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# Second- and Third-Order Elastic Constants of Aluminum and Lead[†]

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The second- and third-order elastic constants of Al and Pb are calculated as the second and third derivatives of the binding energy with respect to the finite deformation parameter. The binding energy is derived from a local pseudopotential by use of second-order perturbation theory. It is shown that the binding energy satisfies not only the diagonal equilibrium condition, but also the off-diagonal equilibrium condition, i.e., the first derivative of the binding energy with respect to a volume change as well as with respect to shear deformations is zero. Accordingly, the present method of calculation is based on a stable lattice model. The results of the present calculation of the third-order elastic constants of Al are found to be in qualitative agreement with the experimental data obtained by Thomas. The complete experimental set of the third-order elastic constants of Pb is not yet available; however, the calculated pressure derivatives of the second-order elastic constants are in agreement with the experimental data of Miller and Schuele. On the other hand, the method initiated by Leigh, which is based on a rigid-band model, cannot reproduce the experimentally observed third-order elastic constants of Al. This is an indication that the pseudopotential method is to be preferred to the rigid-band method as far as the calculation of second- and third-order elastic constants is concerned.

## I. INTRODUCTION

In the calculation by the method of uniform deformation,[1–5] the elastic constants are defined as derivatives of the cohesive energy or the binding energy of a crystal with respect to deformation parameters which specify uniform deformations of the crystal. Accordingly, there are two problems which enter into the calculation of elastic constants by this method. The first is to find a proper expression for the binding energy or cohesive energy.[6] The second is to define parameters to specify the uniform deformations. For a given binding-energy expression, a relationship can be established between different sets of elastic constants defined by different sets of deformation parameters. The relationships between the Brugger elastic constants and the Fuchs elastic constants are described by Suzuki, Granato, and Thomas[7] (abbreviated as SGT hereafter).

In this paper, a calculation of the second- and third-order elastic constants of Al and Pb, based on the binding-energy expression derived from a pseudopotential theory, will be presented and compared with the previous calculation by Leigh,[8] who extended Fuchs's[9,10] calculation of elastic constants of alkali metals to the calculation of the shear elastic constants of Al.

## II. FUCHS-LEIGH CALCULATION

Fuchs calculated the second-order elastic constants of alkali metals from the cohesive-energy expression of Wigner and Seitz, which consists of three terms. The total energy $E$ per electron is given by

$$E = E^0 + E^L + E^F ,$$

where $E^0$ denotes the energy of a conduction electron in its lowest state (i.e., at rest in the lattice), $E^L$ denotes the electrostatic interaction energy between atomic polyhedrons, and $E^F$ is the kinetic energy of a conduction electron. To a good approximation, $E^F$ for alkali metals was assumed to be given by the expression for the kinetic energy of free electrons,

$$E^F = \frac{3\hbar^2}{10m}\left(\frac{3Z\pi^2}{\Omega}\right)^{2/3} , \qquad (2.1)$$

where $\Omega$ is the atomic volume, $\hbar$ is Planck's constant divided by $2\pi$, $m$ is the free-electron mass, and $Z$ is the valency (1 for alkali metals, 3 for Al, 4 for Pb, etc.). The electrostatic interaction energy $E^L$ is given in terms of the lattice structure and the effective charge $Z_{eff}$, which is determined by the electron density near the surface of the atomic sphere.

Leigh[8] extended Fuchs's[9,10] calculation of elastic constants of alkali metals to the calculation of shear elastic constants of Al by taking into account the deviation of the kinetic energy $E^F$ of the conduction electrons in Al from that of free electrons given by Eq. (2.1). Because the number of conduction electrons per atom is more than sufficient to fill the first Brillouin zone in Al, the effect on $E^F$ due to the Brillouin-zone distortion associated with shear deformations was expected to be much larger than in alkali metals. The effect of the movement of the Brillouin zone on $E^F$ in alkali metals was considered to be negligible by Fuchs.

Leigh expressed $E^F$, which is a function of momentum, in terms of four parameters which were supposed to be consistent with experimental data on the Fermi surface in the undeformed state. The derivatives of $E^F$ with respect to the shear deformation parameters were calculated under the assumption that $E^F$ changed because of the displacement of the energy gap present at the Brillouin-zone boundaries and because of the accompanying redistribution of electrons within and between Brillouin zones. Moreover, the energy vs momentum relationship on either side of the zone boundaries was assumed to remain the same during the deformation. This assumption was referred to as "the rigid-band model" by Harrison.[11]

The electron density near the surface of an atomic sphere, which was necessary for Leigh's calculation of the electrostatic interaction energy $E^L$, was another adjustable parameter, since the Schrödinger equation for Al could not be solved to determine the wave function and the energy of conduction electrons. In addition, the bulk modulus, which requires a knowledge of $E^0$ in addition to $E^F$ and $E^L$, was not calculated by Leigh. Hence, his calculation was limited to the shear elastic constants. As a result, he adjusted these five parameters to the four available experimental results, namely, the two shear elastic constants $\frac{1}{2}(C_{11}-C_{12})$ and $C_{44}$, the electronic specific heat, and the width of the soft x-ray emission spectrum.

The calculation of shear elastic constants based on the rigid-band model was extended to magnesium, $\beta$ brass, and $\alpha$-phase copper and silver alloy by Reitz and Smith,[12] Jones,[13] and Collins,[14] respectively.

When Daniels[15] extended Fuchs's calculation[9,10] of the second-order elastic constants of alkali metals to the calculation of the pressure derivatives of the second-order shear elastic constants, he found that it was necessary to assume the effective charge $Z_{\text{eff}}$ in the electrostatic interaction energy $E^L$ to be pressure dependent. Similarly, in the calculation of the pressure derivatives of the second-order elastic constants of Al and Mg, Schmunk and Smith[16] found it necessary to add one more adjustable parameter, namely, the pressure dependence of the effective charge, to the parameters already used in the rigid-band-model calculations of second-order elastic constants.

Five Fuchs third-order elastic constants, which do not contain a contribution from the volume-dependent energy $E^0$, were calculated by Thomas,[17] who extended Leigh's procedure to the third-order elastic constants. Starting from the same expression for the cohesive energy as used by Leigh, Thomas found it impossible to reproduce the experimental Fuchs elastic constants when using the five parameters which are compatible with the experimental data on the Fermi surface of Al. Since it was impossible to calculate the volume-dependent energy $E^0$ for polyvalent metals by the direct extension of the Wigner-Seitz method, Leigh's calculation[8] and other calculations[12,13] based on a rigid-band model of polyvalent metals were limited to the calculation of shear elastic constants, which do not contain contributions from $E^0$. Furthermore, there was no way to check whether the calculation was based on a stable model of the crystal lattice.

## III. PSEUDOPOTENTIAL CALCULATION

### A. Binding-Energy Expression

In pseudopotential theory,[18-21] the energy $E(\vec{k})$ of a conduction electron as a function of momentum $\vec{k}$ is calculated by second-order perturbation theory, whereas in the Fuchs-Leigh calculation $E(\vec{k})$ was expressed in terms of adjustable parameters. The energy of a conduction electron in a perfect crystal is given by

$$E(\vec{k})=\frac{\hbar^2k^2}{2m}+\langle\vec{k}|w|\vec{k}\rangle+\sum_{\vec{q}}{}'\,\frac{\langle\vec{k}+\vec{q}\,|w|\,\vec{k}\rangle\langle\vec{k}\,|w|\,\vec{k}+\vec{q}\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}\,|^2)}\ , \tag{3.1}$$

where the summation extends over all the reciprocal-lattice points $\vec{q}$ except the origin. The matrix element of the screened pseudopotential between two plane waves $\langle\vec{k}+\vec{q}\,|w|\,\vec{k}\rangle$ is obtained from the matrix element of a bare ion pseudopotential $\langle\vec{k}+\vec{q}\,|w_b|\,\vec{k}\rangle$ by use of a dielectric function. The total energy of the conduction electrons is obtained by summing the above expression for $E(\vec{k})$ up to the free-electron Fermi surface and subtracting the electron-electron interaction energy. [The electron-electron interaction energy is counted twice when we perform the summation with respect to $\vec{k}$, since $E(\vec{k})$ represents the energy of an electron in the field of ions and other electrons.]

The total binding energy $E$ of the crystal is obtained by adding the electrostatic energy between positive ions to the total energy of the conduction electrons. The expression for the total binding energy thus obtained is rewritten as a sum of three terms, the free-electron energy $E_1$, the electrostatic energy $E_2$, and the band-structure energy $E_3$. The free-electron energy $E_1$ (per ion), which includes the exchange and correlation energy, is defined as follows:

$$E_1=Z\left\{\frac{3}{10}\,\frac{\hbar^2}{m}\left(\frac{3\pi^2Z}{\Omega}\right)^{2/3}-\frac{0.916\,e^2}{2r_s}\right.$$
$$\left.-\left[0.115-0.031\ln\left(\frac{me^2r_s}{\hbar^2}\right)\right]\frac{me^4}{2\hbar^2}\right.$$

$$+\int_0^{k_F} \langle\vec{\mathrm{k}}|\, w_b+(Ze^2/r)\,|\vec{\mathrm{k}}\rangle\, d^3\vec{\mathrm{k}} \Big/ \int_0^{k_F} d^3\vec{\mathrm{k}} \Bigg\} \; . \tag{3.2}$$

Here $e$ is the electronic charge and $r_s$ is given in terms of the atomic volume $\Omega$ and valence $Z$ by

$$\tfrac{4}{3}\,\pi r_s^3 = \Omega/Z \; . \tag{3.3}$$

Every quantity in Eqs. (3.2) and (3.3) is expressed in cgs units. The free-electron energy $E_1$ is dependent solely upon the atomic volume.

The electrostatic energy $E_2$ is the classical electrostatic energy of a lattice of positive point charges $Ze$ imbedded in a uniform background of compensating negative charge. The electrostatic interaction energy $E^L$ in the Fuchs-Leigh calculation is equal to the same electrostatic energy $E_2$ (with $Z = Z_{\mathrm{eff}}$) minus the electrostatic energy of the atomic sphere. Hence, although $E_2$ is not equal to $E^L$, the derivatives of $E_2$ and $E^L$ with respect to volume-conserving shear deformations are equal.

The band-structure energy $E_3$ is derived from the second-order perturbation term of Eq. (3.1), with care taken to count electron-electron interactions only once. $E_3$ is given as a summation of an energy-wave-number characteristic $F(q)$ over all reciprocal-lattice points except the origin:

$$E_3 = \sum_{\vec{\mathrm{q}}}{}' F(\vec{\mathrm{q}}) \; . \tag{3.4}$$

In the present paper, a simple local pseudopotential, which corresponds to the local part of the Heine-Abarenkov-Animalu[22–24] model potential

$$\begin{aligned} w_b(r) &= -\,Ze^2/r \quad (r > r_c) \\ &= U_0 \qquad\quad (r \le r_c) \; , \end{aligned} \tag{3.5}$$

is used together with both the Hubbard-Sham and Hartree dielectric functions to calculate the band-structure energy $E_3$ and the last term of the free-electron energy $E_1$. From this potential, we obtain the energy–wave-number characteristic

$$F(q) = \frac{q^2}{8\pi e^2 \Omega}\left[-\left(\frac{4\pi Z e^2}{q^2} + \frac{4\pi U_0 r_c}{q^2}\right)\cos q r_c + \frac{4\pi U_0}{q^3}\sin q r_c\right]^2 \frac{1-\epsilon(q,k_F)}{\epsilon(q,k_F)} \; , \tag{3.6}$$

where $q = |\vec{\mathrm{q}}|$, and $k_F$ is the radius of the free-electron Fermi sphere,

$$k_F = (3\pi^2 Z/\Omega)^{1/3} \; . \tag{3.7}$$

$\epsilon(q, k_F)$ represents either the Hubbard-Sham dielectric function[25]

$$\epsilon(q,k_F) = 1 + \frac{me^2}{2\pi k_F \hbar^2 \eta^2}\left(\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| + 1\right) \times\left(1 - \frac{\eta^2}{2\eta^2 + \frac{1}{2} + 1/\pi a_0 k_F}\right) \; , \tag{3.8}$$

or the Hartree dielectric function, which is obtained from the above expression by replacing the last factor by unity. Here, $\eta = q/2k_F$ and $a_0$ is the Bohr radius. The last term of the free-electron energy $E_1$, calculated from the pseudopotential of Eq. (3.5), is given as

$$\int_0^{k_F} \left\langle \vec{\mathrm{k}} \left| w_b + \frac{Ze^2}{r} \right| \vec{\mathrm{k}} \right\rangle d^3\vec{\mathrm{k}} \Big/ \int_0^{k_F} d^3\vec{\mathrm{k}} = \frac{4\pi}{\Omega}\left(\tfrac{1}{3} U_0 r_c^3 + \tfrac{1}{2} Z e^2 r_c^2\right) \; . \tag{3.9}$$

By combining the free-electron energy $E_1$, the electrostatic energy $E_2$, and the band-structure energy $E_3$, we obtain the expression for the total binding energy per ion.

In this paper, the equilibrium conditions for Al and Pb were checked by taking the first derivatives of the binding-energy expression with respect to diagonal as well as off-diagonal components of $\eta_{ij}$. The second and third derivatives of the binding-energy expression with respect to both the diagonal and the off-diagonal components of the finite deformation parameter, i.e., the complete set of second- and third-order elastic constants, were calculated by the same method as used by SGT in the case of the alkali metals. Since the alkali metals are cubic, there are six independent third-order elastic constants; however, only three independent relations (i.e., the pressure derivatives of three second-order elastic constants) have been measured[15, 26–28] experimentally. The complete set of third-order elastic constants of Al has recently been measured by Thomas.[29] The experimental data for Al give the first complete check of a calculation of third-order elastic constants based on a pseudopotential method.

### B. Equilibrium Condition for the Binding-Energy Expression

#### 1. *Equilibrium Condition with Respect to* $\eta_{ii}$

Because the expression for the volume-dependent free-electron energy $E_1$ contains the approximate expression for the correlation and exchange energy, the entire expression for the binding energy does not necessarily have a minimum at the observed electron density or lattice spacing. In the expression for the binding energy proposed by Ashcroft and Langreth[20] and also used in SGT, the equilibrium condition with respect to uniform expansion of the lattice was forced to fit the observed lattice spacing by adjusting the last term of the free-electron energy $E_1$ given by Eq. (3.2). Hence, the expression for the binding energy contained one additional implicit parameter besides the adjustable parameter in the assumed pseudopotential. Furthermore, the expression for the binding energy was not entirely consistent with the assumed pseudopotential. In this paper, however, the last term of the free-electron energy is directly calculated from the pseudopotential [Eq. (3.9)]. For each value of the core radius used, the depth of the well $U_0$ is chosen so that the present expression for the binding energy is minimum at the observed atomic volume (extrapolated to 0 °K). In Table I, the values of the two parameters in the assumed pseudopotential are shown, together with the binding energy and the three second-order elastic constants calculated from the pseudopotential with the corresponding parameters. Also shown in Table I are the observed values of the binding energy and the linearly extrapolated values (to 0 °K) of the observed second-order elastic constants of Al and Pb.[30,31] In the case of Al, the choice of the parameters $r_c = 2.2$ a.u. and $U_0 = -1.62$ a.u. (with the Hartree dielectric function) or $U_0 = -1.58$ a.u. (Hubbard-Sham dielectric function) in the pseudopotential reproduced the observed binding energy and the three second-order elastic constants reasonably well at the observed lattice spacing. In the case of Pb, it is found that the calculated binding energy never becomes larger than the observed binding energy. The choice of $r_c = 1.60$ a.u. and $U_0 = -1.70$ a.u. (with the Hartree dielectric function) or $U_0 = -1.67$ a.u. (Hubbard-Sham dielectric function) reproduced the best possible values of the binding energy and the three second-order elastic constants at the observed lattice spacing within the framework of the present calculation.

It is noticed that the values of the parameters in the pseudopotential thus determined are rather close to those adopted by Animalu *et al.*[32] in their local pseudopotential calculation of the phonon dispersion curves. They have chosen their values from the observation that the orthogonalized-plane-wave (OPW) form factor calculated from the local pseudopotential is a good approximation to the OPW form factor calculated from the Heine-Abarenkov-Animalu model potential for $|\vec{q}| < 2k_F$ and converges quickly to zero for $|\vec{q}| > 3k_F$. Accordingly, the convergence of the summation of the energy–wave-number characteristic, as well as its various derivatives, is also found to be very fast. The summation over the reciprocal-lattice points $|\vec{q}| \leq 3k_F$ is sufficient to ensure numerical accuracy of 1%.

### 2. *Equilibrium Condition with Respect to* $\eta_{ij}$ $(i \neq j)$

Next, we have to show that our expression for the binding energy also satisfies the equilibrium condition with respect to shear deformations, i.e.,

TABLE I. Parameters in pseudopotential, binding energy, and second-order elastic constants.

| | Core radius $r_c$ (a.u.) | Depth of well $U_0$ (a.u.) | Calculated binding energy ($10^{11}$ erg) | Observed binding energy ($10^{11}$ erg) | Calculated second-order elastic constants $C_{11}$ ($10^{11}$ dyn/cm$^2$) | $C_{12}$ | $C_{44}$ | Observed (extrapolated to 0 °K) second-order elastic constants $C_{11}$ ($10^{11}$ dyn/cm$^2$) | $C_{12}$ | $C_{44}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Al Hartree | 1.8 | −1.77 | 10.03 | | 9.88 | 7.84 | 4.71 | | | |
| | 2.0 | −1.71 | 9.95 | | 9.65 | 7.55 | 4.58 | | | |
| | 2.2 | −1.62 | 9.76 | | 9.22 | 6.93 | 4.47 | | | |
| | 2.4 | −1.51 | 9.48 | | 9.40 | 6.29 | 4.98 | | | |
| | 2.6 | −1.41 | 9.17 | | 11.28 | 6.31 | 6.60 | | | |
| | | | | 9.06 | | | | 11.70 | 6.26 | 3.26[a] |
| Al Hubbard-Sham | 1.8 | −1.67 | 9.63 | | 11.67 | 8.83 | 6.25 | | | |
| | 2.0 | −1.64 | 9.58 | | 11.52 | 8.64 | 6.22 | | | |
| | 2.2 | −1.58 | 9.50 | | 11.53 | 8.40 | 6.41 | | | |
| | 2.4 | −1.49 | 9.35 | | 11.77 | 8.03 | 6.98 | | | |
| | 2.6 | −1.41 | 9.16 | | 13.01 | 8.02 | 8.33 | | | |
| Pb Hartree | 2.0 | −1.49 | 13.43 | | 8.40 | 5.92 | 4.34 | | | |
| | 2.2 | −1.68 | 13.63 | | 7.98 | 5.85 | 4.10 | | | |
| | 2.4 | −1.70 | 13.70 | | 7.98 | 5.87 | 4.09 | | | |
| | 2.6 | −1.67 | 13.67 | | 7.94 | 5.79 | 4.11 | | | |
| | 2.8 | −1.61 | 13.51 | | 8.12 | 5.72 | 4.33 | | | |
| | | | | 15.77 | | | | 5.27 | 4.24 | 1.96[b] |
| Pb Hubbard-Sham | 2.0 | −1.45 | 13.36 | | 10.12 | 6.91 | 5.87 | | | |
| | 2.2 | −1.64 | 13.64 | | 9.79 | 6.94 | 5.50 | | | |
| | 2.4 | −1.67 | 13.67 | | 9.72 | 6.94 | 5.42 | | | |
| | 2.6 | −1.65 | 13.62 | | 9.74 | 6.91 | 5.48 | | | |
| | 2.8 | −1.60 | 13.51 | | 9.94 | 6.87 | 5.76 | | | |

[a] G. N. Kamm and G. A. Alers (Ref. 30).

[b] D. L. Waldorf and G. A. Alers (Ref. 31).

$\partial E/\partial \eta_{ij} = 0$ $(i \neq j)$.

Because the free-electron energy $E_1$ is solely dependent on the volume of the crystal,

$$\frac{\partial E_1}{\partial \eta_{ij}} = \frac{\partial E(v)}{\partial v} \frac{\partial v}{\partial \eta_{ij}} .$$

The derivative of the relative volume change $v$ with respect to the off-diagonal component of the finite deformation parameter is always zero:

$$\frac{\partial v}{\partial \eta_{ij}} = 0 \quad (i \neq j) .$$

Hence, the free-electron energy $E_1$ satisfies the off-diagonal equilibrium condition, i.e., $\partial E_1/\partial \eta_{ij} = 0$ $(i \neq j)$.

The electrostatic energy $E_2$, which is a central interaction term, can be written as a summation of pairwise interaction energies $W$, which depend solely on the distance or, equivalently, the square of the distance between two particles, $r^2$. Hence,

$$\frac{\partial E_2}{\partial \eta_{ij}} = \frac{1}{2} \sum_{\substack{\text{all} \\ \text{particles}}} \frac{\partial W(r^2)}{\partial \eta_{ij}} = \frac{1}{2} \sum \frac{W(r^2)}{\partial r^2} \frac{\partial r^2}{\partial \eta_{ij}} .$$

The derivative of the square of the distance is given in terms of the coordinates $r_i$ before deformation as

$$\frac{\partial r^2}{\partial \eta_{ij}} = 2 \sum_{i,j} r_i r_j \eta_{ij} .$$

Accordingly, if every particle in the crystal is located at a center of symmetry, as in the case of Al, the first derivative of the summation of the pairwise interaction energy $W$ is zero. Hence,

$$\frac{\partial E_2}{\partial \eta_{ij}} = 0 \quad (i \neq j) .$$

The energy–wave-number characteristic $F(q, k_F)$ derived from a local pseudopotential is a function of the magnitude of the reciprocal-lattice vector $q$ and the radius of the free-electron Fermi sphere $k_F$. Hence, the derivative of the band-structure energy $E_3$ with respect to $\eta_{ij}$ $(i \neq j)$ is given by[33]

$$\frac{\partial E_3}{\partial \eta_{ij}} = \sum_q{}' \left( \frac{\partial F}{\partial q} \frac{\partial q}{\partial \eta_{ij}} + \frac{\partial F}{\partial k_F} \frac{\partial k_F}{\partial \eta_{ij}} \right) .$$

Here, the derivative of the radius of the free-electron Fermi sphere with respect to the off-diagonal component of the deformation parameter is zero because it is dependent solely on the total volume of the crystal. The square of the magnitude of the reciprocal-lattice vector, $q^2$, is given in terms of the primitive reciprocal-lattice vectors $g_1$, $g_2$, and $g_3$ of the simple cubic lattice such that

$$q^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} m_i m_j g_i g_j ,$$

where $m_1$, $m_2$, and $m_3$ are integers chosen so as to represent a bcc lattice in reciprocal space, if the real lattice under consideration is fcc (e.g., Al and Pb) or vice versa. It is shown in the Appendix that

$$\frac{\partial}{\partial \eta_{ij}} g_1 g_1 = \frac{\partial}{\partial \eta_{ij}} g_2 g_2 = \frac{\partial}{\partial \eta_{ij}} g_3 g_3 = 0 \quad (i \neq j) .$$

Hence, we obtain

$$\frac{\partial E_3}{\partial \eta_{ij}} = \sum_{m_1, m_2, m_3}{}' \frac{\partial F}{\partial q} \frac{1}{2q} \frac{\partial}{\partial \eta_{ij}} \times (2 m_1 m_2 g_1 g_2 + 2 m_2 m_3 g_2 g_3 + 2 m_3 m_1 g_3 g_1).$$

The origin of the reciprocal lattice of bcc or fcc structures is a center of symmetry. Accordingly, the first derivative of the band-structure energy with respect to the off-diagonal component of the finite deformation parameter $\eta_{ij}$ $(i \neq j)$ is zero. In summary, the binding energy $E$, which consists of three parts, the free-electron energy $E_1$, the electrostatic energy $E_2$, and the band-structure energy $E_3$, satisfies the off-diagonal equilibrium condition

$$\frac{\partial E}{\partial \eta_{ij}} = 0 \quad (i \neq j)$$

for fcc and bcc structures.

### C. Elastic Constants

The second- and third-order elastic constants of Al and Pb were calculated for the values of the parameters shown in Table I. The second- and third-order Fuchs elastic constants, which are derivatives of the binding energy with respect to the deformation parameters $v$, $\epsilon_i$, and $\gamma_i$ $(i = 1, 2$, or $3)$, were calculated and then related to the Brugger elastic constants by methods discussed in SGT. The second derivatives of the electrostatic energy $E_2$ for bcc and fcc structures were calculated by Fuchs, and the third derivatives for these structures were calculated by Cousins[34] and also by Suzuki and Granato.[35] The derivatives of the band-structure energy $E_3$ were calculated by summing the derivatives of the energy–wave-number characteristic $F(q)$ up to the 5th neighbor of the reciprocal lattice instead of the 76th neighbor as in SGT; the summation is reduced because of the improved convergence of the energy–wave-number characteristic used in the present calculation.

The Brugger third-order elastic constants of Al and Pb, calculated with the parameters which best reproduced the binding energy and second-order elastic constants, are shown in Tables II and III. The experimental third-order elastic constants obtained by Thomas[29] are included in Table II. As far as the present author is aware, this is the first case where pseudopotential calculations of the third-

TABLE II. Third-order elastic constants of Al ($10^{12}$ dyn/cm$^2$).

| | Hartree<br>$r_c = 2.2$ a.u.<br>$U_0 = -1.62$ a.u. | Hubbard-Sham<br>$r_c = 2.2$ a.u.<br>$U_0 = -1.58$ a.u. | Experimental[a] |
|---|---|---|---|
| $C_{111}$ | $-6.86$ | $-7.66$ | $-10.76 \pm 0.30$ |
| $C_{112}$ | $-3.22$ | $-4.19$ | $-3.15 \pm 0.10$ |
| $C_{123}$ | 1.42 | 1.45 | $+0.36 \pm 0.15$ |
| $C_{144}$ | 0.49 | 0.58 | $-0.23 \pm 0.05$ |
| $C_{166}$ | $-3.47$ | $-4.54$ | $-3.40 \pm 0.10$ |
| $C_{456}$ | 0.92 | 0.73 | $-0.30 \pm 0.30$ |

[a] Experimental data at 25 °C by J. F. Thomas, Jr. (Ref. 29). Strictly speaking, calculated values should be compared with the linear extrapolation of experimental data to 0 °K. However, experimental data on the temperature dependence of the complete set of the third-order elastic constants are not available at present.

order elastic constants can be compared with the experimental data; however, a forthcoming work by Naimon *et al.*[36] will present comparisons of theory with experiment for the third-order elastic constants of Mg. The results of the present calculation reproduce the qualitative features of the observed third-order elastic constants, including weak Cauchy relationships.

The pressure derivatives of the second-order elastic constants of Al and Pb, determined from the calculated third-order elastic constants, are also presented in Tables II and III and compared with the linear extrapolations (0 °K) of the observed values of the pressure derivatives of Al (Ho and Ruoff[37]) and Pb (Miller and Schuele[38]) in Table IV. The complete set of third-order elastic constants of Pb is not yet available experimentally. On the basis of the agreement for the pressure derivatives, it can be conjectured that the calculated values of the third-order elastic constants of Pb shall be at least qualitatively in good agreement with the future experimental data.

## IV. SUMMARY AND DISCUSSIONS

The second-order elastic constants of some of the simple metals, including alkali metals and Al, were previously calculated from the rigid-band model. Because the dominant contribution to the second-order elastic constants of alkali metals comes from the electrostatic energy, it may be argued whether or not a pseudopotential calculation is more valid. However, the calculation of the second-order shear elastic constants of Al and other metals based on the rigid-band model could not be completely checked with experimental data. The number of independent experimental parameters available at the time the calculations were carried out was not substantially larger than the number of adjustable parameters in these calculations.

TABLE III. Third-order elastic constants of Pb ($10^{12}$ dyn/cm$^2$).

| | Hartree<br>$r_c = 2.4$ a.u.<br>$U_0 = -1.70$ a.u. | Hubbard-Sham<br>$r_c = 2.4$ a.u.<br>$U_0 = -1.68$ a.u. |
|---|---|---|
| $C_{111}$ | $-5.47$ | $-6.24$ |
| $C_{112}$ | $-3.16$ | $-3.82$ |
| $C_{123}$ | 0.72 | 0.86 |
| $C_{144}$ | 0.41 | 0.43 |
| $C_{166}$ | $-3.23$ | $-4.05$ |
| $C_{456}$ | 0.61 | 0.46 |

The complete set of the third-order elastic constants recently measured by Thomas[29] clearly supports the pseudopotential interpretation. The failure of the rigid-band model to explain the three Fuchs elastic constants $\partial^3 E/\partial\epsilon_1^2\,\partial\epsilon_2$, $\partial^3 E/\partial\epsilon_2\,\partial\gamma_1^2$, and $\partial^3 E/\partial\gamma_3\,\partial\gamma_2\,\partial\gamma_1$ indicates the inadequacy of this model; these third derivatives conserve volume and, in contrast to those derivatives which describe changes of the second-order elastic constants with pressure, do not allow for the introduction of additional adjustable parameters into the rigid-band model.

In this paper, it has been shown that (i) the expression for the binding energy, which is based on a local pseudopotential, satisfies not only the diagonal equilibrium condition but also the nondiagonal equilibrium condition and (ii) the derivatives of the same expression with respect to deformation parameters reproduce reasonably well the experimental data of the second- and third-order elastic constants of Al and the second-order elastic constants and their pressure derivatives of Pb, without introducing any additional parameters besides those used in the expression for the binding energy itself. The procedure adopted in this paper to satisfy the diagonal equilibrium condition is found to have another advantage besides the formal consistency discussed in Sec. III B 1. Although the pro-

TABLE IV. Pressure derivatives of second-order elastic constants.

| | | $\dfrac{\partial C'}{\partial p}$[a] | $\dfrac{\partial C_{44}}{\partial p}$ | $\dfrac{\partial B}{\partial p}$[a] |
|---|---|---|---|---|
| Al | Hartree | 0.74 | 1.60 | 3.37 |
| | Hubbard-Sham | 0.55 | 1.78 | 3.52 |
| | Experimental[b] (extrapolated to 0 °K) | 1.63 | 2.22 | 4.57 |
| Pb | Hartree | 0.514 | 1.86 | 3.89 |
| | Hubbard-Sham | 0.446 | 2.02 | 3.88 |
| | Experimental[c] (extrapolated to 0 °K) | 0.216 | 1.80 | 5.28 |

[a] $C' = \frac{1}{2}(C_{11} - C_{12})$, $B = \frac{1}{3}(C_{11} + 2C_{12})$.

[b] P. S. Ho and A. L. Ruoff (Ref. 37).

[c] R. A. Miller and D. E. Schuele (Ref. 38).

cedure in SGT reproduced reasonable values of the second- and third-order elastic constants of Al, it has failed for Pb. However, the procedure presented in this paper reproduced the second-order elastic constants and their pressure derivatives of both Al and Pb with the same number of adjustable parameters as in SGT.

The qualitative success of the present calculation for Al and Pb based on a simple local pseudopotential indicates that this approach is more promising in predicting elastic constants than is the rigid-band model. It is expected that the accuracy of the pseudopotential calculation will be improved with use of a nonlocal pseudopotential. If a nonlocal pseudopotential is used, the positive ion charge $Z$ in the electrostatic energy $E_2$ cannot be exactly equal to the valence, and the orthogonalization hole must be taken into account.[39]

The use of the Hubbard-Sham dielectric function did not produce any definite improvement of the results obtained from use of the Hartree dielectric function. However, it has to be investigated whether the new approach to the problem of correlation and exchange proposed by Shaw and Pynn[40] improves the calculation of the third-order elastic constants of simple metals.

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## APPENDIX

The proof that

$$\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_1\cdot\vec{g}_1=\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_2\cdot\vec{g}_2=\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_3\cdot\vec{g}_3=0\quad(i\neq j)$$

is given as follows. The primitive recriprocal-lattice vector of a simple cubic lattice $\vec{g}_1$ ($\vec{g}_2$ or $\vec{g}_3$) is given in terms of the primitive lattice vectors of the simple cubic lattice $\vec{\tau}_1$, $\vec{\tau}_2$, and $\vec{\tau}_3$:

$$\vec{g}_1=2\pi\frac{\vec{\tau}_2\times\vec{\tau}_3}{\vec{\tau}_1\cdot(\vec{\tau}_2\times\vec{\tau}_3)}\ .$$

Hence, we obtain

$$\vec{g}_1\cdot\vec{g}_1=(2\pi)^2\,\frac{(\vec{\tau}_2\cdot\vec{\tau}_2)(\vec{\tau}_3\cdot\vec{\tau}_3)-(\vec{\tau}_2\cdot\vec{\tau}_3)(\vec{\tau}_3\cdot\vec{\tau}_2)}{[\vec{\tau}_1\cdot(\vec{\tau}_2\times\vec{\tau}_3)]^2}\ .$$

The derivative of the denominator of this expression with respect to the off-diagonal component of the finite deformation parameter $\eta_{ij}$ is zero:

$$\frac{\partial}{\partial\eta_{ij}}\,[\vec{\tau}_1\cdot(\vec{\tau}_2\times\vec{\tau}_3)]^2=0;$$

$\vec{\tau}_1\cdot(\vec{\tau}_2\times\vec{\tau}_3)$ represents the volume of the unit cell of a simple cubic lattice, and the derivative of the volume with respect to the off-diagonal component of the finite deformation parameter is zero. The derivative of the numerator is given by

$$\begin{aligned}\frac{\partial}{\partial\eta_{ij}}\,&[(\vec{\tau}_2\cdot\vec{\tau}_2)(\vec{\tau}_3\cdot\vec{\tau}_3)-(\vec{\tau}_2\cdot\vec{\tau}_3)(\vec{\tau}_3\cdot\vec{\tau}_2)]\\&=(\vec{\tau}_2\cdot\vec{\tau}_2)\frac{\partial}{\partial\eta_{ij}}(\vec{\tau}_3\cdot\vec{\tau}_3)+(\vec{\tau}_3\cdot\vec{\tau}_3)\frac{\partial}{\partial\eta_{ij}}(\vec{\tau}_2\cdot\vec{\tau}_2)\\&\qquad-(\vec{\tau}_2\cdot\vec{\tau}_3)\frac{\partial}{\partial\eta_{ij}}(\vec{\tau}_3\cdot\vec{\tau}_2)-(\vec{\tau}_3\cdot\vec{\tau}_2)\frac{\partial}{\partial\eta_{ij}}(\vec{\tau}_2\cdot\vec{\tau}_3);\end{aligned}$$

$(\vec{\tau}_2\cdot\vec{\tau}_3)$ and $(\vec{\tau}_3\cdot\vec{\tau}_2)$, however, are zero by definition. Furthermore, by use of the relation which gives the change of the scalar product of two vectors $\vec{A}(A_1,\,A_2,\,A_3)$ and $\vec{B}(B_1,\,B_2,\,B_3)$,

$$\Delta\vec{A}\cdot\vec{B}=2\sum_{k,l}A_kB_l\eta_{kl}\ ,$$

we can see that

$$\frac{\partial}{\partial\eta_{ij}}\,(\vec{\tau}_2\cdot\vec{\tau}_3)=\frac{\partial}{\partial\eta_{ij}}\,(\vec{\tau}_3\cdot\vec{\tau}_2)=0\quad(i\neq j)\ .$$

Accordingly, we have proved that

$$\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_1\cdot\vec{g}_1=0\quad(i\neq j)\ .$$

By permuting indices, we also have

$$\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_2\cdot\vec{g}_2=\frac{\partial}{\partial\eta_{ij}}\,\vec{g}_3\cdot\vec{g}_3=0\quad(i\neq j)\ .$$

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