Calculation of Thermal Expansion, Compressiblity, an Melting in Alkali Halides: NaCl and KCl

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A parameter-free calculation of the equation of state for KCl and NaCl is presented which gives an accurate prediction of the equilibrium lattice constant over wide-ranging values of pressure and temperature. The results also show a lattice instability which is consistent with melting.

In this Letter I present a parameter-free calculation of the equation of state of a solid. It is the parameter-free aspect of this calculation which is important because it shows that properties derived from an equation of state can be calculated from first principles. Here I have used the *calculated* pair potentials of Gordon and Kim[1] to determine an equation of state for NaCl and KCl.

In order to compute the thermal expansion and compressibility of a cubic crystal in the absence of external fields, we need the free energy, F, of the system as a function of the volume V and the temperature T:

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

where $U(V)$ is the energy of the static lattice (electronic ground-state energy) with volume V, and the $\nu_i(V)$ are the classical normal-mode frequencies of small-amplitude oscillations for the crystal with volume V (see Sect. 4 of Born and Huang[2]). The only assumption needed to derive Eq. (1) (besides the adiabatic approximation) is that the phonon energy levels of the system are those of independent harmonic oscillators with frequencies $\nu_i(V)$, the quasiharmonic approximation.

The term quasiharmonic is often used to refer to that anharmonic effect which gives a volume dependence to the phonon frequencies.[3] In our case we are able to obtain the volume dependence of the frequencies by simply performing harmonic-lattice-dynamics calculations for a large number of selected volumes. This is made possible because the pair potentials are known as a function of separation. If one has the $\nu_i(V)$, then the mode Grüneisen "parameters" [$\gamma_i(V)$ below] are obtained as a function of V by numerical differentiation. Including cubic and higher-order terms in the lattice-dynamical calculation would effectively couple the oscillators and shift their energy levels.

From Eq. (1) and the fact that pressure is given by $P = -(\partial F/\partial V)_T$, we obtain the equation of state,[2]

$$P + dU/dV = f(V, T), \qquad (2)$$

where

$$f(V, T) \equiv V^{-1}\textstyle\sum_i \gamma_i \{\tfrac{1}{2}h\nu_i + h\nu_i/[\exp(h\nu_i/kT) - 1]\} \qquad (3)$$

and

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

In Eq. (2) P is the externally applied pressure while dU/dV and $-f(V, T)$ are internal pressures resulting from changes in the ground-state electronic energy and the vibrational energy, respectively, as a function of volume. The electrons are assumed to remain always in their ground-state (adiabatic) approximation. $f(V, T)$ is sometimes referred to as the thermal pressure although a portion of it, the first term in Eq. (3), is due to vibrations at $T = 0$.

The fundamental quantity required to calculate the equation of state is U, not only as a function of V, but also as a general function of the positions of the nuclei. Both dU/dV and $f(V, T)$ have been determined for KCl and NaCl using the pair potentials of Gordon and Kim.[1] They computed pair potentials for K^+-Cl^- and the Na^+-Cl^- interactions by assuming a free-electron form for the electronic energy as a function of the charge density. The charge density of the molecule was obtained by rigidly overlapping Hartree-Fock charge densities of the free ions.

We choose V to be the volume per molecule. Then, dU/dV is obtained from $U = 6\varphi(r) - \alpha e^2/r$, where α is the Madelung constant, r is the nearest-neighbor separation, e is the electronic charge, and φ is the short-range part of the pair potential. In order to calculate $f(V, T)$ we have solved the dynamical matrix for a rigid-ion crystal[4] as a function of V with the short-range force constants determined by numerically differentiating the short-range part of the pair potential.

In Table I we list calculated ν for NaCl and KCl for wave vectors at the Γ, X, and L points of the Brillouin zone. Results are shown for equilibrium lattice constants at zero pressure, $T = 80$ and 300 K, and the calculated melting temperature (see below). Notice that the computed frequencies for $T = 80$ and 300 K are in reasonably good agreement with experimental results.[5,6]

Having $\nu_i(V)$, and hence $\gamma_i(V)$, it is a simple matter to determine $f(V, T)$ from Eq. (3). The integration (summation over i) was found to be adequately converged for 864 regularly spaced points in the Brillouin zone.

The calculated equation of state for NaCl is shown in Fig. 1 where the external pressure, $P(V, T)$, is plotted as a function of the lattice constant a for several temperatures. The corresponding plot for KCl is qualitatively similar. For NaCl at room temperature and zero pressure we find $a = 5.776$ Å, 2.6% larger than the measured value. For KCl, the calculated value, $a = 6.162$ Å, is 2.0% smaller than the experimental value.

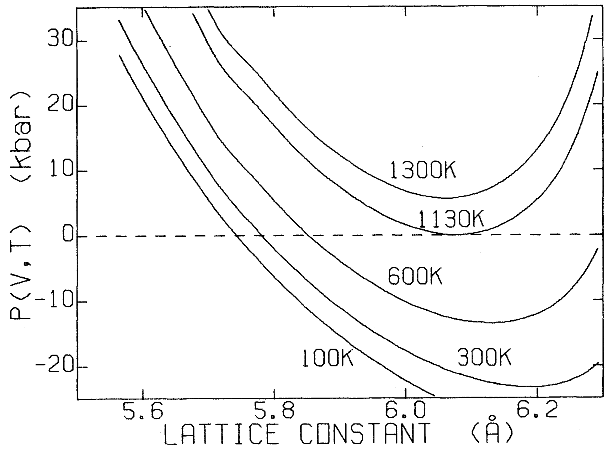

FIG. 1. External pressure, $P(V,T)$, for NaCl as a function of lattice constant for several selected temperatures.

Values of the thermal-expansion parameters $\epsilon \equiv [a(T) - a(293\text{ K})]/a(293\text{ K})$, showing the temperature dependence of the lattice constants of KCl and NaCl at zero pressure, are listed in Table II for comparison with the corresponding data taken from Ref. 7. The pressure dependence

TABLE I. Values of ν_i (in cm^{-1}) for NaCl and KCl for wave vectors at the Γ, X, and L points of the Brillouin zone.

	NaCl					KCl				
	$T = 80^\circ$K		$T = 300^\circ$K		$T = T_m$	$T = 80^\circ$K		$T = 300^\circ$K		$T = T_m$
	$\nu_{exp.}^{a}$	$\nu_{calc.}$	$\nu_{exp.}^{a}$	$\nu_{calc.}$	$\nu_{calc.}$	$\nu_{exp.}^{b}$	$\nu_{calc.}$	$\nu_{exp.}^{b}$	$\nu_{calc.}$	$\nu_{calc.}$
Γ	172	152	163	145	101	149	145	141	139	109
	264	312	261	306	270	218	259	-	254	228
X	87	92	85	93	89	62	75	58	76	79
	142	162	143	155	105	109	151	109	144	110
	180	163	173	155	111	154	156	146	150	113
	192	217	186	215	204	159	167	151	166	162
L	120	102	116	98	72	106	105	-	101	80
	142	126	137	121	89	116	110	110	106	85
	178	190	172	186	163	152	172	146	169	151
	230	234	-	229	202	159	182	155	178	160

[a] Ref. 5.

[b] Ref. 6.

TABLE II. Thermal-expansion parameter, $\epsilon = \{[a(T) - a(293\ \text{K})]/a(293\ \text{K})\} \times 10^5$ for KCl and NaCl at zero pressure. $a(T)$ is the lattice constant at temperature T.

T (K)	KCl ϵ(calc)[a]	KCl ϵ(expt)[b]	NaCl ϵ(calc)[a]	NaCl ϵ(expt)[b]
100	−580	−625	−600	−660
200	−290	−328	−310	−349
400	350	416	380	447
500	690	829	740	892
600	1030	1269	1190	1368
800	1770	2242	2200	2429
1000	2960	3354	3390	3685

[a] Based on my calculated values of $a(293\ \text{K}) = 6.162$ Å KCl and $a(293\ \text{K}) = 5.776$ Å for NaCl.

[b] Data are taken from Ref. 7. $a(293\ \text{K}) = 6.294$ Å for KCl; $a(293\ \text{K}) = 5.640$ Å for NaCl.

TABLE III. Compressibility at room temperature: volume ratio V/V_0 for KCl and NaCl, where V_0 is the volume at zero pressure.

Pressure (kbar)	KCl Calc	KCl Expt	NaCl Calc	NaCl Expt
5	0.976	0.974	0.979	0.980
10	0.956	0.951	0.960	0.962
15	0.936	0.932	0.943	0.947
20	0.917	0.915[a]	0.928	0.932
30			0.900	0.907

[a] Transition to CsCl structure at ~20 kbar.

of the lattice constant at room temperature for these materials is shown in Table III, where calculated values of V/V_0 (V_0 is the volume at $P=0$) are again compared with the corresponding values from Ref. 7. From these results we see that the calculated equation of state gives a remarkably accurate prediction of the density of KCl and NaCl over wide-ranging values of temperature and pressure.

Using the long-wavelength method[2] we find the following expressions for the elastic constants:

$$C_{11} = \varphi''(r)/r - 1.278e^2/r^4, \tag{5a}$$

$$C_{12} = -\varphi'(r)/r^2 + 0.056\,55e^2/r^4, \tag{5b}$$

$$C_{44} = \varphi'(r)/r^2 + 0.639e^2/r^4. \tag{5c}$$

From the equation of state we have r, and hence C_{ij}, as a function of T and P. The calculated temperature dependence of the $P=0$ elastic constants for NaCl is shown in Fig. 1 for comparison with the experimental results of Hunter and Siegel.[8] The values plotted are the bulk moduli $[1/K = \frac{1}{3}(C_{11} + 2C_{12})$, where K is the compressibility] and the shear constants $C_{11} - C_{12}$ and C_{44}. For KCl we find room-temperature values of $1/K$, $C_{11} - C_{12}$, and C_{44} to be (1.96, 3.35, and 0.94) $\times 10^{11}$ dyn/cm^2 while their temperature derivatives are ~(1.7, −3.6, and 0.0) $\times 10^8$ dyn/cm^2 K), respectively. The corresponding experimental results[9] are (1.82, 3.39, and 0.63) $\times 10^{11}$ dyn/cm^2 and (−1.8, −7.6, and −0.33) $\times 10^8$ dyn/cm^2 K, respectively. The agreement is about as good as can be expected because our calculations are based on a rigid-ion approximation of the solid. We also note that we have compared our results to the *adiabatic* experimental values even though the elastic constants calculated from Eq. (5) are, strictly speaking, neither adiabatic nor isothermal. However, the isothermal bulk modulus may be obtained directly from the equation of state.

Now consider what happens, regarding the stability of the lattice, with increasing temperature at zero pressure. There exists some critical temperature, T_m, above which $P(V,T)$ no longer intersects the $P=0$ line (see Fig. 1). In other words, the crystal becomes unstable due to the vanishing of the isothermal bulk modulus, $-V(dP/dV)_T$, at T_m. Above T_m the vibrational pressure, which works to expand the crystal, is too large to be compensated by the electronic ground-state pressure tending to collapse the lattice [see Eq. (2)]. This is the type of instability Herzfeld and Goeppert-Mayer[10] and Kane[11] associated with melting in rare-gas solids. They determined quasiharmonic equations of state using parametrized potentials together with the Debye approximation. Our calculated values for T_m, 1130 and 1050 K for NaCl and KCl, respectively, are in excellent agreement with the measured melting temperatures[7,12] of 1070 and 1040 K. The calculated values of dT_m/dP are in somewhat poorer agreement with experiment. We find $dT_m/dP \cong 40$ K/kbar for both NaCl and KCl while the measured values[10] are ~25 K/kbar for both materials. Although Hunter and Siegel have only measured the adiabatic elastic constants, they point out that the isothermal compressibility is larger than the adiabatic value by an amount proportional to α^2, where α is the thermal-expansion coefficient. They argue that because α increases rapidly near the melting point the isothermal compressibility probably increases monotonically up to the melting point. When T is exactly the melting temperature, the isothermal com-

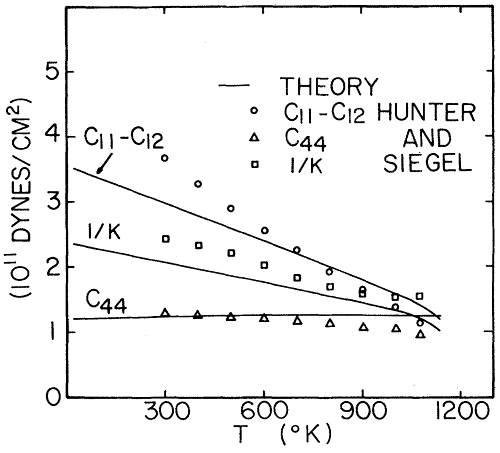

FIG. 2. Calculated and measured shear elastic constants (C_{44} and $C_{11}-C_{12}$) and bulk modulus ($1/K$) for NaCl as a function of temperature.

pressibility of the solid-liquid system is necessarily infinite because of the discontinuous volume change upon melting and the fact that $dT_m/dP \neq 0$.

While the frequencies ν_i decrease with increasing T (see Table I), the melting instability occurs before the lattice becomes intrinsically unstable due to mode softening. Other attempts to explain melting have focused upon the temperature dependence of the elastic constants as the source of the instability.[13,14] Notice from Fig. 2 that our calculated values of $C_{11}-C_{12}$ and C_{44} are substantially greater than zero at T_m. Our results therefore are consistent with the fact that the resistance to elastic shearing (zero in the liquid state) is greater than zero for the solid at the melting temperature. However, I caution again that these are not isothermal quantities.

Whether or not the T_m instability discussed above can be the real cause of melting is still open to question (see Ref. 10 for further discussion of this point). While the results are less accurate at high temperatures (because of the quasiharmonic approximation), the fact that the equations of state are shown to be both accurate and parameter free supports the T_m picture of melting. If it is not the real cause of melting, it at least occurs at approximately the same temperature; a temperature which, as has been demonstrated, can be predicted from a parameter-free calculation.

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