

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.†

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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

$$P = \bar{P} + \frac{\gamma_e E_{\text{vib}}}{V} \quad (1)$$

where P is the pressure, \bar{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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†Present address.

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

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

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

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

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

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

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