

Theoretical Calculation of Plane Wave Speeds for Alkali Metals under Pressure

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SUMMARY

Theoretical calculations of the variation with pressure of small amplitude plane wave speeds are performed for sodium and potassium at zero temperature. The results obtained for wave speeds associated with volume dependent second-order elastic coefficients

show better agreement with experimental data than for wave speeds associated with shear dependent coefficients. This result is believed to be due to omission of the band structure correction to the strain energy density.

RÉSUMÉ

L'influence de la pression sur la vitesse d'ondes planes de faible amplitude a été calculée de manière théorique dans le cas du sodium et du potassium au zéro absolu. Les résultats obtenus dans le cas où la vitesse des ondes est déterminée par les constantes élastiques du second ordre qui dépendent du volume sont en meilleur accord avec les données expérimen-

tales que ceux qui sont obtenus dans le cas où la vitesse des ondes fait intervenir les constantes élastiques qui dépendent du cisaillement. On pense que cette différence est due à l'omission de la correction de structure de bande dans le calcul de la densité d'énergie de déformation.

ZUSAMMENFASSUNG

Die Variation der Ausbreitungsgeschwindigkeit ebener Wellen kleiner Amplitude mit dem Druck wurde für Natrium und Kalium für 0°K theoretisch berechnet. Diejenigen Ausbreitungsgeschwindigkeiten, die mit den volumenabhängigen elastischen Koeffizienten zweiter Ordnung gekoppelt sind, zeigen bessere

Übereinstimmung mit den experimentellen Werten als jene Ausbreitungsgeschwindigkeiten, die mit den scherungsabhängigen Koeffizienten zusammenhängen. Dieses Ergebnis ist vermutlich eine Folge der Vernachlässigung der Bandstrukturkorrektur für die Verformungsenergiedichte.

INTRODUCTION

In previous papers we have shown that by means of a strain energy formulation it is possible to perform, in a general and unified manner, theoretical calculations for constitutive relations, pressure-volume relations, second-order elastic coefficients and the variation of these coefficients with dilatation or pressure for the alkali metals at absolute zero temperature^{1,2}. It should be noted that development of

the strain energy density function mentioned above is independent of classical thermodynamic considerations, which in purely continuum theories of elastic behavior must be employed in order to infer existence of such a function.

The strain energy is expressed as a continuous, differentiable function of the Green-Cauchy deformation tensors, and is based on well established quantum and classical calculations of various contributions to the crystal energy. These include ap-

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 energy³. Even when employing the simplest known local electron-ion pseudopotential suitable for alkali metals, which is the Ashcroft form⁴, 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 coefficients². 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}

$$\begin{aligned} \Sigma = & \left\{ \beta_1 - \frac{1}{\eta^2} \beta_2 \right\} I_3^{-\frac{1}{2}} + \beta_3 I_3^{-\frac{1}{2}} \\ & - \beta_4 I_3^{-\frac{1}{2}} + \beta_5 \ln \{ \beta_6 I_3^{\frac{1}{2}} \} \\ & + \beta_7 I_3^{-\frac{1}{2}} \sum'_m \frac{e^{-\beta_8/\eta^2(m_\alpha m_\beta C_{\alpha\beta}^{\frac{1}{2}})}}{m_\gamma m_\delta C_{\gamma\delta}^{-1}} \\ & + \beta_9 \sum'_n \frac{\operatorname{erfc} \{ \eta \beta_{10} (n_\alpha n_\beta C_{\alpha\beta})^{\frac{1}{2}} \}}{(n_\gamma n_\delta C_{\gamma\delta})^{\frac{1}{2}}} \\ & + \beta_{11} \sum'_n e^{-\beta_{12}(n_\alpha n_\beta C_{\alpha\beta})^{\frac{1}{2}}} \end{aligned} \quad (1)$$

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

$$\begin{aligned} \beta_1 &= \frac{16\pi}{3} \frac{r_0^2}{\Delta^6} & \beta_5 &= \frac{0.062}{\Delta^3} & \beta_9 &= \frac{4}{\Delta^4} \\ \beta_2 &= \frac{4\pi}{\Delta^6} & \beta_6 &= \left(\frac{3}{\pi} \right)^{\frac{1}{2}} \frac{\Delta}{2} & \beta_{10} &= \frac{\Delta}{2} \\ \beta_3 &= \left(\frac{\pi}{3} \right)^{\frac{1}{2}} \frac{17.680\alpha}{\Delta^5} & \beta_7 &= \frac{4}{\pi \Delta^4} & \beta_{11} &= \frac{\tilde{D}}{\Delta^3} \\ \beta_4 &= \left(\frac{\pi}{3} \right)^{\frac{1}{2}} \frac{3.644}{\Delta^4} & \beta_8 &= \frac{\pi^2}{\Delta^2} & \beta_{12} &= \frac{\Delta}{2\mu} \end{aligned}$$

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 Σ'_m, Σ'_n represent triple sums of $\Sigma_{m_1} \Sigma_{m_2} \Sigma_{m_3}$, and $\Sigma_{n_1} \Sigma_{n_2} \Sigma_{n_3}$, 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) | \bar{C}^d (ergs $\times 10^{12}$) | \bar{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 arbitrary 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 $\beta_1, \dots, \beta_{12}$ which include the quantities Δ, α, r_0 and $\bar{D} = \bar{C}e^{2r_c/\mu}$, 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 \bar{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 $\Delta, r_0, \alpha, r_c, \mu, \bar{C}$ and \bar{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

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

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 Swenson¹⁰ 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 $\{\beta_k\}$, $k=1, \dots, 12$, 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, \bar{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

view, material points in each of these configurations (in the same order) will be specified by position vectors \mathbf{R} , $\boldsymbol{\pi}$ and \mathbf{r} , with coordinates (X_α) , (ξ_k) and (x_k) respectively.

The deformations which take $K_0 \rightarrow \tilde{K}$ and $\tilde{K} \rightarrow K(t)$ are specified by the one to one mappings

$$\xi_k = \xi_k(X_\alpha), \quad X_\alpha = X_\alpha(\xi_k) \quad \alpha, k = 1, 2, 3,$$

$$\tilde{J} = \det|\partial \xi_k / \partial X_\alpha| \neq 0 \tag{3}$$

and

$$x_k = x_k(\xi_1, t), \quad \xi_k = \xi_k(x_1, t) \quad k, l = 1, 2, 3$$

$$t > 0$$

$$J' = \det|\partial x_k / \partial \xi_1| \neq 0. \tag{4}$$

The deformations specified by eqns. (3) and (4) are equivalent to passage from the natural to the current configurations such that

$$x_k = x_k(X_\alpha, t), \quad X_\alpha = X_\alpha(x_k, t)$$

$$J = \det|\partial x_k / \partial X_\alpha| \neq 0. \tag{5}$$

Mass densities $\rho_0, \tilde{\rho}$ and ρ associated with configurations K_0, \tilde{K} and $K(t)$ are related to the above Jacobians by

$$\tilde{J} = \rho_0 / \tilde{\rho}, \quad J' = \tilde{\rho} / \rho, \quad J = \rho_0 / \rho. \tag{6}$$

If $\mathbf{u}(\boldsymbol{\pi}, t)$ represents the displacement vector of a material point currently occupying position $\mathbf{r}(t)$, which at time $t=0$ had the initial position $\boldsymbol{\pi}$, then

$$u_k(\xi_1, t) = x_k(\xi_1, t) - \xi_k. \tag{7}$$

While $K_0 \rightarrow \tilde{K}$ may be arbitrary, the superimposed time dependent deformations $\tilde{K} \rightarrow K(t)$ are restricted to infinitesimal magnitudes, i.e., $\partial u_k / \partial \xi_1 \ll 1$ for all $t > 0$.

Relative to the initial configuration \tilde{K} , appropriate constitutive relations for a general theory of elasticity are given by¹³

$$\tilde{t}_{k1} = \tilde{J}^{-1} \left[2 \frac{\partial \Sigma}{\partial \tilde{C}_{\alpha\beta}} \right] \xi_{k,\alpha} \xi_{1,\beta} = \tilde{t}_{1k} \tag{8}$$

$$\tilde{T}_{\alpha\beta} = \tilde{J} \frac{\partial X_\alpha}{\partial \xi_k} \frac{\partial X_\beta}{\partial \xi_1} \tilde{t}_{k1} = 2 \frac{\partial \Sigma}{\partial \tilde{C}_{\alpha\beta}} = \tilde{T}_{\beta\alpha} \tag{9}$$

which are the Cauchy and Kirchhoff–Piola stress tensors respectively, where

$$\tilde{C}_{\alpha\beta} = \xi_{k,\alpha} \xi_{1,\beta} \delta_{k1} = \tilde{C}_{\beta\alpha}, \quad \xi_{k,\alpha} = \frac{\partial \xi_k}{\partial X_\alpha} \tag{10}$$

are the components of the Green–Cauchy deformation tensor. Constitutive relations of this kind

presume the existence of a strain energy density Σ which is a continuous and continuously differentiable function of the $C_{\alpha\beta}$. A mixed Kirchhoff–Piola stress tensor is also defined by the relations

$$\tilde{T}_{\alpha k} = \tilde{J} \frac{\partial X_\alpha}{\partial \xi_1} \tilde{t}_{k1} = \tilde{T}_{\alpha\beta} \xi_{k,\beta} = \frac{\partial \Sigma}{\partial \xi_{k,\alpha}} \tag{11}$$

which in the absence of body force are solutions of the equilibrium equations

$$\tilde{T}_{\alpha k,\alpha} = 0 \tag{12}$$

in the initial configuration \tilde{K} . In the current configuration $K(t)$ these same stress components satisfy the equations of motion

$$T_{\alpha k,\alpha} = \rho_0 \frac{\partial^2 u_k}{\partial t^2}. \tag{13}$$

Expanding $T_{\alpha k}$ in the displacement gradients about \tilde{K}

$$T_{\alpha k} = \tilde{T}_{\alpha k} + [x_{1,\beta} - \xi_{1,\beta}] \left(\frac{\partial \tilde{T}_{\alpha k}}{\partial x_{1,\beta}} \right)_{\mathbf{r}=\boldsymbol{\pi}} + \dots$$

Since the displacement gradients $u_{1,\beta} = (\partial u_1 / \partial \xi_m) \cdot \xi_{m,\beta}$, with $\partial u_1 / \partial \xi_m \ll 1$,

$$T_{\alpha k} = \tilde{T}_{\alpha k} + \tilde{A}_{k\alpha 1\beta} u_{1,\beta} \tag{14}$$

where in view of relations (10) and (11)

$$\tilde{A}_{k\alpha 1\beta} = \frac{\partial \tilde{T}_{\alpha k}}{\partial \xi_{1,\beta}} = \frac{\partial^2 \Sigma}{\partial \xi_{k,\alpha} \partial \xi_{1,\beta}}$$

$$= 4 \frac{\partial^2 \Sigma}{\partial \tilde{C}_{\alpha\gamma} \partial \tilde{C}_{\beta\delta}} \xi_{k,\gamma} \xi_{1,\delta} + 2 \frac{\partial \Sigma}{\partial \tilde{C}_{\alpha\beta}} \delta_{k1}. \tag{15}$$

Linearized equations of motion about the initial configuration in the form

$$[\tilde{A}_{k\alpha 1\beta} u_{1,\beta}]_\alpha = \rho_0 \frac{\partial^2 u_k}{\partial t^2} \tag{16}$$

follow from eqns. (13) and (14), with due account taken of eqn. (12). Relative to the coordinates (ξ_k) of the initial state these equations transform to

$$\frac{\partial}{\partial \xi_p} \left[\tilde{J}^{-1} \tilde{A}_{k\alpha 1\beta} \xi_{p,\alpha} \xi_{q,\beta} \frac{\partial u_1}{\partial \xi_q} \right] = \tilde{\rho} \frac{\partial^2 u_k}{\partial t^2} \tag{17}$$

after use of the identity $(\partial / \partial \xi_p) [\tilde{J}^{-1} \xi_{p,\alpha}] = 0$.

For initial deformations $K_0 \rightarrow \tilde{K}$ which are homogeneous, corresponding deformation gradients $\xi_{k,\alpha}$ as well as the strain energy derivatives in eqns. (15) have constant values throughout \tilde{K} . Equation (17) accordingly reduces to

$$\mathcal{J}^{-1} \tilde{A}_{k\alpha\lambda\beta} \xi_{p,\alpha} \xi_{q,\beta} \frac{\partial^2 u_1}{\partial \xi_p \partial \xi_q} = \tilde{\rho} \frac{\partial^2 u_k}{\partial t^2}. \quad (18)$$

If the displacements superimposed on the homogeneously deformed initial state are small amplitude plane waves

$$\mathbf{u} = \text{Re} [A e^{i(\bar{k}\mathbf{v} \cdot \mathbf{r} - \omega t)}] \quad (19)$$

where \bar{k} is the wave number, \mathbf{v} the propagation direction and ω the frequency, then eqn. (19) will be solutions of the equations of motion (18) if

$$\tilde{A}_{k\alpha\lambda\beta} \xi_{p,\alpha} \xi_{q,\beta} v_p v_q A_1 = \left(\rho_0 \frac{\omega^2}{\bar{k}^2} \right) A_k = \rho_0 U^2 A_k \quad (20)$$

which is a wave propagation condition, with $\omega^2/\bar{k}^2 = U^2$ the wave speeds. The second-order quantities

$$\begin{aligned} \tilde{Q}_{kl}(\mathbf{v}) &= \tilde{A}_{k\alpha\lambda\beta} \xi_{p,\alpha} \xi_{q,\beta} v_p v_q \\ &= \left\{ 4 \frac{\partial^2 \Sigma}{\partial \bar{C}_{\alpha\gamma} \partial \bar{C}_{\beta\delta}} \xi_{p,\alpha} \xi_{q,\beta} \xi_{k,\gamma} \xi_{l,\delta} \right. \\ &\quad \left. + 2 \frac{\partial \Sigma}{\partial \bar{C}_{\alpha\beta}} \xi_{p,\alpha} \xi_{q,\beta} \delta_{kl} \right\} v_p v_q \end{aligned} \quad (21)$$

define components of the acoustical tensor, which reduces the wave propagation condition to the familiar characteristic or eigenvalue equation

$$[\tilde{Q}_{kl}(\mathbf{v}) - (\rho_0 U^2) \delta_{kl}] A_1 = 0 \quad (22)$$

with $\rho_0 U_{(i)}^2$, $i = 1, 2, 3$, the eigenvalues and $A_{(i)1}$ the corresponding eigenvectors (displacement amplitudes) which define the acoustical axes for a given propagation direction \mathbf{v} .

The character of the wave propagation depends on the nature of the matrix $Q = (\tilde{Q}_{kl}(\mathbf{v}))$. The eigenvalues and eigenvectors will be real valued if the components $\tilde{Q}_{kl}(\mathbf{v})$ are real and symmetric. When the eigenvalues are real and distinct the associated eigenvectors define three real mutually orthogonal acoustic axes. If Q is furthermore a positive-definite matrix, *i.e.*, satisfies for every propagation direction \mathbf{v} the so-called strongly elliptic condition

$$\tilde{Q}_{kl}(\mathbf{v}) h_k h_l > 0 \quad (23)$$

for arbitrary non-zero vector \mathbf{h} , then the squared wave speeds will be positive, thereby admitting only real propagation speeds^{11,14}.

Solids which respond elastically are characterized as hyperelastic if they possess a strain energy function which is continuous and continuously differentiable in some measure of the deformation. The

development given above makes this presumption, from which follows, as examination of eqns. (15) and (21) will show, symmetry of the acoustical tensor. Thus for hyperelastic solids the square of the wave speeds and the corresponding acoustical axes are real, and for each direction of propagation there exists at least one mutually orthogonal set of acoustic axes. The wave speeds will not necessarily be real however, unless condition (23) is additionally satisfied.

The strain energy function for the alkali metals at zero temperature, given explicitly by eqn. (1), is of course not presumed but derived. Being continuous and continuously differentiable in the deformation tensor $C_{\alpha\beta}$, it thereby characterizes these metals as hyperelastic and furthermore assures symmetry of the acoustic tensor and real values for the squared wave speeds. The necessary and sufficient conditions which guarantee positive squared wave speeds $U_{(i)}^2$, and thus real wave speeds $U_{(i)}$, for arbitrary initial homogeneous deformation can be obtained from condition (23), where eqn. (1) is used in conjunction with eqn. (21). This calculation however involves several dozens of terms and is much too complicated to permit any interpretation. In the next section theoretical wave speeds for several propagation directions superimposed on different states of initial compression are calculated. The values obtained are all real and positive indicating positive-definite character of the acoustic matrix Q .

As $\bar{K} \rightarrow K_0$, $(\xi_k) \rightarrow (X_k)$ and $\xi_{k,\alpha} \rightarrow \delta_{k\alpha}$. Using the strain energy density eqn. (1) with zero temperature lattice spacing values as given in Table 1,

$$2 \frac{\partial \Sigma}{\partial \bar{C}_{\alpha\beta}} = \bar{T}_{\alpha\beta} \rightarrow T_{\alpha\beta} = 0$$

in the natural state. The quantities (15) correspondingly reduce to

$$\tilde{A}_{k\alpha\lambda\beta} \rightarrow A_{\kappa\alpha\lambda\beta} = \left[4 \frac{\partial^2 \Sigma}{\partial C_{\kappa\alpha} \partial C_{\lambda\beta}} \right]_{C=I} = C_{\kappa\alpha\lambda\beta}$$

which are the second-order elastic coefficients. C is the matrix $(C_{\alpha\beta})$ and I the identity matrix. Theoretical calculation of the $C_{\kappa\alpha\lambda\beta}$ using eqn. (1) compare quite well with experimental values, particularly for potassium, rubidium, and cesium^{1,2}. The equations of motion (16) likewise become the equations of motion of classical linear elasticity for small deformation about the natural configuration K_0

$$A_{\kappa\alpha\lambda\beta} u_{\lambda,\beta\alpha} = \rho_0 \frac{\partial^2 u_\kappa}{\partial t^2}.$$

CALCULATION OF THE VARIATION OF SMALL AMPLITUDE PLANE WAVE SPEEDS WITH PRESSURE

Uniform compression is the simplest of initially deformed configurations from an experimental as well as theoretical point of view, permitting elastic response of real crystals for deformations which may be large.

Setting

$$\xi_k = G_{k\alpha} X_\alpha = \lambda \delta_{k\alpha} X_\alpha, \quad 0 < \lambda < 1 \quad (24)$$

then

$$C_{\alpha\beta} = \xi_{k,\alpha} \xi_{l,\beta} \delta_{kl} = \lambda^2 \delta_{\alpha\beta} \quad (25)$$

In matrix representation

$$C = (C_{\alpha\beta}) = \lambda^2 I, \quad (26)$$

$$C^{-1} = (C_{\alpha\beta}^{-1}) = 1/\lambda^2 I.$$

Relative to the homogeneously compressed configuration \tilde{K}

$$4 \frac{\partial^2 \Sigma}{\partial \tilde{C}_{\kappa\lambda} \partial \tilde{C}_{\mu\nu}} = \left[4 \frac{\partial^2 \Sigma}{\partial C_{\kappa\lambda} \partial C_{\mu\nu}} \right]_{C=\lambda^2 I} = \tilde{C}_{\kappa\lambda\mu\nu}(\lambda) \quad (27)$$

$$2 \frac{\partial \Sigma}{\partial \tilde{C}_{\kappa\lambda}} = \left[2 \frac{\partial \Sigma}{\partial C_{\kappa\lambda}} \right]_{C=\lambda^2 I} = \tilde{T}_{\kappa\lambda}(\lambda) = -\lambda \tilde{p}(\lambda) \delta_{\kappa\lambda} \quad (28)$$

so that

$$\tilde{Q}_{kl}(\mathbf{v}) = [\lambda^4 \tilde{C}_{\kappa\lambda\mu\nu} \delta_{p\kappa} \delta_{k\lambda} \delta_{q\mu} \delta_{l\nu} - \lambda^3 \tilde{p} \delta_{pq} \delta_{kl}] v_p v_q, \quad (29)$$

where $\tilde{C}_{\kappa\lambda\mu\nu}(\lambda)$ are the second-order elastic constants in the compressed state and $\tilde{p}(\lambda)$ the initial pressure. The $\tilde{Q}_{kl}(\mathbf{v})$ can be theoretically calculated for any propagation direction \mathbf{v} by use of eqns. (1) and (26) to calculate $\tilde{C}_{\kappa\lambda\mu\nu}(\lambda)$ and $\tilde{p}(\lambda)^2$.

The square of the wave speeds follows from eqns. (22) and (29) as

$$U^2(\mathbf{v}) = \frac{1}{\rho_0} \frac{A_k A_l}{|A|^2} \tilde{Q}_{kl}(\mathbf{v}) = \frac{1}{\rho_0} \frac{A_k A_l}{|A|^2} \{ \lambda^4 \tilde{C}_{\kappa\lambda\mu\nu} \delta_{p\kappa} \delta_{k\lambda} \delta_{q\mu} \delta_{l\nu} - \lambda^3 \tilde{p} \delta_{pq} \delta_{kl} \} v_p v_q \quad (30)$$

with real values when the right side is positive. In the compressed configuration \tilde{K} the second-order

elastic constants have the same symmetry properties (body-centered cubic) as in the natural state:

$$\begin{aligned} \tilde{C}_{1111} &= \tilde{C}_{2222} = \tilde{C}_{3333} \\ \tilde{C}_{2323} &= \tilde{C}_{1313} = \tilde{C}_{1212} \\ \tilde{C}_{1122} &= \tilde{C}_{1133} = \tilde{C}_{2233}, \end{aligned} \quad (31)$$

all other $\tilde{C}_{\kappa\lambda\mu\nu}$ vanishing. Furthermore, as has been shown both experimentally¹⁵ and theoretically² for sodium

$$\begin{aligned} 0 < \tilde{C}_{2323} < \tilde{C}_{1122} < \tilde{C}_{1111} \\ 0 < \tilde{C}_{1111} - \tilde{C}_{1122} < \tilde{C}_{2323} & \quad 0 < \lambda \leq 1 \\ 0 < \tilde{C}_{1111} - \tilde{C}_{1122} < \tilde{C}_{1111} + \tilde{C}_{1122}. \end{aligned} \quad (32)$$

These inequalities apply for all alkali metals in the natural state, i.e., $\lambda = 1^2$, and can be expected to hold when $\lambda < 1$ for lithium, potassium, rubidium and cesium as well.

For a plane wave front propagating in the ξ_1 direction, $\mathbf{v}:(1, 0, 0)$, the hyperelastic b.c.c. crystal

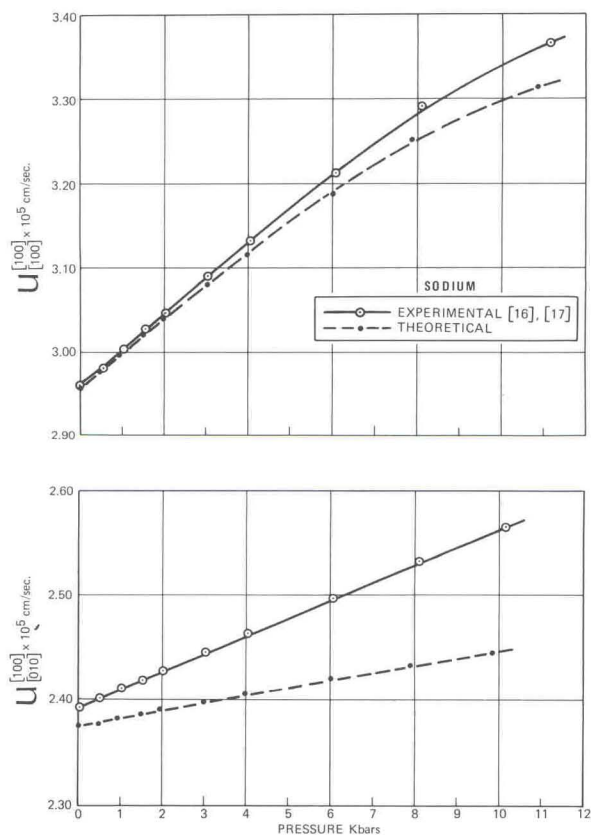


Fig. 1. Variation of $U_{[100][100]}^{[100]}$ and $U_{[100][010]}^{[100]}$ with pressure for sodium.

admits pure longitudinal and transverse waves with propagation speeds

$$U_{[100]}^{[100]} = U_L = \left\{ \frac{1}{\rho_0} \tilde{Q}_{11}[100] \right\}^{\frac{1}{2}} = \left\{ \frac{\lambda^3}{\rho_0} [\lambda \tilde{C}_{1111} - \bar{p}] \right\}^{\frac{1}{2}} \quad (33)$$

$$U_{[010]}^{[100]} = U_{[001]}^{[100]} = U_T = \left\{ \frac{1}{\rho_0} \tilde{Q}_{22}[100] \right\}^{\frac{1}{2}} = \left\{ \frac{\lambda^3}{\rho_0} [\lambda \tilde{C}_{2323} - \bar{p}] \right\}^{\frac{1}{2}} \quad (34)$$

where (32) requires

$$U_T < U_L \quad (35)$$

The upper brace of indices designates the wave front direction while the lower brace denotes the displacement direction or acoustic axes. Calculated values of the wave speeds for sodium and potassium together with experimental data are shown in Figs. 1 and 2. The experimental curves are constructed

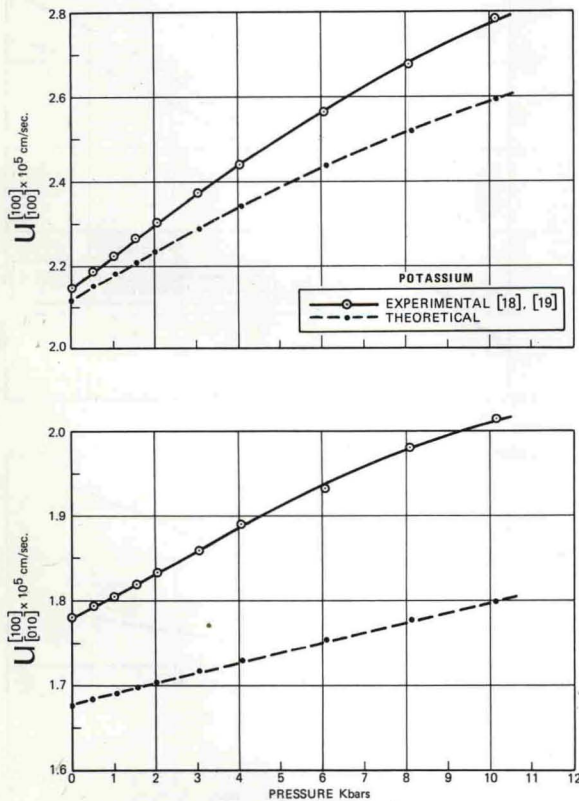


Fig. 2. Variation of $U_{[100]}^{[100]}$ and $U_{[010]}^{[100]}$ with pressure for potassium.

from the low temperature elastic coefficient data^{16,17} and the room temperature data on the pressure variation of the coefficients^{18,19}. The theoretical curves are of course for absolute zero temperature. The rate of increase of wave speed with pressure is seen to be greater for the longitudinal waves, both theoretically and experimentally. It is of interest therefore to note that in addition to inequality (35), both theoretical and experimental results further satisfy Truesdell's stronger inequality¹⁴

$$\frac{4}{3} U_T^2 < U_L^2 \quad (36)$$

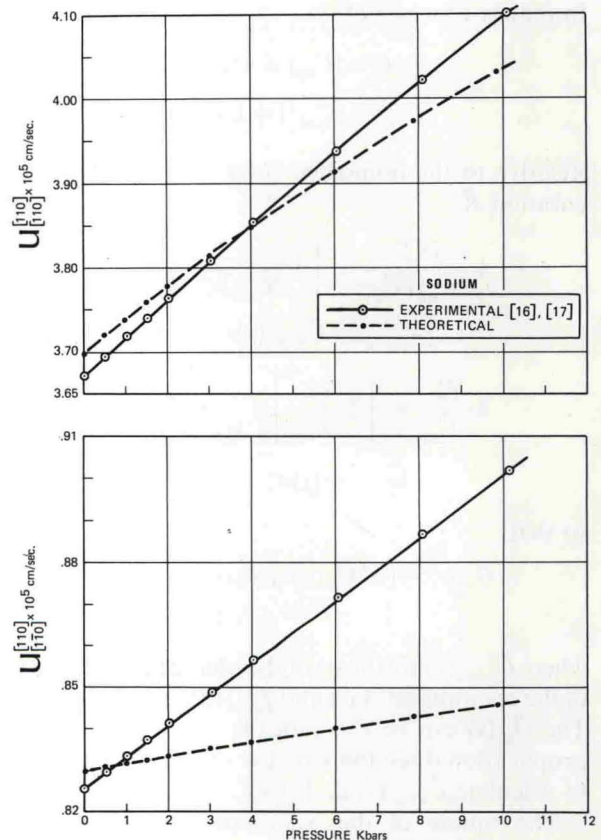


Fig. 3. Variation of $U_{[110]}^{[110]}$ and $U_{[110]}^{[110]}$ with pressure for sodium.

which is a "universal relation", that is, which holds for any state of initial pressure in every solid deforming elastically.

For a plane wave front traveling in the $[110]$ direction, $v : (1/\sqrt{2}, 1/\sqrt{2}, 0)$, there is associated an orthogonal triad of waves with speeds

$$U_{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}} = \left\{ \frac{1}{\rho_0} [\bar{Q}_{11}[110] + \bar{Q}_{12}[110]] \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{\lambda^3}{2\rho_0} [\lambda(\bar{C}_{1111} + \bar{C}_{1122} + 2\bar{C}_{2323}) - 2\bar{p}] \right\}^{\frac{1}{2}} \quad (37)$$

$$U_{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}} = \left\{ \frac{1}{\rho_0} [\bar{Q}_{11}[110] - \bar{Q}_{12}[110]] \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{\lambda^3}{2\rho_0} [\lambda(\bar{C}_{1111} - \bar{C}_{1122}) - 2\bar{p}] \right\}^{\frac{1}{2}} \quad (38)$$

$$U_{\begin{smallmatrix} 110 \\ 001 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 001 \end{smallmatrix}} = U_{\begin{smallmatrix} 100 \\ 001 \end{smallmatrix}}^{\begin{smallmatrix} 100 \\ 001 \end{smallmatrix}} \quad (39)$$

which by virtue of (32) are such that

$$-U_{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}} < U_{\begin{smallmatrix} 110 \\ 001 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 001 \end{smallmatrix}} < U_{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}}. \quad (40)$$

When v has the direction $[111]$, $v: (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$, then

$$U_{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}} = \left\{ \frac{1}{\rho_0} [\bar{Q}_{11}[111] + 2\bar{Q}_{12}[111]] \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{\lambda^3}{3\rho_0} [\lambda(\bar{C}_{1111} + 2\bar{C}_{1122} + 4\bar{C}_{2323}) - 3\bar{p}] \right\}^{\frac{1}{2}} \quad (41)$$

and

$$U_{\begin{smallmatrix} 111 \\ 110 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 110 \end{smallmatrix}} = U_{\begin{smallmatrix} 111 \\ 1\bar{1}0 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 1\bar{1}0 \end{smallmatrix}} = U_{\begin{smallmatrix} 111 \\ 011 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 011 \end{smallmatrix}}$$

$$= \left\{ \frac{1}{\rho_0} [\bar{Q}_{11}[111] - \bar{Q}_{12}[111]] \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{\lambda^3}{3\rho_0} [\lambda(\bar{C}_{1111} - \bar{C}_{1122} + \bar{C}_{2323}) - 3\bar{p}] \right\}^{\frac{1}{2}} \quad (42)$$

where

$$U_{\begin{smallmatrix} 111 \\ 110 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 110 \end{smallmatrix}} < U_{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}. \quad (43)$$

Calculated values together with experimental data for sodium and potassium for the last-named two cases are shown in Figs. 3-6.

The agreement of the calculated and experimental pressure variation of the longitudinal wave speeds is good. For the shear wave speeds the agreement is not good at all. This is because the band structure

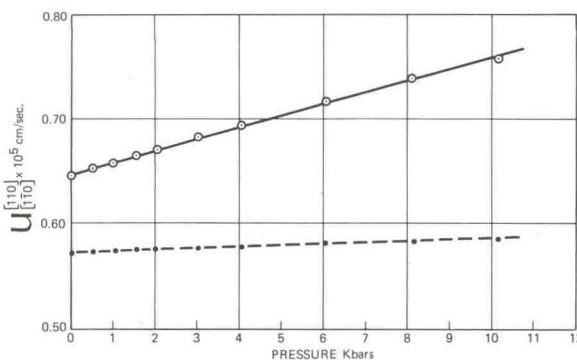
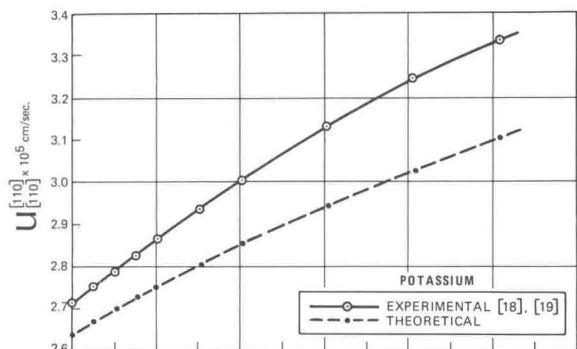


Fig. 4. Variation of $U_{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 110 \end{smallmatrix}}$ and $U_{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}}^{\begin{smallmatrix} 110 \\ 1\bar{1}0 \end{smallmatrix}}$ with pressure for potassium.

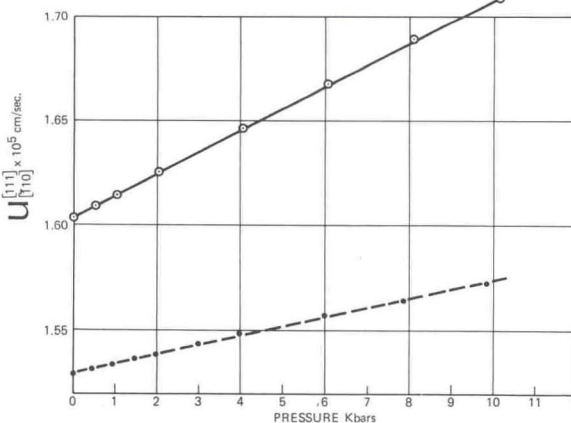
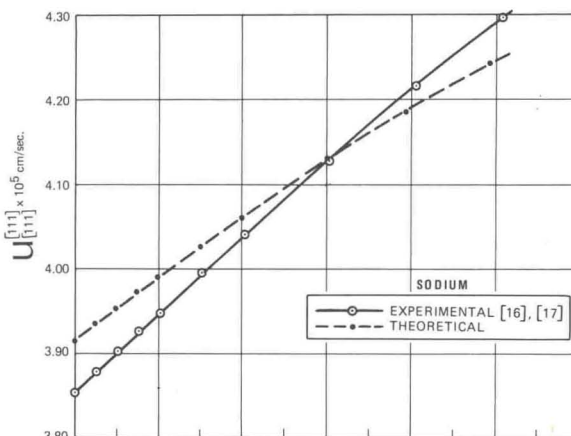


Fig. 5. Variation of $U_{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}$ and $U_{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}^{\begin{smallmatrix} 111 \\ 111 \end{smallmatrix}}$ with pressure for sodium.

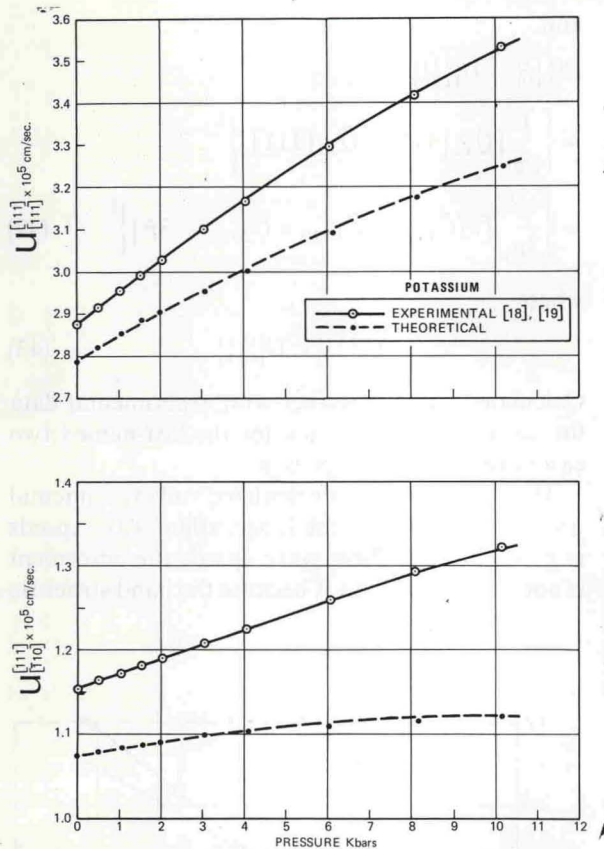


Fig. 6. Variation of $U_{[111]}^{[111]}$ and $U_{[110]}^{[110]}$ with pressure for potassium.

contribution (see Appendix) to the strain energy has been omitted².

The formulation presented here suggests that the experimental data on the wave speeds and their variation with pressure can be compared directly with theoretical models for materials. This method would avoid the errors introduced into the experimental data when the wave speed data are reduced to values for the elastic coefficients.

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APPENDIX

THE BAND STRUCTURE ENERGY

The band structure energy is a second-order perturbation addition to the crystal energy, arising from a pseudopotential correction to the free electron crystal potential which can be shown to have the general form³

$$E_{p2} = \sum_m S^*(\mathbf{K}_m) \cdot S(\mathbf{K}_m) F(\mathbf{K}_m) = \sum_m F(\mathbf{K}_m) \quad (\text{A1})$$

where

$$S(\mathbf{K}_m) = 1$$

$$F(\mathbf{K}_m) = -\frac{\Omega K_m^2}{8\pi e^2} |\langle \mathbf{k} + \mathbf{K}_m | \hat{W} | \mathbf{k} \rangle|^2 \frac{\varepsilon - 1}{\varepsilon}. \quad (\text{A2})$$

The structure factor $S(\mathbf{K}_m)$ is unity for monovalent crystals. $F(\mathbf{K}_m)$ is the energy wave number characteristic with e the electronic charge, \mathbf{k} the wave vector, \hat{W} the local electron-ion pseudopotential, ε the Hartree screening function, Ω the atomic sphere volume and \mathbf{K}_m the reciprocal lattice vector.

The simplest local electron-ion pseudopotential suitable for the alkali metals is the Ashcroft form⁴, wherein

$$|\langle \mathbf{k} + \mathbf{K}_m | \hat{W} | \mathbf{k} \rangle|^2 = \frac{64\pi^2}{\Omega^2 K_m^4} \cos^2 \{r_c |\mathbf{K}_m|\} \quad (\text{A3})$$

Then in atomic units

$$E_{p2}^{\text{a.u.}} = \frac{8\pi}{\Omega_{\text{DL}}} \sum_m \frac{\cos^2 \{r_c |\mathbf{K}_m|\}}{K_m^2} \left(\frac{1}{\varepsilon} - 1 \right) \quad (\text{A4})$$

with

$$\varepsilon = 1 + \frac{4k_F - K_m^2}{2\pi K_m^3} \ln \left| \frac{2k_F/K_m + 1}{2k_F/K_m - 1} \right| + \frac{2k_F}{\pi K_m^2} \quad (\text{A5})$$

$$k_F = \left\{ \frac{6\pi^2}{\Omega_{\text{DL}}} \right\}^{\frac{1}{3}} \quad (\text{A6})$$

where Ω_{DL} is the volume of a unit cell of the direct lattice. The significant contribution of the band structure energy to higher derivatives of the crystal energy comes from the derivatives of the logarithmic term in the screening function ε , which has a singularity at $\mathbf{K}_m = 2\mathbf{k}_F$.

The band structure contribution to the strain energy can be shown to be⁵

$$\frac{2}{\Delta^3 N} E'_{p2} = 4\beta_7 I_3^{-\frac{1}{2}} \sum_m \frac{\cos^2 \{ \beta_{13} (m_\alpha m_\beta C_{\alpha\beta}^{-1})^{\frac{1}{2}} \}}{m_\gamma m_\delta \bar{C}_{\gamma\delta}^{-1}}$$

$$\times \left[\frac{1}{\epsilon'} - 1 \right] \quad (\text{A7})$$

where N is the number of unit cells of the direct lattice,

$$\begin{aligned} \epsilon' = 1 + & \frac{\beta_{14}}{\{m_x m_\beta C_{\alpha\beta}^{-1}\}^{\frac{1}{2}}} \\ & \times \left[\frac{1}{m_\gamma m_\delta C_{\gamma\delta}^{-1} \cdot I_3^{\frac{1}{3}}} - \frac{1}{\beta_{16}^2} \right] L(C_{\alpha\beta}^{-1}, I_3) \\ & + \frac{\beta_{15}}{m_x m_\beta C_{\alpha\beta}^{-1} I_3^{\frac{1}{3}}} \end{aligned} \quad (\text{A8})$$

and

$$L(C_{\alpha\beta}^{-1}, I_3) = \ln \left[\frac{\beta_{16} (m_x m_\beta C_{\alpha\beta}^{-1})^{-\frac{1}{2}} \cdot I_3^{-\frac{1}{6}} + 1}{\beta_{16} (m_x m_\beta C_{\alpha\beta}^{-1})^{-\frac{1}{2}} \cdot I_3^{-\frac{1}{6}} - 1} \right]. \quad (\text{A9})$$

The β_{13} , β_{14} , β_{15} and β_{16} are constants. These expressions involve $C_{\alpha\beta}^{-1}$ and I_3 repeatedly, terms which proliferate upon differentiation with respect to the deformation tensor $C_{\kappa\lambda}$. As a consequence, calculation of higher order derivatives of the band structure contribution with respect to arbitrary deformation becomes extremely tedious.

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