coincide. Therefore,

$$\nu(\eta)=\int_{-\infty}^{\eta} dE\rho(E)=\int_{-\infty}^{\varphi(\eta)} dE\rho^{(0)}(E). \qquad \text{(D3)}$$

This is an equation for φ. The function $\nu(\eta)$, the integrated density of states, increases smoothly from 0 to 1. If $\rho^{(0)}(E)$ is continuous, (D3) determines a unique smooth monotonic function φ. The $s^{(0)}(k)$ given by(D1) is then periodic in k space and smooth although in general not analytic: The second and higher derivatives may be discontinuous at critical points of both ρ and $\rho^{(0)}$. In practice, however, it is possible to fit $s^{(0)}(k)$ by an analytic function.

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Second- and Third-Order Elastic Constants of Alkali Metals*

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The second- and third-order elastic constants of lithium, sodium, potassium, and rubidium in the body-centered cubic structure are calculated. The relationship between Brugger elastic constants and Fuchs elastic constants is worked out. The Brugger elastic constants, which are defined as the derivatives of the energy with respect to the Lagrangian strain, are widely used to express experimental results. The Fuchs elastic constants, which are defined as the derivatives of the energy with respect to homogeneous expansion and volume-conserving homogeneous shear, are often more convenient for calculations in terms of atomistic considerations, and are particularly convenient for calculations with pseudopotentials. They are used here to calculate the contribution of the band-structure energy to the elastic constants using the local pseudopotential proposed by Ashcroft. This pseudopotential contains the core radius as the only adjustable parameter. The contribution of the band-structure energy to the elastic constants is represented as a summation of two kinds of derivatives of the wave-number characteristics over the reciprocal lattice points—those with respect to homogeneous expansion and those with respect to volume-conserving homogeneous shear. The core radius which gives the best fit to the experimental second-order elastic constants agrees with that determined by Ashcroft from data on the Fermi surface or on the resistivity of liquid metals. The band-structure energy term is found to make a small contribution to the second-order elastic constants but an indispensable contribution to the third-order elastic constants.

I. INTRODUCTION

THERE are two methods for calculating the second-order elastic constants of a crystal: the method of homogeneous deformation and the method of long waves. One should be able to calculate the second-order elastic constants using either of the two methods[1] and the results obtained should agree with each other if the same model of the crystal is used in both cases. Fuchs[2,3] calculated the second-order elastic constants of alkali metals by the method of homogeneous deformation and obtained a satisfactory comparison with the data available at that time. However, more recent calculations[4–7] of the second-order elastic constants of alkali metals have been mostly carried out by the method of long waves, except for the calculation of bulk moduli by Ashcroft and Langreth.[8]

Ho and Ruoff[6] based their calculation on a quite different model of an alkali metal which includes closed-core interactions instead of the free-electron energy. Therefore, their results cannot be directly compared with the present calculation. Shyu and Gaspari[5] calculated the effective interatomic potential for alkali metals from the Heine-Abarenkov model potential. They also calculated the second-order elastic constants from the effective interatomic potential by the method of long waves. Their results of the second-order elastic constants are not in as good agreement with the experimental data as the present results, although they used a more sophisticated pseudopotential than that used in the present calculation. However, this is not necessarily evidence against the Heine-Abarenkov pseudopotential,

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[1] D. C. Wallace, Rev. Mod. Phys. **37**, 57 (1965).

[2] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).

[3] K. Fuchs, Proc. Roy. Soc. (London) **A157**, 444 (1936).

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[6] P. S. Ho and A. L. Ruoff, Phys. Status Solidi **23**, 489 (1967).

[7] Besides the works which calculate the second-order elastic constants explicitly, there are many papers on the phonon-dispersion relationship which contain the second-order elastic constants implicitly. As sources for reference to these works we mention the following recent articles: R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. **150**, 487 (1966); in *Phonons in Perfect Lattice and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum Press, Inc., New York, 1966); in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., London, 1965).

[8] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967).

because questionable approximations are inevitably involved in calculating phonon frequencies from the effective interatomic potential. The method of homogeneous deformation has the obvious disadvantage that one cannot calculate the phonon-frequency–wave-number dispersion relationship with it. On the other hand, the calculation of the second-order elastic constants by the method of homogeneous deformation is performed more simply and can be used as a check for the calculation of the dispersion relationship. Also, the calculation can be extended to higher-order elastic constants without essential difficulty. In recent years, experimental data[9–11] for the third-order elastic constants of metals have started to accumulate. This is due to refinements in the technique of measuring very minute changes of sound velocities in crystals under hydrostatic or uniaxial stress. It is worthwhile, then, to try to calculate the higher-order elastic constants of metals as well as the ordinary elastic constants.

In the present paper, as a first step in the attempt to calculate the higher-order elastic constants of metals, the second- and third-order elastic constants of alkali metals in the body-centered cubic (bcc) structure are calculated by the method of homogeneous deformation, neglecting the effect of lattice vibrations. Instead of the expression for the energy given by Wigner and Seitz which was used by Fuchs in his calculation of the second-order elastic constants of alkali metals, we start our calculation of elastic constants from the expression for the energy given by Ashcroft and Langreth[8] in their calculation of bulk moduli and cohesive energy for various simple metals including alkali metals. We show that the expression can be used for the calculation of any kind of elastic constants. The expression for the energy used in the present calculation consists of three parts, the free-electron energy, the electrostatic energy, and the band-structure energy. The band-structure energy is calculated by second-order perturbation theory using the model local pseudopotential proposed by Ashcroft.[12] This pseudopotential contains one adjustable parameter, the core radius. Deformation parameters which are extensions of those originally used by Fuchs[2] are found to be most convenient as independent variables for the derivatives of the band-structure energy. In Sec. II, we discuss the relationship between two kinds of elastic constants, Brugger[13] and Fuchs elastic constants. Brugger second- and third-order elastic constants are widely used to represent experimental data, while Fuchs elastic constants are convenient for the theoretical calculations.

II. RELATIONSHIP BETWEEN BRUGGER AND FUCHS ELASTIC CONSTANTS

In the method of homogeneous deformation, the second-order elastic constants are defined as the second derivatives of the energy with respect to deformation parameters, which specify homogeneous deformations of the crystal. The higher-order elastic constants are defined in a similar way. The first derivatives of the energy with respect to the deformation parameters should vanish, if the crystal under consideration is in equilibrium.

There has been general acceptance of Brugger's[13] definition of the elastic constants as the derivatives of the energy per unit undeformed volume with respect to the Lagrangian strain parameter η_{ij}, which is defined by

$$\eta_{ij}=\frac{1}{2}\left(\sum_t \frac{\partial x_t'}{\partial x_i}\frac{\partial x_t'}{\partial x_j}-\delta_{ij}\right),\quad i,j=1,2,3$$

where x_i and x_i' are the coordinates of a material particle in the undeformed and deformed state, respectively. He has also shown that these elastic constants are the natural generalization of the accepted definition of the second-order elastic constants. The second- and third-order Brugger elastic constants are then given as follows:

$$C_{ijkl}=\left(\frac{\partial^2 E}{\partial\eta_{ij}\partial\eta_{kl}}\right)_{\eta_{ij}=0},$$

$$C_{ijklmn}=\left(\frac{\partial^3 E}{\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}}\right)_{\eta_{ij}=0},$$

where E is the energy of the crystal per unit undeformed. The Voigt abbreviation is used to denote the Brugger elastic constants, i.e.,

$$C_{ijkl\cdots}=C_{JP\cdots},$$

where ij's and J's are related by $11\sim1$, $22\sim2$, $33\sim3$, $23\sim4$, $31\sim5$, and $12\sim6$. Thurston and Brugger[14] have established a convenient procedure for calculating the second- and third-order elastic constants defined above from the experimental data of the change of the natural sound velocity in a crystal due to hydrostatic or uniaxial stress.

Strain parameters other than Lagrangian strain parameters η_{ij} can also be used to define homogeneous but not necessarily infinitesimal deformations of a crystal. The relationship between the elastic constants defined by Wallace[15] and those used here is discussed in Appendix I.

In his calculation of the second-order elastic constants of alkali metals based on the theory of cohesive energy due to Wigner and Seitz, Fuchs[2] used three kinds of

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[9] Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

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[13] K. Brugger, Phys. Rev. **133**, A1611 (1964).

[14] R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).

[15] D. C. Wallace, Phys. Rev. **162**, 776 (1967).

deformation parameters ϵ_i, γ_i, and v. These deformation parameters can be described in terms of rectangular coordinates x, y, and z which are chosen in such a way as to coincide with the cubic axes. ϵ_1 represents an expansion of the lattice in the x direction and contraction in the y direction in such a way that the volume of the crystal is strictly conserved irrespective of the magnitude of the deformation. The relationship between the coordinates after the ϵ_1 deformation, x', y', and z', and the coordinates before the ϵ_1 deformation, x, y, and z, is given as follows:

$$\begin{aligned} x' &= x(1+\epsilon_1), \\ y' &= y/(1+\epsilon_1), \\ z' &= z. \end{aligned}$$

ϵ_2 and ϵ_3 are defined in a similar way.

γ_1 represents a tilting of the y axis in the x-y plane while conserving the height strictly. The relationship between the coordinates after and before the γ_1 deformation is given as follows:

$$\begin{aligned} x' &= x+\gamma_1 y, \\ y' &= y, \\ z' &= z. \end{aligned}$$

γ_2 and γ_3 are defined in a similar way.

v represents a homogeneous expansion or contraction of the crystal, which is given as follows:

$$\begin{aligned} x' &= v^{1/3}x, \\ y' &= v^{1/3}y, \\ z' &= v^{1/3}z. \end{aligned}$$

By taking the derivatives of the energy per unit undeformed volume with respect to these deformation parameters ϵ_i, γ_i, and v, we can define the Fuchs elastic constants. Although Fuchs himself considered only the second derivatives of the energy with respect to the deformation parameters ϵ_1, γ_1, and v, it is natural to extend his definitions for higher-order elastic constants. We have calculated the following 3 second-order and 6 third-order Fuchs elastic constants, i.e.,

$$\frac{\partial^2 E}{\partial v^2},\ \frac{\partial^2 E}{\partial \epsilon_1{}^2},\ \frac{\partial^2 E}{\partial \gamma_1{}^2},$$

$$\frac{\partial^3 E}{\partial v^3},\ \frac{\partial^3 E}{\partial v \partial \epsilon_1{}^2},\ \frac{\partial^3 E}{\partial v \partial \gamma_1{}^2},\ \frac{\partial^3 E}{\partial \epsilon_2 \partial \gamma_1{}^2},\ \frac{\partial^3 E}{\partial \epsilon_1{}^2 \partial \epsilon_2},\ \frac{\partial^3 E}{\partial \gamma_3 \partial \gamma_2 \partial \gamma_1}.$$

This choice of the Fuchs elastic constants is not unique, but represents all the independent second- and third-order elastic constants of a cubic crystal. If the volume dependence of the energy is not known but the shear dependence is, then all but two ($\partial^2 E/\partial v^2$ and $\partial^3 E/\partial v^3$) of these Fuchs constants can still be found.

The relationships between the Brugger and Fuchs elastic constants are established in the following way. The energy per unit undeformed volume of the crystal E is written as a function of the Lagrangian strain parameters η_{ij}. The Lagrangain strain parameters η_{ij} are given as functions of Fuchs deformation parameters v, ϵ_i, and γ_j in Appendix II for those combinations which appear in the Fuchs elastic constants just mentioned. Then, we can express the Fuchs elastic constants, for example $\partial^2 E/\partial \gamma_1{}^2$, by means of the chain rule of differentiation as follows:

$$\begin{aligned} \frac{\partial^2 E}{\partial \gamma_1{}^2} &= \frac{\partial}{\partial \eta_{12}}\left(\frac{\partial E}{\partial \eta_{12}}\frac{\partial \eta_{12}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{22}}\frac{\partial \eta_{22}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{21}}\frac{\partial \eta_{21}}{\partial \gamma_1}\right)\frac{\partial \eta_{12}}{\partial \gamma_1} \\ &\quad +\frac{\partial}{\partial \eta_{22}}\left(\frac{\partial E}{\partial \eta_{12}}\frac{\partial \eta_{12}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{22}}\frac{\partial \eta_{22}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{21}}\frac{\partial \eta_{21}}{\partial \gamma_1}\right)\frac{\partial \eta_{22}}{\partial \gamma_1} \\ &\quad +\frac{\partial}{\partial \eta_{21}}\left(\frac{\partial E}{\partial \eta_{12}}\frac{\partial \eta_{12}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{22}}\frac{\partial \eta_{22}}{\partial \gamma_1}+\frac{\partial E}{\partial \eta_{21}}\frac{\partial \eta_{21}}{\partial \gamma_1}\right)\frac{\partial \eta_{21}}{\partial \gamma_1}. \end{aligned} \tag{2.1}$$

Here, the first derivatives of the energy $\partial E/\partial \eta_{ij}$ should vanish when the crystal under consideration is in equilibrium. The second derivatives of the energy with respect to η_{ij} at $\eta_{ij}=0$ are the second-order Brugger elastic constants. The derivatives of the Lagrangian strain η_{ij} with respect to ϵ_1 are found by differentiating the expression given in Appendix II. Then we obtain

$$\partial^2 E/\partial \gamma_1{}^2 = C_{44}. \tag{2.2}$$

The relationships between the other Fuchs elastic constants and the Brugger elastic constants are established according to similar procedures and are as follows:

$$\partial^2 E/\partial v^2 = \tfrac{1}{3}(C_{11}+2C_{12}), \tag{2.3}$$

$$\partial^2 E/\partial \epsilon_1{}^2 = 2(C_{11}-C_{12}), \tag{2.4}$$

$$\begin{aligned} \partial^3 E/\partial v^3 = \tfrac{1}{9}&(C_{111}+2C_{123}+6C_{112}) \\ &-\tfrac{1}{3}(C_{11}+2C_{12}), \end{aligned} \tag{2.5}$$

$$\begin{aligned} \partial^3 E/\partial v \partial \epsilon_1{}^2 = \tfrac{2}{3}&(C_{111}-C_{123})+(8/3)(C_{11}-C_{12}) \\ &+\tfrac{4}{3}(C_{11}+2C_{12}), \end{aligned} \tag{2.6}$$

$$\begin{aligned} \partial^3 E/\partial v \partial \gamma_1{}^2 = \tfrac{1}{3}&(C_{144}+2C_{155})+\tfrac{1}{3}(C_{11}+2C_{12}) \\ &+\tfrac{4}{3}C_{44}, \end{aligned} \tag{2.7}$$

$$\partial^3 E/\partial \epsilon_2 \partial \gamma_1{}^2 = C_{155}-C_{144}+C_{11}-C_{12}+2C_{44}, \tag{2.8}$$

$$\begin{aligned} \partial^3 E/\partial \epsilon^2 \partial \epsilon_2 = C_{111}&+2C_{123}-3C_{112} \\ &+7(C_{11}-C_{12}), \end{aligned} \tag{2.9}$$

$$\partial^3 E/\partial \gamma_3 \partial \gamma_2 \partial \gamma_1 = C_{456}. \tag{2.10}$$

III. EXPRESSION FOR THE ENERGY

Cohen[16] has shown that the energy of a metal based on the pseudopotential theory consists of three parts, the free-electron energy E_1 which is dependent solely on the density of electrons or the total volume of the

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[16] M. H. Cohen, J. Phys. Radium **23**, 643 (1962).

crystal, the electrostatic energy E_2, and the perturbation energy E_3. In the present calculation of the elastic constants, we adopted the same expressions for E_1, E_2, and E_3 as those used by Ashcroft and Langreth[8] in their calculation of cohesive energy and bulk moduli.

E_1 in cgs units is given by the following:

$$E_1=\frac{1}{\Omega}\left\{\frac{2.21}{r_s^2}\frac{\hbar^2}{2m}-\frac{0.916e^2}{2r_s}-[0.115-0.031\ln](r_sme^2/\hbar^2)\right\}, \quad (3.1)$$

where the first term represents the free-electron Fermi energy, the second term represents the free-electron exchange energy, and the third term is the Pines-Nozières approximate expression for the correlation energy for the free-electron gas. Ω is the atomic volume and r_s is given in terms of the electron density n by

$$\tfrac{4}{3}\pi r_s=n^{-1}. \quad (3.2)$$

In the case of alkali metals, where there is one electron per atom, r_s is equal to the radius of an atomic sphere.

E_2 represents the electrostatic energy of an array of positive point charges embedded in a uniform background of compensating negative charge. The numerical value of this term for the bcc structure was originally calculated by Fuchs[3,17] and recalculated by Coldwell-Horsfall and Maradudin[18] using a simpler method. The value is given by

$$E_2=-(1.792/r_s\Omega)\tfrac{1}{2}e^2. \quad (3.3)$$

The perturbation energy E_3, which represents the deviation of the electron energy from that of free electrons, is calculated by second-order perturbation theory for the simple local pseudopotential proposed by Ashcroft.[12] This assumes perfect cancellation of the effective potential inside the closed core of the positive ion and pure Coulombic behavior outside the core. E_3 is given by

$$E_3=\frac{1}{\Omega}\left\{\frac{3\alpha}{4\pi r_s^3}+{\sum_{\mathbf{G}}}'\frac{\mathbf{G}^2}{8\pi e^2\Omega}\left(\frac{4\pi e^2}{\mathbf{G}^2}\cos|\mathbf{G}|r_c\right)^2\frac{1-\epsilon(\mathbf{G},k_F)}{\epsilon(\mathbf{G},k_F)}\right\}, \quad (3.4)$$

where the first and the second terms represent the first- and the second-order perturbation theory results, respectively, for the pseudopotential, and $\mathbf{G}$ is the reciprocal lattice vector.[19] The prime over the summation means that the origin of the reciprocal lattice is excluded from the summation, r_c is the core radius of the ion, and $\epsilon(\mathbf{G},k_F)$ is the Hartree dielectric function given by

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

Here $\eta=|\mathbf{G}|/2k_F$ and k_F is the radius of the free-electron Fermi sphere, which is given by

$$k_F=(3\pi^2/\Omega)^{1/3}. \quad (3.6)$$

Although the first-order perturbation term, which is dependent only on volume, can be obtained in principle from the assumed pseudopotential, Ashcroft and Langreth determined α by requiring that the lattice be in equilibrium at the observed lattice spacing.

The energy per unit volume E, which is the sum of the three terms E_1, E_2, and E_3, is the basis of our calculation of the elastic constants. After we specify the crystal structure, which is bcc in the present case, the lattice constant and the valency, the sole adjustable parameter is the core radius r_c. In the case of alkali metals, the second-order perturbation of the pseudopotential is very small compared with other terms in the expression for the energy. This is in agreement with the experimentally established fact that the Fermi surface of an alkali metal is very close to a perfect sphere. As discussed in the following sections, however, this does not imply that the contribution of the second-oredr perturbation of the pseudopotential to the elastic constants, especially to the higher-order elastic constants, is negligible compared with the contribution of other terms in the expression for the energy.

IV. DERIVATIVES OF THE VOLUME-DEPENDENT ENERGY

The expressions for the free-electron energy and the first-order perturbation term of the pseudopotential do not depend on the configuration of the positive ions but depend solely on the volume of the crystal or the electron density. Hence, these terms do not make any contribution to those Fuchs elastic constants which are defined as the derivatives of the energy with respect to volume-conserving shear parameters. Those Fuchs elastic constants which are defined as mixed derivatives of the energy, i.e., $\partial^3E/\partial v\partial\epsilon_1^2$ and $\partial^3E/\partial v\partial\gamma_1^2$ also do not depend on the volume-dependent energy, because once the derivative of the energy with respect to a volume-conserving shear is taken, that part of the energy which is solely dependent on volume drops out of the expression. Hence, except for $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$, all other Fuchs elastic constants do not depend on the volume-dependent energy terms.

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[17] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

[18] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. **1**, 395 (1960).

[19] The reciprocal lattice vector $\mathbf{G}$ in the present paper is defined by

$$\mathbf{G}=m_1 2\pi\frac{\boldsymbol{\tau}_2\times\boldsymbol{\tau}_3}{\boldsymbol{\tau}_1(\boldsymbol{\tau}_2\times\boldsymbol{\tau}_3)}+m_2 2\pi\frac{\boldsymbol{\tau}_3\times\boldsymbol{\tau}_1}{\boldsymbol{\tau}_2(\boldsymbol{\tau}_3\times\boldsymbol{\tau}_1)}+m_3 2\pi\frac{\boldsymbol{\tau}_1\times\boldsymbol{\tau}_2}{\boldsymbol{\tau}_3(\boldsymbol{\tau}_1\times\boldsymbol{\tau}_2)},$$

where m_1, m_2, and m_3 are positive and negative integers and $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ are primitive lattice vectors. This definition of the reciprocal lattice vector is different by the factor 2π from that adopted by Born and Huang. Harrison uses wave-number lattice instead of reciprocal lattice for the present definition.

TABLE I. Contributions of energy term Pv^n to the Brugger elastic constants of cubic crystals.

Second-order Brugger elastic constants	Contributions from Pv^n	Third-order Brugger elastic constants	Contributions from Pv^n
C_{11}	$Pn(n-2)$	C_{111}	$Pn(n-2)(n-4)$
C_{12}	Pn^2	C_{112}	$Pn^2(n-2)$
C_{44}	$-Pn$	C_{123}	Pn^3
		C_{144}	$-Pn^2$
		C_{155}	$-Pn(n-2)$
		C_{456}	Pn

However, if we calculate elastic constants according to Brugger's definitions, the situation is quite different. Consider a volume-dependent term Pv^n, where P and n are arbitrary constants, and v designates the ratio of the volume of the crystal after the deformation to that before the deformation. For example, the contribution of a term of this form $\partial^2(Pv^n)/\partial\gamma_1^2$ is zero, but the contribution to the shear Brugger elastic constant $\partial^2(Pv^n)/\partial\eta_{23}^2$ is not zero. The calculation is made by using the relations[20]

$$v=(1+2I_1+4I_2+8I_3)^{1/2},$$

where

$$I_1=\eta_{11}+\eta_{22}+\eta_{33},$$

$$I_2=\eta_{22}\eta_{33}-\eta_{23}\eta_{32}+\eta_{33}\eta_{11}-\eta_{31}\eta_{13}+\eta_{11}\eta_{22}-\eta_{12}\eta_{21},$$

and

$$I_3=\begin{vmatrix}\eta_{11}\eta_{12}\eta_{13}\\ \eta_{21}\eta_{22}\eta_{23}\\ \eta_{31}\eta_{32}\eta_{33}\end{vmatrix}.$$

Hence, one obtains

$$\partial^2(Pv^n)/\partial\eta_{23}^2=-Pn.$$

These results might appear superficially to be in contradiction with the relationships between the Brugger and the Fuchs elastic constants described in Sec. III. But this is not so, because the relationship requires that the crystal under consideration should be in equilibrium, and an energy term of the form Pv^n alone cannot represent a crystal in equilibrium.

Any kind of volume-dependent terms can be represented as linear combinations of terms of the form Pv^n. In Table I, the contribution of an energy term Pv^n to the Brugger elastic constants of a cubic crystal are given.

V. DERIVATIVES OF THE ELECTROSTATIC ENERGY

The electrostatic energy is defined as the electrostatic potential energy of the periodic array of positive ions, which is a bcc array in the present case, embedded in the background of compensating negative charge. Fuchs[2] has shown that this electrostatic potential energy per unit volume E_2 can be reduced to the sum of two terms E_{21} and E_{22}. The term E_{21} is half the potential energy of interaction of a single ion with the other ions, divided by the atomic volume Ω. The term E_{22} is half the potential energy of interaction of a single ion with the uniform background of negative charge, divided by the atomic volume Ω. The terms E_{21} and E_{22} are given by

$$E_{21}=\frac{1}{2\Omega}\sum_l{}'\frac{e^2}{(\mathbf{r}_l^2)^{1/2}},\tag{5.1}$$

and

$$E_{22}=-\frac{n}{2\Omega}\iiint\frac{e^2d\mathbf{r}}{(\mathbf{r}^2)^{1/2}},\tag{5.2}$$

respectively, where the summation is extended over all the lattice points except the one at the origin and similarly the integration is extended over the entire volume of the crystal. The density n of electrons is given by $n=2/a^3$ in the present case.

The second and third derivatives of this electrostatic energy with respect to volume-conserving shear-strain parameters were calculated by Fuchs[2] and Cousins,[21] respectively. The second and third derivatives of this electrostatic energy with respect to the Lagrangian strain parameters η_{ij} were calculated independently by the present authors[22] by using the following procedure. The change of the square of the length of a vector $\mathbf{r}$, which connects two material particles in a homogeneoulsy deformed solid, is given in terms of the Lagrangian strain parameter η_{ij} and the components of the vector before the deformation x_i as[23]

$$\Delta\mathbf{r}^2=2\sum\eta_{ij}x_ix_j.\tag{5.3}$$

Using Eq. (5.3), one obtains the derivatives of the electrostatic energy with respect to η_{ij} as

$$\frac{\partial^2E_2}{\partial\eta_{ij}\partial\eta_{kl}}=\frac{3e^2}{2\Omega}\left(\sum{}'\frac{x_{li}x_{lj}x_{lk}x_{ll}}{(\mathbf{r}_l^2)^{5/2}}-n\iiint\frac{x_ix_jx_kx_l}{(\mathbf{r}^2)^{5/2}}d\mathbf{r}\right)\tag{5.4}$$

and

$$\frac{\partial^2E_2}{\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}}=-\frac{15e^2}{2\Omega}\left(\sum{}'\frac{x_{li}x_{lj}x_{lk}x_{ll}x_{lm}x_{ln}}{(\mathbf{r}_l^2)^{7/2}}-n\iiint\frac{x_ix_jx_kx_lx_mx_n}{(\mathbf{r}^2)^{7/2}}\right)d\mathbf{r}.\tag{5.5}$$

We define the following lattice sums, extending the

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[20] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Dover Publications, Inc., New York, 1967), p. 36.

[21] C. S. G. Cousins, Proc. Phys. Soc. (London) **91**, 235 (1967).

[22] T. Suzuki and A. V. Granato, Bull. Am. Phys. Soc. **12**, 305 (1967).

[23] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Inc., London, 1959), p. 1.

original definitions by Misra,[24]

$$\mathcal{S}_n{}^{(m)}=\sum{}'\frac{l_1{}^{2m}}{(l_1{}^2+l_2{}^2+l_3{}^2)^{n/2}}-\frac{1}{4}\iiint\frac{u_1{}^{2m}du_1du_2du_3}{(u_1{}^2+u_2{}^2+u_3{}^2)^{n/2}},\tag{5.6}$$

$$\mathcal{S}_n{}^{(l,m)}=\sum{}'\frac{l_1{}^{2l}l_2{}^{2m}}{(l_1{}^2+l_2{}^2+l_3{}^2)^{n/2}}-\frac{1}{4}\iiint\frac{u_1{}^{2l}u_2{}^{2m}du_1du_2du_3}{(u_1{}^2+u_2{}^2+u_3{}^2)^{n/2}},\tag{5.7}$$

$$\mathcal{S}_n{}^{(k,l,m)}=\sum{}'\frac{l_1{}^{2k}l_2{}^{2l}l_3{}^{2m}}{(l_1{}^2+l_2{}^2+l_3{}^2)^{n/2}}-\frac{1}{4}\iiint\frac{u_1{}^{2k}u_2{}^{2l}u_3{}^{2m}du_1du_2du_3}{(u_1{}^2+u_2{}^2+u_3{}^2)^{n/2}},\tag{5.8}$$

where l_1, l_2, and l_3 are integers which specify the bcc lattice point and the u_i are defined by $x_i=\frac{1}{2}au_i$, the quantity a being the lattice parameter. Without the integrals, the $\mathcal{S}_n{}^{(k,l,m)}$ become the usual lattice sums $S_n{}^{(k,l,m)}$. These lattice sums must by their definitions satisfy the relationships

$$\mathcal{S}_1{}^{(0)}=3\mathcal{S}_5{}^{(2)}+6\mathcal{S}_5{}^{(1,1)},\tag{5.9}$$

$$\mathcal{S}_1{}^{(0)}=3\mathcal{S}_7{}^{(3)}+18\mathcal{S}_7{}^{(2,1)}+6\mathcal{S}_7{}^{(1,1,1)}.\tag{5.10}$$

These relationships were used to check our calculations of the lattice sums. The same relationships are given by Ghate[25] for the lattice sums pertinent to ionic crystals. The lattice sums which are necessary for the second- and the third-order elastic constants of a metal with bcc structure are calculated by a method described in Appendix III, which is an extension of the technique used by Coldwell-Horsfall and Maradudin[18] in their calculation for $\mathcal{S}_1{}^{(0)}$. The results including $\mathcal{S}_1{}^{(0)}$ are

$$\begin{aligned}\mathcal{S}_1{}^{(0)}&=-1.819629, & \mathcal{S}_7{}^{(3)}&=-0.3078,\\ \mathcal{S}_5{}^{(2)}&=-0.44965, & \mathcal{S}_7{}^{(2,1)}&=-0.07090,\\ \mathcal{S}_5{}^{(1,1)}&=-0.078447, & \mathcal{S}_7{}^{(1,1,1)}&=+0.06336.\end{aligned}\tag{5.11}$$

The contribution of the electrostatic energy to the various Brugger elastic constants for cubic lattices are given in terms of these lattice sums as

$$\frac{\partial^2E_2}{\partial\eta_{11}\partial\eta_{11}}=\frac{4e^2}{a^4}\frac{3}{2}\mathcal{S}_5{}^{(2)},\tag{5.12}$$

$$\frac{\partial^2E_2}{\partial\eta_{11}\partial\eta_{22}}=\frac{\partial^2E_2}{\partial\eta_{23}\partial\eta_{23}}=\frac{4e^2}{a^4}\frac{3}{2}\mathcal{S}_5{}^{(1,1)},\tag{5.13}$$

$$\frac{\partial^3E_2}{\partial\eta_{11}\partial\eta_{11}\partial\eta_{11}}=\frac{4e^2}{a^4}\frac{15}{2}\mathcal{S}_7{}^{(3)},\tag{5.14}$$

$$\frac{\partial^3E_2}{\partial\eta_{11}\partial\eta_{11}\partial\eta_{22}}=\frac{\partial^3E_2}{\partial\eta_{11}\partial\eta_{31}\partial\eta_{31}}=\frac{4e^2}{a^4}\frac{15}{2}\mathcal{S}_7{}^{(2,1)},\tag{5.15}$$

and

$$\frac{\partial^3E_2}{\partial\eta_{11}\partial\eta_{22}\partial\eta_{33}}=\frac{\partial^3E_2}{\partial\eta_{11}\partial\eta_{23}\partial\eta_{23}}=\frac{\partial^3E_2}{\partial\eta_{23}\partial\eta_{31}\partial\eta_{12}}=\frac{4e^2}{a^4}\frac{15}{2}\mathcal{S}_7{}^{(1,1,1)}.\tag{5.16}$$

The contribution of the electrostatic energy E_2 to the Fuchs elastic constants cannot be found by simply inserting these electrostatic components of the Brugger elastic constants into the right-hand sides of Eqs. (2.2)–(2.10) in Sec. II. These equations give the relationships between Fuchs and Brugger elastic constants of the crystal under equilibrium, but cannot give the relationships between the components of two kinds of elastic constants. The components, or contributions, from different terms in the energy are different in the Fuchs and Brugger schemes. The contribution to the elastic constant from a given term in the energy thus has no absolute significance. However, the total elastic constant for a crystal in equilibrium is the same. For this comparison, the proper linear combination, as specified by Eqs. (2.2)–(2.10), has to be used.

The relationships between the two types of components of the elastic constants can be established in the following way. Consider a fictitious solid which is in equilibrium under the influence of electrostatic energy and a term Pv^n, where P is a constant. Because this fictitious solid is in equilibrium, we should be able to establish the relationship between the total Brugger and Fuchs elastic constants of this solid. If we choose $n=-\frac{2}{3}$ our fictitious solid reduces to a jellium model[26,27] of a metal.

All the shear Fuchs elastic constants of this solid do not depend on the term Pv^n and consequently the total Fuchs elastic constants are equal to the expression for the electrostatic contribution given by Fuchs[2] and Cousins.[21] On the other hand, in the Brugger definition of elastic constants, we have to calculate the contribution from the electrostatic energy as well as the volume-dependent term Pv^n. The constant P must satisfy the equilibrium condition $\partial E/\partial v=0$, i.e.,

$$nP-(e^2/3a)\mathcal{S}_1{}^{(0)}=0.\tag{5.17}$$

Inserting this value of P in the expression given in

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[24] R. D. Misra, Proc. Cambridge Phil. Soc. **36**, 173 (1940).

[25] P. B. Ghate, Phys. Rev. **139**, A1666 (1965).

[26] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966) 3rd ed., p. 244.

[27] Because Fuchs did not take into account the band-structure energy in his calculation of shear elastic constants, he effectively calculated the shear elastic constants of a jellium model.

Table I, we obtain the contribution of the term Pv^n to the elastic constants. Adding the electrostatic contribution and the contribution from Pv^n, we obtain the Brugger constants of our fictitious solid as

$$C_{11}=(4e^2/a^4)\tfrac{3}{2}\mathcal{S}_5{}^{(2)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}(n-2)\,, \tag{5.18}$$

$$C_{12}=(4e^2/a^4)\tfrac{3}{2}\mathcal{S}_5{}^{(1,1)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n\,, \tag{5.19}$$

$$C_{44}=(4e^2/a^4)\tfrac{3}{2}\mathcal{S}_5{}^{(1,1)}-(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}\,, \tag{5.20}$$

$$C_{111}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(3)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}\times n(n-2)(n-4)\,, \tag{5.21}$$

$$C_{112}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(2,1)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n^2(n-2)\,, \tag{5.22}$$

$$C_{123}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(1,1,1)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n^3\,, \tag{5.23}$$

$$C_{144}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(1,1,1)}-(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n^2\,, \tag{5.24}$$

$$C_{155}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(2,1)}-(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n(n-2)\,, \tag{5.25}$$

$$C_{456}=-(4e^2/a^4)\tfrac{15}{2}\mathcal{S}_7{}^{(1,1,1)}+(4e^2/a^4)\tfrac{1}{6}\mathcal{S}_1{}^{(0)}n\,. \tag{5.26}$$

When we combine these total Brugger elastic constants according to Eqs. (2.2)–(2.10) of Sec. II, we find that the expression for the electrostatic contribution given by Fuchs[2] and Cousins[21] is in agreement with the combinations [Eqs. (2.2)–(2.10)] of the Brugger elastic constants.

The term Pv^n can be interpreted as the Lagrangian undetermined multiplier which represents volume-conserving constraints. The fictitious volume-dependent term Pv^n or Lagrangain undetermined multiplier always serves to convert the combinations of derivatives with respect to η_{ij} to those with respect to volume-conserving shear parameters. Hence, the contribution of the electrostatic energy to the elastic constants given by Eqs. (5.18)–(5.26) should be used in combination with the Fuchs elastic constants, but not in combination with the contribution of other terms to the Brugger elastic constants.

VI. DERIVATIVES OF THE BAND-STRUCTURE ENERGY

The band-structure energy is given by the second term of Eq. (3.4). The second-order perturbation-theory term is represented as the summation over the reciprocal lattice points of the energy–wave-number characteristic $F(\mathbf{G},k_F)/\Omega$, where F is given by

$$F(\mathbf{G},k_F)=\frac{\mathbf{G}^2}{8\pi e^2\Omega}\left(\frac{4\pi e^2}{\mathbf{G}^2}\cos|\mathbf{G}|r_c\right)^2\frac{1-\epsilon(\mathbf{G},k_F)}{\epsilon(\mathbf{G},k_F)}\,. \tag{6.1}$$

Because the energy–wave-number characteristic contains only the magnitude of the reciprocal lattice vector $\mathbf{G}$, it may be represented as a function of η and r_s.

When a homogeneous deformation is introduced into the lattice in order to calculate the elastic constants, the reciprocal lattice is also homogeneously deformed and the band-structure energy of the deformed lattice is represented as the summation of the same energy–wave-number characteristic $F(\eta,r_s)$ over the homogeneously deformed reciprocal lattice points. Hence, the contribution of the band-structure energy to the elastic constants is calculated[28] as the summation of the derivatives of the energy–wave-number characteristics with respect to the deformation parameter over the reciprocal lattice points.

It is relevant here to note that the variable η does not change for a homogeneous dilatation of the lattice, because both the distance between the reciprocal lattice points and the radius of the Fermi sphere change in inverse proportion to the lattice parameter. On the other hand, the variable r_s does not change for a volume-conserving pure shear. For these reasons, the Fuchs deformation parameters are especially well suited for psuedopotential calculations.

Accordingly, if we take the derivatives of the band-structure energy with respect to v, which designates homogeneous dilatation of the lattice, in order to calculate the Fuchs elastic constants $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$, we have to calculate the derivatives of the energy–wave-number characteristics solely with respect to r_s, because

$$\partial\eta/\partial v=0\,.$$

Hence, the derivatives of the wave-number characteristics with respect to v are given as follows:

$$\frac{\partial F(\eta,r_s)}{\partial v}=\frac{r_s}{3}\frac{\partial F}{\partial r_s}, \tag{6.2}$$

$$\frac{\partial^2 F(\eta,r_s)}{\partial v^2}=\frac{1}{9}r_s{}^2\frac{\partial^2 F}{\partial r_s{}^2}-\frac{2}{9}r_s\frac{\partial F}{\partial r_s}, \tag{6.3}$$

and

$$\frac{\partial^3 F(\eta,r_s)}{\partial v^3}=\frac{1}{27}r_s{}^3\frac{\partial^3 F}{\partial r_s{}^3}-\frac{2}{9}r_s{}^2\frac{\partial^2 F}{\partial r_s{}^2}+\frac{10}{27}r_s\frac{\partial F}{\partial r_s}. \tag{6.4}$$

The second derivative of the energy–wave-number characteristics with respect to the volume-conserving shear, for example γ_1, is calculated in the following way. Applying the chain rule of differentiation, we obtain

$$\frac{\partial^2 F(\eta_1 r_s)}{\partial\gamma_1{}^2}=\frac{\partial^2 F}{\partial\eta^2}\left(\frac{\partial\eta}{\partial\gamma_1}\right)^2+\frac{\partial F}{\partial\eta}\frac{\partial^2\eta}{\partial\gamma_1{}^2}, \tag{6.5}$$

where η is given by the definition

$$\eta=|\mathbf{G}|/2k_F\,. \tag{6.6}$$

$\mathbf{G}$ is given in terms of the primitive reciprocal lattice vectors $\mathbf{g}_1$, $\mathbf{g}_2$, and $\mathbf{g}_3$ of the simple cubic lattice

$$\mathbf{G}=m_1\mathbf{g}_1+m_2\mathbf{g}_2+m_3\mathbf{g}_3\,. \tag{6.7}$$

The reciprocal lattice points of the bcc structure can

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[28] V. Heine and D. Weaire, Phys. Rev. 152, 603 (1966).

be obtained by choosing the integers m_1, m_2, and m_3 according to the rule

$$m_1+m_2+m_3=\text{even},$$

i.e., the fcc lattice rule. Hence

$$|\mathbf{G}|=(\sum_{i=1}^{3}\sum_{j=1} m_i m_j \mathbf{g}_i \mathbf{g}_j)^{1/2}. \tag{6.8}$$

The primitive reciprocal lattice vectors of the simple cubic lattice are given in terms of the primitive lattice vector $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ of the simple cubic lattice:

$$\mathbf{g}_1=2\pi\frac{\boldsymbol{\tau}_2\times\boldsymbol{\tau}_3}{\boldsymbol{\tau}_1(\boldsymbol{\tau}_2\times\boldsymbol{\tau}_3)},\quad \mathbf{g}_2=2\pi\frac{\boldsymbol{\tau}_3\times\boldsymbol{\tau}_1}{\boldsymbol{\tau}_2(\boldsymbol{\tau}_3\times\boldsymbol{\tau}_1)},$$

and

$$\mathbf{g}_3=2\pi\frac{\boldsymbol{\tau}_1\times\boldsymbol{\tau}_2}{\boldsymbol{\tau}_3(\boldsymbol{\tau}_1\times\boldsymbol{\tau}_2)}, \tag{6.9}$$

where $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ are given by

$$\boldsymbol{\tau}_1=(a,0,0),\quad \boldsymbol{\tau}_2=(0,a,0),\quad \text{and } \boldsymbol{\tau}_3=(0,0,a).$$

These primitive lattice vectors $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, and $\boldsymbol{\tau}_3$ are deformed to $\boldsymbol{\tau}_1'$, $\boldsymbol{\tau}_2'$, and $\boldsymbol{\tau}_3'$ by the γ_1 deformation, the transformation matrix of which is given in Appendix II:

$$\begin{aligned}\boldsymbol{\tau}_1'&=(a,0,0),\\ \boldsymbol{\tau}_2'&=(\gamma,a,0),\\ \boldsymbol{\tau}_3'&=(0,0,a).\end{aligned} \tag{6.10}$$

Hence,

$$\begin{aligned}\boldsymbol{\tau}_2'\times\boldsymbol{\tau}_3'&=2\pi a^2(1,-\gamma_1,0),\\ \boldsymbol{\tau}_3'\times\boldsymbol{\tau}_1'&=2\pi a^2(0,1,0),\\ \boldsymbol{\tau}_1'\times\boldsymbol{\tau}_2'&=2a\pi^2(0,0,1).\end{aligned} \tag{6.11}$$

We note here that the denominators of Eq. (6.9) and also the radius of the Fermi sphere k_F do not change for volume-conserving shear deformations such as the γ_1 deformation. Consequently, we obtain

$$\eta=[\pi/(6\pi^2)^{1/3}](m_1^2\gamma_1^2+m_2^2+m_3^3-2\gamma_1 m_1 m_2)^{1/2}. \tag{6.12}$$

By differentiating this expression with respect to γ_1, we obtain the derivatives which are needed in Eq. (6.5):

$$\frac{\partial\eta}{\partial\gamma_1}=\frac{1}{(6\pi^2)^{1/3}}\frac{1}{(m_1^2+m_2^2+m_3^2)^{1/2}}\pi(m_1m_2), \tag{6.13}$$

$$\frac{\partial^2\eta}{\partial\gamma_1^2}=\frac{\pi}{(6\pi^2)^{1/3}}\left\{-\frac{m_1^2m_2^2}{(m_1^2+m_2^2+m_3^2)^{3/2}}+\frac{m_1^2}{(m_1^2+m_2^2+m_3^2)^{1/2}}\right\}. \tag{6.14}$$

Combining (6.5), (6.13), and (6.14), we obtain

$$\frac{\partial^2F(\eta,r_s)}{\partial\gamma_1^2}=\frac{\partial^2F(\eta,r_s)}{\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\frac{m_1^2m_2^2}{m_1^2+m_2^2+m_3^2}+\frac{\partial F(\eta,r_s)}{\partial\eta}\frac{\pi}{(6\pi^2)^{1/3}}\left\{-\frac{m_1^2m_2^2}{(m_1^2+m_2^2+m_3^2)^{3/2}}+\frac{m_1^2}{(m_1^2+m_2^2+m_3^2)^{1/2}}\right\}. \tag{6.15}$$

The other derivatives of the energy–wave-number characteristics with respect to volume-conserving shear deformation parameters are obtained following similar procedures. They are

$$\frac{\partial^2F(\eta,r_s)}{\partial\epsilon_1^2}=\frac{\partial^2F(\eta,r_s)}{\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\frac{(m_2^2-m_1^2)^2}{m_1^2+m_2^2+m_3^2}+\frac{\partial F(\eta,r_s)}{\partial\eta}\frac{\pi}{(6\pi^2)^{1/3}}\times\left\{-\frac{(m_2^2-m_1^2)^2}{(m_1^2+m_2^2+m_3^3)^{3/2}}+\frac{3m_1^2+m_2^2}{(m_1^2+m_2^2+m_3^2)^{1/2}}\right\}, \tag{6.16}$$

$$\begin{aligned}\frac{\partial^3F(\eta,r_s)}{\partial\epsilon_1^2\partial\epsilon_2}=&\frac{\partial^3F(\eta,r_s)}{\partial\eta^3}\frac{\pi^3}{(6\pi^2)^{3/3}}\frac{(-m_1^2+m_2^2)^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^{3/2}}+\frac{\partial^2F(\eta,r_s)}{\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\\&\times\left\{-3\frac{(-m_1^2+m_2^2)^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^2}+\frac{(3m_1^2+m_2^2)(-m_2^2+m_3^2)-4m_2^2(-m_1^2+m_2^2)}{m_1^2+m_2^2+m_3^2}\right\}+\frac{\partial F(\eta,r_s)}{\partial\eta}\frac{\pi}{(6\pi^2)^{1/3}}\\&\times\left\{3\frac{(-m_1^2+m_2^2)^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^{5/2}}-\frac{(3m_1^2+m_2^2)(-m_2^2+m_3^2)-4m_2^2(-m_1^2+m_2^2)}{(m_1^2+m_2^2+m_3^2)^{3/2}}-\frac{2m_2^2}{(m_1^2+m_2^2+m_3^2)^{1/2}}\right\},\end{aligned} \tag{6.17}$$

$$\begin{aligned}\frac{\partial^3F(\eta,r_s)}{\partial\epsilon_2\partial\gamma_1^2}=&\frac{\partial^3F(\eta,r_s)}{\partial\eta^3}\frac{\pi^3}{(6\pi^2)^{3/3}}\frac{(m_1m_2)^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^{3/2}}+\frac{\partial^2F(\eta,r_s)}{\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\left\{-3\frac{m_1^2m_2^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^2}\right.\\&\left.+\frac{m_1^2(-m_2^2+m_3^2)-2m_1^2m_2^2}{m_1^2+m_2^2+m_3^2}\right\}+\frac{\partial F(\eta,r_s)}{\partial\eta}\frac{1}{(6\pi^2)^{1/3}}\left\{3\frac{m_1^2m_2^2(-m_2^2+m_3^2)}{(m_1^2+m_2^2+m_3^2)^{5/2}}-\frac{m_1^2(-m_2^2+m_3^2)-2m_1^2m_2^2}{(m_1^2+m_2^2+m_3^2)^{3/2}}\right\},\end{aligned} \tag{6.18}$$

$$\frac{\partial^3F(\eta,r_s)}{\partial\gamma_3\partial\gamma_2\partial\gamma_1}=-\frac{\partial^3F(\eta,r_s)}{\partial\eta^3}\frac{\pi^3}{(6\pi^2)^{3/3}}\frac{m_1{}^2m_2{}^2m_3{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{3/2}}+\frac{\partial^2F(\eta,r_s)}{\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\left\{3\frac{m_1{}^2m_2{}^2m_3{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^2}-\frac{m_2{}^2m_3{}^2}{m_1{}^2+m_2{}^2+m_3{}^2}\right\}$$
$$+\frac{\partial F(\eta,r_s)}{\partial\eta}\frac{1}{(6\pi^2)^{1/3}}\left\{-3\frac{m_1{}^2m_2{}^2m_3{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{5/2}}+\frac{m_2{}^2m_3{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{3/2}}\right\}. \tag{6.19}$$

The contribution of the energy–wave-number characteristics to the two kinds of Fuchs elastic constants $\partial^3E/\partial v\partial\epsilon_1{}^2$ and $\partial^3E/\partial v\partial\gamma_1{}^2$, which involve both the volume-conserving shear parameters ϵ_i or γ_j and the uniform dilatation parameter v, are simply the derivatives of the two second-order Fuchs elastic constants $\partial^2E/\partial\epsilon_1{}^2$ and $\partial^2E/\partial\gamma_1{}^2$. In these expressions, all factors except the derivatives of energy–wave-number characteristics $F(\eta,r_s)$ with respect to η do not depend on v. Hence, we find

$$\frac{\partial^3F(\eta,r_s)}{\partial v\partial\epsilon_1{}^2}=\frac{r_s}{3}\frac{\partial^3F(\eta,r_s)}{\partial r_s\partial\eta^2}\frac{\pi^2}{(6\pi^2)^{2/3}}\frac{(m_2{}^2-m_1{}^2)^2}{m_1{}^2+m_2{}^2+m_3{}^2}+\frac{r_s}{3}\frac{\partial^2F(\eta,r_s)}{\partial r_s\partial\eta}\frac{\pi}{(6\pi^2)^{1/3}}$$
$$\times\left\{-\frac{(m_2{}^2-m_1{}^2)^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{3/2}}+\frac{3m_1{}^2+m_2{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{1/2}}\right\}, \tag{6.20}$$

$$\frac{\partial^3F(\eta,r_s)}{\partial v\partial\gamma_1{}^2}=\frac{r_s}{3}\frac{\partial^3F(\eta,r_s)}{\partial r_s\partial\eta^2}\frac{\pi}{(6\pi^2)^{2/3}}\frac{m_1{}^2m_2{}^2}{m_1{}^2+m_2{}^2+m_3{}^2}+\frac{r_s}{3}\frac{\partial^2F(\eta,r_s)}{\partial r_s\partial\eta}\frac{\pi}{(6\pi^2)^{1/3}}$$
$$\times\left\{-\frac{m_1{}^2m_2{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{3/2}}+\frac{m_1{}^2}{(m_1{}^2+m_2{}^2+m_3{}^2)^{1/2}}\right\}. \tag{6.21}$$

The derivatives of the energy–wave-number characteristics with respect to r_s and η are concerned with different aspects of the wave-number characteristics. When we take the derivatives of the energy–wave-number characteristics with respect to η, the derivative brings out the logarithmic singularity[29] of the Hartree dielectric function $\epsilon(\eta,r_s)$. If some of the reciprocal lattice points are not too far from the surface of the sphere with radius $2k_F$, where the Hartree dielectric function shows its singularity, the higher-order derivatives of the band-structure energy with respect to η tend to give the more significant contribution to the elastic constants. On the other hand, the derivatives with respect to r_s are not concerned with the logarithmic singularity of the Hartree dielectric function but are concerned mainly with the oscillation of the wave-number characteristics in the reciprocal lattice space.

Although we are able to get a reasonable estimate of the two Fuchs elastic constants $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$, these Fuchs elastic constants are less accurate than the others for two reasons. The first is that, while the other Fuchs elastic constants do not depend on the volume-dependent terms of the energy, these two Fuchs elastic constants do and the volume dependence is known less accurately than the shear dependence at constant volume. The volume dependence is less well known because the expression for the correlation energy is not an exact one but an interpolation formula from the high and low electron-density limit where exact expressions have been obtained and also because the first-order perturbation term is not calculated from the pseudopotential but was determined empirically by Ashcroft and Langreth using an equilibrium condition. The second reason is that, in order to calculate the contribution of the band-structure energy to the Fuchs elastic constants $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$, one has to know in detail the oscillatory behavior of the energy–wave-number characteristics in the region far from the origin of the reciprocal lattice (approximately $3k_F<k<5k_F$), where the pseudopotential is least well known. As we try to obtain higher-order derivatives with respect to the v deformation parameter, the contribution from the oscillatory behavior of the energy–wave-number characteristic becomes more important, and the convergence of the sum of the derivatives of the energy–wave-number characteristics is slower.

VII. RESULTS AND DISCUSSION

In Secs. IV, V, and VI we have discussed procedures for differentiating each of the three energy terms E_1, E_2, and E_3 with respect to Fuchs deformation parameters. The summation of the derivatives of the energy–wave-number characteristics over the reciprocal lattice points has been carried out to the 76th neighbors of the origin by a computer. But it has been found that the results of the summation do not vary appreciably for the shear constants after the summation is carried out to about 6th neighbors. Because the expression for the energy, which forms the basis of our calculation of

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[29] For example, see J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959); W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), p. 51.

TABLE II. Elastic constants (10^{11} dyn/cm^2) and pressure derivatives of Li as a function of core radii (a.u.).

Core radii	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{155}	C_{456}	$\partial C'/\partial p$	$\partial C/\partial p$	$\partial B/\partial p$
0.96	1.220	1.265	0.521	−10.42	−3.53	−2.15	−2.59	−2.95	−3.90	0.109	1.127	3.194
1.06	1.261	1.230	0.691	−11.27	−3.23	−2.71	−3.26	−3.04	−4.17	0.146	1.324	3.232
1.16	1.307	1.210	0.855	−12.16	−2.98	−3.30	−3.91	−3.11	−4.42	0.174	1.487	3.279
1.26	1.381	1.216	1.013	−13.48	−2.91	−3.96	−4.56	−3.23	−4.66	0.226	1.621	3.398
1.36	1.495	1.257	1.164	−14.89	−2.97	−4.66	−5.15	−3.31	−4.84	0.247	1.646	3.497
1.46	1.622	1.324	1.291	−16.14	−3.11	−5.35	−5.65	−3.33	−4.97	0.228	1.579	3.554
1.56	1.770	1.423	1.396	−17.87	−3.47	−6.08	−6.10	−3.40	−5.08	0.240	1.491	3.672

TABLE III. Elastic constants (10^{11} dyn/cm^2) and pressure derivatives of Na as a function of core radii (a.u.).

Core radii	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{155}	C_{456}	$\partial C'/\partial p$	$\partial C/\partial p$	$\partial B/\partial p$
1.39	0.623	0.597	0.365	−5.67	−1.57	−1.45	−1.74	−1.52	−2.01	0.156	1.425	3.299
1.49	0.651	0.597	0.435	−6.23	−1.52	−1.73	−2.03	−1.57	−2.12	0.203	1.568	3.400
1.59	0.696	0.610	0.505	−6.89	−1.54	−2.04	−2.30	−1.63	−2.21	0.242	1.643	3.513
1.69	0.751	0.635	0.569	−7.47	−1.58	−2.35	−2.55	−1.66	−2.28	0.238	1.625	3.571
1.79	0.808	0.668	0.624	−8.06	−1.66	−2.66	−2.78	−1.68	−2.34	0.226	1.567	3.629
1.89	0.877	0.715	0.673	−8.90	−1.84	−2.99	−2.99	−1.72	−2.40	0.244	1.497	3.742
1.99	0.996	0.777	0.715	−9.83	−2.08	−3.33	−3.17	−1.76	−2.43	0.253	1.368	3.832

elastic constants, contains only the core radius r_c as an adjustable parameter, the results are obtained as a function of r_c for various alkali metals. The Fuchs elastic constants thus obtained are converted to the Brugger elastic constants by means of Eqs. (2.2)–(2.10). The values of the second-order elastic constants, their pressure derivatives and the third-order elastic constants of Li, Na, K, and Rb are given as a function of the core radius r_c in Tables II–V.

It is interesting to note that the predicted sets of the third-order elastic constants of alkali metals have the common features that C_{111} is negative and its absolute magnitude is appreciably larger than that of the other third-order elastic constants. However, there are no experimental data available for individual third-order elastic constants. Our knowledge about the volume-dependent terms of energy is less reliable than the knowledge about the electrostatic energy and the band-structure energy. Consequently, the Fuchs elastic constants $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$ are less accurate than the other Fuchs elastic constants. If more reliable information about the volume-dependent term of the energy becomes available, these two Fuchs elastic constants will be modified while other Fuchs elastic constants are not affected. The elastic constants shown in Tables II–V are the Brugger elastic constants obtained from the Fuchs elastic constants by means of Eqs. (2.2)–(2.10). Therefore, any new information on the volume-

TABLE IV. Elastic constants (10^{11} dyn/cm^2) and pressure derivatives of K as a function of core radii (a.u.).

Core radii	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{115}	C_{456}	$\partial C'/\partial p$	$\partial C/\partial p$	$\partial B/\partial p$
1.94	0.298	0.271	0.203	−2.935	−0.723	−0.832	−0.956	−0.734	−0.927	0.235	1.651	3.544
2.04	0.320	0.280	0.230	−3.185	−0.739	−0.956	−1.061	−0.757	−0.959	0.245	1.667	3.611
2.14	0.342	0.292	0.255	−3.409	−0.760	−1.081	−1.158	−0.767	−0.984	0.230	1.633	3.648
2.24	0.366	0.307	0.277	−3.678	−0.802	−1.210	−1.252	−0.782	−1.009	0.230	1.591	2.713
2.34	0.395	0.326	0.298	−4.041	−0.878	−1.347	−1.343	−0.807	−1.034	0.253	1.539	3.819
2.44	0.431	0.351	0.317	−4.441	−0.975	−1.488	−1.424	−0.829	−1.051	0.268	1.441	3.904
2.54	0.472	0.380	0.333	−4.779	−1.074	−1.620	−1.488	−0.828	−1.056	0.246	1.284	3.917

TABLE V. Elastic constants (10^{11} dyn/cm^2) and pressure derivatives of Rb as a function of core radii (a.u.).

Core radii	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{155}	C_{456}	$\partial C'/\partial p$	$\partial C/\partial p$	$\partial B/\partial p$
2.29	0.265	0.228	0.197	−2.647	−0.601	−0.837	−0.898	−0.603	−0.755	0.230	1.647	3.667
2.39	0.283	0.239	0.214	−2.851	−0.633	−0.934	−0.969	−0.615	−0.775	0.230	1.609	3.729
2.49	0.305	0.253	0.230	−3.123	−0.688	−1.038	−1.039	−0.636	−0.794	0.253	1.565	3.832
2.59	0.332	0.271	0.245	−3.430	−0.760	−1.145	−1.104	−0.655	−0.809	0.272	1.481	3.920
2.69	0.362	0.293	0.258	−3.702	−0.835	−1.248	−1.157	−0.659	−0.815	0.259	1.342	3.945
2.79	0.392	0.316	0.268	−3.921	−0.908	−1.342	−1.197	−0.649	−0.814	0.221	1.174	3.923
2.89	0.422	0.341	0.274	−4.148	−0.991	−1.432	−1.228	−0.637	−0.812	0.194	1.020	3.915

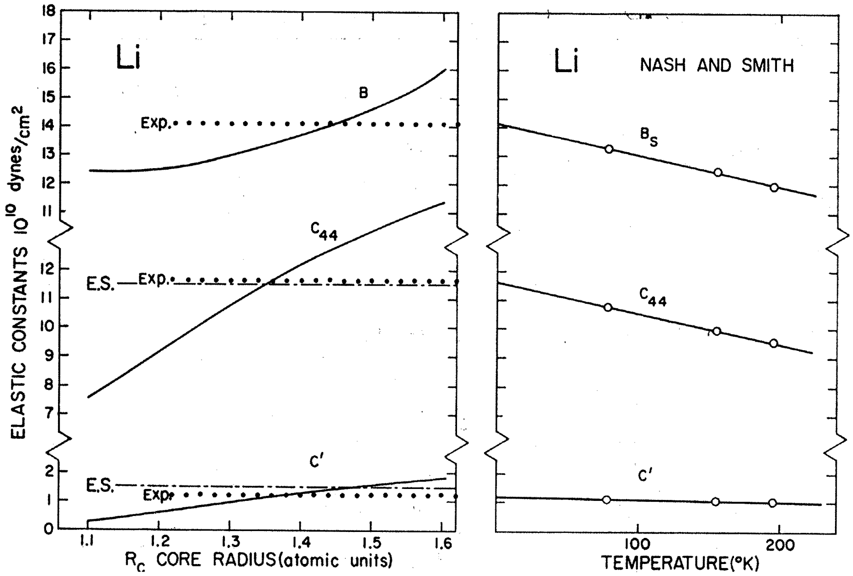

FIG. 1. Second-order elastic constants of lithium. The solid lines in the left half of the figure show the results of the calculation as a function of the core radius r_c. Dotted lines show the data which are obtained from the linear extrapolation of the experimental data shown in the right half of the figure. Dashed lines indicate the electrostatic contributions to the shear elastic constants. B and C' stand for $\frac{1}{3}(C_{11}+2C_{12})$ and $\frac{1}{2}(C_{11}-C_{12})$, respectively.

dependent term of the energy would inevitably affect almost all values of the Brugger elastic constants shown in the tables even though only two of the Fuchs elastic constants would be changed.

Before we compare the results of the calculation with the experimental data, we recall that our calculation does not include the effect of the lattice vibrations. Consequently, the data which are compared with the present calculations should be obtained by a linear extrapolation[30] of the experimental data as shown on the right-hand sides of Figs. 1–4. The lattice parameter a is also obtained from a linear extrapolation of the temperature dependence of the lattice parameter.[31] The values used were 3.485, 4.215, 5.124, and 5.5715 Å for Li, Na, K, and Rb, respectively.

The temperature-dependent second-order elastic constants of alkali metals are taken from the work of Nash and Smith,[32] Diederich and Trivisonno,[33] Marquardt and Trivisonno,[34] and Guttman and Trivisonno.[35] We notice that a value of the adjustable parameter r_c which is

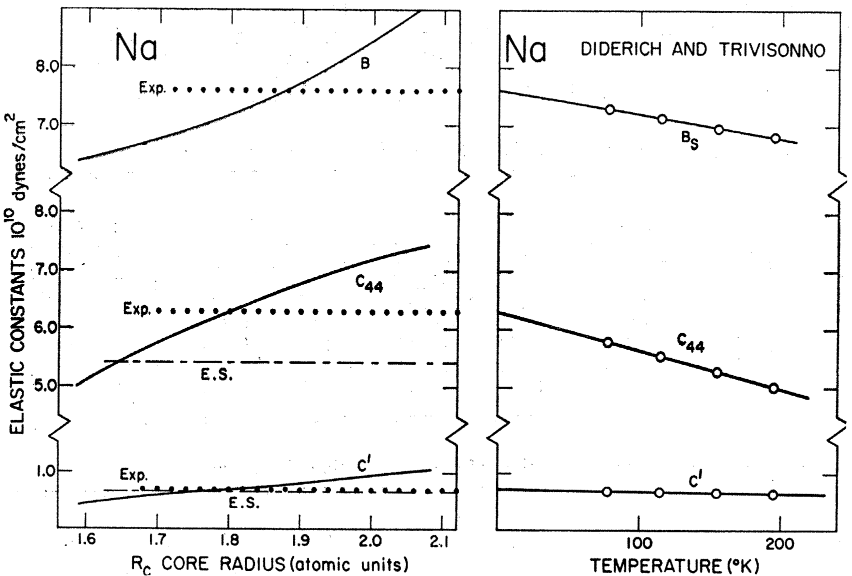

FIG 2. Second-order elastic constants of sodium. Notations are the same as Fig. 1.

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[30] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963) Vol. XII.

[31] C. S. Barrett, Acta Cryst. **9**, 67 (1956).

[32] H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).

[33] M. E. Diederich and J. Trivisonno, J. Phys. Chem. Solids **27**, 637 (1966).

[34] W. R. Marquardt and J. Trivisonno, J. Phys. Chem. Solids **26**, 273 (1965).

[35] E. J. Gutman and J. Trivisonno, J. Phys. Chem. Solids **28**, 805 (1967).

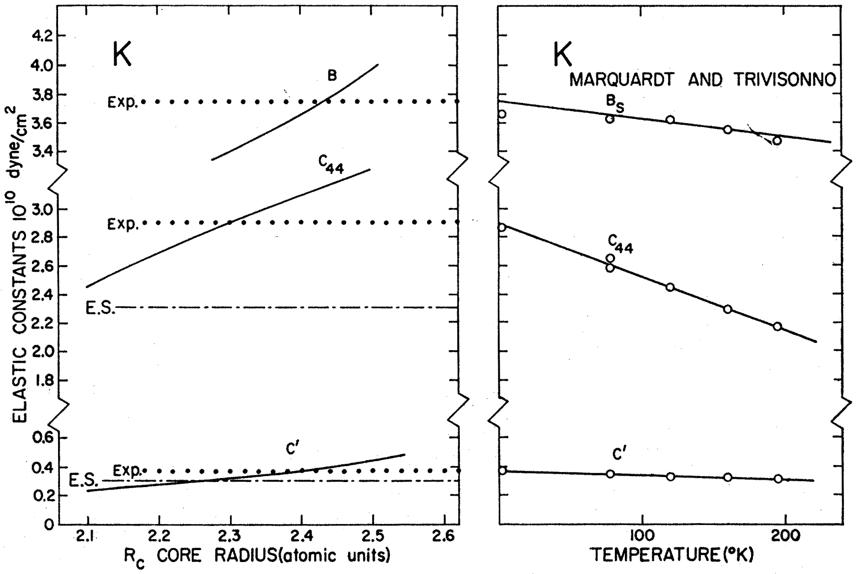

Fig. 3. Second-order elastic constants of potassium. Notations are the same as Fig. 1.

reasonably consistent with the two shear elastic constants can be determined only after a linear extrapolation of the experimental data. The values of the core radii r_c thus determined are shown in Table VI together with the core radii determined by Ashcroft and Langreth[8] from the data on the Fermi surface or on the liquid-metal resistivity. The values of ionic radii compiled by Pauling[36] are also shown in Table VI. The reasonable agreement between the core radii determined from the different kinds of experimental data supports the validity of the model pseudopotential proposed by Ashcroft.[12]

Dashed lines in Figs. 1–4 indicate the electrostatic contribution to the shear elastic constants. Because the volume-dependent terms of the energy do not contribute to the shear elastic constants, the difference between the calculated curves for the two shear elastic constants and the dashed lines indicates the contribution from the band-structure energy. The contribution from the band-structure energy to the two shear elastic constants is not a major contribution to the shear elastic constants of alkali metals. This explains why the calculation of the second-order shear elastic constant of alkali metals by Fuchs is qualitatively satisfactory. Because the contribution from the band-structure energy is small, it is found essential to use the linear extrapolation of the experimental value for determining the core radius which in turn determines the contribution of the band-

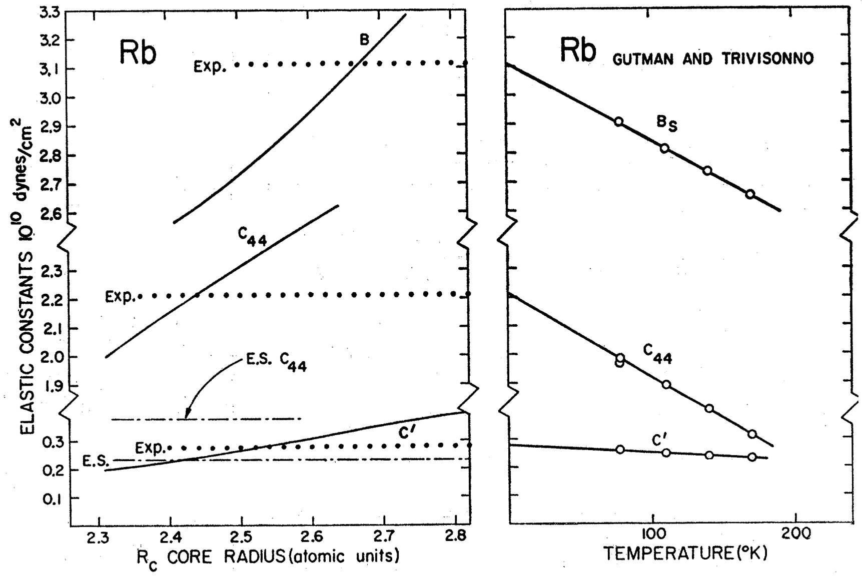

Fig. 4. Second-order elastic constants of rubidium. Notations are the same as Fig. 1.

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[36] L. Pauling, *Nature of Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1945), p. 326.

[37] M. Born and R. D. Misra, Proc. Cambridge Phil. Soc. **36**, 466 (1940).

TABLE VI. Core radii (a.u.).

	Shear elastic constants[a]	Fermi surface[b]	Resistivity of[b] liquid metal	Ionic radii[c]
Li	1.36	···	1.06	1.13
Na	1.79	···	1.67	1.79
K	2.34	2.14	···	2.51
Rb	2.49	2.61	···	2.79

[a] Present authors. [b] Reference 8. [c] Reference 36.

structure energy. When we compare the results in Figs. 1–4, we notice a systematic increase of the contribution of the band-structure energy to the shear elastic constants as we go from Li to Rb. As the contribution of the band-structure energy to the shear elastic constants increases, a small difference between the core radii determined from the two values of the linear extrapolations of the shear elastic constants becomes noticeable in K and Rb.

Although the difference is small, the calculated curves of the bulk moduli do not cross over the experimental data exactly at the value of r_c shown in Table VI. This is not surprising for the reasons already given about the volume dependence of the energy.

However, we believe that the present scheme gives a fairly accurate account of the second-order elastic constants of alkali metals. Once the core radius is determined from the data of the second-order elastic constants, we are able to predict the values of the third-order elastic constants which are consistent with our choice of r_c, by use of Tables II–V. The values of the third-order elastic constants thus determined should be compared to the linearly extrapolated values of the third-order elastic constants. However, neither the temperature dependence nor the values of the third-order elastic constants of alkali metals are available at present. The pressure dependence of the second-order elastic constants of Li, Na, and K at room temperature has been measured by Jain,[38] Daniels,[39] and Smith and Smith,[40] respectively. The predicted values of these quantities are in good agreement with the experimental data for Na and K as shown in Table VII. If we excluded band-structure energy in the calculation of $\partial C/\partial p$ and $\partial C'/\partial p$ of Na, K, and Rb, we would obtain values smaller by about 40% than the values shown in Tables III–V. This shows that although the band-structure energy contributes a small correction to the second-order elastic constants, the same energy makes an indispensable contribution to the third-order elastic constants.

TABLE VII. Pressure derivatives of second-order elastic constants of alkali metals.

		Core radii (a.u.)	$\partial C'/\partial p$	$\partial C/\partial p$	$\partial B/\partial p$
Li	Calculation	0.92	0.085	1.034	3.173
	Calculation	1.36	0.247	1.646	3.497
	Experiment	a	0.081	1.01	···
Na	Calculation	1.79	0.226	1.567	3.629
	Experiment	b	0.226	1.63	3.60
K	Calculation	2.34	0.253	1.539	3.819
	Experiment	c	0.281	1.88	3.97
Rb	Calculation	2.49	0.253	1.565	3.832
	Experiment	···	···	···	···

[a] A. L. Jain, Phys. Rev. 123, 1234 (1961).
[b] W. B. Daniels, Phys. Rev. 119, 1246 (1960).
[c] P. A. Smith and C. S. Smith, J. Phys. Chem. Solids 26, 279 (1965).

There are appreciable differences between the calculated values and the experimental values of $\partial C/\partial p$ and $\partial C'/\partial p$ of Li. At the present time, we do not know whether this is due to the temperature dependence of the pressure derivatives of the second-order elastic constants or due to the failure of the pseudopotential theory for Li. However, comparing the curves of Fig. 1 to those of Figs. 2–4, it is clear that Li is quite different from the other alkali metals. The band-structure energy always gives a positive contribution to the shear elastic constants for the alkali metals except for Li. The band-structure energy makes a very small positive contribution to C and a negative contribution to C', in the case of Li. The calculated values of the pressure derivatives of the second-order elastic constants of all alkali metals except for Li do not depend critically on the choice of r_c. In the case of Li, if we choose the value $r_c = 0.92$ a.u., we can obtain good agreement between the calculated pressure derivatives and the experimental data, but at the same time, the agreement with the second-order elastic constants is reduced. The value of the core radius determined by Ashcroft and Langreth from the data of the resistivity of the liquid metal, $r_c = 1.06$ a.u., is a good compromise for the second-order elastic constants of Li and their pressure derivatives.

By this comparison with the limited amount of data available so far, it is apparent that the band-structure energy makes a small but important contribution to the second-order elastic constants, and has a major impact on the third-order elastic constants. By the use of the psuedopotential, the mechanical and electrical properties have become closely related.

ACKNOWLEDGMENTS

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APPENDIX I

Different strain parameters as independent variables lead to different kinds of elastic constants. The litera-

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[38] A. L. Jain, Phys. Rev. 123, 1234 (1961).

[39] W. B. Daniels, Phys. Rev. 119, 1246 (1960).

[40] P. A. Smith and C. S. Smith, J. Phys. Chem. Solids 26, 279 (1965).

ture on this subject is large and confused. Recently, Wallace[15] has given a general theory of thermoelasticity in which he reviews and clarifies this subject. Wallace defines five different sets of thermoelastic coefficients. These are all equivalent when the reference state is the unstressed state, but are all different when the reference state is a stressed state. The five different sets include (1) the second-order elastic constants $C_{\alpha\beta}$, which contain the rotational invariance conditions and always have Voigt symmetry, and (2) the Fuchs coefficients $F_{\alpha\beta}$ for which the independent variables are quantities which are convenient for calculations of elastic properties from atomic considerations.

Wallace refers to the $C_{\alpha\beta}$ coefficients as elastic constants and the other four sets of coefficients as elastic coefficients. To distinguish the general case from the unstressed reference state case, the latter are designated by barred symbols, e.g., $\bar{C}_{\alpha\beta}$. In the present paper, all elastic constants are referred to the unstressed state, and we wish to emphasize a somewhat different distinction between the different elastic constants. For this purpose we would propose two changes in notation and nomenclature which we believe would still preserve the useful distinctions made by Wallace. The first is to drop the bar notation for the unstressed case, as this notation becomes clumsy in cases, such as the present one, for which only such quantities are considered. Also this is a unique state, depending only on the crystal forces, and not on external stresses. A possibility for the stressed-state coefficients might be to simply indicate explicitly the stress dependence, for example $C_{\alpha\beta}(p)$. The second is to refer to elastic *coefficients* in all cases where the reference state is stressed and elastic *constants* in all cases where the reference state is unstressed. Then the $\bar{C}_{\alpha\beta}$ of Wallace become the Brugger elastic constants $C_{\alpha\beta}$.

As we still find it useful to distinguish between the Brugger and Fuchs schemes for calculating elastic constants from atomic considerations, we should like to use these terms to distinguish different combinations of elastic constants for the unstressed state. That is, just as the A, B, C constants of Fuchs $[A=F_{11}-F_{12}$, $B=\frac{1}{2}F_{44}$, and $C=\frac{1}{6}(F_{11}+2F_{12})]$, or the C', C, B constants of Zener $[C'=\frac{1}{2}(C_{11}-C_{12})$, $C=C_{44}$, and $B=\frac{1}{3}(C_{11}+2C_{12})]$ are preferred linear combinations for physical reasons in second-order, so also are certain linear combinations of third-order elastic constants preferred. These are given in the text as extensions of Fuchs definitions. We believe that reference to these useful combinations as Fuchs elastic constants will not violate Wallace's scheme, particularly if the independent variables are explicitly indicated, for example F_{vv} instead of the Wallace-Fuchs constants $F_{\alpha\beta}$. In fact, in the present paper, the distinction is made even more explicit by writing the Fuchs elastic constants explicitly as second derivatives.

APPENDIX II

(1) v deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} v^{1/3}-1 & 0 & 0\\ 0 & v^{1/3}-1 & 0\\ 0 & 0 & v^{1/3}-1\end{bmatrix},$$

$$(\eta_{\alpha\beta})=\begin{bmatrix} (v^{1/3}-1)+\frac{1}{2}(v^{1/3}-1)^2 & 0 & 0\\ 0 & (v^{1/3}-1)+\frac{1}{2}(v^{1/3}-1)^2 & 0\\ 0 & 0 & (v^{1/3}-1)+\frac{1}{2}(v^{1/3}-1)^2\end{bmatrix}.$$

(2) ϵ_1 deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} \epsilon_1 & 0 & 0\\ 0 & -\epsilon_1/(1+\epsilon_1) & 0\\ 0 & 0 & 0\end{bmatrix},\qquad (\eta_{\alpha\beta})=\begin{bmatrix} \epsilon_1+\frac{1}{2}\epsilon_1^2 & 0 & 0\\ 0 & -\epsilon_1/(1+\epsilon_1)+\frac{1}{2}\epsilon_1^2/(1+\epsilon_1)^2 & 0\\ 0 & 0 & 0\end{bmatrix}.$$

(3) γ_1 deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} 0 & \gamma_1 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix},\qquad (\eta_{\alpha\beta})=\begin{bmatrix} 0 & \frac{1}{2}\gamma_1 & 0\\ \frac{1}{2}\gamma_1 & \frac{1}{2}\gamma_1^2 & 0\\ 0 & 0 & 0\end{bmatrix}.$$

(4) $v\epsilon_1$ deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} (1+\epsilon)v^{1/3}-1 & 0 & 0\\ 0 & v^{1/3}/(1+\epsilon)-1 & 0\\ 0 & 0 & v^{1/3}-1\end{bmatrix},$$

$$(\eta_{\alpha\beta})=\begin{bmatrix} (1+\epsilon)v^{1/3}-1+\frac{1}{2}\{(1+\epsilon)v^{1/3}-1\}^2 & 0 & 0\\ 0 & v^{1/3}/(1+\epsilon)-1+\frac{1}{2}\{v^{1/3}/(1+\epsilon)-1\}^2 & 0\\ 0 & 0 & v^{1/3}-1+\frac{1}{2}(v^{1/3}-1)^2\end{bmatrix}.$$

(5) $v\gamma_1$ deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} v^{1/3}-1 & \gamma v^{1/3} & 0 \\ 0 & v^{1/3}-1 & 0 \\ 0 & 0 & v^{1/3}-1 \end{bmatrix},$$

$$(\eta_{\alpha\beta})=\begin{bmatrix} v^{1/3}-1+\frac{1}{2}(v^{1/3}-1)^2 & \frac{1}{2}\gamma v^{1/3}+\frac{1}{2}\gamma v^{1/3}(v^{1/3}-1) & 0 \\ \frac{1}{2}\gamma v^{1/3}+\frac{1}{2}\gamma v^{1/3}(v^{1/3}-1) & v^{1/3}-1+\frac{1}{2}\gamma^2 v^{2/3}+(v^{1/3}-1)^2 & 0 \\ 0 & 0 & (v^{1/3}-1)+\frac{1}{2}(v^{1/3}-1)^2 \end{bmatrix}.$$

(6) $\epsilon_1\epsilon_2$ deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} \epsilon_1 & 0 & 0 \\ 0 & \dfrac{1+\epsilon_2}{1+\epsilon_1}-1 & 0 \\ 0 & 0 & \dfrac{1}{1+\epsilon_2}-1 \end{bmatrix}, \quad (\eta_{\alpha\beta})=\begin{bmatrix} \epsilon_1+\frac{1}{2}\epsilon_1{}^2 & 0 & 0 \\ 0 & \dfrac{1+\epsilon_2}{1+\epsilon_1}-1+\frac{1}{2}\left(\dfrac{1+\epsilon_2}{1+\epsilon_1}-1\right)^2 & 0 \\ 0 & 0 & \dfrac{1}{1+\epsilon_2}-1+\frac{1}{2}\left(\dfrac{1}{1+\epsilon_2}-1\right)^2 \end{bmatrix},$$

(7) $\epsilon_2\gamma_1$ deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} 0 & 0 & 0 \\ \gamma_1(1+\epsilon_2) & \epsilon_2 & 0 \\ 0 & 0 & 1/(1+\epsilon_2)-1 \end{bmatrix},$$

$$(\eta_{\alpha\beta})=\begin{bmatrix} \frac{1}{2}\gamma^2(1+\epsilon_2)^2 & \frac{1}{2}\gamma_1(1+\epsilon_2)+\frac{1}{2}\gamma_1(1+\epsilon_2)\epsilon_2 & 0 \\ \frac{1}{2}\gamma_1(1+\epsilon_2)+\frac{1}{2}\gamma_1(1+\epsilon_2)\epsilon_2 & \epsilon_2+\frac{1}{2}\epsilon_2{}^2 & 0 \\ 0 & 0 & 1/(1+\epsilon_2)-1+\frac{1}{2}[1/(1+\epsilon_2)-1]^2 \end{bmatrix}.$$

(8) $\gamma_3\gamma_2\gamma_1$ deformation:

$$(u_{\alpha\beta})=\begin{bmatrix} \gamma_1\gamma_2\gamma_3 & \gamma_2\gamma_3 & \gamma_3 \\ \gamma_1 & 0 & 0 \\ \gamma_1\gamma_2 & \gamma_2 & 0 \end{bmatrix}, \quad (\eta_{\alpha\beta})=\begin{bmatrix} \gamma_1\gamma_2\gamma_3+\frac{1}{2}(\gamma_1{}^2\gamma_2{}^2\gamma_3{}^2+\gamma_1{}^2+\gamma_1{}^2\gamma_2{}^2) & (12) & (13) \\ \frac{1}{2}(\gamma_1+\gamma_2\gamma_3)+\frac{1}{2}(\gamma_1\gamma_2{}^2\gamma_3{}^2+\gamma_1\gamma_2{}^2) & \frac{1}{2}(\gamma_2{}^2\gamma_3{}^2+\gamma_2{}^2) & \frac{1}{2}\gamma_2 \\ \frac{1}{2}(\gamma_3+\gamma_1\gamma_2)+\frac{1}{2}(\gamma_1\gamma_2\gamma_3{}^2) & \frac{1}{2}\gamma_2 & \gamma_3{}^2 \end{bmatrix}.$$

APPENDIX III

Because all the lattice sums are calculated by similar procedures, we show in detail the calculation only for the following typical sum:

$$\sum{}' \frac{l_1{}^4}{(l_1{}^2+l_2{}^2+l_3{}^2)^{5/2}}-\frac{1}{4}\int\int\int\frac{u_1{}^4du_1du_2du_3}{(u_1{}^2+u_2{}^2+u_3{}^2)^{5/2}}. \tag{A1}$$

By means of a Laplace transformation

$$\frac{1}{Z^k}=\frac{1}{\Gamma(k)}\int_0^\infty t^{k-1}e^{-zt}dt, \tag{A2}$$

the lattice sum can be rewritten as follows:

$$\frac{1}{\Gamma(\frac{5}{2})}\left\{\sum\int_0^\infty t^{3/2}l_1{}^4\exp[-(l_1{}^2+l_2{}^2+l_3{}^2)t]dt \right.$$
$$-\frac{1}{4}\int\int\int\int_0^\infty t^{3/2}u_1{}^4$$
$$\left.\times\exp[-(u_1{}^2+u_2{}^2+u_3{}^2)t]du_1du_2du_3dt\right\}.$$

The restriction on the integers l_1, l_2, l_3 can be removed by rewriting the first term as a sum of two terms:

$$\sum\int_0^\infty t^{3/2}l_1{}^4\exp[-(l_1{}^2+l_2{}^2+l_3{}^2)t]dt$$
$$=\int_0^\infty t^{3/2}\left\{\frac{\partial^2}{\partial t^2}\sum_{-\infty}^{+\infty}\exp[-4l^2t]\right\}\left\{\sum_{-\infty}^{+\infty}\exp[-4l^2t]\right\}^2dt$$
$$+\int_0^\infty t^{3/2}\left\{\frac{\partial^2}{\partial t^2}\sum_{-\infty}^{+\infty}\exp[-4(l-\tfrac{1}{2})^2t]\right\}$$
$$\times\{\sum_{-\infty}^{+\infty}\exp[-4(l-\tfrac{1}{2})^2t]\}^2dt. \tag{A3}$$

On the right-hand side, l runs all over the integers $-\infty$ to $+\infty$. The integration is split up into two parts, i.e., 0 to ϵ and ϵ to ∞ where ϵ is a positive constant chosen in a way discussed shortly. The integrations ϵ to ∞ are simple and given in terms of integrals defined by

$$\phi_m(x)=\int_1^\infty t^m e^{-xt}dt \tag{A4}$$

as follows:

$$\int_\epsilon^\infty t^{3/2}\left\{\frac{\partial^2}{\partial t^2}\sum \exp(-4l^2t)\right\}\{\sum \exp(-4l^2t)\}^2dt$$
$$=\epsilon^{\frac{3}{2}+1}[32\phi_{3/2}(4\epsilon)+128\phi_{3/2}(8\epsilon)+128\phi_{3/2}(12\epsilon)+512\phi_{3/2}(16\epsilon)+\cdots],$$

$$\int_\epsilon^\infty t^{3/2}\left\{\frac{\partial^2}{\partial t^2}\sum \exp[-4(l-\tfrac{1}{2})^2t]\right\}\times\{\sum \exp[-4(l-\tfrac{1}{2})^2t]\}^2dt$$
$$=\epsilon^{\frac{3}{2}+1}[8\phi_{3/2}(3\epsilon)+664\phi_{3/2}(11\epsilon)+1296\phi_{3/2}(19\epsilon)+\cdots]. \tag{A5}$$

By means of the following formulas

$$\sum_{l=-\infty}^{\infty}\exp(-l^2t)=\left(\frac{\pi}{t}\right)^{1/2}\sum_{l=-\infty}^{\infty}\exp\left(-\frac{\pi^2}{t}l^2\right),$$

$$\sum_{l=-\infty}^{\infty}\exp[-4(l-\tfrac{1}{2})^2]t=\tfrac{1}{2}\left(\frac{\pi}{t}\right)^{1/2}\sum_{l=-\infty}^{\infty}(-1)^l\times\exp\left(-\frac{\pi^2}{4t}l^2\right),$$

the integrals from 0 to ϵ are converted as follows:

$$\int_0^\epsilon t^{3/2}\left\{\frac{\partial^2}{\partial t^2}\sum \exp(-4l^2t)\right\}\{\sum \exp(-4l^2t)\}^2dt+\int_0^\epsilon t^{3/2}\{\sum \exp[-4(l-\tfrac{1}{2})^2t]\}\{\sum \exp[-4(l-\tfrac{1}{2})^2t]\}^2dt$$
$$=\int_0^\epsilon \frac{\pi^{3/2}}{2^4}3t^{-2}dt+\frac{3}{2^4}\pi^{3/2}\frac{1}{\epsilon}\left[12\phi_0\left(\frac{2\pi^2}{4\epsilon}\right)+6\phi_0\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]-\frac{6}{2^5}\pi^{7/2}\frac{1}{\epsilon^2}\left[8\phi_1\left(\frac{2\pi^2}{4\epsilon}\right)+8\phi_1\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]$$
$$+\frac{1}{2^6}\pi^{11/2}\frac{1}{\epsilon^3}\left[8\phi_2\left(\frac{2\pi^2}{4\epsilon}\right)+32\phi_2\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]. \tag{A6}$$

The second term of the lattice sum is integrated as follows

$$-\tfrac{1}{4}\int_0^\infty\int\int\int t^{3/2}u_1^4\exp[-(u_1^2+u_2^2+u_3^2)t]du_1du_2du_3dt=-(\pi^{3/2}/2^4)3\int_0^\infty t^{-2}dt. \tag{A7}$$

We notice that the divergent integrals in Eqs. (A6) and (A7) cancel each other. The positive constant ϵ is chosen in such a way that the series in Eqs. (A5) and (A6) converges at approximately the same speed. On our calculation we used $\epsilon=\frac{1}{2}\pi$; however, the results of the calculation are not critically dependent on the choice of ϵ, as long as a sufficient number of terms are summed in the calculation of the series in Eqs. (A5) and (A6).

Finally, adding (A5) ,(A6), and (A7), we obtain the expression for the lattice sum

$$\frac{1}{\Gamma(\frac{5}{2})}\left\{\epsilon^{5/2}[32\phi_{3/2}(4\epsilon)+128\phi_{3/2}(8\epsilon)+128\phi_{3/2}(12\epsilon)+512\phi_{3/2}(16\epsilon)+\cdots]\right.$$
$$+\epsilon^{5/2}[8\phi_{3/2}(3\epsilon)+664\phi_{3/2}(11\epsilon)+1296\phi_{3/2}(19\epsilon)+\cdots]+\frac{3}{2^4}\pi^{3/2}\frac{1}{\epsilon}\left[12\phi_0\left(\frac{2\pi^2}{4\epsilon}\right)+6\phi_0\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]$$
$$\left.-\frac{6}{2^5}\pi^{7/2}\frac{1}{\epsilon^2}\left[8\phi_1\left(\frac{2\pi^2}{4\epsilon}\right)+8\phi_1\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]+\frac{1}{2^6}\pi^{11/2}\frac{1}{\epsilon^3}\left[8\phi_2\left(\frac{2\pi^2}{4\epsilon}\right)+32\phi_2\left(\frac{4\pi^2}{4\epsilon}\right)+\cdots\right]+\int_\epsilon^\infty\frac{\pi^{3/2}}{2^4}3t^{-2}dt\right\}.$$

Using the table for the integral $\phi_n(x)$ provided by Misra and Born[37] we obtain the result for $S_5^{(2)}$ given in Eq.(5.11).