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Pseudopotential Calculation of the Third-Order Elastic Constants of Copper and Silver*

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The third-order elastic constants of copper and silver have been calculated by the method of homogeneous deformation from a total energy expression consisting of four terms: a free-electron energy, an electrostatic energy, a band-structure energy, and an ion-core overlap energy. The band-structure energy has been expressed in terms of a local pseudopotential. The overlap energy has been approximated by a Born-Mayer potential. The total-energy expression includes five adjustable parameters which have been chosen to fit the binding energy, lattice spacing, and three second-order elastic constants to experiment. The ion-core repulsive energy makes the dominant contribution to the third-order elastic constants. The other contributions are not negligible but tend to cancel. The calculated third-order elastic constants of copper and silver are in good agreement with low-temperature experimental values. An attempt to apply the five-parameter fitting procedure to gold was unsuccessful.

I. INTRODUCTION

Pseudopotential theory has been remarkably successful in the calculation of structural properties, such as elastic constants and phonon spectra of simple (*sp*-bonded) metals. Unfortunately, the situation is quite the opposite for the transition metals. There is now no distinct approach of comparable power applicable to this important class of materials. This is true, also, for the noble metals copper, silver, and gold which, in many respects, form a link between the simple metals and the transition series.

Several years ago, Harrison¹ proposed a scheme by which the pseudopotential formalism could be applied to transition metals. The key result was that hybridization between the *d* bands and conduction band could be included in a weak pseudopotential. Perturbation theory could then be used in the usual way to obtain an analytical expression for the lattice energy as a function of the ion positions.² Harrison's approach has been developed by Moriarty.³⁻⁵ He recently completed numerical calculations of the total energy of the noble metals and applied the results to predict crystal structure and calculate phonon spectra with moderate, yet encouraging, success.⁵

The purpose of this work is to calculate the third-order elastic (TOE) constants of the noble

metals. Interest in TOE constants, which measure the anharmonic part of the interatomic potentials, has centered on information which can be obtained regarding the lattice energy or interatomic potential. For example, by symmetry, there are six TOE constants for a cubic crystal. Experimental values of these parameters for the noble metals,⁶⁻¹⁰ including some measurements at low temperature,⁸⁻¹⁰ are available to fit or verify a theoretical interatomic potential.

We have calculated the TOE constants by the method of homogeneous deformation. The total-energy expression used in the calculation is based upon the work of Harrison¹ and Moriarty.⁵ However, we have made several simplifying assumptions, including the use of a local-empirical pseudopotential, to keep the calculation of the required energy derivatives tractable. To partially compensate, we have included five adjustable parameters in the total-energy expression. These have been chosen to fit the binding energy, lattice spacing, and three second-order elastic (SOE) constants to their experimental values. The total-energy expression consists of four terms: the free-electron energy U_{fe} , the electrostatic energy U_{es} , the band-structure energy U_{bs} , and the overlap energy U_{o1} . The energy term U_{o1} , which measures the exchange interaction between neighboring ion cores, has been approximated in terms of the

well-known Born-Mayer potential. We find that U_{01} makes the dominant contribution to the TOE constants of the noble metals. The calculated TOE constants of copper and silver are in good agreement with low-temperature experimental values. It was not possible to perform the required five-parameter fit for gold, and no results for the elastic constants are included here.

In addition to Moriarty's work on the noble metals,⁵ there have been other calculations of the phonon spectrum and elastic constants of copper based on a pseudopotential approach. However, none have included TOE constants or even pressure derivatives of the SOE constants. Most recently, Prakash and Joshi¹¹ calculated the phonon spectrum of copper. They included the effects of hybridization in a parametrized-dielectric screening function, but neglected ion-core overlap. They obtained fair agreement with experiment for longitudinal modes, but the calculated frequencies for the transverse modes were low. Sinha¹² also calculated the phonon spectrum of copper using a pseudopotential formalism with three parameters fit to the SOE constants. He included an explicit ion-core overlap term. Sinha's calculated phonon spectrum is in good agreement with experiment. Using a different approach, Collins¹³ fit the SOE constants of copper and silver in a rigid-band calculation. Collins also included an explicit ion-core overlap energy term.

In Sec. II of this paper, we present a short discussion of the method of homogeneous deformation. In Sec. III we describe the total-energy expression. In Sec. IV the results of the calculation are presented, and these are discussed in Sec. V.

II. METHOD OF HOMOGENEOUS DEFORMATION

The relation between the elastic constants and the strain-dependent lattice energy can be written

$$U = U_0 + \frac{1}{2} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{6} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} + \dots \quad (1)$$

Here the elastic constants of any order are defined as

$$C_{ijklmn\dots} = \left(\frac{\partial^n U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn} \dots} \right)_{\eta=0} \quad (2)$$

This definition was first proposed by Brugger¹⁴ and has been widely accepted. In these expressions, U is the total energy of the crystal per unit mass, and the η_{ij} are components of the Lagrangian strain tensor

$$\eta_{ij} = \frac{1}{2} (\alpha_{ik} \alpha_{jk} - \delta_{ij}) \quad (3)$$

The deformation tensor

$$\alpha_{ik} = \frac{\partial r_i}{\partial a_k} \quad (4)$$

relates the initial and final coordinate vectors \vec{a}

and \vec{r} of an infinitesimal element in the deformed solid. Any deformation for which $\det(\alpha_{ik}) = 1$ will define a strictly volume-conserving (shear) deformation.

The method of homogeneous deformation dates to the work of Fuchs.¹⁵ He defined two shear deformations which isolated the cubic elastic constants $C' = \frac{1}{2}(C_{11} - C_{12})$ and $C = C_{44}$. Elastic-shear constants were emphasized because they do not depend upon terms in the total energy which depend solely on crystal volume. The method of homogeneous deformation was extended to the third order by Cousins¹⁶ and by Suzuki, Granato, and Thomas.¹⁷ The procedure used here closely parallels that of Suzuki *et al.* except for the use of slightly different deformation parameters. Hence, the four deformation parameters used here will be defined.

The first deformation (χ) contracts the lattice along the [001] direction and expands it uniformly in the plane perpendicular to this direction so as to maintain constant volume. The deformation tensor is

$$\alpha_{ij}(\chi) = \begin{pmatrix} \chi^{1/3} & 0 & 0 \\ 0 & \chi^{1/3} & 0 \\ 0 & 0 & \chi^{-2/3} \end{pmatrix} \quad (5)$$

The second deformation (λ) contracts the lattice along the [111] direction and expands it in the plane perpendicular to this direction to maintain constant volume. The deformation tensor is

$$\alpha_{ij}(\lambda) = \frac{1}{3} \lambda^{1/3} \begin{pmatrix} \lambda^{-1} + 2 & \lambda^{-1} - 1 & \lambda^{-1} - 1 \\ \lambda^{-1} - 1 & \lambda^{-1} + 2 & \lambda^{-1} - 1 \\ \lambda^{-1} - 1 & \lambda^{-1} - 1 & \lambda^{-1} + 2 \end{pmatrix} \quad (6)$$

The third deformation (κ) contracts the lattice along the [110] direction and expands it in the plane perpendicular to this direction to maintain constant volume. The deformation tensor is

$$\alpha_{ij}(\kappa) = \kappa^{1/3} \begin{pmatrix} \frac{1}{2}(\kappa^{-1} + 1) & \frac{1}{2}(\kappa^{-1} - 1) & 0 \\ \frac{1}{2}(\kappa^{-1} - 1) & \frac{1}{2}(\kappa^{-1} + 1) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (7)$$

In addition, we require a deformation defining a simple volume change. This is taken to be

$$\alpha_{ij} = \nu^{1/3} \delta_{ij} \quad (8)$$

where ν is the reduced volume, $\nu = (V/V_0)$.

The three shear deformations defined above have been chosen to distort the lattice along directions of high symmetry. Each can be obtained from the others by means of a similarly transformation referred to the cubic crystallographic axes. In addition, we note that the deformations have been defined in terms of parameters which approach unity at the equilibrium configuration. This is allowable as there is no need to construct a series expansion in terms of the deformation parameters,

TABLE I. Relation between Fuchs and Brugger cubic second- and third-order elastic constants and energy derivatives with respect to the deformation parameters defined in the text.

$C' = \frac{1}{2}(C_{11} - C_{12})$	$\frac{3}{4} \frac{\partial^2 U}{\partial \lambda^2}$
$C = C_{44}$	$\frac{3}{4} \frac{\partial^2 U}{\partial \lambda^2}$
$B = \frac{1}{3}(C_{11} + 2C_{12})$	$\frac{\partial^2 U}{\partial \nu^2}$
$C_{XXX} = \frac{1}{8}(C_{111} - 3C_{112} + 2C_{123})$	$-\frac{1}{16} \left(9 \frac{\partial^3 U}{\partial \lambda^3} + 45 \frac{\partial^2 U}{\partial \lambda^2} \right)$
$C_{\lambda\lambda\lambda} = C_{456}$	$-\frac{1}{16} \left(9 \frac{\partial^3 U}{\partial \lambda^3} + 45 \frac{\partial^2 U}{\partial \lambda^2} \right)$
$C_{KKK} = \frac{1}{2}(C_{166} - C_{144})$	$-\frac{1}{16} \left(8 \frac{\partial^3 U}{\partial \kappa^3} + \frac{\partial^3 U}{\partial \lambda^3} + 15 \frac{\partial^2 U}{\partial \lambda^2} + 30 \frac{\partial^2 U}{\partial \lambda^2} \right)$
$C_{XXV} = 2B + \frac{1}{2}(C_{111} - C_{123})$	$\frac{3}{4} \left(3 \frac{\partial^3 U}{\partial \lambda^2 \partial \nu} - 4 \frac{\partial^2 U}{\partial \lambda^2} \right)$
$C_{\lambda\lambda\nu} = 3B + C_{144} + 2C_{166}$	$\frac{3}{4} \left(3 \frac{\partial^3 U}{\partial \lambda^2 \partial \nu} - 4 \frac{\partial^2 U}{\partial \lambda^2} \right)$
$C_{\nu\nu\nu} = \frac{1}{9}(C_{111} + 6C_{112} + 2C_{123})$	$\frac{\partial^3 U}{\partial \nu^3} + \frac{\partial^2 U}{\partial \nu^2}$

and this choice results in the calculations becoming somewhat less tedious.

The elastic constants which we calculate from the derivatives of the total energy with respect to the above deformation parameters are summarized in Table I. This table defines the notation to be used in this paper for relating Fuchs elastic constants (C' , C_{XXX} , etc.) to Brugger elastic constants (C_{11} , C_{111} , etc.) and the energy derivatives. Three of the Fuchs TOE constants, C_{XXX} , $C_{\lambda\lambda\lambda}$, and C_{KKK} , have previously been identified by Cousins¹⁶ as third-order shear constants. The other three Fuchs TOE constants, C_{XXV} , $C_{\lambda\lambda\nu}$, and $C_{\nu\nu\nu}$, measure the volume derivatives of the SOE constants. Finally, we note that seven of the nine Fuchs elastic constants for a cubic crystal, all except B and $C_{\nu\nu\nu}$, will be independent of lattice energy terms which depend solely on crystal volume.

III. TOTAL ENERGY EXPRESSION

The work of Harrison¹ and Moriarty³⁻⁵ has shown that the total energy of a noble metal can be written in a pseudopotential approach as the sum of four terms,

$$U = U_{f_e} + U_{es} + U_{bs} + U_{o1} \quad (9)$$

The reader is referred to the references cited for basic accounts of these energy terms. The treatment here is approximate. In addition, we introduce five adjustable parameters. The energy expressions given below are written in atomic units with lengths measured in Bohr radii ($a_0 = 0.529 \text{ \AA}$) and energies measured in rydbergs (1 Ry = 13.6 eV).

For conversion purposes one would use $\hbar = 2m_e = \frac{1}{2} e^2 = 1$. In addition, we have used valence $Z = 1$ throughout.

The free-electron energy U_{f_e} depends only on the volume of the crystal and is unchanged during a shear deformation. We write it as follows:

$$U_{f_e} = 2.21/r_s^2 - 0.916/r_s - (0.115 - 0.031 \ln r_s) + 3\alpha/4\pi r_s^3 \quad (10)$$

Here the first term represents the Fermi energy, the second term represents the exchange energy, and the third term represents the Nozières-Pines approximate expression for the correlation energy of a free-electron gas.¹⁸ The parameter r_s is the radius per conduction electron. For the monovalent noble metals, r_s is related to the atomic volume Ω_0 by $\Omega_0 = (\frac{4}{3}\pi)r_s^3$. In the fourth term in Eq. (10) we introduce the adjustable parameter α to measure that component of the energy U_{f_e} depending on volume as r_s^{-3} . This volume dependence would be correct for the first-order perturbation energy term for a simple metal treated in terms of a local pseudopotential. However, for a noble metal, the pseudopotential includes the effects of hybridization, and nonlocal effects should also be important. In addition, U_{f_e} should account for the volume-dependent energy of the d electrons for which an energy term varying as r_s^{-3} is only a first approximation.¹⁹ Limiting U_{f_e} to the four terms in Eq. (10) with a single adjustable parameter is a serious approximation. In a certain respect it is necessary, though, as our procedure will not accommodate another adjustable parameter. Hopefully, the results of our calculation will indicate the extent to which this approximation is justified.

The electrostatic energy U_{es} represents the classical electrostatic energy of an array of positive point charges embedded in a uniform-compensating electron gas. The volume dependence of U_{es} can be written as

$$U_{es} = -1.792/r_s \quad (11)$$

and U_{es} also depends on the configuration of the ions. The numerical coefficient is appropriate for any fcc lattice.²⁰ In pseudopotential calculations which include the effect of the energy dependence of the potential, the electrostatic energy is multiplied by the square of an effective valence, Z^* , to account for the exclusion of charge from the core of a pseudoatom. Since energy-dependent effects are not explicitly included here, we take $Z^* = 1$ for the monovalent noble metals.

The band-structure energy U_{bs} represents the deviation of the energy of the conduction electrons from that of a free-electron gas. In particular, it is calculated from the second-order perturbation energy of a conduction electron in an expan-

sion in terms of the pseudopotential. For a Bravais lattice, U_{bs} can be written

$$U_{\text{bs}} = \sum'_{q=\vec{G}} F(q), \quad (12)$$

where $F(q)$ is called the energy-wave-number characteristic, \vec{G} is a reciprocal-lattice vector, and the prime on the sum indicates that the term with $\vec{G}=0$ should be excluded. We have chosen to approximate the energy-wave-number characteristic $F(q)$ in terms of a local-model pseudopotential and a linear screening function corrected for exchange and correlation among the conduction electrons. In this case, $F(q)$ can be written²¹

$$F(q) = w_0^2(q) [\chi(q)/\epsilon(q)] D(q), \quad (13)$$

where

$$w_0(q) = \Omega_0^{-1} [-8\pi/q^2 + \beta/(1+q^2r_c^2)^2], \quad (14)$$

$$\epsilon(q) = 1 - (16\pi/\Omega_0 q^2) [1-f(q)] \chi(q), \quad (15)$$

$$\chi(q) = -\frac{3}{8} k_F^{-2} \left(1 + \frac{1-\eta^2}{2\eta} \ln \left| \frac{\eta+1}{\eta-1} \right| \right), \quad (16)$$

$$f(q) = \frac{1}{2} \eta^2 / [\eta^2 + \frac{1}{4} + (2k_F \pi)^{-1}], \quad (17)$$

$$D(q) = e^{-0.0258\eta^4}. \quad (18)$$

In these expressions, k_F is the free-electron Fermi wave number, $k_F = (\frac{9}{4}\pi)^{1/3} r_s^{-1}$, and $\eta = |\vec{G}|/2k_F$.

For the bare-ion pseudopotential form factor $w_0(q)$, Eq. (14), we have chosen Harrison's modified point-ion form.² This includes the adjustable parameters β and r_c . There is, of course, no theoretical justification for choosing a local pseudopotential with no explicit account of hybridization. We have done so to keep the calculation of the second and third derivatives of $F(q)$ tractable. However, it is interesting to note that, by adjusting the values of β and r_c , the screened form factor w_0/ϵ calculated here can be brought into general agreement with that calculated by Moriarty⁵ for $q \gtrsim 2k_F$. This is the region of concern in the elastic-constant calculation.

For the dielectric screening function $\epsilon(q)$, Eqs. (15)–(17), we have used the Hubbard–Sham form.²² This is equivalent to the Hartree dielectric function with the factor $[1-f(q)]$ inserted to correct approximately for correlation and exchange among the conduction electrons. The factor $\chi(q)$ includes the logarithmic singularity arising from the assumption of a sharp Fermi surface.

The function $D(q)$ is not usually included in the energy-wave-number characteristic. We have included it here to improve the convergence of sums over $F(q)$ and its derivatives. The coefficient in the exponent was arbitrarily chosen so that $F(q)$ would be down by e^{-1} at $q = 5k_F$ and converge rapidly for higher q . There is little effect

on $F(q)$ in the region near $q \approx (2-3)k_F$ where the principal contributions to the elastic constants occur.

The overlap energy U_{o1} represents the exchange energy due to the overlap of d -electron states on neighboring ion cores. In the noble metals, the ion cores have the closed-shell configuration d^{10} , and the electron states on neighboring ions must be orthogonal. This results in an interaction energy which varies rapidly with interatomic distance. We have chosen to parametrize this energy term by the well-known Born–Mayer form

$$U_{o1} = \frac{1}{2} \sum_i A e^{B[(|\vec{r}_i|/r_0)^{-1}]} \quad (19)$$

Here r_0 is the nearest-neighbor distance, and A and B are adjustable parameters. The sum in Eq. (19) will be performed over the 12-nearest neighbors only.

IV. CALCULATIONS AND RESULTS

The expression for the total energy contains five adjustable parameters. These have been chosen to fit the experimental values of the binding energy and SOE constants and to assure crystal equilibrium, $\partial U/\partial r_s = 0$, at the observed lattice spacing. The relevant constants for copper and silver are summarized in Table II. The experimental binding energy²³ is the sum of the cohesive energy plus the first ionization energy of the free atom. Since the method of homogeneous deformation treats the crystal as an anisotropic continuum at 0°K ignoring zero-point vibrations, we have tabulated experimental values of the lattice constant²⁴ and elastic constants^{25,26} extrapolated linearly to 0°K.

We used the following procedure to choose the values of the adjustable parameters: The pseudopotential parameters β and r_c were set, and the band structure and electrostatic energies and energy derivatives were calculated. The Born–Mayer parameters A and B could then be obtained from the experimental values of the second-order shear constants, and the overlap energy and its derivatives could then be calculated. The parameter α in the free-electron energy could then be

TABLE II. Cohesive properties of copper and silver at 0°K.

	Copper	Silver
Binding energy ^a (Ry/ion)	0.825	0.774
Lattice constant ^b (Å)	3.597	4.063
Elastic constants (10 ¹² dyn cm ⁻²)		
$C' = \frac{1}{2}(C_{11} - C_{12})$	0.266 ^c	0.173 ^d
$C = C_{44}$	0.832 ^c	0.517 ^d
$B = \frac{1}{3}(C_{11} + 2C_{12})$	1.439 ^c	1.097 ^d

^aReference 23.

^cReference 25.

^bReference 24.

^dReference 26.

TABLE III. Final values of the adjustable parameters in the total-energy expressions for copper and silver.

Energy term	Parameter	Copper	Silver
U_{fe}	α (Ry a_0^3)	2.92	22.41
U_{bs}	β (Ry a_0^3)	59.10	69.00
	$r_c(a_0)$	0.516	0.457
U_{o1}	A (Ry)	4.62×10^{-3}	4.21×10^{-3}
	B	14.95	15.26

adjusted to obtain lattice equilibrium. The procedure was repeated for different pseudopotential parameters until agreement with experiment was obtained for the binding energy and bulk modulus. The procedure was successful for copper and silver, and the final values of the adjustable parameters for these metals are summarized in Table III. The procedure was not successful for gold. The experimental values of the binding energy and bulk modulus of gold could not be obtained simultaneously with reasonable values of the pseudopotential parameters. This is discussed further in Sec. V.

The elastic constants summarized in Table I have been calculated from the equivalent energy derivatives. The free-electron energy U_{fe} contributes only to the elastic constants B and $C_{\nu\nu\nu}$. The contributions of the electrostatic energy U_{es} and the overlap energy U_{o1} to the second- and third-order elastic shear constants have recently been summarized by Cousins.¹⁶ The contributions of these energy terms to the elastic constants B , $C_{\lambda\lambda\nu}$, $C_{\lambda\nu\nu}$, and $C_{\nu\nu\nu}$ can be calculated from the results of Cousins and the volume dependence. The calculation of the contribution of the band-structure

TABLE IV. Calculated lattice energy contributions to the Fuchs second-order elastic constants of copper and silver in units of 10^{12} dyn cm^{-2} .

	$C' = \frac{1}{2}(C_{11} - C_{12})$	$C = C_{44}$	$B = \frac{1}{3}(C_{11} + 2C_{12})$
Copper			
U_{bs}	-0.020	-0.202	0.054
U_{es}	0.029	0.261	-0.562
U_{fe}	0	0	0.485
U_{o1}	0.257	0.773	1.462
Total	0.266	0.832	1.439
Silver			
U_{bs}	-0.017	-0.155	-0.198
U_{es}	0.018	0.160	-0.345
U_{fe}	0	0	0.679
U_{o1}	0.172	0.512	0.961
Total	0.173	0.517	1.097

TABLE V. Calculated Fuchs third-order elastic constants of copper and silver in units of 10^{12} dyn cm^{-2} .

	C_{xxx}	$C_{\lambda\lambda\lambda}$	$C_{\kappa\kappa\kappa}$	$C_{\lambda\lambda\nu}$	$C_{\lambda\nu\nu}$	$C_{\nu\nu\nu}$
Copper						
U_{bs}	-0.25	-0.49	0.60	0.13	2.24	-0.30
U_{es}	0.35	0.35	-0.80	-0.14	-1.31	0.75
U_{fe}	0	0	0	0	0	-0.96
U_{o1}	1.36	0.26	-4.13	-4.13	-12.90	-7.83
Total	1.46	0.12	-4.33	-4.14	-11.97	-8.34
Silver						
U_{bs}	-0.17	-0.50	0.48	0.18	2.17	-0.12
U_{es}	0.22	0.21	-0.49	-0.09	-0.80	0.46
U_{fe}	0	0	0	0	0	-1.37
U_{o1}	0.90	0.17	-2.77	-2.83	-8.71	-5.24
Total	0.95	-0.12	-2.78	-2.74	-7.34	-6.27

energy U_{bs} to the elastic constants is equivalent to that of Suzuki *et al.*¹⁷ except for the use of the different strain parameters defined in Sec. II. This calculation is straightforward, but lengthy, and will not be summarized here. In calculating U_{bs} and its derivatives, $F(q)$ and its derivatives have been summed over the nearest 258 reciprocal-lattice vectors, which extend to a distance $q = 7.7k_F$.

The decomposition of the Fuchs SOE constants of copper and silver into contributions from the various energy terms is presented in Table IV. We note that the overlap energy makes the dominant contribution to the three SOE constants, and that the electrostatic energy and band-structure energy contributions to the second-order shear constants nearly cancel. In addition, the band-structure energy contribution to the shear constant C is approximately an order of magnitude greater than the contribution to the shear constant C' for both copper and silver. This relationship is in agreement with the calculations of Sinha¹² and Collins¹³ mentioned previously. It is related to the fact that the Fermi surface of a noble metal intersects the $\{111\}$ planes of the Brillouin zone, and it is the motion of these planes that is the predominant feature of the shear deformation (λ) defining C . In fact, the band-structure contribution to C is approximately equal to that part of the sum arising from the eight nearest $\langle 111 \rangle$ reciprocal-lattice vectors.

The final results for the Fuchs TOE constants of copper and silver along with the decomposition into contributions from the various energy terms are presented in Table V. The most striking feature here is that, as for the second-order constants, the overlap-energy contributions are predominant. In each case, the electrostatic and band-structure energy contributions are opposite in sign and nearly equal in magnitude. We also note that, as for the second-order shear constants, the band-structure contribution of $C_{\lambda\lambda\nu}$ is an order

TABLE VI. Comparison of the calculated Brugger third-order elastic constants of copper and silver with experimental values (units of 10^{12} dyn cm^{-2}).

	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
Copper						
Present calculation	-17.02	-9.65	-0.10	+0.34	-8.32	+0.12
Hiki and Granato ^a (300 °K)	-12.71	-8.14	-0.50	-0.03	-7.80	-0.95
Salama and Alers ^b (300 °K)	-15.0	-8.5	-2.5	-1.35	-6.45	-0.16
(4.2 °K)	-20.0	-12.2	-5.0	-1.32	-7.05	+0.25
Silver						
Present calculation	-12.64	-7.12	-0.57	+0.17	-5.40	-0.11
Hiki and Granato ^a (300 °K)	-8.43	-5.29	+1.89	+0.56	-6.37	+0.83

^aReference 6.^bReference 8.

of magnitude larger than the contribution to C_{xxv} . The analogous situation for the third-order shear constants is not as transparent. However, in this case, the band-structure contribution to the third derivative $\partial^3 U / \partial \lambda^3$ is much larger than the contributions to $\partial^3 U / \partial \chi^3$ and $\partial^3 U / \partial \kappa^3$.

We have calculated the Brugger TOE constants from the Fuchs TOE constants using the relations in Table I. Our results for the Brugger TOE constants of copper and silver are presented in Table VI and compared to the available experimental values. The experimental results of Hiki and Granato⁶ at 300 °K and of Salama and Alers⁸ at both 300 and 4.2 °K were obtained from stress derivatives of pure-mode sound velocities. Since our TOE constants were calculated by the method of homogeneous deformation, we should expect agreement with low-temperature experimental values.

The hydrostatic-pressure derivatives of the SOE constants can be calculated from the TOE constants. In the notation used here the pressure derivatives are given by

$$\frac{\partial C'}{\partial P} = \frac{-(C' + C_{xxv})}{3B}, \quad (20)$$

$$\frac{\partial C}{\partial P} = \frac{-(C + C_{\lambda\lambda v})}{3B}, \quad (21)$$

$$\frac{\partial B}{\partial P} = \frac{-C_{vvv}}{B}. \quad (22)$$

Our results for the hydrostatic-pressure derivatives of the SOE constants of copper and silver and the available experimental values are presented in Table VII. The experimental results of Hiki and Granato⁶ and of Daniels and Smith⁷ were obtained at 300 °K. The pressure derivatives attributed to Salama and Alers⁸ were calculated by us from their 300 and 4.2 °K TOE constants. The pressure derivatives of Ho, Poirer, and Ruoff⁹ for silver were obtained from 300 to 77 °K.

The magnitude of the temperature dependence

of the pressure derivatives for copper obtained from the results of Salama and Alers is significantly larger than that obtained by Ho *et al.* for silver. In fact, Ho *et al.* conclude that, within experimental error, the pressure derivatives for silver may be independent of temperature. The large temperature dependence obtained by Salama and Alers has been questioned by Peters, Breazeale, and Pare.¹⁰ They measured three linear combinations of the TOE constants of copper determined by the generation of the second harmonic of an ultrasonic wave propagating in each of three pure-mode crystallographic directions. These combinations, termed nonlinearity parameters, were determined as a function of temperature from 300 to 77 °K, and the results were extrapolated to 0 °K. The magnitude of the temperature dependence determined by Peters *et al.* is much smaller than that obtained by Salama and Alers. Nonlinearity parameters determined from the TOE constants

TABLE VII. Comparison of calculated elastic-constant hydrostatic-pressure derivatives of copper and silver with experimental values (dimensionless).

	$\frac{\partial C'}{\partial P}$	$\frac{\partial C}{\partial P}$	$\frac{\partial B}{\partial P}$
Copper			
Present calculation	0.90	2.58	5.80
Hiki and Granato ^a (300 °K)	0.38	2.63	5.44
Daniels and Smith ^b (300 °K)	0.58	2.35	5.59
Salama and Alers ^c (300 °K)	0.50	2.37	5.90
(4.2 °K)	0.70	2.43	8.07
Silver			
Present calculation	0.78	2.07	5.72
Hiki and Granato ^a (300 °K)	0.76	3.04	4.11
Daniels and Smith ^b (300 °K)	0.64	2.31	6.18
Ho <i>et al.</i> ^d (300 °K)	0.66	2.32	6.07 ^e
(77 °K)	0.64	2.27	5.96 ^e

^aReference 6.^dReference 9.^bReference 7.^eIsothermal bulk modulus.^cReference 8.

TABLE VIII. Comparison of calculated nonlinearity parameters of copper with experimental values (units of 10^{12} dyn/cm²).

Direction	Nonlinearity parameter	Present calculation	Peters <i>et al.</i> , ^a	
			0 °K	300 °K
[100]	C_{111}	-17.0	-15.1	-13.9
[110]	$\frac{1}{4}(C_{111} + 3C_{112} + 12C_{166})$	-36.5	-33.2	-31.2
[111]	$\frac{1}{3}(C_{111} + 6C_{112} + 2C_{123} + 12C_{144} + 24C_{166} + 16C_{456})$	-29.9	-28.7	-25.7

^aReference 10.

of copper calculated here are compared to the 300 and 0 °K values obtained by Peters *et al.* in Table VIII. The calculated values are in good agreement with the low-temperature experimental values. In balance, from the comparisons in Tables VI–VIII, we believe that the calculated TOE constants of copper and silver are in good agreement with the available low-temperature experimental values.

V. DISCUSSION

The calculation of the TOE constants of copper and silver is based upon a modified pseudopotential expression for the total energy which contains five adjustable parameters. Final values for these parameters have been presented in Table III.

The band-structure energy U_{bs} has been written in terms of the local, point-ion potential containing the parameters β and r_c . We hoped that these could be adjusted to account approximately for hybridization as well as other components of the electron-ion potential. It was noted earlier that the shape of the screened form factors w_0/ϵ is in reasonable agreement with those calculated by Moriarty⁵ for $q \geq 2k_F$. However, one difficulty is that the final values of β and r_c result in a stronger potential for silver than for copper. This is not in accord with the general experimental observation that the Fermi surface of silver is less distorted

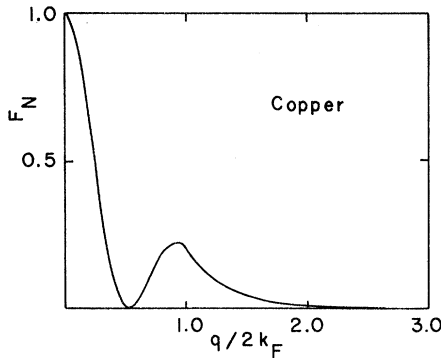


FIG. 1. Normalized energy-wave-number characteristic F_N vs reduced wave number $q/2k_F$ for copper.

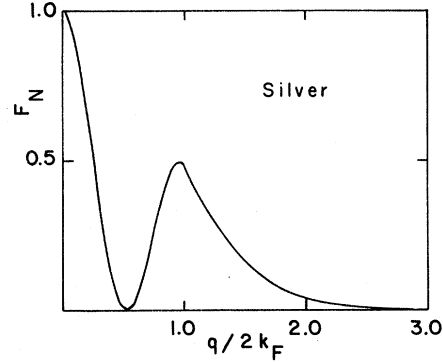


FIG. 2. Normalized energy-wave-number characteristic F_N vs reduced wave number $q/2k_F$ for silver.

than that of copper.

The contribution of the band-structure energy to the elastic constants depends directly on the energy-wave-number characteristic $F(q)$ and its derivatives. This function is most conveniently presented in the normalized form

$$F_N(q) = -(\Omega_0 q^2 / 4\pi) F(q) \quad (23)$$

The functions $F_N(q)$ for copper and silver are shown in Figs. 1 and 2, respectively. We note that the maxima of $F_N(q)$ occur before the position of the first reciprocal-lattice vectors, $G = 2.22k_F$, for both copper and silver. For copper, the maximum in $F_N(q)$ is about twice as large as that calculated by Moriarty.⁵ The larger maximum in $F_N(q)$ for silver is a measure of the stronger potential just discussed. This probably occurs because the fitting procedure depends more on the slope and curvature of $F(q)$ than its magnitude. In fact, the magnitudes of the band-structure contributions to the elastic constants are generally smaller for silver than for copper. In the limit of a smooth potential, these contributions would vanish. A possible conclusion here is that we have not built the correct volume dependence into the expression for the total energy.

The overlap energy U_{o1} has been written in terms of a Born-Mayer potential. The two Born-Mayer parameters A and B presented in Table III are in good agreement with previous estimates.^{12, 13, 27, 28} The values of the hardness parameter B imply a rapidly varying potential and fully support limiting the sum in U_{o1} [Eq. (19)] to nearest neighbors only. Moriarty⁵ has expressed his overlap energy in terms of a Born-Mayer form modified by a polynomial factor. His calculated U_{o1} is much softer than that obtained here; but he notes that, for copper, a harder potential would improve agreement of his calculated phonon frequencies with experiment.

One important result of our calculation is that

the overlap energy makes the dominant contribution to the TOE constants of copper and silver. The contributions of the electrostatic energy and band-structure energy are significant, but these cancel to a remarkable degree. Several years ago, Hiki and Granato⁶ proposed that the measured TOE constants of the noble metals could be interpreted by considering solely the overlap energy. They argued that, since this interaction must vary rapidly with ion separation, it would become increasingly important in the higher-order elastic constants. The results of our calculation help to explain the success of this approximation.

As a final comment, we consider the fact that the fitting procedure used here was not successful for gold. We choose to discuss this in terms of the failure of the Cauchy condition, the magnitude of the difference $C_{12} - C_{44}$. The author has recently

shown how this quantity can be obtained from solely volume-dependent terms in the total energy.²⁹ For copper, silver, and gold we have $C_{12} - C_{44} = 0.430, 0.465, \text{ and } 1.251 \times 10^{12} \text{ dyn cm}^{-2}$, respectively.^{25,26} The situation for gold is clearly anomalous. It is not surprising that an energy expression with the simplified volume dependence considered here is unable to account for the elastic properties of gold in spite of the considerable success achieved for copper and silver.

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