

First-principles equation-of-state calculations for alkali halides

L. L. Boyer

Naval Research Laboratory, Washington, D.C. 20375

(Received 28 July 1980)

Results of first-principles (parameter-free) equation-of-state calculations are reported for sixteen alkali halides. The theory adopts the methods of Gordon and Kim for computing pair potentials for closed-shell systems. Specifically, the electronic ground-state energy is assumed to be that of an electron gas with the total charge density obtained by rigidly overlapping the free-ion charge densities. A number of properties are treated within this framework: lattice dynamics, elastic behavior, structure determination, thermal expansion, compressibility, and the overall stability of the lattice as a function of temperature and pressure. At high temperatures a lattice instability develops in which above a certain critical temperature (T_c) the vibrational and static pressures cannot balance each other at any volume. It is argued that this instability plays a role in causing solids to melt. An attempt is made to ascribe trends in the discrepancies between theory and experiment to particular approximations of the theory. From this analysis it appears that (a) the pair-potential approximation is in greatest need of improvement, (b) anharmonic corrections tend to raise T_c by about 20%, and (c) lattice imperfections are not an important factor for temperatures up to about 90% of the melting temperature.

I. INTRODUCTION

Several years ago Gordon and Kim¹ developed a theory from which reliable pair potentials for closed-shell systems could be readily calculated from the charge densities of the free-atom (ion) constituents. To accomplish this they assumed that the ground-state energy could be expressed in terms of the charge density of the system, as though it were a free-electron gas, with the total charge density approximated by rigidly overlapping the free atoms (ions). Following their initial success there has been a considerable effort to both refine the method and apply the potentials in the calculation of various physical properties.^{2,3} The most significant aspect of this work, in my view, is that the method is truly parameter free, or "first principles," in the sense that no experimental quantities (other than Planck's constant, Boltzmann's constant, the charge of the electron, the mass of the electron, the mass of the nuclei, and the atomic number) are required as input. Recently I reported some results of equation-of-state calculations for two alkali halides⁴ based on the potentials of Gordon and Kim. There I attempted to stress the importance of the first-principles nature of the calculation.

In this paper I report results of similar calculations of the equations of state for sixteen alkali halides (XY where $X = \text{Li, Na, K, and Rb}$, and $Y = \text{F, Cl, Br, and I}$) in both the NaCl and the CsCl structures. Due to the simplifying approximations and the parameter-free nature of the theory, the results are generally less accurate than those derived from parametrized models of the solid. On the other hand, a first-principles approach, however approximate, has certain advantages over

model calculations. First of all, any discrepancies between quantities calculated from first principles and the corresponding measured values result from the breakdown of certain well defined approximations rather than from any real or imagined flaw in a model. The procedure for improving a first-principles calculation is obviously to use better approximations without compromising its first-principles character. While this may not be the easiest way to obtain more accurate results it necessarily leads to the correct physics. Another advantage of a first-principles approach is of course that the results have a genuine predictive capability, while model calculations are usually limited to the role of interpreting existing experimental results. The equations of state for the alkali halides are already well characterized experimentally, and as such, provide an ideal system for assessing the overall accuracy of the theory. This is precisely what I have striven to accomplish in this work. Also, by studying an entire class of compounds it is possible to see trends in the discrepancies between theory and experiment which suggest which approximations may be in greatest need of improvement. Finally I note that the success of the theory in agreeing with observations on well characterized materials generates confidence in applying the same approaches in a predictive manner for less well understood systems.

Previous efforts to determine equations of state for solids from first principles have focused mainly on rare-gas crystals.⁵ For these materials the basic forces involved are the van der Waals type, which are relatively well understood. However, the explicit form of the interatomic potential still contains parameters derived from experimentally

determined properties of the solid. That is, they are not truly first principles. There has also been a considerable effort to compute equation-of-state properties for alkali halides using models of varying degrees of sophistication.⁶⁻⁹ Of these, Decker's⁷ model holds special significance due to its use in calibrating high-pressure measurements.

The key ingredient for an equation-of-state calculation is an expression for the "interatomic forces"; that is, the electronic ground-state energy as a function of the positions of the nuclei. The electrons are assumed to stay in their ground state as the nuclei move (adiabatic approximation). The method for computing the interatomic forces adopts, in the spirit of the Hohenberg-Kohn¹⁰ theorem, the approximations employed by Gordon and Kim¹ for expressing the ground-state energy solely in terms of the charge density. Specifically, I have used the computer program of Green and Gordon¹¹ to calculate pair potentials from free-ion Hartree-Fock wave functions.¹² The interatomic forces for the two crystal structures discussed were then expressed as a sum of these pairwise interactions. Two additional approximations were made in the calculation of the equation of state from the interatomic forces; the quasiharmonic approximation and the assumption that the solid remains free of lattice imperfections. All these approximations are discussed in Sec. II. The numerical methods of the calculations are discussed in Sec. III.

The results are presented and compared with experimental data in Sec. IV. In this section the results are classified, somewhat arbitrarily, as (a) lattice-dynamical properties, (b) properties directly related to the equation of state, or (c) properties pertaining to the stability of the lattice (melting and polymorphism). In fact, these properties are, of course, interrelated. Of particular interest is the relationship between a thermodynamic instability of the lattice and the phenomenon of melting. Upon comparing the calculated results with experimental data we are led to believe that a perfect crystal would melt when the repulsive pressure due to the phonons becomes too large to be canceled by the static pressure. This aspect of the results has been discussed earlier¹³ and is further elucidated here and elsewhere.¹⁴

In Sec. V the overall accuracy of the results is assessed in the light of the approximations which enter the theory. In general, the results are remarkably accurate for a first-principles, parameter-free, theory. At the same time, trends in the departures from the experimental results are evident which single out the approximations in greatest need of improvement.

II. APPROXIMATIONS

A. Adiabatic approximation

The adiabatic approximation results from assuming that the free energy of the system of electrons and nuclei does not involve excited states of the electrons. That is, the free energy depends solely on the electronic *ground*-state energy as a function of the positions of the nuclei. This is an excellent approximation for the alkali halides at all temperatures of interest because the band gaps in these materials are about two orders of magnitude higher than their melting temperatures and several orders of magnitude larger than their phonon frequencies.

B. Electronic ground-state energy

Three approximations have been used to express the electronic ground-state energy, U , as a function of the positions of the nuclei. The first two, the electron gas approximation (EGA) and the rigid-ion approximation (RIA) were used by Gordon and Kim¹ to calculate pair potentials for closed-shell atom (ion) pairs. The third approximation is obtained by writing U for the solid as a sum of these calculated pair potentials (PPA). The theorem of Hohenberg and Kohn¹⁰ states that the electronic ground-state energy is a universal functional of the charge density. The EGA is obtained by choosing this functional, which is not known exactly, to be that of a free-electron gas. In the RIA the total charge density of the system of ions is that obtained by simply summing up the charge densities of the free ions. Here I have used free-ion charge densities obtained from the Hartree-Fock approximation.¹² The PPA treats every ion pair as though it were isolated from the rest of the solid. Then the total contribution is obtained by summing over the pairwise interactions.

C. Perfect-crystal approximation

The solid is assumed to be in the form of an infinitely extended perfect crystal. The present calculations do not account for thermally induced lattice imperfections such as vacancies, dislocations, or surfaces. Such defects may have some important effects on the thermodynamic properties of the system at high temperatures.

D. Quasiharmonic approximation

For ease of discussion, consider a crystal whose structure is given by a single parameter, V , its volume; or think of V as a set of structure parameters. Given the interatomic forces one can calculate the normal mode frequencies, $\nu_i(V)$, using the well known theory of lattice dynamics in the

harmonic approximation.^{15,16} The $\nu_i(V)$ are the classical frequencies of small amplitude oscillations about the configuration given by V . At this point we are not concerned whether the crystal structure is stable or not. We simply note that once the interatomic forces are known, meaningful harmonic lattice-dynamics calculations can be performed for any volume we choose.

Let V_s be the volume for which static equilibrium is achieved at zero pressure. The dynamical matrix for V_s has some special properties. It is rotationally invariant because the conditions for rotational invariance are identical to those obtained by requiring the crystal to exert zero stress on its surroundings.¹⁷ Also, at V_s the Cauchy relations are satisfied for central pairwise forces. Lattice-dynamics calculations are normally done for V near V_s because of the availability of experimental data from which model parameters may be determined. Thus, such models may be unreliable if the external conditions force V too far from V_s . On the other hand, a first-principles lattice-dynamics calculation can be done for any volume, within the limits of the approximations used to derive the interatomic forces, with equal confidence in the values of $\nu_i(V)$.

If we assume that the vibrational energy levels of the system are those of independent harmonic oscillators with frequencies $\nu_i(V)$, then the free energy takes the simple form (Sec. IV of Ref. 15):

$$F(V, T) = U(V) + \frac{1}{2} \sum_i h \nu_i(V) + kT \sum_i \ln \{1 - \exp[-h \nu_i(V)/kT]\}, \quad (1)$$

where T is the temperature, h is Planck's constant, and k is Boltzmann's constant. Oddly enough this assumption is referred to as the quasiharmonic approximation (QHA) rather than the harmonic approximation, and we will also adopt this definition. Others use the term in a vague way to refer to the volume dependence of the frequencies,⁶ in spite of the fact that the volume dependence can be obtained from a sequence of harmonic lattice-dynamics calculations at selected volumes. In the discussion that follows I will occasionally refer to these frequencies as phonon frequencies, but it should be remembered that they are only such to the extent that the QHA is valid.

The volume dependence of F is implicit in the volume dependence of U and ν_i . For quasiharmonic model calculations it is convenient to extract an explicit dependence of F on V by expanding in a power series relative to some reference volume near V_s .⁸ The order of the expansion is limited by the experimental data available. For a first-principles calculation it is more convenient to simply

evaluate Eq. (1) for a sufficiently large number of selected volumes. In principle, one could determine the free energy from a single fully anharmonic calculation for an arbitrarily chosen V . However, except perhaps for diatomic molecules, this is not practical. The simpler approach is to obtain harmonic results as a function of volume and add any needed anharmonic corrections to the quasiharmonic results.

From Eq. (1) and the fact that pressure is given by $P = -(\partial F/\partial V)$, we obtain the following equation of state:

$$P + \frac{dU}{dV} = f(V, T), \quad (2)$$

where

$$f(V, T) \equiv V^{-1} \sum_i \gamma_i \left\{ \frac{1}{2} h \nu_i + h \nu_i / [\exp(h \nu_i/kT) - 1] \right\} \quad (3)$$

and

$$\gamma_i \equiv (-V/\nu_i) d\nu_i/dV. \quad (4)$$

In the above expressions, ν_i , γ_i , and dU/dV are functions of volume. In Eq. (2), P is the externally applied pressure, $f(V, T)$ is a pressure due to the vibration of the nuclei (vibrational pressure), and dU/dV is a pressure due to volume dependence of the electronic ground-state energy (static pressure).

III. NUMERICAL METHODS

In my earlier work⁴ I used the published tables¹ of potential values for the $\text{Na}^+ - \text{Cl}^-$ and $\text{K}^+ - \text{Cl}^-$ interactions to determine an equation of state for NaCl and KCl. The first (second) derivatives of the short-range part of the potentials were obtained numerically by (a) taking the first (second) differences from the tabulated values and (b) using polynomial interpolation to obtain values for an arbitrary separation. This is not the best method for getting accurate values for these derivatives unless one has *very* accurate values for the potentials at small intervals of separation. Inaccuracies in the values for the potential can cause spurious structure in the volume dependence of the vibrational pressure as a result of this method. The appearance of slight shoulders in the higher-temperature curves in Fig. 1 of Ref. 4 near $a = 5.8 \text{ \AA}$ is such an effect. A transcription error¹⁸ in Table IV of Ref. 1 was easily discovered because it produced a large oscillation in $f(V, T)$.

For this work I have adopted a least-squares-fitting procedure which avoids the difficulties posed by small inaccuracies in the computed values of the potential. The total interaction for an

ion pair is the sum of a long-range part ($\sim 1/r$) and a short-range part. The short-range part has contributions from the electrostatic, kinetic, exchange, and correlation energies of the overlapping electrons. Each of these short-range contributions has an approximately exponential behavior in the range of separations of interest here. I used an exponential form

$$\phi(r) = Ce^{-\beta r} \quad (5)$$

to fit each of the short-range contributions. The values for C and β were obtained by least-squares fitting to about 12 values of ϕ obtained from program POTLSURF.¹¹ The resultant values are listed in Table I, along with the range of separations, r , used for their determination. The following rationale was used selecting the ranges r_i to r_u given in Table I. For the alkali-halide interactions the range was chosen to correspond to that for which the material in the rocksalt structure is intrinsically stable, or possesses only real phonon frequencies. In all cases it was found that the intrinsically stable region was bounded below (above) at a value of r for which $C_{44} = 0$ ($C_{11} - C_{12} = 0$). These two conditions determine approximately the range of r values for the alkali-halide interactions shown

in Table I. The range used for fitting a particular interaction between like ions was selected to correspond to the lattice constants for the four compounds in which it is found. For example, the minimum value of r used in the fit to the $\text{Cl}^- - \text{Cl}^-$ interaction is roughly that found in LiCl , while the maximum is that for RbCl . However, somewhat smaller values of r were used to fit the short-range part of the electrostatic interaction between alkali ion pairs because it is difficult to calculate the short-range electrostatic contribution accurately when the interaction is weak.

The accuracy of this method of fitting the numerical potential to an analytic form was checked by varying the number and range of the fitted points and by adding an r^2 term in the exponential of Eq. (5). Variations in the results due to the different fitting techniques were found to be small compared to discrepancies with experiment; that is small compared to errors which result from the essential approximations outlined in Sec. II.

The volume dependence of the quantities entering Eqs. (1)–(4) were obtained by simply doing the requisite computations for a sufficiently large number of volumes in the range of interest. Typically, about 15 different lattice constants, a , on a

TABLE I. Values obtained for C and β by fitting the exponential from $Ce^{-\beta r}$ to calculated values of the short-range Coulomb (SRC), kinetic (KE), exchange (EX), and correlation (CORR) contributions to the indicated pair potentials in the range r_i to r_u . Results are in atomic units with energy in hartrees.

Ion pair	C				β				r_i	r_u
	SRC	KE	EX	CORR	SRC	KE	EX	CORR		
LiF	1.140	14.48	-1.920	-0.051	1.692	1.882	1.583	1.184	3.1	3.9
LiCl	4.044	14.63	-2.158	-0.063	1.581	1.565	1.341	1.024	4.0	5.1
LiBr	5.197	14.77	-2.227	-0.067	1.521	1.485	1.277	0.982	4.3	5.4
LiI	4.785	16.12	-2.474	-0.076	1.346	1.397	1.207	0.936	4.8	6.0
NaF	-8.949	42.70	-5.196	-0.130	1.869	1.776	1.509	1.146	3.8	4.7
NaCl	-8.069	48.78	-6.374	-0.174	1.569	1.521	1.312	1.017	4.7	5.8
NaBr	-9.234	52.47	-6.386	-0.190	1.525	1.459	1.261	0.983	5.0	6.2
NaI	-12.08	52.88	-7.281	-0.212	1.508	1.362	1.188	0.934	5.5	6.8
KF	-36.47	85.03	-9.201	-0.229	1.788	1.672	1.373	1.037	4.4	5.4
KCl	-44.35	97.07	-11.77	-0.316	1.557	1.460	1.220	0.937	5.1	6.3
KBr	-49.54	102.37	-12.55	-0.344	1.504	1.403	1.176	0.908	5.4	6.6
KI	-47.10	102.19	-13.42	-0.381	1.404	1.315	1.114	0.865	5.8	7.1
RbF	-59.92	115.19	-11.22	-0.274	1.756	1.629	1.323	0.997	4.7	5.7
RbCl	-76.78	134.79	-14.57	-0.384	1.544	1.435	1.185	0.908	5.4	6.6
RbBr	-85.88	143.82	-15.61	-0.422	1.492	1.383	1.145	0.882	5.7	6.9
RbI	-74.88	139.02	-16.60	-0.468	1.378	1.293	1.085	0.841	6.1	7.4
LiLi	-20.91	74.96	-4.721	-0.421	4.512	3.791	3.019	2.753	4.8	6.0
NaNa	-191.5	355.3	-16.82	-1.443	3.389	2.956	2.339	2.133	6.2	8.6
KK	-828.4	3422	-144.1	-18.81	2.586	2.433	1.942	1.833	7.0	9.2
RbRb	-5663	3391	-151.5	-18.92	2.621	2.173	1.734	1.631	7.4	9.8
FF	-18.97	23.03	-2.721	-0.127	1.568	1.388	1.092	0.859	5.4	7.4
ClCl	-85.21	60.85	-7.016	-0.310	1.399	1.210	0.955	0.756	6.8	8.8
BrBr	-122.1	87.00	-9.078	-0.398	1.336	1.166	0.915	0.726	7.4	9.2
II	-138.4	98.98	-10.90	-0.479	1.202	1.063	0.841	0.666	8.0	9.8

grid with $\Delta a \approx 0.1$ a.u. was found to be adequate. I found no advantage in evaluating Eq. (3) for the vibrational pressure as opposed to numerically differentiating the quantities in Eq. (1), except as a check on the results.

The summation over i in Eqs. (1) and (3) includes all normal modes in a crystal with volume V . Periodic boundary conditions were invoked in the usual way by replacing V by Nv , where v is the volume per primitive cell, and \sum_i by $\sum_j \sum_q$ where j is the branch index of the phonon dispersion curves ($j=1, 2, \dots, 6$ for the alkali halides) and \sum_q includes N regularly spaced points, q , in the Brillouin zone. The summation over q was found to be adequately converged for $N \sim 1000$.

The frequencies for a particular q are obtained by diagonalizing the dynamical matrix for that q . General expressions for the dynamical matrix of an ionic crystal with pairwise short-range forces are listed in Ref. 17. It is worthwhile to note how the volume dependence enters these expressions. The long-range Coulomb part is independent of v except for a multiplicative factor of $1/v$. The volume dependence of the short-range part enters solely through changes in the force constants. The total short-range part may be written as a sum of the contributions from each force constant, and the force constant may be factored from each term. For the NaCl structure I included short-range contributions to the dynamical matrix from nearest-neighbor alkali-alkali, halide-halide and alkali-halide interactions. This yields six terms which contribute to the short-range part of the dynamical matrix due to the first and second derivatives of the potentials for each type of interaction. Thus, seven matrices for each q (the seventh coming from the long-range part) can be computed one time and used for all volumes and all materials with the appropriate structure. For the CsCl structure an additional shell of halide-halide interactions were included.

The static energy per unit cell, $u = U/N$, is given by

$$u = 6\phi_{\text{AH}}(a/2) + 6\phi_{\text{AA}}(\sqrt{2}a/2) + 6\phi_{\text{HH}}(\sqrt{2}a/2) - 3.4952 e^2/a \quad (6)$$

for the NaCl structure, and

$$u = 8\phi_{\text{AH}}(\sqrt{3}a/2) + 3\phi_{\text{AA}}(a) + 3\phi_{\text{HH}}(a) + 6\phi_{\text{HH}}(\sqrt{2}a) - 2.0354 e^2/a \quad (7)$$

for the CsCl structure, where a is the corresponding lattice constant and e is the electronic charge. The static pressure is given by du/dv where $v = (a^3/4)(v = a^3)$ for the NaCl (CsCl) structure. As with the vibrational pressure, there is no real advantage in formally (as opposed to numerically)

differentiating Eqs. (6) and (7).

Once the potentials are specified the main computational problem in an automated determination of the equation of state is clearly the calculation of the vibrational pressure. However, this part of the calculation is not particularly time consuming for either human or computer. I found that a table of about 500 values on a suitable temperature and volume grid was sufficient for later use in an automated determination of equation-of-state properties, such as thermal expansion. The computation of the vibrational pressure table for a given material was accomplished by a single run requiring less than one minute of CP time using a Texas Instruments Advanced Scientific Computer.

IV. RESULTS

Many properties of materials can be calculated once the interatomic potentials are known. Here I report results for a number of properties of alkali halides which illustrate the kind of accuracy that can be achieved, given the approximations of Sec. II. In the analysis of these results we will be particularly concerned about any systematic discrepancies that may suggest the breakdown of one or more of the key approximations. Several properties will be considered: phonon frequencies and elastic constants, temperature and pressure dependence of the lattice constant, i.e., thermal expansion and compressibility, and the overall stability of the crystal (melting and polymorphism).

The previous work of Cohen and Gordon¹⁹ examines various *static* lattice properties of the alkali halides, with particular attention given to the polymorphism. Basu and Sengupta²⁰ have also employed Gordon-Kim potentials in harmonic lattice-dynamics calculations on alkali halides. The latter work does not consider temperature and pressure effects, but they offer a first-principles method for removing the rigid-ion approximation.

A. Lattice dynamics

The calculated phonon frequencies for NaCl at the symmetry points Γ , X , and L of the Brillouin zone are listed in Table II for comparison with experimental values. Also listed are the corresponding values of γ_i for comparison with the deformation dipole model calculations of Hardy and Karo.⁸ The results in Table II are for $a = 10.6$ a.u. which is approximately the lattice constant predicted for 0 K (see below). While the results show some significant discrepancies ($\sim 25\%$) the overall accuracy is reasonably good and representative of the rest of the alkali halides as well. However, the Li compounds and some of the heavier halides have larger discrepancies, like that seen for the

TABLE II. Phonon frequencies (ν_i) and mode Grüneisen parameters (γ_i) for NaCl at selected symmetry points in the Brillouin zone.

Wave vector	$\nu(\text{cm}^{-1})$		γ	
	Calc. ^a	Expt. ^b	Calc. ^a	Model ^c
Γ	175	172	2.4	2.4
Γ	332	264	1.0	0.9
X	95	87	-0.1	0.1
X	185	142	2.1	2.4
X	188	180	2.4	2.5
X	227	192	0.7	0.4
L	120	120	2.2	2.3
L	144	142	2.2	2.1
L	204	178	1.2	1.6
L	249	230	1.0	0.9

^a Present results for $a = 10.6$ a.u. or $T \sim 0$ K.

^b Experimental results for $T = 80$ K (Ref. 22).

^c Deformation dipole model (Ref. 8).

elastic constants (below). These results differ slightly from those reported earlier⁴ for two reasons: (1) there are small differences in alkali-halide potentials owing to improvements in the charge densities²¹ and interpolation procedures, and (2) alkali-alkali and halide-halide interactions, included in this work, were not included in the earlier work.

Expressions for the elastic constants are obtained by comparing the long-wavelength limit of the dynamical matrix with the corresponding results from elasticity theory.¹⁵ For the NaCl structure this yields

$$C_{11} = -1.2780 \frac{e^2}{r_1^4} + \frac{1}{r_1} \left(\phi_{\text{AH}}'' + \phi_{\text{HH}}'' + \phi_{\text{AA}}'' + \frac{1}{r_2} (\phi_{\text{HH}}' + \phi_{\text{AA}}') \right), \quad (8)$$

TABLE III. Comparison of the calculated (static values) and measured bulk moduli ($1/K$) and shear elastic constants ($C_{11} - C_{12}$ and C_{44}) for the alkali halides at zero pressure and room temperature in units of 10^{11} dynes/cm².

		$1/K$				$C_{11} - C_{12}$				C_{44}			
		F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
Calc.	Li	7.01	3.41	2.81	2.32	3.05	4.26	3.92	5.42	7.01	2.59	2.00	0.88
	Na	4.35	2.29	1.92	1.53	6.06	4.16	3.70	3.67	3.08	1.30	1.01	0.56
	K	3.31	1.96	1.70	1.41	6.14	4.12	3.70	3.54	1.82	0.92	0.75	0.46
	Rb	2.82	1.72	1.50	1.25	5.58	3.80	3.43	3.18	1.44	0.74	0.60	0.39
Expt. ^a	Li	6.96	3.17	2.56	1.88	6.59	2.66	2.07	1.45	6.35	2.46	1.93	1.35
	Na	4.85	2.50	2.06	1.59	7.27	3.65	2.92	2.14	2.81	1.26	0.99	0.74
	K	3.16	1.82	1.54	1.22	5.10	3.39	2.91	2.31	1.25	0.63	0.51	0.37
	Rb	2.77	1.62	1.38	1.11	4.13	3.02	2.66	2.21	0.92	0.46	0.38	0.28
% dev.	Li	1	8	10	23	-54	60	89	274	10	5	4	-35
	Na	-10	-8	-7	-4	-17	14	27	71	10	3	2	-24
	K	5	8	10	16	20	22	27	53	46	46	47	24
	Rb	2	6	9	13	35	26	29	44	57	61	58	39

^a Reference 23.

$$C_{12} = 0.0565 \frac{e^2}{r_1^4} + \frac{1}{r_1} \left(\frac{-1}{r_1} \phi_{\text{AH}}' + \frac{1}{2} (\phi_{\text{HH}}'' + \phi_{\text{AA}}'') - \frac{5}{2r_2} (\phi_{\text{HH}}' + \phi_{\text{AA}}') \right), \quad (9)$$

and

$$C_{44} = 0.6390 \frac{e^2}{r_1^4} + \frac{1}{r_1} \left(\frac{1}{r_1} \phi_{\text{AH}}' + \frac{1}{2} (\phi_{\text{HH}}'' + \phi_{\text{AA}}'') + \frac{3}{2r_2} (\phi_{\text{HH}}' + \phi_{\text{AA}}') \right), \quad (10)$$

where the derivatives of the ϕ_{AH} potential are evaluated at $r_1 = a/2$, and the derivatives of ϕ_{AA} and ϕ_{HH} at $r_2 = \sqrt{2}a/2$. Since these expressions give the elastic behavior of the static lattice as a function of volume we shall refer to them as the static elastic constants. Experimentally the elastic behavior can be determined dynamically, which gives the elastic response in an adiabatic environment, or through a static measurement in an isothermal environment, which of course gives the isothermal response. The distinction between the static and isothermal bulk modulus will be clarified below. At low temperatures (here $T \lesssim 300$ K) such distinctions are not significant compared to limitations in accuracy imposed by the fundamental approximations. It is convenient to express the elastic properties in terms of the bulk modulus and the two shear elastic constants. They are, respectively, $1/K = (C_{11} + 2C_{12})/3$, $C_{11} - C_{12}$, and C_{44} , where K is the compressibility. The room-temperature bulk and shear elastic constants, obtained by substituting the room-temperature calculated value of a (see below) into the expressions above, are listed and compared with experimental values in Table III. Except for the (lithium) compounds, and also the iodides, the calculated values for

TABLE IV. Comparison of the calculated (static values) and measured temperature derivative of the elastic constants (units of 10^8 dyne/cm² K).

		$-d(1/K)/dT$				$-d(C_{11}-C_{12})/dT$				$-dC_{44}/dT$			
		F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
Calc.	Li	3.9	1.4	1.2	0.7	4.6	2.4	2.0	1.7	0.8	0.1	0.1	-0.1
	Na	2.0	1.2	1.0	0.7	3.6	2.4	2.1	1.7	0.0	0.0	0.0	-0.1
	K	1.5	1.0	0.9	0.7	3.2	2.2	1.9	1.6	-0.1	-0.1	-0.1	-0.1
	Rb	1.4	0.9	0.8	0.6	3.0	2.0	1.8	1.6	-0.1	-0.1	-0.1	-0.1
Expt. ^a	Li	2.5	1.8	1.5		7.5	4.3	3.8		1.8	1.0	0.9	
	Na	1.8	1.2	1.1	0.9	6.6	4.2	3.5	2.9	0.6	0.3	0.2	0.2
	K	1.3	0.9	0.7	0.6	5.1	3.8	3.4	2.9	0.3	0.1	0.1	0.1
	Rb	1.3	0.8	0.7	0.6	4.5	3.5	3.1	2.7	0.2	0.1	0.1	0.1

^a Reference 23.

$1/K$ and $C_{11} - C_{12}$ are in rather good agreement with the experimental values. A substantial portion of the discrepancy for the lithium compounds can be blamed on the pair-potential approximation (see discussion below). The calculated values for C_{44} are in good agreement with experimental results for the sodium compounds, but progressively worse agreement is seen for the potassium and rubidium compounds. These discrepancies may also result from the breakdown of the pair-potential approximation because the errors are largest for those materials which show the greatest violation of the Cauchy relation, $C_{12} = C_{44}$. The calculated elastic constants only satisfy the Cauchy condition at $V = V_s$ the static equilibrium volume, but the experimentally observed violations of the Cauchy relation are too large to be explained as a volume effect. This is especially true for the rubidium compounds for which we find the largest errors in C_{44} . We are therefore led to suspect the breakdown of the pair-potential approximation as the source of the large errors in C_{44} for the Rb compounds, and to a lesser extent, for the K compounds. However, errors in C_{44} do not affect very much the equation of state because C_{44} is only weakly temperature dependent (Table IV).

The most significant volume dependence of the phonon frequencies, in so far as the equation of state is concerned, can be understood by looking at the volume dependence of $C_{11} - C_{12}$ and C_{44} . Generally speaking, the frequencies decrease with increasing volume, but for sufficiently small r_1 the ϕ'_{AH}/r_1^2 term in Eq. (10), which is negative, begins to dominate and pull the corresponding acoustic branch to zero. The signs of the Coulomb and ϕ'_{AH} terms are reversed for the $C_{11} - C_{12}$ branch; thus, for a sufficiently large volume $C_{11} - C_{12} = 0$. Approximate values of r_1 where C_{44} and $C_{11} - C_{12}$ are zero are given in Table I (see discussion in Sec. III). The temperature dependence of the phonon frequencies is, within the QHA, given implicitly

through the temperature dependence of the volume. Above room temperature the elastic constants are essentially linear in T for both theory (see Fig. 3 of Ref. 4) and experiment.²³ The computed gradients are compared with experimental results in Table IV. We find the agreement is similar to that found for the elastic constants themselves.

B. The equation of state

The lattice constant and its dependence on pressure and temperature is obtained from the equation of state [Eq. (2)], which may be shown graphically by plotting both dU/dV and the family of curves $f(V, T)$ as a function of lattice constant [$a = (4v)^{1/3}$ for the rocksalt structure]. Alternatively $P(V, T)$ may be plotted, as in Ref. 4, but I believe it is more instructive to see the separate contributions. Figure 1 shows the static and vibrational pressure contributions to the equation of state for NaCl. Qualitatively similar results are obtained for the rest of the alkali halides. The temperature dependence of the $P=0$ lattice constant is given by

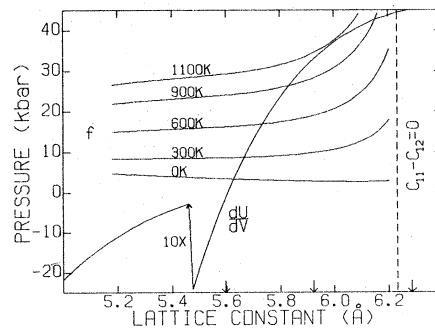


FIG. 1. Plot of the electron pressure and phonon pressure (for selected temperatures) for NaCl as a function of lattice constant. The arrows on the abscissa indicate the measured volumes of the solid at 0 K and T_m (Ref. 24) and of the liquid at T_m (Ref. 25).

the points on the abscissa where the static pressure curve intersects the vibrational pressure curves. The $P \neq 0$ values are obtained in the same way after first shifting the static pressure curve by the amount P . We note that for $P = 0$ the lattice becomes unstable at about 1090 K. Above this critical temperature, T_c , the magnitude of the vibrational pressure is larger than the static pressure for all volumes. In terms of the free energy, the critical temperature is defined as that temperature above which there is no longer a minimum as a function of volume. Below T_c a given vibrational-pressure curve intersects the static-pressure curve in two places; the first corresponds to a minimum in F , and the second, a maximum.

We note that as $T \rightarrow T_c$ the isothermal bulk modulus β_T , goes to zero. β_T is not to be confused with $1/K$ above; the latter is just the slope of the static pressure curve while β_T is $1/K$ minus the slope of the vibrational-pressure curve. The reason for the sharp increase in the vibrational-pressure curves above $a \cong 5.8 \text{ \AA}$ is due to the onset of the intrinsic shear instability $C_{11} - C_{12} = 0$, which occurs at $a = 6.25 \text{ \AA}$. The actual solid can never reach the volume where $C_{11} - C_{12} = 0$ because β_T necessarily goes to zero first¹⁴ as the temperature is increased.

The accuracy of the equation-of-state calculations can be assessed from the results in Tables V–VII and Fig. 2. The computed values of the lattice constant at zero pressure and temperatures

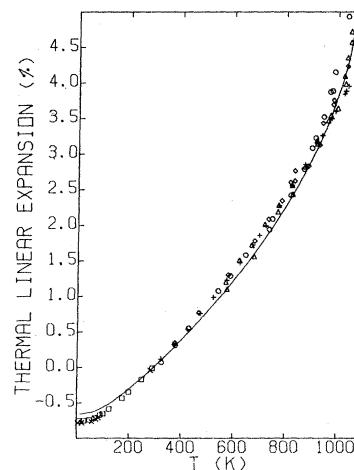


FIG. 2. Comparison of calculated thermal expansion for NaCl (solid curve) with selected experimental data (\square —Ref. 31, \times —Ref. 32, $+$ —Ref. 33, \circ —Ref. 34, \diamond —Ref. 35, and \triangle —Ref. 36) as tabulated in Ref. 24.

$T = 0, 300, 500,$ and 800 K , are compared with experimental values in Table V. The thermal-expansion coefficients, $\alpha = (1/a)(\partial a/\partial T)$, are given in Table VI for $T = 300 \text{ K}$ and $P = 0$. The pressure dependence of the lattice constant is shown in terms of the $T = 300 \text{ K}$ volume ratios V_p/V_0 in Table VII. The measured critical pressures were used to compute the volume ratios for the compounds undergoing transformations to the CsCl structure. Figure 2 shows the temperature de-

TABLE V. Comparison of the calculated and measured lattice constants, a , for the alkali halides at $T = \sim 0, 300, 500,$ and 800 K . Measured results are from Ref. 26 unless otherwise specified.

	$a(300 \text{ K})$		$\sim 0 \text{ K}$		$[\Delta a/a(300 \text{ K})](10^{-5})$		800 K	
	Calc.	Expt. ^a	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
LiF	4.062	4.028	-623	-505	1120	777		2226
LiCl	4.960	5.140	-450 ^b	-654 ^b	714	962 ^d	2160	
LiBr	5.290	5.502	-462 ^b	-756 ^b	705	1056 ^e	2080	
LiI	5.564	6.000	-347 ^b	-902 ^b	532		1510	
NaF	4.706	4.634	-557	-547	710	712	2170	1912
NaCl	5.666	5.640	-670	-766	762	900	2240	2429
NaBr	5.991	5.978	-546 ^b	-656 ^b	761	896 ^d	2260	2560 ^d
NaI	6.381	6.474	-677	-967	694	945 ^d	2030	
KF	5.221	5.348	-451 ^b	-491 ^{b,d}	670	701 ^d	1970	
KCl	6.060	6.294	-660	-745	703	829	2090	2242
KBr	6.342	6.596	-714	-833	720	851	2110	2361
KI	6.716	7.066	-692	-893	677	942	1946	2602
RbF	5.534	5.630	-614		683		1990	
RbCl	6.347	6.582	-701	-772 ^d	717	837 ^c	2150	2248 ^c
RbBr	6.626	6.890	-762	-852 ^d	738	812 ^c	2150	2158 ^c
RbI	7.006	7.342	-749	-942 ^d	704	837 ^c	2040	2321 ^c

^a Reference 27.

^d Reference 24.

^b Values for 123 K.

^e Reference 29.

^c Reference 28.

TABLE VI. Comparison of the calculated and measured thermal-expansion coefficients for zero pressure and room temperature in units of 10^{-6} K^{-1} . Measured results are from Ref. 26 unless specified otherwise.

	LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI
Calc.	40.5	31.1	31.2	26.8	31.4	34.5	34.7	31.7
Expt.	33.2	43.2	49.8	59.4	31.7	39.7	42.3 ^a	45.5
% dev	22	-28	-37	-55	-1	-13	-18	-30
	KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
Calc.	30.1	32.2	33.1	31.3	30.9	32.8	34.0	32.5
Expt.	31.7	37.1	38.7	40.8	34.0 ^b	36.1 ^a	37.8 ^a	38.0 ^a
% dev	-5	-13	-14	-23	-9	-9	-10	-15

^a Reference 24.

^b Reference 30.

pendence of α for NaCl. Overall, these results constitute a reasonably accurate prediction of $\alpha(P, T)$ considering that they were derived from first principles.

C. Melting

In a proper theory of melting the melting temperature is defined by the equality of the free energies of the liquid and solid phases. However,

TABLE VII. Room-temperature volume ratios, V_P/V_0 , for selected alkali halides (V_P is the volume at pressure P and V_0 the volume at zero pressure).

P (kbar)	NaCl		NaI			
	Calc.	Expt. ^a	Calc.	Expt. ^a		
5	0.981	0.980	0.972	0.970		
10	0.964	0.962	0.948	0.944		
20	0.934	0.932	0.909	0.902		
50	0.867	0.864	0.825	0.813		
100	0.793	0.788				
	KCl		KBr		KI	
	Calc.	Expt. ^a	Calc.	Expt. ^a	Calc.	Expt. ^a
5	0.978	0.974	0.975	0.970	0.970	0.965
10	0.958	0.951	0.953	0.944	0.945	0.935
20	{0.925 0.805 ^b	{0.915 0.807}	0.798 ^b	0.800	0.767 ^b	0.802
50	0.750	0.737	0.738	0.724	0.705	0.718
100	0.690	0.678	0.674	0.663	0.640	0.650
	RbCl		RbBr		RbI	
	Calc.	Expt. ^a	Calc.	Expt. ^a	Calc.	Expt. ^a
5	0.975	0.970	0.972	0.967	0.966	0.965
	0.835 ^b	0.830	0.830 ^b	0.834	0.808 ^b	0.839
10	0.819	0.811	0.813	0.811	0.789	0.807
20	0.794	0.780	0.784	0.780	0.759	0.762
50	0.738	0.706	0.724	0.704	0.695	0.672
100	0.677	0.635	0.660	0.635	0.630	0.600

^a Reference 26.

^b Transition to the CsCl structure.

this does not exclude the possibility that melting may be controlled or conditioned by an instability in one of the separate phases. It can be argued that the instability described above, which has $\beta_T \rightarrow 0$ as $T \rightarrow T_c$ plays an important role in causing solids to melt.^{4, 13, 14, 41-44} First of all, we note from the results in Tables V, VI, and VIII that the calculated values for T_c are in good agreement with the corresponding melting temperatures (T_m) for those compounds that have similarly good agreement with thermal-expansion data. In other words, if the interatomic forces are predicted accurately by the present theory then T_c is close to T_m . This point will be further discussed and refined to include qualitatively the effect of anharmonic corrections in the next section. Also, from

TABLE VIII. Comparison of T_c with T_m and dT_c/dP with dT_m/dP at $P=0$.

Compound	(K)		(K/kbar)	
	T_c	T_m	dT_c/dP	dT_m/dP
LiF	630	1143 ^a	7.5	
LiCl	1060	887 ^a 878 ^b	21	24.2 ^b
LiBr	1130	820 ^a	24	
LiI	1600	719 ^a	35	
NaF	1030	1265 ^{a,b,c}	17	15.1 ^b 18.0 ^c
NaCl	1090	1073 ^{a,b,c}	29	23.6 ^b 24.1 ^c
NaBr	1110	1028 ^a 1014 ^{b,c}	34	28.7 ^b 27.1 ^c
NaI	1270	924 ^a 928 ^{b,c}	51	33.2 ^b 35.6 ^c
KF	1150	1153 ^a 1124 ^d	22	22.6 ^d
KCl	1150	1063 ^a 1043 ^{b,d}	36	29.1 ^b 26.5 ^d
KBr	1170	1003 ^a 1006 ^d	42	37.8 ^d
KI	1270	996 ^a 957 ^d	53	64.2 ^d
RbF	1160	1033 ^a 1071 ^e	27	15.1 ^e
RbCl	1140	1018 ^a 990 ^{b,e}	43	25.0 ^b 25.6 ^e
RbBr	1140	955 ^a 950 ^e	48	32.2 ^e
RbI	1220	915 ^a 913 ^e	58	32.4 ^e

^a Reference 26.

^b Reference 37.

^c Reference 38.

^d Reference 39.

^e Reference 40.

the results in Table VIII we see that the pressure derivatives of T_c and T_m are in favorable agreement with each other.

Others have noted the proximity of T_c to T_m for rare-gas solids but prefer not to make any causal connection between the $\beta_T \rightarrow 0$ instability and melting. Dobbs and Jones,⁴⁹ in reviewing the work of Kane⁴² and Herzfeld and Goepfert-Mayer,⁴¹ dismiss the correlation as a "defect" in the theory because it predicts $T_c < T_m$ and (consequently) gives too rapid an increase in thermal expansion at high temperatures. For the reasons stated below, I claim that the "defect" is quantitative in nature, owing mainly to the quasiharmonic approximation and not because of anything essentially wrong with the basic idea. Using self-consistent phonon theory and Green's-function techniques, Plakida and Siklas⁵⁰ obtain the $\beta_T \rightarrow 0$ instability for a simple model of an fcc lattice. While they note that T_c must be an upper bound to T_m they do not suggest that any real connection exists between melting and the $\beta_T \rightarrow 0$ instability. Here I argue that the onset of the $\beta_T \rightarrow 0$ instability is important in explaining why solids melt, with any difference between the anharmonically corrected T_c and T_m ascribed to lattice imperfections.

It is natural to associate the volume for which $C_{11} - C_{12} = 0$ to that of the liquid because in either case there is no resistance to elastic shear; some theories of melting are based entirely on this connection.^{51,52} When this is done we find that not only does the present theory give a reasonably accurate prediction of thermal expansion up to the melting temperature (for those compounds with $T_c \cong T_m$), but the volume discontinuity that occurs upon melting is also accurately predicted. This is illustrated by the three small arrows on the abscissa in Fig. 1; they mark the measured volume of the solid at $T = 0$ and $T = T_m$, and the liquid at $T = T_m$.

Further evidence that the $\beta_T \rightarrow 0$ instability plays a role in melting can be seen in high-temperature thermal-expansion data for the alkali halides. Specifically, the greater-than-linear increase in α seen at high temperatures, can be satisfactorily interpreted as the onset of the $\beta_T \rightarrow 0$ instability. This idea has been quantified for NaCl,¹³ for which an abundance of high-temperature thermal-expansion data exists. In the high-temperature limit ($T \rightarrow T_c$) the present theory gives

$$a(T) = a_0 + a_1(T_c - T)^{1/2}. \quad (11)$$

This follows by expanding the static and vibrational pressure curves to second order in a and noting that in the high-temperature limit the phonon pressure is linear in T . When a_0 , a_1 , and T_c are

treated as adjustable parameters Eq. (11) gives a substantially better fit to the high-temperature thermal-expansion data than can be achieved by the usual polynomial fits. For NaCl the optimum value of T_c is found to be within 10% of the melting temperature ($T_m < T_c \lesssim 1.1 T_m$), but accurate data are needed to fix T_c within this range.

Collectively the above results show, rather convincingly I believe, that the $\beta_T \rightarrow 0$ instability plays a role in melting. Yet, it would be misleading to say that it is *the* cause of melting. Remember that the $\beta_T \rightarrow 0$ instability is itself caused by the decreasing value of $C_{11} - C_{12}$ with increasing volume. It is reasonable to expect the properties of the solid *very* near T_m to be largely controlled by lattice imperfections (e.g., vacancies, dislocations, and surfaces). In fact, theories of melting have been constructed based on lattice imperfections.⁵³⁻⁵⁶ The increasingly important role for lattice imperfections, as $T \rightarrow T_m$, would be enhanced by the diminishing value of β_T because the thermal generation of such defects would be made easier by the low value of β_T . The question of how near the temperature must be to the melting temperature before lattice imperfections play a dominant role is therefore indicated by the value of $T_c - T_m$. As was mentioned above, when T_c is deduced from thermal-expansion data within the present theory we find $T_c - T_m \lesssim 0.1 T_m$. Anharmonic corrections to T_c could be included in the manner described below (Sec. V), but greater accuracy in the high-temperature data would still be required to draw more quantitative conclusions about the value of $T_c - T_m$.

With increasing pressure the theoretical results for dT_c/dP are nearly constant within the quasiharmonic approximation. If, as argued below, anharmonic corrections tend to compress the phonon pressure curves at high temperatures, then the anharmonically corrected dT_c/dP may even increase with increasing pressure. However, experimental results show a gradual decrease in dT_m/dP with increasing pressure. Together these trends suggest that T_c moves to a relatively higher value above T_m as pressure increases, which in turn implies a more dominant role for lattice imperfections in describing the properties of the solid near melting at elevated pressures.

D. Polymorphism

Cohen and Gordon¹⁹ have previously treated the problem of polymorphism in the alkali halides within the static lattice approximation. They calculated critical pressures (P_c) above which the crystal transforms to the CsCl structure, by evaluating the static Gibbs energy, $G = U + PV$, for both structures. To justify the static lattice ap-

proximation they noted that experiments show that P_c has little temperature dependence. I have performed similar calculations of P_c with the vibrational contributions to the Gibbs energy included ($G=F+PV$), and find P_c to be essentially independent of temperature, confirming the static lattice approximation in this case. This is illustrated in Fig. 3 where G for KCl is plotted for selected temperatures as a function of pressure. The results for the rest of the alkali halides are qualitatively similar.

The calculated and measured values of P_c are compared in Table IX. The calculated values differ somewhat from those of Cohen and Gordon, primarily because they used a scaled electron-gas approximation for computing pair potentials while I have retained the original coefficients in the electron-gas formulas. The comparison with experiment is not as good as one might expect from the equation-of-state results. The wrong $P=0$ structure is predicted in some cases ($P_c < 0$) and P_c for NaCl (for which a quite accurate equation of state is obtained) is much too low. Using the scaled EGA improves this situation somewhat,¹⁹ but large discrepancies still remain. On the other hand, certain trends in P_c for these compounds are correctly predicted; compounds with light alkali ions show a marked preference for the rock-salt structure, and similarly for the fluorides. Below I argue that the large errors in the values predicted for P_c are likely caused by a breakdown in the pair-potential approximation.

V. DISCUSSION

In this section I offer an analysis of the discrepancies between theory and experiment, which is mostly qualitative, but nevertheless seems to

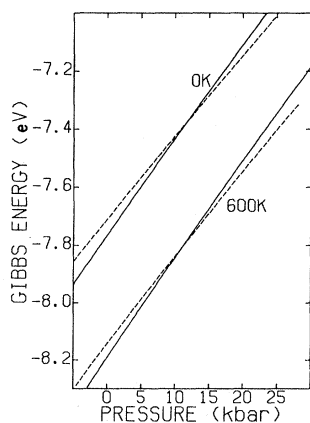


FIG. 3. Calculated pressure dependence of the Gibbs free energy for KCl, at $T=0$ and 600 K, in the NaCl (solid line) and CsCl (dashed line) structures.

TABLE IX. Critical pressures (P_c) for polymorphism in the alkali halides.

Compound	P_c (kbar)	
	Calc.	Expt. ^a
LiF	>200	>100
LiCl	>200	>100
LiBr	96	>100
LiI	-27	>100
NaF	>200	>200
NaCl	46	300
NaBr	30	>100
NaI	-7	>100
KF	75	>100
KCl	12	20
KBr	7	19
KI	-10	19
RbF	61	>100
RbCl	4	5
RbBr	0	5
RbI	-9	4

^a As tabulated in Ref. 19.

point out which approximations are in greatest need of improvement. First let us consider the EGA. Waldman and Gordon³ have recently modified the EGA by scaling the kinetic, exchange, and correlation energies to match the correct atomic values. I have investigated the effect of using the scaled EGA on the equation of state for selected alkali halides. In some cases there is a modest improvement, but for others the agreement is worsened. For example for NaI the EGA yields a value for the thermal-expansion coefficient that is 30% too low while the scaled EGA improves this discrepancy to 18% (still too low). However, for NaF the EGA value for α is in rather good agreement with experiment but the scaled EGA is about 20% too high. The scaled EGA results for polymorphic critical pressures¹⁹ offer a modest improvement over the EGA results (Table IX) but still large discrepancies remain. In short, we must look to other approximations to correct the larger discrepancies between theory and experiment.

The main effect of non-rigid-ion-type behavior on the lattice dynamics of alkali halides is known from model calculations to be a lowering of the LO branch of the phonon dispersion curves.⁵⁷ While this substantially improves the agreement for the phonon frequencies, its effect on the equation of state would be small because the LO branch is only weakly volume dependent. Thus, the RIA does not appear to be responsible for the larger discrepancies either.

The greatest error made by the present theory, at least at low temperature, seems to come from

the PPA. This can be seen by noting that the magnitudes of the errors are related to the relative sizes of the ions. Large errors are found for those compounds with a big difference between the sizes of the constituent ions. This is most evident in the thermal expansion results (see Table VI). For example, the predicted values of α for the iodides are in all cases considerably too small, with progressively worse agreement going from Rb to Li. The reason why a large size difference between constituent ions produces large errors in the PPA can be understood from a simple geometrical argument. In the calculation of a pair potential the largest contribution comes from the region where there is greatest overlap of the two charge densities. However, in a solid a substantial portion of the *total* charge density in the overlap region of a given ion pair can come from neighboring ions as well. This is especially true if one ion is much smaller than the other. The fact that this simple picture correlates well with the major discrepancies between theory and experiment points to the PPA as the main source of error in the present theory.

The generally poorer agreement between theory and experiment for the polymorphic critical pressures is also an indication of a breakdown in the PPA. Here the values obtained for P_c depend on a comparison of energies computed for two different crystal structures with different coordination numbers. Thus, zeroth-order corrections to the PPA energies are important in the calculation of P_c , but do not contribute to the equation of state for a single structure because the latter requires only derivatives of energy.

As discussed above, the amount by which the Cauchy relation is violated can be used as a measure of the validity of the PPA. The present theory predicts that at room temperature C_{44} will be about 10% larger than C_{12} , owing to the more rapid decrease in C_{12} with increasing volume. Indeed, we find best results for materials with $C_{12} \approx C_{44}$ (e.g., NaF and NaCl). However, we also find reasonably good equations of state for the lighter potassium and rubidium compounds, for which C_{44} is 10 to 30% less than C_{12} . Since the error made by the PPA in this case is primarily in overestimating C_{44} , and since C_{44} is relatively volume independent (both theoretically and experimentally), it introduces little error in the equation of state.

In the previous section we noted that a good prediction of the thermal expansion is obtained over the entire temperature range (0 K to melting) for those compounds which have $T_c \approx T_m$ (see Fig. 2). If T_c is much larger than T_m , as is the case for the iodides, then the thermal expansion is too low. If T_c is much smaller than T_m , as it is for LiF,

then the thermal expansion is too high. On closer scrutiny, however, we see that if T_c is very near T_m , as it is for NaCl, then the thermal expansion is predicted a little too low at low temperatures and a little too high at high temperatures. If the thermal expansion is more accurately predicted at low temperatures, as for NaF, then T_c falls somewhat below T_m . This can be interpreted as a gradual worsening of the QHA with increasing temperature. (A good low-temperature result is an indication that the interatomic forces are accurately predicted.) Including anharmonic corrections to the QHA would therefore (in order to bring agreement at high temperatures) reduce the vibrational pressure at high temperatures and thus postpone the $\beta_T \rightarrow 0$ instability to a value of T_c near or somewhat greater than T_m . This anharmonic lowering of the vibrational pressure at high temperatures is consistent with the results of Feldman *et al.*⁵⁸ who showed that anharmonic corrections for rare-gas solids effectively reduce γ . This type of anharmonic effect has a simple physical interpretation. As the temperature and vibrational amplitude increases, so does the anharmonic part of the restoring force. This prohibits the phonon frequencies from decreasing with temperature as fast as they would in the QHA which, in turn, lowers the effective γ .

One could incorporate anharmonic effects in the analytic form of $a(T)$ near T_c [Eq. (11)] by replacing T by a more slowly varying function of T , say T^ρ with $\rho < 1$. However, this would not alter significantly the qualitative features of the thermal expansion at high temperatures [$a(T)$ would still attain an infinite slope ($\alpha \rightarrow \infty$) at $T = T_c$]. It might lead to a better estimate of the proximity of T_c to T_m if the uncertainties in the high-temperature thermal-expansion data can be resolved. But currently the QHA result for NaCl ($T_m < T_c \approx 1.1 T_m$) is about as good as one can do given these uncertainties.

The amount by which T_c lies above T_m is an indication of the influence of lattice imperfections on the properties of the solid at high temperatures. The present results suggest that lattice imperfections are not an important factor for temperatures up to at least $0.9 T_m$. However, the fact that dT_m/dP decreases with pressure, contrary to the prediction for dT_c/dP , implies an increasingly important role for lattice imperfections near T_m at high pressures.

ACKNOWLEDGMENTS

Helpful discussions with J. R. Hardy, J. L. Feldman, B. M. Klein, and H. B. Rosenstock, throughout the course of this work, are gratefully acknowledged.

- ¹R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**, 3122 (1972).
- ²For a review and references before 1978, see M. J. Clugston, *Adv. Phys.* **27**, 893 (1978).
- ³M. Waldman and R. G. Gordon, *J. Chem. Phys.* **71**, 1325 (1979); **71**, 1340 (1979); **71**, 1353 (1979).
- ⁴L. L. Boyer, *Phys. Rev. Lett.* **42**, 584 (1979).
- ⁵See, for example, *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976).
- ⁶H. D. Merchant, K. K. Srivastava, and H. D. Pandey, *Crit. Rev. Solid State Sci.* **3**, 451 (1973) and references therein.
- ⁷D. L. Decker, *J. Appl. Phys.* **36**, 157 (1965); **42**, 3239 (1971).
- ⁸R. J. Hardy and A. M. Karo, *J. Phys. Chem. Solids* **31**, 905 (1977).
- ⁹R. W. Roberts and R. Ruppini, *Phys. Rev.* **4**, 2041 (1971).
- ¹⁰P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹¹S. Green and R. G. Gordon, Quantum Chemistry Program Exchange, QCPE Program No. 251, Chemistry Department, Indiana University (unpublished).
- ¹²E. Clementi and C. Roetti, *Atomic Data and Nuclear Tables* (Academic, New York, 1974).
- ¹³L. L. Boyer, *Proc. 7th International Thermal Expansion Symposium*, Nov. 1979, in press.
- ¹⁴L. L. Boyer, *Phys. Rev. Lett.* **45**, 1858 (1980).
- ¹⁵M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).
- ¹⁶A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Theory of Lattice Dynamics in the Harmonic Approximation*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963).
- ¹⁷L. L. Boyer, *Phys. Rev. B* **9**, 2684 (1974).
- ¹⁸The short-range part of the potential for $R=6.0$ should be 0.2311 $D-2$ (R. G. Gordon, private communication).
- ¹⁹A. J. Cohen and R. G. Gordon, *Phys. Rev. B* **12**, 3228 (1975).
- ²⁰A. N. Basu and S. Sengupta, *Phys. Rev. B* **14**, 2633 (1976).
- ²¹The present work uses charge densities derived from the 1974 Clementi and Roetti Table (Ref. 12), whereas the results published in Ref. 1 were based on similar 1965 Table [E. Clementi, *IBM J. Res. Dev. Suppl.* **9**, 2 (1965)].
- ²²G. Raunio, L. Almquist, and R. Stedman, *Phys. Rev.* **178**, 1496 (1969).
- ²³S. Haussühl, *Z. Phys.* **159**, 223 (1960); and K. Sprangenberg and S. Haussühl, *Z. Kristall.* **109**, 422 (1957).
- ²⁴*Thermal Expansion of NonMetallic Solids*, Vol. 13 of *Thermophysical Properties of Matter*, edited by Y. S. Touloukian and C. Y. Ho (Plenum, New York, 1977).
- ²⁵G. J. Janz, F. W. Dampier, G. R. Lakshminarayanan, P. K. Lorenz, and R. P. Tomkins, U. S. National Bureau of Standards, National Standards Reference Data Series—15 (U.S. GPO, Washington, D. C., 1968).
- ²⁶American Institute of Physics Handbook, edited by D. E. Gray (McGraw-Hill, New York, 1972), 3rd edition.
- ²⁷M. P. Tosi, *Solid State Phys.* **16**, 1 (1964).
- ²⁸K. K. Srivastava and H. D. Merchant, *J. Phys. Chem. Solids* **34**, 2069 (1973).
- ²⁹J. E. Rapp and H. D. Merchant, *J. Appl. Phys.* **44**, 3919 (1973).
- ³⁰C. S. Sahagian and C. A. Pitha, AFCRL-72-0170 special reports No. 135 (unpublished).
- ³¹P. P. M. Meincke and G. M. Graham, *Can. J. Phys.* **43**, 1853 (1965).
- ³²G. K. White, *Proc. R. Soc. London* **80**, 373 (1962).
- ³³F. D. Enck and J. G. Dommel, *J. Appl. Phys.* **36**, 839 (1965).
- ³⁴E. Laredo, *J. Phys. Chem. Solids* **30**, 1037 (1969).
- ³⁵H. F. Fischmeister, *Acta Crystallogr.* **9**, 416 (1956).
- ³⁶M. V. Smirnov, M. M. Vasipevskaya, and G. V. Vupov, *Tr. Inst. Elektrokhim. Akad. Nauk SSSR, Ural. Fil.* **13**, 82 (1970).
- ³⁷S. P. Clark, *J. Chem. Phys.* **31**, 1526 (1959).
- ³⁸C. W. F. T. Pistorius, *J. Chem. Phys.* **45**, 3513 (1966).
- ³⁹C. W. F. T. Pistorius, *J. Phys. Chem. Solids* **26**, 1543 (1965).
- ⁴⁰C. W. F. T. Pistorius, *J. Chem. Phys.* **43**, 1557 (1965).
- ⁴¹K. F. Herzfeld and M. Goeppert-Mayer, *Phys. Rev.* **46**, 995 (1934).
- ⁴²G. Kane, *J. Chem. Phys.* **7**, 603 (1939).
- ⁴³J. L. Feldman and L. L. Boyer, *Physica* **99B**, 347 (1980).
- ⁴⁴The theory of melting due to Ida (see Refs. 45–48) is based on a different kind of instability of the lattice, but one which leads to similar high-temperature properties. Thus, the arguments Ida uses to make the connection between lattice stability and melting are in some respect similar to that found here.
- ⁴⁵Y. Ida, *Phys. Rev.* **187**, 951 (1969).
- ⁴⁶Y. Ida, *Phys. Rev. B* **1**, 2488 (1970).
- ⁴⁷K. Ishizak, P. Bolsaitis, and I. L. Spain, *Phys. Rev.* **7**, 5412 (1973).
- ⁴⁸Y. Ida, *Phys. Rev. B* **7**, 5416 (1973).
- ⁴⁹E. R. Dobbs and G. O. Jones, *Rep. Prog. Phys.* **20**, 516 (1957).
- ⁵⁰N. M. Plakida and T. Siklóš *Acta Phys. Acad. Sci. Hung.*, Tomus **45**, 37 (1978).
- ⁵¹M. Born, *J. Chem. Phys.* **7**, 591 (1939).
- ⁵²J. L. Tallon, W. H. Robinson, and S. I. Smedley, *Philos. Mag.* **36**, 741 (1977); and *Nature* **266**, 337 (1977).
- ⁵³T. Goreck, *Z. Metallk.* **65**, 426 (1974).
- ⁵⁴D. Kuhlmann-Wilsdorf, *Phys. Rev.* **140**, A1599 (1965).
- ⁵⁵R. M. J. Cotterill, *Philos. Mag.* **32**, 1283 (1975).
- ⁵⁶L. Pietronero and E. Tosatti, *Solid State Commun.* **32**, 255 (1979).
- ⁵⁷J. R. Hardy and A. M. Karo, *Lattice Dynamics and Statics of Alkali Halide Crystals* (Plenum, New York, 1979).
- ⁵⁸C. Feldman, J. L. Feldman, G. K. Horton, and M. L. Klein, *Proc. Phys. Soc. London* **90**, 1182 (1967).