Second and Third-Order Elastic Constants

of Aluminum and Lead*

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY
DATE 3-27-70

Tetsuro Suzuki[†]

Department of Metallurgy and Mining Engineering

Department of Physics and Materials Research Laboratory

University of Illinois, Urbana, Illinois 61801

MASTER

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission, makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe upon privately owned rights; or

It is the policy of the Commission to make available as soon as possible to all persons upon request and at a charge not exceeding the cost of reproduction, any patentable and non-patentable inventions, designs, drawings, or processes, or any information, apparatus, method, or process disclosed in this report, by any person acting on behalf of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor, prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

*This work was supported by the U.S. Atomic Energy Commission under Contract AT(11-1)-1198, and the U.S. Air Force Office of Scientific Research under Contract AF-OSR-803-65.

P4629

[†]Present address: University of Missouri at Rolla, Rolla, Missouri.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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,^{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 in 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 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^{7/} (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,^{8/} who extended Fuchs'^{9,10/} 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,

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

where Ω is the atomic volume, $\hbar$ is Planck's constant divided by 2π , 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_{eff} , which is determined by the electron density near the surface of the atomic sphere.

Leigh^{8/} extended Fuchs^{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.^{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 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_{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

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

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 $\langle k + q | w | k \rangle$ is obtained from the matrix element of a bare ion pseudopotential $\langle k + q | w_b | k \rangle$ 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,

$$E_1 = \left(\int_0^{k_F} \frac{\hbar^2 k^2}{2m} d^3k + \int_0^{k_F} \langle k | w_b + \frac{Ze^2}{r} | k \rangle d^3k \right) / \int_0^{k_F} d^3k \quad (3.2)$$

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 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 $Z = Z_{\text{eff}}$) 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:

$$E_3 = \sum'_{\mathbf{q}} F(\mathbf{q}). \quad (3.3)$$

In the present paper, the one by Ashcroft and Langreth^{18/} and also SGT, a simple local base ion pseudopotential proposed by Ashcroft,^{19/}

$$\left. \begin{aligned} w_b(r) &= -\frac{Ze^2}{r} \quad r > r_c \\ &= 0 \quad r \leq r_c \end{aligned} \right\} \quad (3.4)$$

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,

$$\epsilon(q, k_F) = 1 + \frac{me^2}{2\pi k_F^2 \eta^2} \left(\frac{1-\eta^2}{2\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| + 1 \right) \quad (3.5)$$

we obtain the following energy-wavenumber characteristic

$$F(q) = \frac{q^2 Z}{8\pi e^2 \Omega} \left(\frac{4\pi Z e^2}{q^2} (\cos |q| r_c) \right)^2 \frac{1 - \epsilon(q, k_F)}{\epsilon(q, k_F)}.$$

where $q = |\vec{q}|$, $\eta = q/2k_F$ 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 Ω by

$$k_F = \left(\frac{3\pi^2 Z}{\Omega} \right)^{1/3} \quad (3.6)$$

Ashcroft and Langreth^{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

$$\int_0^{k_F} \langle k | w_b + \frac{Ze^2}{r} | k \rangle d^3k = \frac{4\pi r_c^2 Z h^4}{\Omega 2m^2 e^2} \quad (3.7)$$

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:

$$E_1 = Z \left\{ \frac{3}{10} \frac{h^2}{m} \left(\frac{3\pi^2 Z}{\Omega} \right)^{2/3} - \frac{0.916e^2}{2r_s} - (0.115 - 0.031 \ln \left(\frac{r_s}{\frac{h^2}{me^2}} \right)) \frac{me^4}{2h^2} + \frac{3\alpha}{4\pi r_s^3} \frac{h^4}{2m^2 e^2} \right\} \quad (3.8)$$

where r_s is given in terms of the atomic volume Ω and valence Z by

$$\frac{4}{3}\pi r_s^3 = \frac{\Omega}{Z} \quad (3.9)$$

Here, every quantity is expressed in c.g.s. units, except α 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 moduli 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 η_{ij} , but did not consider derivatives with respect to the off-diagonal components of the finite deformation parameter η_{ij} ($i \neq j$), where η_{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.^{23/} 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 $4\pi r_c^4 / 2m^2 e^2 \Omega$ (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, $(\alpha/4\pi)^{1/2}$ 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 η_{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. $\partial E / \partial \eta_{ij} = 0$ ($i \neq j$).

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 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. $\partial E_1 / \partial \eta_{ij} = 0$ ($i \neq j$).

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

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

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

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

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 pair-wise interaction energy W is zero. Hence,

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

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 η_{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 and 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 and 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. 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

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

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 η_{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 v , ϵ_i and γ_i ($i = 1, 2$ 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, ϵ_i or γ_i , ($\partial^2 E / \partial \epsilon^2$, $\partial^2 E / \partial \gamma^2$, $\partial^3 E / \partial v \partial \epsilon^2$, $\partial^3 E / \partial v \partial \gamma^2$, $\partial^3 E / \partial \epsilon_2 \partial \gamma_1^2$, $\partial^3 E / \partial \epsilon_1^2 \partial \epsilon_2$ and $\partial^3 E / \partial \gamma_3 \partial \gamma_2 \partial \gamma_1$) 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^{9/} and the third derivatives for the same structures were calculated by Cousins^{25/} and also by Sukuki and Granato.^{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^{8/} and other previous calculations^{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 constants $\partial^2 E / \partial v^2$, $1/4 \cdot \partial^2 E / \partial \epsilon_1^2$ and $\partial^2 E / \partial \gamma^2$ 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

$$B = (C_{11} + 2 C_{12})/3$$

$$C' = (C_{11} - C_{12})/2$$

$$C = C_{44}$$

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 experimental 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^{18/} 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.^{23/} 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^{28/} 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,^{29/} 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.^{16/} 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.^{16/}

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.^{30/} Although the calculated bulk modulus for a core radius of 1.12 atomic units, the value obtained by Ashcroft and Langreth^{18/} 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 $\partial^3 E / \partial \epsilon_1^2 \partial \epsilon_2$, $\partial^3 E / \partial \epsilon_2 \partial \gamma_1^2$ 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 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

	$(\alpha/4\pi)^{1/2}$	r_c
Al	1.216 a.u.	1.12 a.u.
Pb	1.368 a.u.	1.12 a.u.

TABLE II

Third Order Fuchs Elastic Constants of Aluminum
 $(10^{12} \text{dyne/cm}^2)$

	Electrostatic Energy Contribution	Band Structure Energy Contribution	Calculated Elastic Constants	Experimental Elastic Constants
$\frac{\partial^3 E}{\partial v \partial \epsilon_1^2}$	-0.50	-1.82	-2.32	-4.14
$\frac{\partial^3 E}{\partial v \partial \gamma_1^2}$	-0.22	-0.82	-1.04	-1.21
$\frac{\partial^3 E}{\partial \epsilon_1^2 \partial \epsilon_2}$	18.69	-12.58	6.10	2.65
$\frac{\partial^3 E}{\partial \epsilon_2 \partial \gamma_1^2}$	-5.89	2.05	-3.84	-2.14
$\frac{\partial^3 E}{\partial \gamma_3 \partial \gamma_2^2 \partial \gamma_1}$	2.03	-1.42	-0.62	-0.30

TABLE III
Third Order Elastic Constants
(10^{12} dyne/cm²) of Aluminum

	Calculated Values for $r_c = 1.12$ a.u.	Experimental Values at 25°C by J. F. Thomas, Jr.
C_{111}	-8.39	-10.76 ± 0.30
C_{112}	-3.32	-3.15 ± 0.10
C_{123}	+0.99	$+0.36 \pm 0.15$
C_{144}	+1.02	-0.23 ± 0.05
C_{166}	-4.00	-3.40 ± 0.10
C_{456}	+0.61	-0.30 ± 0.30

TABLE IV
Pressure Derivatives of Second Order
Elastic Constants of Al

	Calculated Values $r_c = 1.12$ a.u.	Experimental Values at 25°C by Schmunk and Smith	Experimental Values at 25°C by Thomas
$\partial C' / \partial P^a$	1.03	1.62	1.45
$\partial C / \partial P$	2.05	2.31	2.10
$\partial B / \partial P$	3.96	5.19	4.42

a. $C' = (C_{11} - C_{12})/2$, $C = C_{44}$, $B = (C_{11} + 2C_{12})/3$

TABLE V
Pressure Derivatives of Second Order
Elastic Constants of Lead

	Core Radii (atomic units)	$\partial C'/\partial P^a$	$\partial C/\partial P$	$\partial B/\partial P$
Experimental Value at	195°K ^b	0.28	1.97	5.45
	0.62	0.071	0.306	2.941
	0.72	0.049	0.351	2.891
	0.82	-0.035	0.335	2.771
Calculation	0.92	-0.040	0.383	2.840
	1.02	-0.158	0.291	2.803
	1.12	-0.060	0.398	3.154

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

b. R. A. Miller and D. E. Schuele, J. Phys. Chem. Solids 30, 589 (1969).

REFERENCES

1. H. B. Huntington, Solid State Physics, Vol. VII, edited by F. Seitz and Turnbull (Academic Press Inc., New York, 1963), p. 213.
2. M. Bom and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, London, 1962), p. 129.
3. D. C. Wallace, Rev. Mod. Phys. 37, 57 (1965).
4. M. Lax, Lattice Dynamics, edited by R. F. Wallis (Pergamon Press, London, 1965), p. 583.
5. D. C. Wallace, Phys. Rev. 182, 778 (1969).
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.
7. T. Suzuki, A. V. Granato and J. F. Thomas, Jr., Phys. Rev. 175, 766 (1968).
8. R. S. Leigh, Phil. Mag. 42, 139 (1951).
9. K. Fuchs, Proc. Roy. Soc. A153, 622 (1936).
10. K. Fuchs, Proc. Roy. Soc. A157, 444 (1936).
11. W. A. Harrison, Pseudopotential in the Theory of Metals (Benjamin, New York, 1966), p. 195.

12. J. R. Reitz and C. S. Smith, Phys. Rev. 104, 1253 (1956).
13. H. Jones, Phil. Mag. 43, 105 (1952).
14. J. G. Collins, Phys. Rev. 155, 663 (1967).
15. W. B. Daniels, Phys. Rev. 119, 1246 (1960).
16. R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids 9, 100 (1959).
17. See, e.g., W. A. Harrison, Pseudopotential in the Theory of Metals, (Benjamin, New York, 1966).
18. N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967).
19. N. W. Ashcroft, Phys. Letters 23, 48 (1966).
20. F. D. Murnaghan, Finite Deformation of an Elastic Solid (Dover, New York, 1957).
21. A. L. Jain, Phys. Rev. 123, 1234 (1961).
22. P. A. Smith and C. S. Smith, J. Phys. Chem. Solids 26, 279 (1965).
23. J. F. Thomas, Jr., Phys. Rev. 175, 955 (1968).
24. F. D. Murnaghan, *ibid*, p. 36.
25. C.S.G. Cousins, Proc. Phys. Soc. (London) 91, 235 (1967).
26. T. Suzuki and A. V. Granato, Bull. Am. Phys. Soc. 12, 305 (1967).
27. G. N. Kamm and G. A. Alers, J. Appl. Phys. 35, 327 (1964).
28. J. F. Thomas, Jr., Ph.D. Thesis (University of Illinois, Urbana, Illinois, 1968).
29. Y. Hiki and A. V. Granato, Phys. Rev. 144, 411 (1966).
30. D. L. Waldorf and G. A. Alers, J. Appl. Phys. 33, 3266 (1962).
31. R. A. Miller and D. E. Schuele, J. Phys. Chem. Solids 30, 589 (1969).
32. R. W. Shaw and W. A. Harrison, Phys. Rev. 163, 604 (1967).
33. J. R. Anderson and A. V. Gold, Phys. Rev. 139, A1459 (1965).

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