Second and Third-Order Elastic Constants
of Aluminum and Lead*

Tetsuro Suzuki†

Department of Metallurgy and Mining Engineering
Department of Physics and Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801

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 derivatives of the binding energy with respect to a volume change as well as shear deformations are zero. Accordingly, the present method of calculation is based on a stable lattice model. The results of the present calculation for the third order elastic constants of Al are found to be in satisfactory agreement with the experimental data of the complete set of

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†Present address: University of Missouri at Rolla, Rolla, Missouri.
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third order elastic constants obtained by Thomas. 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 in as far as the calculation of second and third order elastic constants is concerned. 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 not in agreement with the experimental data by Miller and Schuele. This perhaps indicates the necessity of a more accurate pseudopotential, namely a non-local one, for the calculation of the elastic constants of Pb.
1. INTRODUCTION

In the calculation by the method of uniform deformation, 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 in the calculation of elastic constants by this method. The first is to find a proper expression for the binding energy or cohesive energy. The second problem 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 relationship between the Brugger elastic constants and the Fuchs elastic constants is described by Suzuki, Granato and Thomas (abbreviated as SGT hereafter).

In this paper, a calculation of 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, who extended Fuchs' calculation of elastic constants of alkali metals to the calculation of the shear elastic constants of Al.

2. 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 the conduction electron. $E^F$ for alkali metals was assumed to be given to a good approximation by the expression for the kinetic energy of free electrons,

$$E^F = \frac{3\pi^2}{10m} \left( \frac{32\pi^2}{\Omega} \right)^{2/3}$$

(2.1)

where $\Omega$ is the atomic volume, $\hbar$ is Planck's constant divided by $2\pi$, $m$ the free electron mass and $Z$ 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 $Z_{\text{eff}}$, which is determined by the electron density near the surface of the atomic sphere.

Leigh\textsuperscript{8/} extended Fuchs\textsuperscript{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 the shear deformation 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 the change of $E^F$ due to shear deformations was due to the displacement of the energy gap present at the Brillouin zone boundaries and to the accompanying redistribution of electrons within and between Brillouin zones; moreover the energy versus 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.

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 Schrodinger equation for Al could not be solved to determine the wavefunction and the energy of conduction electrons. In addition, the bulk modulus, which requires the lowest energy $E_0$ of the conduction electron 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 data, namely the two shear elastic constants, $(C_{11} - C_{12})/2$ 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,\(^{12/}\) by Jones\(^{13/}\) and by Collins\(^{14/}\) respectively.

When Daniels\(^{15/}\) extended Fuchs' 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.

3. PSEUDOPOTENTIAL CALCULATION

3.1 Binding Energy Expression

In pseudopotential theory,\(^{17/}\) the energy of a conduction electron \(E(k)\) as a function of momentum \(k\) is calculated by second order perturbation theory whereas in the Fuchs–Leigh calculation \(E(k)\) was expressed in terms of adjustable parameters. The energy of a conduction electron in a perfect crystal is given by

\[
E(k) = \frac{\hbar^2 k^2}{2m} + \langle k | \bar{w} | k \rangle + \sum_q \frac{\langle k + q | \bar{w} | k \rangle \langle k | \bar{w} | k + q \rangle}{\hbar^2/2m (k^2 - |k + q|^2)} \tag{3.1}
\]
where the summation extends over all the reciprocal lattice points \( q \) except the origin. The matrix element of the screened pseudopotential between two plane waves \( \langle k + q \mid w \mid k \rangle \) is obtained from the matrix element of a bare ion pseudopotential \( \langle k + q \mid w_b \mid k \rangle \) by use of a dielectric function. The total energy of the conduction electrons is obtained by summing the above expression for \( E(k) \) 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 \( k \), since \( E(k) \) represents the energy of an electron in the field of ions and other electrons.

The total binding energy of the crystal \( E \) 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 \( E_1 \) is defined as follows,

\[
E_1 = \left( \int_0^{k_F} \frac{k^2}{2m} \, d^3k + \int_0^{k_F} \langle k \mid w_b \rangle + \frac{Z e^2}{r} \mid k \rangle d^3k \right) / \int_0^{k_F} d^3k \quad (3.2)
\]

and is dependent solely on the total volume of the crystal. Here, \( e \) is the electronic charge and \( Z \) is the valence.

The electrostatic energy \( E_2 \) is the classical electrostatic energy of a lattice of positive point charges \( Z e \) 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 \( Z = Z_{\text{eff}} \)) 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 the values of a energy-wavenumber characteristic $F(q)$ at all reciprocal lattice points except the origin:

$$E_3 = \sum' F(q).$$  \hspace{1cm} (3.3)

In the present paper, the one by Ashcroft and Langreth\textsuperscript{18} and also SGT, a simple local base ion pseudopotential proposed by Ashcroft,\textsuperscript{19} is used together with the Hartree dielectric function to calculate the band structure energy $E_3$. $r_c$ is the "core radius" and is the sole adjustable parameter. From this pseudopotential and the Hartree dielectric function,

$$\varepsilon(q,k_F) = 1 + \frac{me^2}{2\pi k_F^2\hbar^2} \left( \frac{1-n^2}{2n} \ln \left| \frac{1+n}{1-n} \right| + 1 \right)$$  \hspace{1cm} (3.5)

we obtain the following energy-wavenumber characteristic

$$F(q) = \frac{q^2Z}{8\pi e^2 \hbar^2} \left( \frac{4\pi Ze^2}{q^2} \left( \cos q r_c \right)^2 \right)^2 \frac{1 - \varepsilon(q,k_F)}{\varepsilon(q,k_F)}.$$
where \( q = |q| \), \( n = q/2k_F \) and \( k_F \) is the radius of the free electron Fermi sphere, which is given in terms of the valence \( Z \) and the atomic volume \( \Omega \) by

\[
k_F = \left( \frac{3\pi^2 Z}{\Omega} \right)^{1/3}
\]

(Ashcroft and Langreth\textsuperscript{18} have introduced two modifications into the free electron energy \( E_1 \). First, they have added the approximate formula for the correlation and exchange energy to the kinetic energy of a free electron given by the first term in Eq. (3.2). Second, they have adjusted the value of the second term in Eq. (3.2) so that the total expression for the binding energy is minimum at the observed lattice spacing. However, if the total binding energy expression is, at least approximately, internally consistent, the adjusted value should be approximately equal to the value directly calculated from the assumed pseudopotential, namely

\[
\int_0^{k_F} <k|\omega_b + \frac{Ze^2}{r} |k> d^3k = \frac{4\pi r_c^2 Z\hbar^4}{\Omega 2m^2 e^2}
\]

(3.7)

The internal consistency will be checked for Al and Pb in the following section.

As a result of these modifications, the free electron energy \( E_1 \) (per atom) is now given by:

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

(3.8)
where $r_s$ is given in terms of the atomic volume $\Omega$ and valence $Z$ by

$$\frac{4}{3} \pi r_s^3 = \frac{\Omega}{Z} \tag{3.9}$$

Here, every quantity is expressed in c.g.s. units, except $a$ in Eq. (3.8) and $r_c$ in Eq. (3.7), which are measured in atomic units for convenience of comparison with the table given by Ashcroft and Langreth.\(^{19}\)

Ashcroft and Langreth have shown that the binding energy expression thus obtained from the pseudopotential of Eq. (3.4) and the second derivative with respect to volume change can reproduce the experimentally observed binding energies and bulk modulii of Li, Na, K, Rb, Cs, Mg, Zn, Al and Pb, with use of the appropriate core radii. These core radii are at the same time consistent with the experimental data of the resistivity of the liquid phase or Fermi surface data of these simple metals. However, they did not consider the derivatives of their expression with respect to shear deformations. In other words, they considered the derivative of the binding energy expression with respect to the diagonal component of the finite deformation parameter $\eta_{ij}$, but did not consider derivatives with respect to the off-diagonal components of the finite deformation parameter $\eta_{ij}(i \neq j)$, where $\eta_{ij}$ is defined by

$$\eta_{ij} = \frac{1}{2} \sum_k \left( \frac{\partial x_k}{\partial a_i} \cdot \frac{\partial x_k}{\partial a_j} - \delta_{ij} \right)$$

Here, $a_k$ and $x_k$ are the coordinates of ions before and after the deformation.
In this paper, the first derivatives of the binding energy expression with respect to diagonal as well as off-diagonal components of $n_{ij}$ were checked as the equilibrium conditions for Al and Pb. The second and third derivatives of the binding energy expression with respect to the diagonal as well as the off-diagonal components of the finite deformation parameter, the complete set of second and third order elastic constants of Al and Pb, were calculated by the same method as used by SGT in the case of the alkali metals. For the alkali metals only three independent relations (i.e., the pressure derivatives of three second order elastic constants) have been measured, whereas experimentally there are six independent third order elastic constants for cubic crystals. The complete set of third order elastic constants of Al have recently been measured by Thomas. The experimental data for Al give the first complete check of a calculation of third order elastic constants based on a pseudopotential method.

3.2 EQUILIBRIUM CONDITION FOR THE BINDING ENERGY EXPRESSION

A. Equilibrium Condition With Respect to $n_{ij}$

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 and also used in the present calculation as well as 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. (3.8). This term, when directly calculated from the assumed pseudopotential, is equal to $4\pi r_c^2 n^4/2m^2 e^2 \Omega (r_c$ in atomic units, the rest in c.g.s. units), while the last term in $E_1$ of the binding energy expression used in the present calculation has a different value of $\alpha Z^4/2m^2 e^2 \Omega$. In order to check whether or not the resulting binding energy expression is nearly consistent, $(a/4\pi)^{1/2}$ is compared with the core radius $r_c$ in the Ashcroft pseudopotential in Table I. Upon comparison we can see that the internal consistency is better for Al than for Pb.

B. 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.,

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

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 change of volume $v$ 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. $\frac{\partial E_1}{\partial n_{ij}} = 0 \ (i \neq j)$.

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

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

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

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

Accordingly, if every particle in the crystal is located at a center of symmetry, as in the case of $\text{al}$, the first derivative of the summation of the pair-wise interaction energy $W$ is zero. Hence,

$$
\frac{\partial E_2}{\partial n_{ij}} = 0 \ (i \neq j)
$$

The energy-wavenumber 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 $n_{ij} \ (i \neq j)$ is given by.
\[ \frac{\partial E_3}{\partial \eta_{ij}} = \sum_q \left( \frac{\partial F}{\partial q} \frac{\partial q}{\partial \eta_{ij}} + \frac{\partial F}{\partial k_F} \frac{\partial k_F}{\partial \eta_{ij}} \right) \]

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 \( g_1, g_2, g_3 \) of the simple cubic lattice in the following way:

\[ q^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} m_i m_j g_{i} g_{j}, \]

where \( m_1, m_2, m_3 \) are integers chosen so as to represent a b.c.c. lattice in reciprocal space, if the real lattice under consideration is f.c.c. (e.g. A \( \alpha \) and Pb) or vice versa. It is shown in the Appendix that

\[ \frac{\partial}{\partial \eta_{ij}} g_{i} g_{i} = \frac{\partial}{\partial \eta_{ij}} g_{j} g_{j} = \frac{\partial}{\partial \eta_{ij}} g_{k} g_{k} = 0 \quad (i \neq j) \]

Hence, we obtain

\[ \frac{\partial E_3}{\partial \eta_{ij}} = \sum_{m_1, m_2, m_3} \frac{\partial F}{\partial q} \frac{1}{2q} \frac{\partial}{\partial \eta_{ij}} (2m_1 m_2 g_{i} g_{j} + 2m_2 m_3 g_{j} g_{k} + 2m_3 m_1 g_{k} g_{i}) \]

The origin of the reciprocal lattice of b.c.c. or f.c.c. structures is the 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 first derivative of 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 f.c.c. and b.c.c. structures.

### 3.3 Elastic Constants

The second and third order elastic constants of Al and Pb were calculated for various values of the core radius, the sole adjustable parameter in the expression for the binding energy. The second and third order Fuchs elastic constants, which are derivatives of the expression for the binding energy with respect to the deformation parameters \( \nu, \varepsilon_1 \) and \( \gamma_i \) \((i = 1, 2 \text{ or } 3)\) are calculated and then converted into Brugger elastic constants by means of the relationships in S.G.T.

Those Fuchs elastic constants which contain at least one volume concerning shear deformation parameter, \( \varepsilon_1 \) or \( \gamma_i \), \((\partial^3 E/\partial \varepsilon_1^2, \partial^3 E/\partial \gamma_1^2, \partial^3 E/\partial \gamma_i^2, \partial^3 E/\partial \nu \partial \varepsilon_1^2, \partial^3 E/\partial \varepsilon_2 \partial \gamma_1^2, \partial^3 E/\partial \varepsilon_1 \partial \gamma_i^2 \text{ and } \partial^3 E/\partial \gamma_j \partial \gamma_i \partial \gamma_k)\) do not contain any contribution from the volume dependent energy term \( E_1 \). These seven elastic constants are calculated as the sum of the derivatives of the electrostatic energy \( E_2 \) and the band structure energy \( E_3 \). The second derivatives of the electrostatic energy \( E_2 \) for B.C.C. and F.C.C. structures...
were calculated by Fuchs\textsuperscript{9} and the third derivatives for the same structures were calculated by Cousins\textsuperscript{25} and also by Sukuki and Granato.\textsuperscript{26} The derivatives of the band structure energy $E_3$ are calculated as the summation of the derivatives of the wavenumber characteristic $F(q)$ up to the 260th neighbor of the reciprocal lattice instead of the 76th neighbor as in the case of alkali metals; this was done to retain the same accuracy in spite of the increase of the radius of the free electron Fermi sphere due to the higher valence.

There are nine independent Fuchs second and third order elastic constants for cubic crystals; seven have just been discussed. The remaining two, $\partial^2 E / \partial v^2$ and $\partial^3 E / \partial v^3$, contain contributions from all three terms of the expression for the binding energy, $E_1$, $E_2$ and $E_3$. The calculation of these two derivatives are easier than the calculation of other kinds of derivatives, once the explicit expression for the volume dependent term $E_1$ is known. Leigh's calculation\textsuperscript{8} and other previous calculations\textsuperscript{12,13} of elastic constants of polyvalent metals were limited to the calculation of shear elastic constants and their pressure derivatives, since it was impossible to calculate the volume dependent energy $E^0$ for polyvalent metals by the direct extension of the Wigner-Seitz method. In the present calculation, the free electron energy $E_1$ contains the Nozieres-Pines approximation for the exchange and correlation energy. Note that this approximation has nothing to do with the pseudopotential and hence cannot be checked with other kinds of experimental data than the elastic properties. Because the volume dependent term does contain this approximation it is likely that these two elastic constants, together with the equilibrium condition discussed earlier, contain more errors than the other second and third order Fuchs elastic constants.
The results of the calculations for three second order elastic
costants \( \frac{\partial^2 E}{\partial \nu^2} \), \( \frac{1}{4} \cdot \frac{\partial^2 E}{\partial e_i^2} \) and \( \frac{\partial^2 E}{\partial \gamma^2} \) for Al and Pb are shown as
a function of the core radius in Figs. 1 and 2. These are the bulk
modules B and the two shear elastic constants C and C' of cubic crystals,
which are related to the Brugger elastic constants \( C_{11}, C_{12} \) and \( C_{44} \) by

\[
\begin{align*}
B &= \frac{(C_{11} + 2 C_{12})}{3} \\
C' &= \frac{(C_{11} - C_{12})}{2} \\
C &= C_{44}
\end{align*}
\]

Dashed lines in Figs. 1 and 2 indicate the electrostatic contribution to
the two shear elastic constants, C and C'. In the case of Al, this is
identical to the electrostatic contribution considered by Leigh, except
he assumed the effective charge of \( Z = 2.64 \) instead of \( Z = 3.00 \) as in the
present calculation. The difference between the solid line and the dashed
line indicates the contribution from the band structure energy \( E_3 \) in the
present calculation. In Leigh's calculation, this was interpreted in
terms of the movement of the Brillouin zone boundaries, while the band
structure represented by four adjustable parameters was assumed to be
rigid with respect to the boundaries during shear deformations.

In Fig. 1, the calculated curves for Al cross over the linear
extrapolation (to 0°K) of the experimental data of Kamm and Alers\(^{27}\)
which are indicated by dotted lines, at slightly different values of \( r_c \),
indicating the approximate nature of the simple local pseudopotential
proposed by Ashcroft. We have chosen \( r_c = 1.12 \) (atomic units) as the
value of the core radius approximately consistent with the three experi-
mental values of second order elastic constants; this turns out to be in
agreement with the value of the core radius determined by Ashcroft and Langreth from Fermi-surface data.

Five third order Fuchs elastic constants of Al, which consist of the contributions from the electrostatic energy $E_2$ and the band structure energy $E_3$, are calculated and compared with the experimental data in Table II. The band structure energy is calculated for the value of the core radius $r_c = 1.12$ atomic units, which is determined by use of the experimental data of the second order elastic constants. The experimental data shown in Table II are those calculated from the Brugger elastic constants experimentally determined by Thomas. It is to be noted that the calculated total Fuchs elastic constants often come out as the difference of large numbers.

These five Fuchs third order elastic constants were also calculated by Thomas who extended the Leigh's procedure to the third order elastic constants starting from the same expression for the cohesive energy as used by Leigh. The contributions to the second and third order elastic constants from the two kinds of electrostatic terms, $E^L$ or $E_2$, are the same, except for the differences of effective charge, as previously discussed. Thomas found it impossible to reproduce the experimental Fuchs elastic constants with the adjustment of the five parameters in $E^F$ (four parameters) and $E^L$ (one parameter), which are compatible with the experimental data on the Fermi surface of Al.

The complete set of the Brugger third order elastic constants was calculated by combining the five Fuchs elastic constants shown in Table III and the one remaining Fuchs elastic constant, the third derivative of the expression for the binding energy with respect to the deformation...
parameter $v$, which indicates the uniform expansion of the volume. As far as the present author is aware, this is the first case where the calculation of the third order elastic constants based on the pseudo-potential can be compared with the experimental data. In spite of the rather critical competition of the contributions from three terms of the energy, the result of the calculation reproduces the qualitative features of the observed third order elastic constants, including the weak Cauchy relationship, with the value of the parameter $r_c$ compatible with the Fermi surface data as well as three second order elastic constants. The pressure derivatives of the second order elastic constants are also calculated from the third order elastic constants for the same value of the core radius, $r_c = 1.12$ a.u., and compared in Table IV with the experimental value obtained by Schmunk and Smith. These pressure derivatives are calculated without adding any parameters to those already used in the calculation of the second order elastic constants, in contrast to the calculation by Schmunk and Smith.

In Fig. 2, the calculated curves for three second order elastic constants of lead are compared with the linear extrapolation (to 0°K) of the experimental data of Waldorf and Alers. Although the calculated bulk modulus for a core radius of 1.12 atomic units, the value obtained by Ashcroft and Langreth from Fermi surface data, is approximately equal to the experimental data, the calculated shear elastic constants for the same core radius do not agree with experimental data. This is due to the fact that, while the contributions from the band structure energy $E_3$ and electrostatic energy $E_2$ to the bulk modulus are smaller than the contribution from the free electron energy $E_1$, the shear elastic
constants are determined solely by the contribution from the band structure energy $E_3$ and the electrostatic energy $E_2$. In other words, the comparison of the calculated and experimental values of the bulk modulus does not offer as sensitive a check of the assumed pseudopotential as does the comparison of the shear elastic constants. The complete set of third order elastic constants of lead is not yet available experimentally. The pressure derivatives of the three second order elastic constants measured by Miller and Schuele$^{31}$ are compared in Table V with the calculated values for core radii of 0.62 to 1.12 atomic units. It is found impossible to find a single value of the core radius which is approximately consistent with the experimental values of second order elastic constants and their pressure derivatives for Pb.

4. 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 the experimental data. The number of independent experimental data available at the time when the calculations were carried out was not substantially larger than the number of adjustable parameters in these calculations.
The pressure derivatives of the second order shear elastic constants of these metals were calculated by introducing a parameter, the pressure dependence of the effective charge, in addition to the parameters already included in the rigid band model. The pressure dependence of the effective charge is a quantity which cannot be compared directly with experimental data other than the pressure dependence of second order elastic constants. On the other hand, in SGT, the pressure derivatives of the second order elastic constants of alkali metals were calculated from a pseudopotential without introducing any additional parameters to those already contained in the total binding energy expression. The results obtained in SGT are in good agreement with the experimental data of the pressure dependence of the second order elastic constants for Na and K.

The complete set of the third order elastic constants recently measured by Thomas clearly support the interpretation based on a pseudopotential. The failure of the rigid band model to explain the three Fuchs elastic constants $\frac{\partial^3 E}{\partial \varepsilon_1^2 \partial \varepsilon_2}$, $\frac{\partial^3 E}{\partial \varepsilon_2 \partial \gamma_1}$, and $\frac{\partial^3 E}{\partial \gamma_3 \partial \gamma_2 \partial \gamma_1}$ 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 1) the expression for the binding energy proposed by Ashcroft and Langreth, which is based on a local pseudopotential, satisfies not only the diagonal equilibrium condition but also the non-diagonal equilibrium condition and 2) 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, without introducing any additional parameters besides those used in the expression for the binding energy itself. The qualitative success of the present calculation for Al 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 non-local pseudopotential. If a non-local pseudopotential is used, the positive ion charge $Z$ in the electrostatic energy $E_2$ cannot exactly be equal to the valence, and the orthogonalization hole must be taken into account.\(^{32}\)

As with the results obtained in the calculation of electronic properties by use of a pseudopotential, the results obtained in the present calculation are consistently better for Al than for Pb. There are many problems to be solved before quantitatively satisfactory results for Pb can be expected. A pseudopotential which is non-local and which also takes into account spin-orbit interaction\(^{17,33}\) will be needed for Pb. Furthermore, due to the presence of d and f shells, the assumption of the rigid pseudopotential, which is adopted in the present calculation instead of the rigid band model, may have to be considered more carefully.

ACKNOWLEDGMENT

The author would like to thank R. M. Thomson for his encouragement and support for the study and A. V. Granato for a critical reading of the manuscript. He also wishes to thank J. F. Thomas, Jr. for many stimulating discussions and E. R. Naimon for his assistance in calculations.
TABLE I

Check of Internal Consistency
With Respect to Volume Change

<table>
<thead>
<tr>
<th></th>
<th>$(a/4\pi)^{1/2}$</th>
<th>$r_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.216 a.u.</td>
<td>1.12 a.u.</td>
</tr>
<tr>
<td>Pb</td>
<td>1.368 a.u.</td>
<td>1.12 a.u.</td>
</tr>
</tbody>
</table>
TABLE II
Third Order Fuchs Elastic Constants of Aluminum

\((10^{12} \text{ dyne/cm}^2)\)

<table>
<thead>
<tr>
<th>Electrostatic Energy Contribution</th>
<th>Band Structure Energy Contribution</th>
<th>Calculated Elastic Constants</th>
<th>Experimental Elastic Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{\partial^3 E}{\partial \nu \partial \varepsilon_1^2})</td>
<td>-0.50</td>
<td>-1.82</td>
<td>-2.32</td>
</tr>
<tr>
<td>(\frac{\partial^3 E}{\partial \nu \partial \gamma_1^2})</td>
<td>-0.22</td>
<td>-0.82</td>
<td>-1.04</td>
</tr>
<tr>
<td>(\frac{\partial^3 E}{\partial \varepsilon_1^2 \partial \varepsilon_2})</td>
<td>18.69</td>
<td>-12.58</td>
<td>6.10</td>
</tr>
<tr>
<td>(\frac{\partial^3 E}{\partial \varepsilon_2 \partial \gamma_2^2})</td>
<td>-5.89</td>
<td>2.05</td>
<td>-3.84</td>
</tr>
<tr>
<td>(\frac{\partial^3 E}{\partial \gamma_3 \partial \gamma_2^2 \partial \gamma_1})</td>
<td>2.03</td>
<td>-1.42</td>
<td>-0.62</td>
</tr>
</tbody>
</table>
TABLE III

Third Order Elastic Constants

\((10^{12} \text{dyne/cm}^2)\) of Aluminum

<table>
<thead>
<tr>
<th></th>
<th>Calculated Values for (r_c = 1.12) a.u.</th>
<th>Experimental Values at 25°C by J. F. Thomas, Jr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{111})</td>
<td>(-8.39)</td>
<td>(-10.76 \pm 0.30)</td>
</tr>
<tr>
<td>(C_{112})</td>
<td>(-3.32)</td>
<td>(-3.15 \pm 0.10)</td>
</tr>
<tr>
<td>(C_{123})</td>
<td>(+0.99)</td>
<td>(+0.36 \pm 0.15)</td>
</tr>
<tr>
<td>(C_{144})</td>
<td>(+1.02)</td>
<td>(-0.23 \pm 0.05)</td>
</tr>
<tr>
<td>(C_{166})</td>
<td>(-4.00)</td>
<td>(-3.40 \pm 0.10)</td>
</tr>
<tr>
<td>(C_{456})</td>
<td>(+0.61)</td>
<td>(-0.30 \pm 0.30)</td>
</tr>
</tbody>
</table>
TABLE IV
Pressure Derivatives of Second Order
Elastic Constants of Al

<table>
<thead>
<tr>
<th>Calculated Values</th>
<th>Experimental Values at 25°C by Schmunk and Smith</th>
<th>Experimental Values at 25°C by Thomas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\partial C' / \partial P^a$</td>
<td>1.03</td>
<td>1.62</td>
</tr>
<tr>
<td>$\partial C / \partial P$</td>
<td>2.05</td>
<td>2.31</td>
</tr>
<tr>
<td>$\partial B / \partial P$</td>
<td>3.96</td>
<td>5.19</td>
</tr>
</tbody>
</table>

a. $C' = (C_{11} - C_{12})/2$, $C = C_{44}$, $B = (C_{11} + 2C_{12})/3$
<table>
<thead>
<tr>
<th>Core Radii (atomic units)</th>
<th>$\frac{\partial C'}{\partial P}$</th>
<th>$\frac{3B}{3P}$</th>
<th>$\frac{3C}{3P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Value at $195^\circ K$</td>
<td>0.28</td>
<td>1.97</td>
<td>5.45</td>
</tr>
<tr>
<td>0.62</td>
<td>0.071</td>
<td>0.306</td>
<td>2.941</td>
</tr>
<tr>
<td>0.72</td>
<td>0.049</td>
<td>0.351</td>
<td>2.891</td>
</tr>
<tr>
<td>0.82</td>
<td>-0.035</td>
<td>0.335</td>
<td>2.771</td>
</tr>
<tr>
<td>Calculation</td>
<td>0.92</td>
<td>-0.040</td>
<td>0.383</td>
</tr>
<tr>
<td>1.02</td>
<td>-0.158</td>
<td>0.291</td>
<td>2.803</td>
</tr>
<tr>
<td>1.12</td>
<td>-0.060</td>
<td>0.398</td>
<td>3.154</td>
</tr>
</tbody>
</table>

a. $C' = \frac{(C_{11} - C_{12})}{2}$, $C = C_{49}$ and $B = \frac{(C_{11} + 2C_{12})}{3}$

REFERENCES


6. The binding energy is defined as the difference of the energies between the completely ionized state and the metallic state. On the other hand, the cohesive energy is defined as the difference of energies between the neutral atomic state and the metallic state. Accordingly, the binding energy is equal to the cohesive energy plus the ionization energy of the atom under consideration. However, for the purpose of the calculation of the elastic constants, which is concerned with the configuration of ions in the metallic state, the difference between the binding energy and the cohesive energy does not matter.


24. F. D. Murnaghan, ibid, p. 36.
FIGURE CAPTIONS

Fig. 1  Second order elastic constants of aluminum
indicates the linear extrapolation of the experimental
data to 0°K.

indicates the electrostatic contribution of two shear
elastic constants, \( C' = (C_{11} - C_{12})/2 \) and \( C = C_{44} \).

Fig. 2  Second order elastic constants of lead
indicates the linear extrapolation of the experimental
data to 0°K.

indicates the electrostatic contribution of two shear
elastic constants, \( C' = (C_{11} - C_{12})/2 \) and \( C = C_{44} \).
Fig. 1
Fig. 2