proximations for the Fermi, exchange, correlation and ground state energies of the valence electrons, the lattice electrostatic energy and the core–core overlap repulsion contribution. Omitted are several small energy contributions arising from ion core oscillations and core–core polarization effects, which are of the order of 10^{-3} to 10^{-5} ryd/ion for alkali metals. Also omitted is a second-order perturbation correction to the free electron approximation inherent in calculation of the valence electron contributions to the crystal energy, the so-called band structure energy[3]. Even when employing the simplest known local electron-ion pseudopotential suitable for alkali metals, which is the Ashcroft form[4], one finds the resulting band structure energy contribution to the strain energy to be so complex as to render near hopeless any calculation of higher order derivatives with respect to arbitrary deformations. (See Appendix.)

Nevertheless, comparisons with experimental data show that omission of the band structure term has little effect on those elastic properties which involve up to two derivatives of the strain energy, e.g., pressure–volume and second-order elastic coefficient calculations. In theoretical calculation of the pressure variation of these coefficients (up to 10^4 atmospheres), which in effect involves a third derivative of the strain energy, fairly good comparisons with available experimental data were obtained for the volume dependent coefficients[2]. For the shear dependent coefficients, however, it appears that inclusion of the band structure energy may be necessary in order to give these coefficients a more accurate pressure variation.

In this paper theoretical calculations of the variation of small amplitude plane wave speeds with pressure are performed for sodium and potassium at zero temperature. The formalism developed in our previous work is particularly well suited for calculations of this type since the problem is essentially one in which small amplitude plane waves are superimposed on initial homogeneously compressed crystal states.

What emerges from the calculations given here, as in our previously cited papers, is the realization that the problem of crystal elasticity can be given a consistent, unified and general structure through a strain energy formulation. The predictive accuracy of such a formulation of course centers on the extent to which the underlying crystal energy calculation includes, with sufficient accuracy, all significant energy contributions. When such is the case for

any given solid or class of solids; as it appears to be for the smaller ion core metallic crystals, theoretical calculation of all quantities which characterize elastic material response is then a straightforward matter. The practical difficulties of such a program lie in the complexity of some of the energy contributions and their derivatives with respect to arbitrary deformations, e.g., the band structure term.

CRYSTAL STRAIN ENERGY DENSITY

In the approximation which omits the band structure contribution (eqns. (A7)–(A9) of the Appendix) the strain energy density per unit volume of the undeformed crystal at absolute zero temperature, in atomic units, has the form[1,5]

$$\Sigma = \left\{\beta_1 - \frac{1}{\eta^2}\beta_2\right\} I_3^{-\frac{1}{2}} + \beta_3 I_3^{-\frac{1}{3}}$$
$$- \beta_4 I_3^{-\frac{1}{6}} + \beta_5 \ln\left\{\beta_6 I_3^{\frac{1}{3}}\right\}$$
$$+ \beta_7 I_3^{-\frac{1}{2}} \sum_m{}' \frac{e^{-\beta_8/\eta^2(m_\alpha m_\beta C_{\alpha\beta}^{-1})}}{m_\gamma m_\delta C_{\gamma\delta}^{-1}}$$
$$+ \beta_9 \sum_n{}' \frac{\text{erfc}\left\{\eta\beta_{10}(n_\alpha n_\beta C_{\alpha\beta})^{\frac{1}{2}}\right\}}{(n_\gamma n_\delta C_{\gamma\delta})^{\frac{1}{2}}}$$
$$+ \beta_{11} \sum_n{}' e^{-\beta_{12}(n_\alpha n_\beta C_{\alpha\beta})^{1/2}} \tag{1}$$

where constants $\beta_1, \ldots, \beta_{12}$ have the values

$$\beta_1 = \frac{16\pi}{3}\frac{r_0^2}{\Delta^6} \qquad \beta_5 = \frac{0.062}{\Delta^3} \qquad \beta_9 = \frac{4}{\Delta^4}$$

$$\beta_2 = \frac{4\pi}{\Delta^6} \qquad \beta_6 = \left(\frac{3}{\pi}\right)^{\frac{1}{3}}\frac{\Delta}{2} \qquad \beta_{10} = \frac{\Delta}{2}$$

$$\beta_3 = \left(\frac{\pi}{3}\right)^{\frac{1}{3}}\frac{17.680\alpha}{\Delta^5} \qquad \beta_7 = \frac{4}{\pi\Delta^4} \qquad \beta_{11} = \frac{\tilde{D}}{\Delta^3}$$

$$\beta_4 = \left(\frac{\pi}{3}\right)^{\frac{1}{3}}\frac{3.644}{\Delta^4} \qquad \beta_8 = \frac{\pi^2}{\Delta^2} \qquad \beta_{12} = \frac{\Delta}{2\mu}$$

In this equation $C_{\alpha\beta}, C_{\alpha\beta}^{-1}$ ($\alpha, \beta = 1, 2, 3$) are the direct and inverse Green–Cauchy deformation tensors referred to the coordinates (X_α) of the undeformed state (see the following section), I_3 is the third principal invariant of $C_{\alpha\beta}$. The summation signs $\sum_m'$, $\sum_n'$ represent triple sums of $\sum_{m_1}\sum_{m_2}\sum_{m_3}$, and $\sum_{n_1}\sum_{n_2}\sum_{n_3}$, respectively, where $m_1, m_2, m_3, n_1, n_2, n_3$ are positive and negative integers which must satisfy certain restrictions in order properly to incorporate the in-

TABLE 1: TABLE OF LATTICE AND ATOMIC CONSTANTS

Element	Δ (bu)	$r_0{}^a$ (bu)	α^b	$r_c{}^c$ (bu)	μ^d (bu)	$\tilde{C}^d$ (ergs × 10^{12})	$\tilde{D}$ (ryd)
Lithium	7.249	2.84	0.730	0.90	0.652	2.00	1.4
Sodium	8.138	3.00	1.009	1.65	0.652	1.25	9.2
Potassium	9.791	3.78	1.066	2.24	0.652	1.25	56.8
Rubidium	10.278	3.94	1.148	2.49	0.652	1.25	121.9
Cesium	11.029	4.27	1.206	2.75	0.652	1.25	267.0

[a] Reference 6, [b] reference 7, [c] reference 8, [d] reference 9.

herent anisotropy of the lattice structure. Erfc represents the complementary error function, while η is a positive but otherwise aribitrary number which is chosen so as to effect rapid simultaneous convergence of the lattice sums in which it appears. The strain energy Σ can be shown to be invariant with respect to the numerical choice of η^5. The prime on the lattice sums is taken to mean omission of the reference lattice site. The set of constants $\beta_1, ..., \beta_{12}$ which include the quantities Δ, α, r_0 and $\tilde{D} = \tilde{C} e^{2r_c/\mu}$, together with the allowed values of n_α, m_α, characterize both the atomic and lattice structure of the solid since Δ is the crystal lattice spacing at absolute zero temperature, r_0 is the value of the atomic radius for which the valence electron ground state energy is minimum, α is the effective valence electron mass ratio near the bottom of the conduction band and is the measure of the "freeness" of the valence electrons, while r_c is the effective ion core radius in a rigid ion core approximation. The constants $\tilde{C}$ and μ, which appear in the Born–Mayer central force potential used to approximate the core–core overlap repulsion, are obtained from alkali halide crystal data where the ion–ion interaction is basically of this form. Numerical values of the quantities Δ, r_0, α, r_c, μ, $\tilde{C}$ and $\tilde{D}$ used in subsequent calculations are shown in Table 1.

The zero temperature lattice spacing values listed above were obtained from the condition that in the natural (undeformed) state the components of the stress tensor

$$T_{\kappa\lambda} = 2 \frac{\partial \Sigma}{\partial C_{\kappa\lambda}} \qquad (2)$$

assuming a perfect crystal, vanish everywhere. For $\kappa \neq \lambda$ this condition is readily satisfied. However, for $\kappa = \lambda$ the right-hand side of eqn. (2) will not be exactly zero because of the approximations inherent in the crystal energy calculation. Consequently we choose the zero temperature lattice spacing such that the right side of eqn. (2) vanishes identically,

yielding values of Δ which differ from the experimental values of Swenson[10] by the following percentages: Li($+11.89$), Na($+2.01$), K(-0.31), Rb (-2.01) and Cs(-1.43).

The functional form $\Sigma = \Sigma(C_{\alpha\beta}, n_\alpha, m_\alpha, \{\beta_k\})$, eqn. (1), which is continuous and differentiable in $C_{\alpha\beta}$, is properly invariant both with respect to allowable coordinate transformations and with respect to changes of frame of reference, *i.e.*, time dependent orthogonal transformation of coordinates. The anisotropy of the body-centered cubic crystal lattice is directly accounted for by the allowed values of the integers n_α and m_α in the lattice sums, which are taken along the crystallographic axes of the undeformed direct and reciprocal lattices. In this form the set of quantities $\{\beta_k\}$, $k = 1, ..., 12$, can be interpreted as material structure parameters.

THE ACOUSTICAL TENSOR FOR SMALL AMPLITUDE PLANE WAVES SUPERIMPOSED ON HOMOGENEOUSLY DEFORMED EQUILIBRIUM CONFIGURATIONS

When crystals are given an initial homogeneous deformation, the elastic propagation of superimposed small amplitude plane waves can be studied in terms of the properties of an associated acoustical tensor[11,12]. The components of this tensor, for any given wave propagation direction, can be theoretically determined whenever the strain energy density of the crystal is explicitly known. It will be useful for purposes of discussion, within the present context, to outline the derivation leading to definition of an acoustical tensor together with the condition for wave propagation.

Let K_0, $\tilde{K}$ and $K(t)$ represent the natural (undeformed), initially deformed and current configurations respectively, of any crystal solid, where t designates the time variable. All three configurations are referred to some common rectangular coordinate system. Adopting a continuum point of