2. Lattice dynamical calculations

2.1. *Background*

Conventional lattice dynamics generally treats the entire frequency spectrum of harmonic vibrations of a lattice at a particular volume. (For a recent review article, see COCHRAN, 1971.) By considering a small perturbation of the volume, many authors (for example, BARRON, 1957; ACHAR and BARSCH, 1971 a,b; NAMJOSHI et al., 1971) have calculated the zero pressure Grüneisen parameter as a function of temperature, getting fairly good agreement with experiment. By assuming a functional form of the interatomic potential, a number of authors have attempted to predict the elastic properties and equation of state of the NaCl lattice at high pressure (ANDERSON and LIEBERMANN, 1970; SAMMIS, 1970, 1971; ANDERSON, 1970; ANDERSON and DEMAREST, 1971; BARSCH and SHULL, 1971; DEMAREST, 1972). None of these authors attempted to treat the entire frequency spectrum at high pressure, although ANDERSON and DEMAREST (1971) did calculate a Grüneisen parameter based only on the low-frequency acoustic modes of vibration. In the present paper, I have extended previous work (DEMAREST, 1972) to include the entire frequency spectrum. The quasiharmonic approximation, in which the frequencies are assumed to be functions of volume but not of temperature, is used. The results are a set of equations which can be used to predict virtually any thermodynamic property of the crystal at arbitrary pressure and temperature.

2.2. *Central force model*

I have assumed that the potential energy per ion pair of the crystal is given by

$$\tilde{\phi} = \sum_{i=1}^{\infty} \pm \frac{z^2 e^2}{r_i} + \sum_{i=1}^{6} b \exp\left(-r_i/\rho\right)$$
$$+\frac{1}{2} \sum_{i=1}^{12} \varepsilon_0 \left[\left(\frac{r_m}{r_i}\right)^{12} - 2\left(\frac{r_m}{r_i}\right)^{6}\right]. \quad (1)$$

The tilde over ϕ indicates that vibrational effects are neglected.

The first term is the electrostatic energy summed over all ions in the lattice. The second term gives the repulsive energy between nearest neighbours, and the third term gives the interaction between anions.

There is little justification for using the Lennard–Jones 6–12 potential between anions, although its qualitative features were verified by WEIDNER and SIMMONS (1972) and by DEMAREST (1972). The neglect of noncentral or multibody forces in this model will not cause serious error in the alkali halides, where such effects can be shown to be small, but the central force assumption is invalid for MgO, AgCl and AgBr, and may be equally invalid for many geophysically important materials.

A more serious defect of the model is the neglect of the polarizability of the anion. Although polarizability does not affect the elastic constants in a centrosymmetric lattice, it has a strong effect on the optic modes of vibration. Treatment of the polarizability is possible through the shell model. Its neglect in the present rigid ion model calculation leads to calculated optic frequencies which are 10% to 40% too high at zero pressure. This in turn will lead to an underestimation of the specific heat and will directly affect the accuracy of the calculated mode Grüneisen parameters, which are discussed in the next section. Since the macroscopic Grüneisen parameter represents an average over all modes of vibration, the error caused by this neglect of polarizability will probably cancel to some extent in the summations. The resulting error in the Grüneisen constant should not be more than about 10%.

The equations for the pressure, the elastic constants and their pressure derivatives in the model were derived in DEMAREST (1972). The procedure for calculating the frequency of vibration for arbitrary wavevector, based on a potential function such as the above, has been adequately discussed in COCHRAN's (1971) review article. Detailed applications to the NaCl lattice are given by KELLERMANN (1940), COWLEY (1962) and PECKHAM (1967). The mode Grüneisen parameters, $\gamma_i = \partial \ln v_i / \partial \ln V$, can be calculated by the straightforward application of perturbation theory (WALLACE, 1972, p. 179).

2.3. *Thermal effects*

The total energy in the lattice is the sum of two terms, corresponding to the static lattice and the vibrational energy:

$$\phi = \tilde{\phi} + \sum_i h v_i \left[\frac{1}{2} + (\exp\left(h v_i / kT\right) - 1)^{-1}\right]. \quad (2)$$

In this equation the v_i are the frequencies of vibration of the normal modes. In my calculations, I have carried

out the summation over a representative sample of 282 frequencies corresponding to 47 wavevectors. WALLACE (1972) has discussed the procedure for carrying out the summation.

The vibrational contribution to pressure is obtained by differentiating eq. (2):

$$P = \tilde{P} + V^{-1} \gamma_e E_{vib},\qquad(3)$$

$$\gamma_e \equiv \sum_i \gamma_i E_i / (\sum_i E_i).\qquad(4)$$

E_{vib} is the vibrational energy corresponding to the summation term in eq. (2), and E_i is the ith vibrational term within the summation. V is the volume. The vibrational pressure term in eq. (3) includes the effect of zero point motion. In this respect it differs from the expression of BARRON (1955), who chose to incorporate the zero point effect into his potential $\tilde{\phi}$.

Except at high temperature, γ_e is not the same as the thermal Grüneisen parameter γ_{th}, which is given by

$$\gamma_{th} \equiv \frac{V\beta K_T}{C_v} = \frac{\sum \gamma_i C_{vi}}{\sum C_{vi}},\qquad(5)$$

where β is the volume thermal expansion coefficient, K_T is the isothermal bulk modulus, C_v is the heat capacity at constant volume, and C_{vi} is the contribution of an individual mode to the heat capacity.

Although it is possible to develop an analytic expression for the thermal corrections to the isothermal bulk modulus K_T (WALLACE, 1972, p. 194). I have determined this correction by numerical differentitation. The formula for converting K_T to the adiabatic bulk modulus K_s is well known. The thermal correction to dK_s/dP was also determined by numerical differentiation.

The quasiharmonic approximation suggests that there should be no thermal correction to the shear elastic constants. However, at least for the alkali halides, this assumption is empirically more correct for the thermodynamic than the effective elastic constants, and I have made thermal corrections accordingly. [The effective elastic constants are those which appear in the equations of motion. The effective shear constants are less than the thermodynamic ones by the quantity P. For further discussion of this distinction, see THURSTON (1965).]

2.4. Determination of arbitrary parameters

There are five arbitrary parameters in eq. (1): z, b, ρ, ε_0 and r_m. These were determined in order to make the calculated and experimental values of five quantities agree: $P = 0$ (the equilibrium condition), K_s, dK_s/dP, the shear elastic constant C_{44} and its pressure derivative dC_{44}/dP. The elastic constants and their pressure derivatives can be measured very accurately by modern acoustical experiments and are a very sensitive measure of the interatomic forces.

It is important to point out several differences between the above procedure and those used by others. The vibrational corrections to the pressure, elastic constants and pressure derivatives, discussed in the previous section, permit a calculation of thermal effects which is exact within the framework of the quasi-harmonic approximation. Without this exact thermal treatment, it has been necessary to extrapolate the experimental values to either zero temperature (DE-MAREST, 1972) or to a static reference state (SAMMIS, 1971), necessitating experimental data at several temperatures.

There are several alternatives to fitting the arbitrary parameters to the pressure derivatives of the elastic constants. For example, in a similar model, SAMMIS (1971) assumed that the parameters in the Lennard-Jones 6–12 potential between anions were the same as for the isoelectronic inert gases. In their model for the NaCl structure, BARSCH and SHULL (1971) and CHANG and BARSCH (1971) used parameters estimated by TOSI (1964) and others. This procedure sometimes leads to rather poor agreement with experimental elastic constants and pressure derivatives and is therefore inappropriate for extrapolations to high pressure.

In calculations similar to the present ones (DEMAREST, 1972), I tried to correct for thermal effects by extrapolating the elastic constants to zero temperature. The parameters in eq. (1) which fitted the elastic constant data for 12 alkali halides were all reasonable, although the anion–anion force constant ε_0 was 5–10 times larger than SAMMIS (1971) had assumed.

With the more exact thermal treatment of the present paper, the parameters are slightly different. The improvement in the effective ionicity Z is noteworthy. In the earlier calculations the ionicity varied from 0.86–1.03, in a manner which could not be explained physically. When the explicit thermal corrections are included, the variation is from 0.96–1.04. Most of the remaining variation can be explained by errors in the measured elastic constants. I regard this relatively small variation