frac{\partial^2 \Phi^R}{\partial r_\alpha(\mu, \nu)\partial r_\beta(\mu, \nu)} e^{i[\mathbf{k} \cdot \mathbf{r}(\mu, \nu)]} \quad (4)$$

where the indices μ, $\nu = 1$ or 2 refers to the anion or cation, separated by the vector $\mathbf{r}$, and $\mathbf{k}$ is the

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

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

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

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

where

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

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

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

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.

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

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

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

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

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

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

$$C_{\text{shear}} = \tilde{C}_{\text{shear}} - \frac{\gamma_e E_{\text{vib}}}{V}. \tag{10}$$

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.

of the elastic constants from reference[42]. Then the $\tilde{P}$, $\tilde{C}_{44}$, and $\tilde{K}$ 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 $Y^2 e^2/k$.

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 $\tilde{P}$, $\tilde{K}$ and $d\tilde{K}/d\ln V$ 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, $Y^2 e^2/k$ 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	$b_{+-}(10^{-10}$ ergs)	ρ_-(Å)	ρ_+(Å)	$C(10^{60}$ rthd vm^6) This paper	[54]	Y	$k(10^5$ dyn/cm)	Electronic polarizability $Y^2 e^2/k$ (Å^3) 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_s. 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_s. 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

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

	$\tilde{\Delta}$ (kbar)	$\tilde{\Delta}/K_r$	$d\tilde{\Delta}/dP$
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].

the Cauchy failure due to multi-body or noncentral forces. This athermal Cauchy failure, $\tilde{\Delta}$ is given in Table 3 as well as the dimensionless parameter $\tilde{\Delta}/K_r$ and the pressure derivative $d\tilde{\Delta}/dP$. There seems to be a general trend of $\tilde{\Delta}/K_r$ increasing in the sequences Li–Na–K–Rb and F–Cl–Br–I. Trends in $d\tilde{\Delta}/dP$ 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, $\tilde{\Delta}$ 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 Ruppin [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 4. Comparison of experimental and theoretical values of $\partial \ln \gamma / \partial \ln V$ and δ_s at 295°K

	γ_{th}		$\dfrac{\partial \ln \gamma}{\partial \ln V}$					δ_s			
	Theory	Experiment	Theory This paper	[12]	[13]	Experiment		Theory This paper	[13]	Experiment	
		[a]				[b]	[c]			[b]	[c]
LiBr	2·48	1·94	3·5			2·0[d]		8·7		4·1[d]	
LiI	2·38	2·19	3·4			1·9[e]		8·4		4·0[e]	
NaF	1·86	1·51	2·3			1·22		5·3		3·75	
NaCl	1·69	1·62	2·0			1·40		4·8		3·87	
NaBr	1·75	1·65	1·9			1·75		4·8		4·13	
NaI	1·72	1·71	1·9	1·44	0·05[f]	1·77	0·67[f]	4·6	2·58[f]	4·16	3·22
KF	1·71	1·52	2·4			1·57		5·3		4·12	
KCl	1·59	1·49	2·1	1·64		1·77		4·9		4·41	
KBr	1·69	1·50	2·0			1·37		5·1		4·05	
KI	1·27	1·54	2·0	1·37	− 0·40[f]	1·26	0·47[f]	4·7	2·14[f]	3·98	2·94
RbF	1·66	1·40	2·9			2·07		5·7		5·05	
RbCl	1·45	1·39	2·2	1·82	1·44[f]	2·14	1·92[f]	5·0	4·06[f]	5·02	4·68[f]
RbBr	1·37	1·42	2·2	1·86	1·09[f]	1·99	1·58[f]	4·9	3·74[f]	4·81	4·44[f]
RbI	1·32	1·56	2·4	1·91	0·12[f]	1·91	1·34[f]	5·1	3·05[f]	4·35	4·10[f]
NaCl (i)	1·70							4·8			
NaCl (ii)	1·82							5·1			
NaCl (iii)	1·70							4·8			

[a] Tabulated in Refs. [43, 45, 48].
[b] Tabulated in Ref. [12].
[c] Tabulated in Ref. [13].
[d] Calculated from data in Refs. [43, 42].
[e] Calculated from data in Refs. [43, 44].
[f] Calculated at $V(P = 0, T = 0)$.
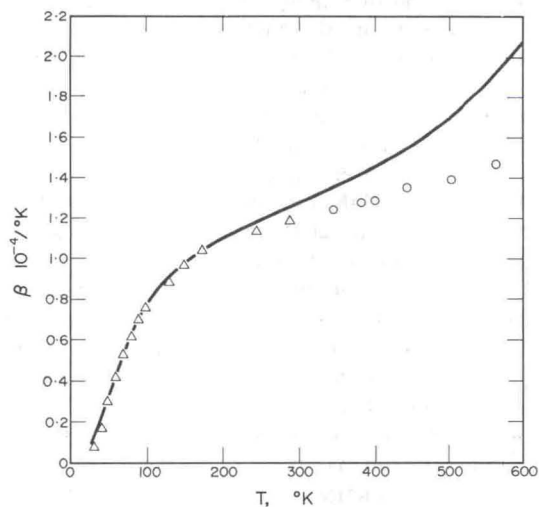
Fig. 1. Coefficient of thermal expansion in NaCl as a function of temperature. ——— lattice model calculation. Experimental data: ○ Ref. [58], △ Ref. [57].

amount which increases with temperature. The inclusion of higher order anharmonic terms would help to correct this problem[7].

The predictions of $\partial \ln \gamma / \partial \ln V$ are in general better than those of Barsch and Achar[13], but somewhat worse than those of Roberts and Ruppin[12]. The large errors for LiBr, LiI, NaF and NaCl are probably a result of the neglected anharmonic terms. While this correction would also improve the calculated results for the other alkali halides, it is unlikely to be large enough to bring them into agreement.

δ_s does not depend as strongly on thermal effects as does $\partial \ln \gamma / \partial \ln V$. The present calculation is in better agreement with experiment than that of Ref. [13], although the error is somewhat larger than expected.

Most of the experimental and theoretical values for $\partial \ln \gamma / \partial \ln V$ and δ_s from Ref. [13] refer to a slightly contracted volume corresponding to $P = 0$ at $T = 0$. The correction back to zero pressure at room temperature is smaller than the experimental error in these quantities.

6. CALCULATIONS AT HIGH PRESSURE

6.1 The behavior of γ at high pressure

Uncertainty as to the variation of the Grüneisen parameter with volume is a major problem in high pressure physics. Figure 2 plots the present model calculation of γ along the Hugoniot as a function of volume for fourteen alkali halides. The different plots are displaced vertically for clarity on this log–log graph.
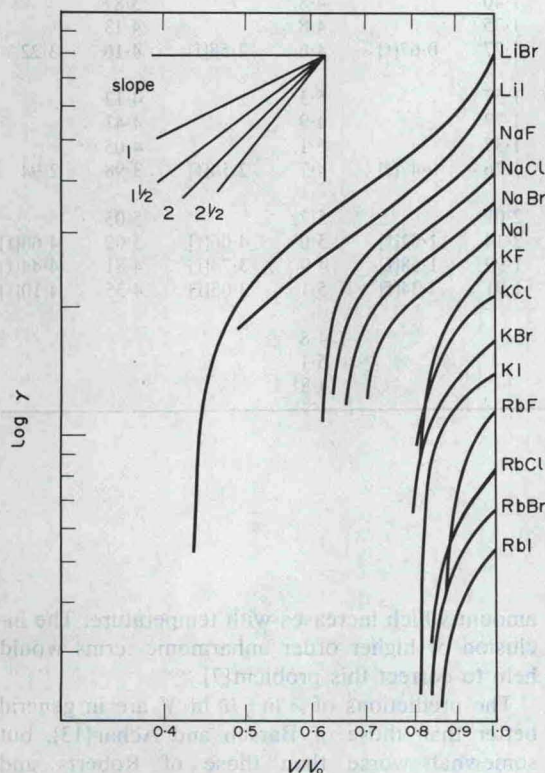

Fig. 2. Model calculation of the Grüneisen parameter as a function of volume for fourteen alkali halides. Graphs are displaced vertically for clarity.

Three different types of behavior of $\gamma(V)$ can be seen. They are:

(i) An initial steep slope caused essentially by the fact that under pressure the coulombic forces increase less rapidly than the short range forces. This effect is most noticeable in LiBr, LiI and NaF, but is mostly canceled by other factors in the other alkali halides.

(ii) A region of nearly linear decrease, with a relatively shallow slope.

(iii) Another region of sharp decrease, arising from soft modes.

The third region is a precursor of an instability caused by a zero frequency transverse acoustic mode occuring, in the present model calculation, in the $(1, 0, 0)$ direction at the Brillouin Zone boundary. In actual practice, a phase transition to the B2(CsCl) structure occurs before this steep dip is too pronounced. However, the soft modes are also important in determining the slope in region (ii) and in counteracting the coulomb effect in region (i).

The calculated instabilities are generally consistent with known transitions that occur under pressure, although the calculated instabilities in NaBr ($P \approx 265$ kbar, $V/V_0 \approx 0.65$) and NaI ($P \approx 150$ kbar, $V/V_0 \approx 0.69$) seem suspiciously low, and it is unlikely that there exist undiscovered transitions at such easily accessible pressures in such common compounds.

It is interesting to note that according to the present model, for all alkali-halides the assumption that $\gamma = \gamma_0(V/V_0)^q$ with $q = 1.75$ or 2.0 would only be in error by about 10%, from zero pressure up to the region of a transition. Other simple assumptions such as that made by finite strain theory [24, 27] may be equally valid. However setting q equal to the zero pressure slope of γ in LiBr, LiI, and NaF might lead to a serious underestimation of γ at high compression.

Previous calculations of this type used a six–twelve anion–anion interaction [23]. In these calculations, there was no instability at high pressure in the sodium halides, and $\gamma(V)$ decreased to a minimum and then increased under pressure. This strange behavior of $\gamma(V)$ was a result of two related factors: a lack of mode softening under pressure, and an anion–anion force of the power law form, which increased in strength faster than the anion–cation exponential force.

While the present model calculations are more likely to be valid than the previous ones, there may exist crystals in which there are no soft modes over a wide pressure range, and in which one type of short-range force gradually becomes dominant over another. Although γ probably behaves monotonically in all the NaCl type alkali halides, it may have a local minimum in some crystals. It has generally been assumed that $\gamma(V)$ is a smooth monotonic function. A more fundamental assumption is that the potential function be composed of terms which are smooth functions of interatomic separation. This type of assumption does not necessarily imply that $\gamma(V)$ will behave monotonically. A $\gamma(V)$ which has a local minimum may be unusual, but it is not unreasonable.

6.2 Calculation of Hugoniots

The most accurate information on solids at high pressure is available from shock wave experiments. The relevant equations are well known[59]

$$u_s = V_0 \sqrt{\frac{P_1 - P_0}{V_0 - V_1}} \qquad (11)$$

$$u_p = \sqrt{(P_1 - P_0)(V_0 - V_1)} \qquad (12)$$

and

$$E_1 - E_0 = \tfrac{1}{2}(P_1 + P_0)(V_0 - V_1) \qquad (13)$$

where u_s is the shock velocity, u_p is the particle velocity, and the subscripts 0 and 1 refer to the initial and final states, respectively.

At a given volume, equation (13) was solved numerically using tabulated values of $P(T)$ and $E(T)$ from (5) and (6). The calculated pressure was then inserted into (11) and (12) giving the theoretical Hugoniot curve in the shock-particle velocity plane. These theoretical curves are plotted along with the experimental data from Refs. [60–64] for LiBr, LiI, NaF, NaCl, NaBr and NaI in Figs. 3–8. In most cases, Hugoniots corresponding to zero and two percent porosity are plotted. Data of
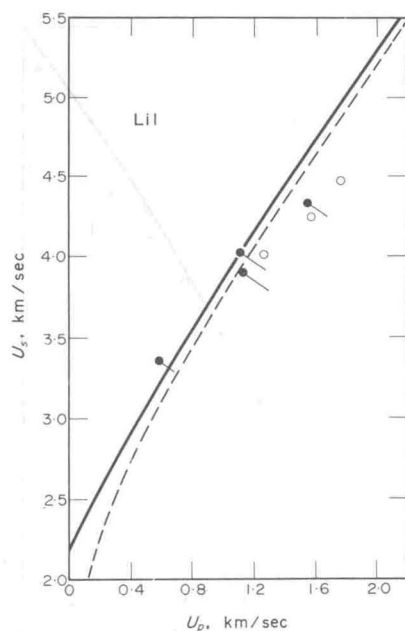
Fig. 4. Hugoniot of LiI. ——— lattice model calculation. ––– model calculation for 24 porous sample. ○ Single crystal experiment[61], ● Pressed sample[62], corrected to single crystal Hugoniot.
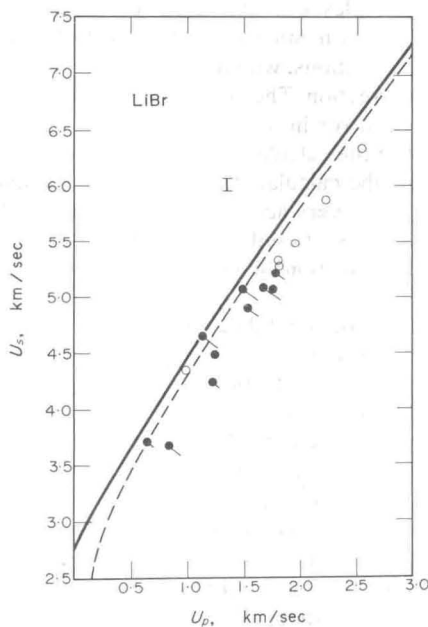
Fig. 3. Hugoniot of LiBr. ——— lattice model calculation. ––– model calculation for 2 per cent porous sample. ○ Single Crystal Experiment[60]; ● Pressed Sample[61], corrected to single crystal Hugoniot.
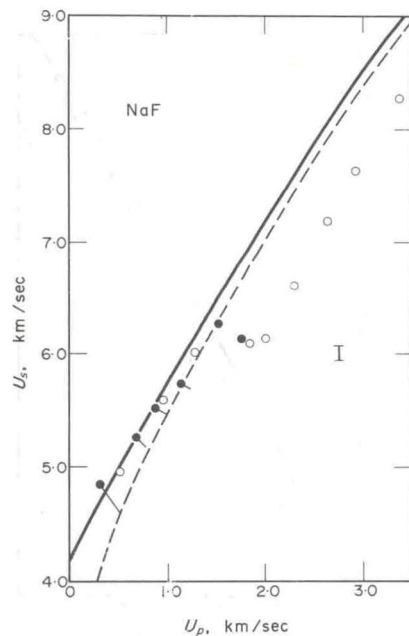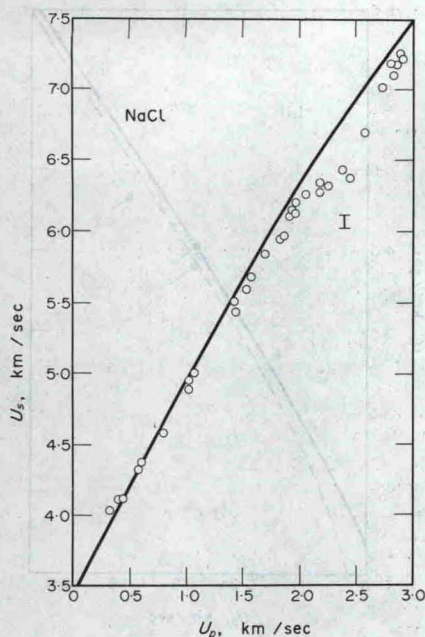

Fig. 5. Hugoniot of NaF. ——— lattice model calculation. ––– model calculation for 2 per cent porous sample. ○ Single crystal experiment[60]. ● Pressed sample[61], corrected to single crystal Hugoniot.

Fig. 6. Hugoniot of NaCl. ——— lattice model calcula-
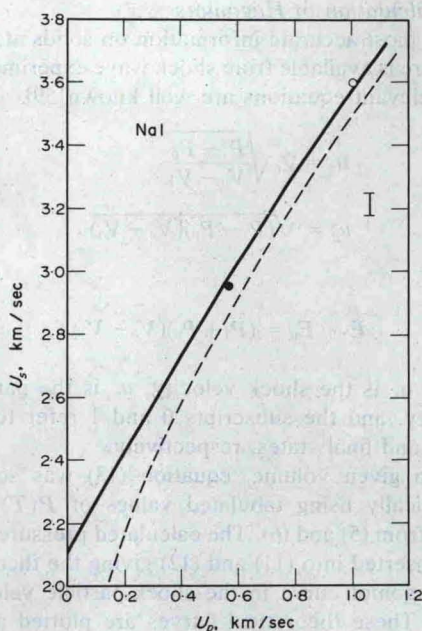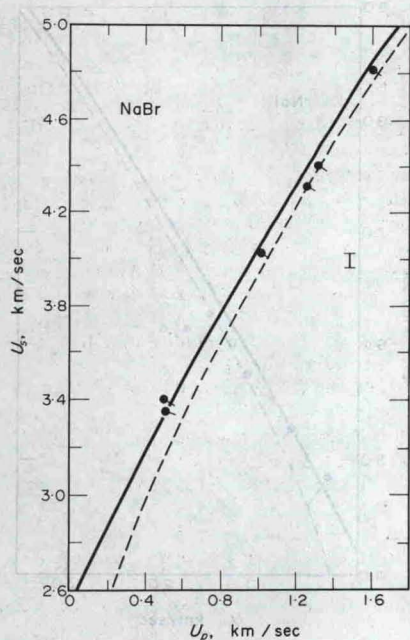tion. ○ Single crystal data [63].

Fig. 7. Hugoniot of NaBr. ——— lattice model calcula-
tion. --- model calculation for 2 per cent porous sample.
● experimental data from pressed sample [61], corrected
to zero porosity.

Fig. 8. Hugoniot of NaI. ——— lattice model calculation.
● Single crystal data [61]. ○ single crystal data [64].

porous samples was corrected to a zero porosity
Hugoniot in a manner consistant with the present
model calculations, with a line on the graph indicat-
ing the correction. The error bars refer to a nominal
1 per cent error in u_s.

Because the calculated γ at room temperature is
too large, the calculated Hugoniot of LiBr and LiI
should not be very accurate. The experimental data
is sparse and scattered, and does not contradict the
present calculation at compressions of less than
$\Delta V / V_0 = 0.25$.

The new Hugoniot data for NaF (Fig. 5) shows a
phase change initiating at a pressure somewhere be-
tween 210 and 270 kbar on the Hugoniot. The
possibility of a phase change at this point was
recently suggested by Ahrens and Thomsen [27] on
the basis of Christian's [61] single data point falling
within the transition region. Just prior to the
transition, the Hugoniot prediction of the present
lattice model calculation is slightly more accurate
than the prediction of Ahrens and Thomsen based
on finite strain theory [27].

In NaCl (Fig. 6), the predictions of lattice theory
and finite strain theory [27] are both fairly accurate
up to the phase transition, which occurs at a
compression of about 0.35.

The predicted Hugoniots in NaBr and NaI are in

excellent agreement with experiment, more so than the finite strain theory predictions. The calculated instabilities prevented comparison with experiment at compressions higher than those plotted ($\Delta V/V_0 = 0\cdot33$ and $0\cdot28$ respectively).

7. CONCLUSIONS

The present quasi-harmonic lattice model calculations provide a self-consistent framework for the calculation of macroscopic physical properties of crystals at arbitrary pressure and temperature. The calculated Grüneisen γ, $\partial \ln \gamma / \partial \ln V$, and δ_s are in reasonable agreement with experiment for most alkali halides. The inclusion of higher order anharmonic terms would improve the situation. The variation of γ with volume is initially dominated by coulomb effects. At very modest compressions this effect suddenly diminishes and $\gamma(V)$ is controlled mainly by the short range portion of the interatomic potential. Although simple analytic functions can adequately describe $\gamma(V)$, the presence of coulomb effects at zero pressure makes it difficult to extrapolate smoothly through this region of sudden change using low pressure experimental data.

The model calculations are in good agreement with experimental Hugoniots in cases for which the quasiharmonic theory was adequate at room temperature (NaCl, NaBr and NaI). The agreement is worse in cases for which anharmonic effects are important at room temperature (LiBr, LiI and NaF). In all cases the present theory compares favorably with recent finite strain theory calculations.

REFERENCES

1. Anderson O. L., *J. geophys. Res.* **73**, 5187 (1968).
2. Knopoff L. and Shapiro J. N., *J. geophys. Res.* **74**, 1439 (1969).
3. Vetelino J. F., Namjoshi K. V. and Mitra S. S., *J. appl. Phys.* **41**, 5141 (1970).
4. Hardy R. J. and Karo A. M., *J. appl. Phys.* **41**, 5144 (1970).
5. Namjoshi K. V., Mitra S. S. and Vetelino J. F., *Phys. Rev.* **B3**, 4398 (1971).
6. Ruppin R., *Solid State Commun.* **9**, 1387 (1971).
7. Cowley E. R., *J. Phys. C* **4**, 988 (1971).
8. Achar B. N. N. and Barsch G. R., *Phys. Status Solidi* **A6**, 247 (1971).
9. Achar B. N. N. and Barsch G. R., *Phys. Rev.* **B3**, 4352 (1971).
10. Ruppin R. and Roberts R. W., *Phys. Rev.* **B3**, 1406 (1971).
11. Ruppin R., *J. Phys. Chem. Solids* **33**, 945 (1972).
12. Roberts R. W. and Ruppin R., *Phys. Rev.* **B4**, 2041 (1971).
13. Barsch G. R. and Achar B. N. N., *AIP Conf. Proc.* **3**, 211 (1972).
14. Anderson O. L. and Liebermann R. C., *Phys. Earth Planet. Interiors* **3**, 61 (1970).
15. Anderson O. L., *J. geophys. Res.* **75**, 2719 (1970).
16. Sammis C. G., *Geophys. J.* **19**, 258 (1970).
17. Anderson O. L. and Demarest H. H., Jr., *J. geophys. Res.* **76**, 1349 (1971).
18. Barsch G. R. and Shull H. E., *Phys. Status Solidi* **B43**, 637 (1971).
19. Chang Z. P. and Barsch G. R., *J. Phys. Chem. Solids* **32**, 27 (1971).
20. Sammis C. G., PhD Thesis, California Institute of Technology (1971).
21. Demarest H. H., Jr., *J. geophys. Res.* **77**, 848 (1972).
22. Spetzler H., Sammis C. G. and O'Connell R. J., *J. Phys. Chem. Solids* **33**, 1727 (1972).
23. Demarest H. H., Jr., *Phys. Earth Planet. Interiors*, **6**, 146 (1972).
24. Thomsen L., *J. Phys. Chem. Solids* **31**, 2003 (1970).
25. Thomsen L., *J. geophys. Res.* **76**, 1342 (1971).
26. Thomsen L., *J. Phys. Chem. Solids* **33**, 363 (1972).
27. Ahrens T. J. and Thomsen L., *Phys. Earth Planet. Interiors* **5**, 282 (1972).
28. Decker D. L., *J. appl. Phys.* **36**, 157 (1965).
29. Weaver J. S., Takahashi T. and Bassett W. A., In: *Accurate Characterization of the High Pressure Environment* (Edited by E. C. Lloyd), p. 189. Nat. Bur. Std. Spec. Publ. 326 (1971).
30. Barsch G. R. and Chang Z. P., In: *Accurate Characterization of the High Pressure Environment* (Edited by E. C. Lloyd), p. 173. Nat. Bur. Std. Spec. Publ. 326 (1971).
31. Decker D. L., *J. appl. Phys.* **42**, 3239 (1971).
32. Schroder U., *Solid State Commun.* **4**, 347 (1966).
33. Peckham G., *Proc. Phys. Soc.* **90**, 657 (1967).
34. Cowley R. A., *Proc. R. Soc. Lond.* **A268**, 109 (1962).
35. Cowley R. A., *Proc. R. Soc. Lond.* **A268**, 121 (1962).
36. Kellermann E. W., *Phil. Trans. R. Soc. Lond.* **238**, 513 (1940).
37. Wallace D. C., *Thermodynamics of Crystals*, p. 129. Wiley, New York (1972).
38. Wallace D. C., *Thermodynamics of Crystals*, p. 456. Wiley, New York (1972).
39. Thurston R. N., *J. acoust. Soc. Am.* **37**, 348 (1965).
40. Wallace D. C., *op. cit.*, p. 226.
41. Miller R. A. and Smith C. S., *J. Phys. Chem. Solids* **25**, 1279 (1964).
42. Haussuhl S., *Z. Phys.* **159**, 223 (1960).
43. McLean K. O. and Smith C. S., *J. Phys. Chem. Solids* **33**, 279 (1972).
44. McLean K. O. and Smith C. S., *J. Phys. Chem. Solids* **33**, 275 (1972).
45. Roberts R. W. and Smith C. S., *J. Phys. Chem. Solids* **31**, 619 (1970).
46. Bartels R. A. and Schuele D. E., *J. Phys. Chem. Solids* **26**, 537 (1965).
47. Reddy P. J. and Ruoff A. L., In: *Physics of Solids at High Pressures* (Edited by C. T. Tomizuko and R. M.

Emrick), p. 510. Academic Press, New York (1965).

48. Roberts R. W. and Smith C. S., *J. Phys. Chem. Solids* **31**, 2397 (1970).

49. Ghafelehbashi M. and Koliwad K. M., *J. appl. Phys.* **41**, 4010 (1970).

50. Hojendahl K., *Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd.* **16**, 1 (1938).

51. Andeen C., Fontanella J. and Schuele D., *Phys. Rev.* **B2**, 5068 (1970).

52. Jones G. O., Martin D. H., Mawer P. A. and Perry C. H., *Proc. R. Soc. Lond.* **A261**, 10 (1961).

53. Jones B. W., *Phil Mag. Lond.* **16**, 1805 (1967).

54. Mayer J. E., *J. chem. Phys.* **1**, 270 (1933).

55. Tessman J. R., Kahn A. H. and Shockley W., *Phys. Rev.* **92**, 890 (1953).

56. Pauling L., *The Nature of the Chemical Bond*, 3rd ed., p. 99. Cornell University Press, Ithaca (1960).

57. Meincek P. P. M. and Graham G. M., *Can. J. Phys.* **43**, 1853 (1965).

58. Leadbetter A. J. and Newsham D. M. T., *J. Phys. C.* **2**, 210 (1969).

59. Rice M. H., McQueen R. G. and Walsh J. M., In: *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 6, p. 1. Academic Press, New York (1958).

60. Carter W. J., *High Temp.-High Press* **5**, 313 (1973).

61. Christian R. H., Equation of State of Alkali Halides (thesis), UCRL-4900, May 16, 1957, University of California, Livermore, as cited by Van Thiel, Ref [62].

62. Van Theil M., *Compendium of Shock Wave Data*, UCRL-50108, Vol. 1. University of California, Livermore (1967).

63. Fritz, J. N., Marsh S. P., Carter W. J. and McQueen R. G., In: *Accurate Characterization of the High Pressure Environment* (Edited by E. C. Lloyd), p. 201. Nat. Bur. Std. Spec. Publ. 326 (1971).

64. Al'tshuler L. V., Pavlovskii M. N., Kuleshova L. V. and Simakov G. V., *Soviet Phys.-solid State* **5**, 203 (1963) as cited by Van Thiel, Ref.[62].