$$\left(\frac{\partial B}{\partial p}\right)=\frac{(B_0^{(1)}-B_\infty^{(1)})B_0}{B(p)}+B_\infty^{(1)}. \tag{3.12}$$

$B_\infty^{(1)}$ is the limiting value of the pressure coefficient of the bulk modulus for infinite pressure. Kean's equation of state is obtained by twofold integration of (3.12) in connection with (3.4) [3, 4]:

$$\pi_K=(B_0^{(1)}/B_\infty^{(1)})^2)\ [R^{-B_\infty^{(1)}}-1] + [(B_0^{(1)}/B_\infty^{(1)})-1]\ln R. \tag{3.13}$$

By comparing the Taylor expansion of (3.13) with (3.3) and (3.6) the third parameter, $B_\infty^{(1)}$ can be expressed in terms of the second pressure derivative of the bulk modulus as follows:

$$B_\infty^{(1)}=B_0^{(1)}+(B_0B_0^{(2)}/B_0^{(1)}). \tag{3.14}$$

The two assumptions of Keane ($B(p)$ monotonously increasing with p, $(\partial B/\partial p)$ monotonously decreasing with p) lead to the following condition for the bulk modulus and its first two pressure derivatives:

$$-(B_0^{(1)})^2<B_0B_0^{(2)}<0. \tag{3.15}$$

Both inequalities are fulfilled for the experimental data of CsCl, CsBr, and CsI listed in tables 1 and 2 so that it is consistent to use, for these materials, Keane's expression (3.13) for the representation of the equation of state.

3.2. A Lattice Theoretical Equation of State and Comparison With the Phenomenological Equations of Section 3.1

An ionic crystal, such as one of the alkali halides, seems ideally suited for deriving a theoretical equation of state because the interatomic forces can be described quite adequately and successfully in terms of Coulomb and van der Waals attraction, and in terms of a Born-Mayer type repulsive potential with empirical or adjustable parameters. In view of the considerable success of the classical theory of ionic crystals, it is not surprising that this approach has been used also for the equation of state of alkali halides [12–14, 35]. It should be remembered, however, that these equations of state are semi-empirical, and that their accuracy is limited by the accuracy of the empirical quantities that were used for the determination of the parameters in the repulsive potential. Since these parameters are determined from experimental data measured at low pressure one must expect that the effect of their errors increases with increasing pressure. Thus from this point of view there would be no advantage in using a lattice "theoretical" equation of state instead of a phenomenological equation as discussed in section 3.1, provided the phenomenological equation selected converges sufficiently fast and differs in the pressure range considered from the lattice theoretical equation with the same number of parameters by an amount smaller than the effect of the experimental error of the input data.

Another limitation of the kind of lattice theoretical equation of state considered is that it is based on several simplifying assumptions and that their effect on the results is not easy to determine and would require a much higher theoretical effort. First, it has been noted that the inverse power law for the van der Waals potential should be screened at smaller interatomic separations due to the interpenetration of the electronic shells [36]. Also, the use of an exponential law for the repulsive interaction is only an approximation because the radial dependence of the electronic wave functions corresponds to a series of terms consisting of products of polynomials and exponential functions and is reflected in the radial dependence of the cohesive energy [37, 38]. More specific approximations of dubious justification made in previous lattice theoretical equations of state consist of the use of an inverse power potential for the repulsive interaction and neglect of second nearest neighbor effects [35], or of the evaluation of the repulsive parameters for the second nearest neighbor interaction from the electronic polarizabilities [13]. The equation of state of Decker is further based on the Debye-Grueneisen approximation, and the Grueneisen constant and its first pressure derivative are determined jointly with the first nearest neighbor repulsive parameters from empirical data of the thermal expansion as a function of temperature [13].

In view of the considerable difficulties encountered in deriving a sufficiently reliable lattice theoretical equation of state, the question arises whether an empirical ultrasonic equation of state based on any of the phenomenological equations discussed in section 3.1 agrees within the uncertainty limit caused by the experimental error of the empirical parameters with the corresponding lattice theoretical equation of state. In order to explore this possibility, a simple lattice theoretical equation of state with four empirical parameters was compared with the phenomenological equations discussed in section 3.1. This equation of state is based on the expression

$$\phi=-\frac{\alpha e^2}{r}-\frac{C}{r^6}-\frac{D}{r^8}+A_1e^{-\frac{r}{\rho_1}}+A_2e^{-\frac{(2/\sqrt{3})r}{\rho_2}} \tag{3.16}$$

for the lattice energy per ion pair where the symbols have the usual meaning [39], and the effect of thermal motion has been neglected. This expression contains the usual Coulomb and van der Waals terms, and first and second nearest neighbor repulsive interaction. In general, two exponential terms

are required for the second nearest neighbor interaction, but these two reduce to one if it is assumed that the same constant ρ_2 describes both cation-cation and anion-anion interaction. The van der Waals constants C, D were taken from references [40] and [41], respectively, and the repulsive constants A_1, A_2, ρ_1, ρ_2 were determined from the zero pressure values of the lattice constant, and of the bulk modulus and its first two pressure derivatives.

The equation of state based on (3.16) according to

$$p=-\frac{\partial\phi}{\partial v_c}=-\frac{1}{2r^2}\frac{\partial\phi}{\partial r} \tag{3.17}$$

was compared with (a) Murnaghan's first-order equation (3.9); (b) Birch's equation (3.7) in first-order approximation; (c) Murnaghan's second-order equation (3.10); (d) Birch's equation (3.10) in second-order approximation; and (e) Keane's equation (3.13). The same ultrasonic values for the bulk modulus and its first two pressure derivatives were used for these phenomenological equations so that the difference $\Delta p = p_{\text{lattice}} - p_{\text{phen.}}$ between the lattice theoretical equation of state based on (3.16) and the phenomenological equations (a) to (d) arises from differences in the second and higher pressure coefficients of the bulk modulus (cases (a) and (b)), or from differences in the third and higher order pressure derivatives of the bulk modulus (cases (c) to (e)). This difference Δp is therefore an indication of the quality of the different phenomenological equations in approximating the lattice theoretical equation based on (3.16), and a measure of the rate of convergence of the various Taylor-expansions underlying the phenomenological equations (a) to (e). Although the exact or true potential energy of the lattice will be given only approximately by (3.16) and the thermal energy has been neglected, one may expect that the difference between the two values of Δp referred to (3.16) and to the volume dependence of the true free energy is a higher order quantity, so that for ionic crystals the difference Δp based on (3.16) may be considered as a fair estimate of the deviation of the phenomenological equations from the true equation of state.

The difference $|\Delta p|$ is plotted for CsI in figure 1 for the five cases (a) to (e) as a function of pressure. The ultrasonic data of table 2 were used in connection with the room temperature value of the lattice constant from reference [30]. For CsCl and CsBr curves very similar to those of figure 1 were obtained. It is apparent that in the entire pressure range up to 500 kbar the quality of the second-order Birch equation in approximating the lattice theoretical equation is one order of magnitude better than Keane's equation, and about two orders of magnitude better than the second order Murnaghan equation. As all three equations contain the same number of three empirical parameters, this drastic

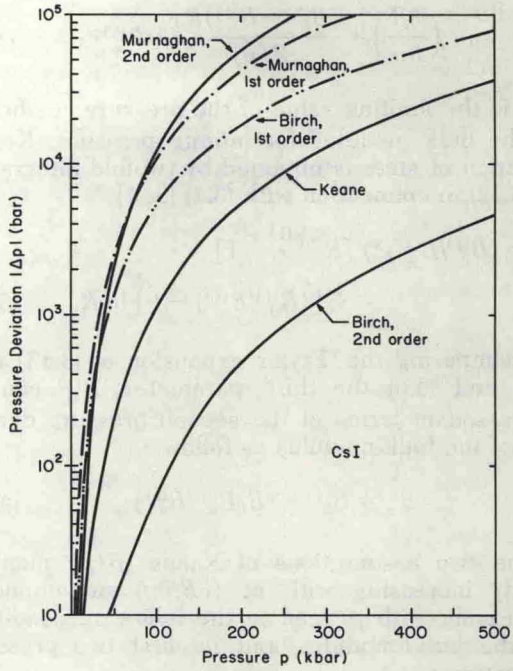

FIGURE 1. *Pressure difference between phenomenological and lattice theoretical equation of state versus pressure for* CsI.

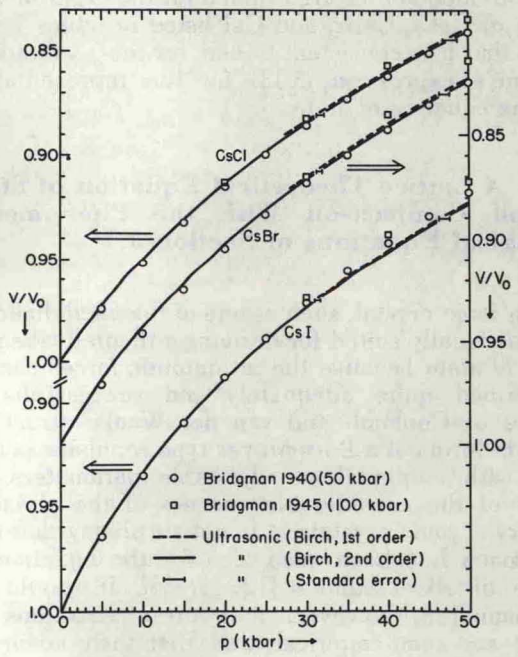

FIGURE 2. *Comparison of compression data for* CsCl, CsBr, *and* CsI *by Bridgman* [9, 10] *with ultrasonic Birch equation of state in first- and second-order approximation.*

superiority of Birch's equation is quite surprising. The first-order Birch equation also can be seen to be superior to the first-order Murnaghan equation, but the difference is not quite as pronounced. As expected, the two three-parameter equations accord-