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Volumetric and structural contributions to the interatomic potentials and elastic moduli of cubic metals

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A popular model for metals considers the binding energy E_{bind} to consist of a structure-dependent part E_{str} and a volume-dependent part E_{vol}. An analysis of each part's contributions to the pressure, the bulk modulus κ, and the shear moduli μ and μ' reveals combinations of elastic moduli that are evidently fundamental as is evidenced by their systematic variation in the Periodic Table. If κ_{vol} and P_{vol} are the contributions of E_{vol} to κ and P, respectively, at arbitrary applied pressure P, $\kappa_{\text{vol}}-2P_{\text{vol}}=\kappa-2P-\mu'-\frac{2}{3}\mu$. If nearest-neighbor interactions provide the dominant contributions to the structure-dependent parts of κ, μ, and μ', for fcc crystals, $\kappa_{\text{vol}}=\kappa-\frac{1}{3}(9\mu'-10\mu)$ and $P_{\text{vol}}=2\mu-\mu'+P$. For aluminum, $\kappa_{\text{vol}}/\kappa\approx 1$ (i.e., $\mu/\mu'\approx 0.9$); this is considered to be more basic (and is more accurate) than the "usual" expression of aluminum's high isotropy (i.e., $\mu/\mu'\approx 1$). Similar elastic behavior is predicted for the fcc metals calcium and strontium. For the metals copper, silver, nickel, and lead, $\kappa_{\text{vol}}/\kappa$ is small; i.e., $\kappa\approx\frac{1}{3}(9\mu'-10\mu)$. Theoretical and empirical considerations suggest the utility of a specific analytical form for E_{bind} for the noble metals copper, silver, and gold; the form has four model-adjusting constants, the values of which are determined from experimental values of the zero pressure atomic volume and elastic moduli κ, μ, and μ'. The resultant expressions for E_{bind} are used to compute P_{vol}, κ_{vol}, theoretical pressure-versus-volume relations, and the first and second pressure derivatives of κ, μ, and μ'. The results compare favorably with experiment and with other (more complex) theoretical computations.

INTRODUCTION

Models for atomic binding of crystals are used in theoretical studies of many solid-state phenomena, including elasticity, general deformation, theoretical strength, lattice vibrations, and phase stability and transformations. Since computations of such phenomena based upon first principles are extremely complicated, models that are simple and accurate are of particular value; i.e., they allow computations to be performed and provide physical insight. A model popularly used in studies[1-9] of the lattice dynamics of metals considers the binding energy per atom E_{bind} to consist of a structure-dependent part E_{str} and a volume-dependent part E_{vol},

$$E_{\text{bind}}=E_{\text{str}}+E_{\text{vol}}\ , \tag{1}$$

where E_{str} is taken as a summation over pairwise energies ϕ depending only upon interatomic separation r and E_{vol} is attributed to the energy associated with the electron gas; E_{str} is generally taken to include only nearest-neighbor or nearest- and next-nearest-neighbor interactions, although longer-range interactions can be included, in principle. The present paper concerns several aspects of this model.

First, despite the basic simplicity of the model, a fair amount of controversy can be found in the technical literature[1-14] regarding (i) the conditions for crystal equilibrium and (ii) the relationships between the elastic moduli of the crystal and P_{vol} and κ_{vol} (the contributions of the volume-dependent part of the binding energy to the total pressure and bulk modulus, respectively, of the crystal). Here we show that the formalism developed by Milstein and Hill[15-17] to treat the elastic moduli of cubic crystals at arbitrary pressure is able to provide a clear perspective. Second, a general expression is derived for $\kappa_{\text{vol}}-2P_{\text{vol}}$ in terms of the elastic moduli of the crystal; the expression is general in that it applies at arbitrary pressure P and for arbitrary mathematical forms for E_{vol} and E_{str} (without need of truncating the lattice summation comprising E_{str} after some arbitrarily small number of terms). Next, for fcc crystals, in which, to a reasonable approximation, the E_{str} lattice summation can be truncated after just nearest-neighbor interactions, separate (general) expressions are derived for κ_{vol} and P_{vol} in terms of the elastic moduli [specifically, $\kappa_{\text{vol}}=\kappa-\frac{1}{3}(9\mu'-10\mu)$ and $P_{\text{vol}}=2\mu-\mu'+P$, where κ, μ, and μ' are the bulk and two shear moduli and P is the external pressure]; these expressions are also applicable at arbitrary pressure and for arbitrary mathematical forms of E_{vol} and E_{str}. Experimental values of elastic moduli are then used to compute theoretical values of κ_{vol} and P_{vol} for a number of fcc metals, and the results are discussed in terms of the nature of metallic binding and the positions of the metals in the Periodic Table. Although based upon a simplified model, the combinations of elastic moduli that comprise κ_{vol} and P_{vol} evidently represent fundamental quantities; i.e., they exhibit a systematic variation in the Periodic Table that is not present among the individual moduli κ, μ, and μ' (or among the moduli C_{ij}). The expression for κ_{vol} allows us to obtain insight into the high degree of isotropy of aluminum; i.e., for Al, $\kappa_{\text{vol}}/\kappa\approx 1$ so $\mu/\mu'\approx 0.9$. We consider this to be a more fundamental and technically correct statement of the elastic behavior of aluminum than is the "usual" expression $\mu/\mu' \approx 1.0$ (the experimental value is 0.83 at 0 K). The positions of calcium and strontium in the Periodic Table lead us to predict similar behavior for these fcc structures. For other fcc metals (specifically copper, silver, lead, and nickel), $\kappa_{\rm vol}/\kappa$ is small, so to a good approximation $\kappa \approx \frac{1}{3}(9\mu'-10)$; Milstein and Rasky[18] recently proposed this as a theoretical relation for fcc crystals and they showed that it agrees with experimental data better than the Cauchy relation $\kappa=\mu'+2\mu/3$ (or $C_{12}=C_{44}$) for fcc metals and inert-gas solids. The present development shows that the expression of Milstein and Rasky[18] becomes "exact" (i.e., for the simplified model under consideration) if $\kappa_{\rm vol}$ is zero and $E_{\rm str}$ consists of nearest-neighbor interactions only.

Finally, for the purpose of illustration and of obtaining some useful forms of $E_{\rm bind}$, pseudopotential theory is used to suggest a form for $E_{\rm vol}$, and specific expressions for $E_{\rm bind}$ are determined for the noble metals Au, Ag, and Cu based upon experimental values of the zero-pressure atomic volume and elastic moduli κ, μ, and μ'. These expressions are then used to compute $P_{\rm vol}$, $\kappa_{\rm vol}$, the pressure derivatives of the elastic moduli κ, μ, and μ', and the pressure-volume relations. The theoretical computations are compared with experimental results and with computations made using the full pseudopotential model; good agreement with both is obtained.

CONTRIBUTIONS TO THE ELASTIC MODULI

Milstein and Hill adopted the view that the bulk modulus κ and "the shear moduli μ and μ' provide a more direct, physically meaningful measure of the elastic response of cubic crystals at nonzero pressure"[16] than other moduli that have been discussed in the literature, where "κ is the ordinary bulk modulus, $-(\lambda/3)dP/d\lambda$, while μ and μ' are the usual shear moduli in the relations between the cubic-axes components of the Cauchy stress increment $\delta\sigma_{ij}$ and the rotationless strain increment $\delta\epsilon_{ij}$ (reckoned conventionally, relative to the *current* configuration);"[19] the term "current" refers to the cubic crystal at any given atomic volume Ω, under equilibrium pressure P; thus, P represents the external pressure required to hold the crystal at atomic volume Ω; at $P=0$, $\Omega=\Omega_0$; the stretch $\lambda=(\Omega/\Omega_0)^{1/3}$. Milstein and Hill[15,16] derived the following expressions for the structure-dependent contributions to κ, μ, and μ' (to our knowledge, the prior literature does not contain explicitly the lattice summations for μ and μ'):

$$3\kappa_{\rm str}=\frac{na}{2^3}\sum[(m_1^4+2m_1^2m_2^2)\phi''(r^2)]+P_{\rm str}\,, \tag{2}$$

$$\mu_{\rm str}=\frac{na}{2^4}\sum[(m_1^4-m_1^2m_2^2)\phi''(r^2)]-P_{\rm str}\,, \tag{3}$$

$$\mu'_{\rm str}=\frac{na}{2^3}\sum[m_1^2m_2^2\phi''(r^2)]-P_{\rm str}\,, \tag{4}$$

with

$$P_{\rm str}=-\frac{n}{4a}\sum m_1^2\phi'(r^2) \tag{5}$$

from which

$$\kappa_{\rm str}-2P_{\rm str}=\mu'_{\rm str}+\tfrac{2}{3}\mu_{\rm str}\,, \tag{6}$$

where a is the current lattice parameter; n is the number of atoms in a conventional cubic cell; the m_i are integers appropriate to the particular cubic lattice (the quantity $m_1+m_2+m_3$ must be even for each lattice site in an fcc crystal and the m_i are all even or all odd at each bcc site); the summations are over the allowed values of the indices m_i; $\phi'(r^2)$ and $\phi''(r^2)$ are, respectively, the first and second derivatives of ϕ with respect to r^2. Equations (2)–(6) are applicable to the crystal at any given atomic volume Ω. For the "special case" in which $E_{\rm bind}=E_{\rm str}$ (i.e., if $E_{\rm vol}$ is not included in the expression for the binding energy), Eq. (5) gives the total, externally applied pressure P (required for equilibrium) and Eqs. (2)–(4) give 3κ, μ, and μ', respectively, for the crystal under pressure P. In that case, Eq. (6) relates the pressure and crystal moduli, and furthermore, if $P=0$, $\kappa=\mu'+\frac{2}{3}\mu$ is equivalent to the Cauchy condition $C_{12}=C_{44}$.

If $E_{\rm bind}$ is given by Eq. (1), however, the following statements are valid for the crystal (at any given volume Ω).

(1) Equations (2)–(6) give the structural contributions (i.e., resulting from the pairwise interactions) to the total pressure P and crystal moduli κ, μ, and μ' for the crystal at atomic volume Ω.

(2) The total externally applied pressure P necessary for equilibrium of the crystal is given by

$$P=P_{\rm str}+P_{\rm vol}\,, \tag{7}$$

which follows from Eq. (1) and the relations $P=-dE_{\rm bind}/d\Omega$,

$$P_{\rm str}\equiv-\frac{dE_{\rm str}}{d\Omega}\ \text{and}\ P_{\rm vol}\equiv-\frac{dE_{\rm vol}}{d\Omega}\,.$$

($P_{\rm vol}$ is thus seen to be the contribution to the total pressure resulting from the volume-dependent part of the energy; it is usually attributed to the pressure resulting from the conduction electrons, although the development in the present section of this paper does not require a mechanistic model or particular mathematical form for $E_{\rm vol}$ apart from its explicit dependence upon Ω.)

(3) The bulk modulus κ of the crystal at volume Ω and pressure P is given by

$$\kappa=\kappa_{\rm str}+\kappa_{\rm vol}\,, \tag{8}$$

which follows from $\kappa=-\Omega dP/d\Omega$, $\kappa_{\rm str}\equiv-\Omega dP_{\rm str}/d\Omega$, $\kappa_{\rm vol}\equiv-\Omega dP_{\rm vol}/d\Omega$, and Eq. (7); $\kappa_{\rm vol}$ is thus the contribution to the bulk modulus κ resulting from the volume-dependent part of the binding energy.

(4) At any given atomic volume, the term $E_{\rm vol}$ does not contribute to the shear moduli μ and μ' of the crystal ($\mu_{\rm vol}=\mu'_{\rm vol}=0$); thus

$$\mu=\mu_{\rm str}\ \text{and}\ \mu'=\mu'_{\rm str}\,. \tag{9}$$

We can now substitute (7), (8), and (9) into (6) to obtain

$$\kappa_{\rm vol}-2P_{\rm vol}=\kappa-2P-\mu'-\tfrac{2}{3}\mu\,, \tag{10}$$

which gives the relation between the elastic moduli of the crystal (κ, μ, and μ'), the equilibrium pressure P applied to the crystal, and the contributions, κ_{vol} and P_{vol}, of the volume-dependent part of the binding energy to the bulk modulus κ and pressure P, respectively. Equation (10) is valid at arbitrary applied pressure P (and, of course, at $P=0$).

Equation (10) can be rewritten in terms of sets of elastic moduli C_{ij} using the following relations, derived by Hill and Milstein.[19] For the Green moduli

$$\kappa=\frac{\lambda}{3}(C_{11}+2C_{12})+\frac{P}{3},\quad \mu=\frac{\lambda}{2}(C_{11}-C_{12})-P\ ,$$
$$\mu'=\lambda C_{44}-P\ . \tag{11}$$

For the stretch moduli

$$\kappa=\frac{1}{3\lambda}(C_{11}+2C_{12})+\frac{2P}{3},\quad \mu=\frac{1}{2\lambda}(C_{11}-C_{12})-\frac{P}{2}\ ,$$
$$\mu'=\frac{C_{44}}{\lambda}-\frac{P}{2}\ . \tag{12}$$

For the Milstein moduli,

$$\kappa=\frac{1}{3\lambda}(C_{11}+2C_{12})+\frac{2P}{3},\quad \mu=\frac{1}{2\lambda}(C_{11}-C_{12})-\frac{P}{2}\ ,$$
$$\mu'=\frac{C_{44}}{\lambda^3}-P\ . \tag{13}$$

[Elastic moduli C_{ij} are defined according to

$$C_{ij}=\frac{1}{\Omega_0}\frac{\partial^2 E_{\text{bind}}}{\partial q_i \partial q_j}\ ,$$

where the q_i are any suitable set of geometric parameters. In Eq. (11) the q_i are the elements of the Green strain tensor; in Eq. (12) the q_i are the elements of the stretch tensor;[20] in Eq. (13) the q_i are the edges of the conventional cubic cell and their included angles. The C_{ij} depend upon the level of strain in the crystal and upon the choice of q_i. It is emphasized that Eqs. (11), (12), and (13) are model *independent*. Also, analogous sets of equations could be derived for other appropriate choices of q_i.] If we consider the case where the applied pressure P is zero ($\lambda=1$), substitution of Eqs. (11), (12), *or* (13) into Eq. (10) yields

$$\kappa_{\text{vol}}-2P_{\text{vol}}=C_{12}-C_{44}\ . \tag{14}$$

Equation (14) was derived earlier by Thomas,[21] but for the special case of fcc and bcc crystals in which E_{str} consists of nearest-neighbor interactions only and E_{vol} is given by terms of the form $C\Omega^n$ where C and n are constants. The present development shows that Eq. (14) is valid even with E_{str} containing arbitrarily long-range interactions and for arbitrary forms for E_{vol}. Furthermore, Eq. (10), which does not seem to have appeared in the prior literature, is a preferred form, since it is applicable at arbitrary pressure. (In order to relate $\kappa_{\text{vol}}-2P_{\text{vol}}$ to the C_{ij} under nonzero P, separate equations would be needed, in general, for each choice of geometric parameters q_i; thus, for the Green, stretch, and Milstein moduli, three distinct equations are needed.) Thomas correctly pointed out the error in the work of deLaunay;[3,10] evidently he and his followers had set $C_{12}-C_{44}$ equal to κ_{vol} alone; this error was also pointed out in papers by Cousins[22] and Bhatia.[2] The error results, in effect, from the unwarranted assumption that the contributions of E_{vol} to $\frac{1}{2}(C_{11}-C_{12})$ and to C_{44} are zero. If these contributions are designated as $\frac{1}{2}(C_{11_{\text{vol}}}-C_{12_{\text{vol}}})$ and $C_{44_{\text{vol}}}$, the nature of the error is made explicit by allowing Eqs. (11) to represent the volume-dependent parts, and setting $\mu_{\text{vol}}=\mu'_{\text{vol}}=0$, i.e.,

$$\tfrac{1}{2}(C_{11_{\text{vol}}}-C_{12_{\text{vol}}})=P_{\text{vol}}/\lambda,\quad C_{44_{\text{vol}}}=P_{\text{vol}}/\lambda\ . \tag{15}$$

Note that Eq. (15) applies specifically to the Green moduli; for the stretch moduli, from Eqs. (12),

$$\tfrac{1}{2}(C_{11_{\text{vol}}}-C_{12_{\text{vol}}})=\frac{\lambda P_{\text{vol}}}{2},\quad C_{44_{\text{vol}}}=\frac{\lambda P_{\text{vol}}}{2}\ , \tag{16}$$

and for the Milstein moduli, from (13),

$$\tfrac{1}{2}(C_{11_{\text{vol}}}-C_{12_{\text{vol}}})=\frac{\lambda P_{\text{vol}}}{2},\quad C_{44_{\text{vol}}}=\lambda^3 P_{\text{vol}}\ . \tag{17}$$

This illustrates that the quantities $\frac{1}{2}(C_{11_{\text{vol}}}-C_{12_{\text{vol}}})$ and $C_{44_{\text{vol}}}$ are not only nonzero, but their specific dependencies upon P_{vol} are not independent of the choice of variable q_i used in specifying strain. The above development further illustrates the physical and conceptual advantages of working with the set of moduli κ, μ, and μ' versus any of the sets C_{ij}, since it is specifically the shear moduli μ and μ' that are unaffected by E_{vol}, irrespective of its particular mathematical form. [Note that while E_{vol} does not contribute to μ and μ' for a cubic crystal *at a given volume*, the addition of an E_{vol} contribution to a crystal (previously described by an E_{str} contribution only) will change the equilibrium volume (and equilibrium pressure), in general, and that will of course affect the values of the shear moduli of the crystal.]

Our expressions for κ_{vol} and P_{vol} (which are often referred to as the bulk modulus and pressure of the electron gas) can be sharpened further if we consider that only nearest-neighbor interactions contribute to the $\phi''(r^2)$ summations in Eqs. (2)–(4); Eq. (5) may still retain an arbitrarily large number of terms, or may be truncated after any given number of terms are included. For an fcc crystal, Eqs. (2)–(4) then become

$$\begin{aligned}3\kappa_{\text{str}}&=8\sqrt{2}r_1\phi''(r_1^2)+P_{\text{str}}\ ,\\ \mu_{\text{str}}&=\sqrt{2}r_1\phi''(r_1^2)-P_{\text{str}}\ ,\\ \mu'_{\text{str}}&=2\sqrt{2}r_1\phi''(r_1^2)-P_{\text{str}}\ ,\end{aligned} \tag{18}$$

where r_1 is the current nearest-neighbor distance. Equations (6)–(10) are also valid in this "nearest-neighbor" approximation for κ_{str}, μ_{str}, and μ'_{str}; in addition, eliminating P_{str} and $r_1\phi''(r_1^2)$ from Eqs. (18) gives

$$3\kappa_{\text{str}}=9\mu'_{\text{str}}-10\mu_{\text{str}}\ . \tag{19}$$

Combining Eq. (19) with Eqs. (8) and (9), we have

$$\kappa_{\text{vol}}=\kappa-\tfrac{1}{3}(9\mu'-10\mu)\ , \tag{20}$$

at any pressure P. Substitution of Eq. (20) into (10) then yields

$$P_{\text{vol}}=2\mu-\mu'+P\ , \tag{21}$$

which is also valid at any pressure P. If we now consider the "special case," in which the (externally applied) equilibrium pressure P is zero, and substitute Eqs. (11), (12), or (13) into (20) and (21), we obtain

$$\kappa_{\text{vol}}=2C_{11}-C_{12}-3C_{44} \tag{22}$$

and

$$P_{\text{vol}}=C_{11}-C_{12}-C_{44}\ . \tag{23}$$

Equations (20) [or (22)] and (21) [or (23)] thus provide theoretical expressions relating the elastic moduli of fcc crystals to the volume-dependent contributions to κ and P [Eqs. (20) and (21) are to be preferred since they apply at arbitrary pressure P]. Furthermore, the relations can be used to compute theoretical values of κ_{vol} and P_{vol} from experimental values of the elastic moduli; some values are listed in Table I.

Table I reveals several interesting features that are understandable in terms of relatively simple, well-known concepts of atomic binding. Consider first the noble metals Cu, Ag, and Au. To a good approximation, the elastic properties and existence of close-packed crystal structures in these metals can be understood in terms of an essentially "hard-sphere" model, wherein E_{vol} contains the volumetric part of the electrostatic attraction between the ionic cores and the valence electrons, which is assumed to "force the atoms together," and E_{str} consists primarily of short-range, repulsive, d-band interactions between the relatively large, closed-shell, ionic cores of neighboring atoms. Thus, P_{vol} for these metals is negative. [Since P_{vol} is the contribution to the externally applied pressure P, a negative value of P_{vol} (at $P=0$) implies that the E_{vol} contribution "forces the atoms together" while the E_{str} part "pushes them apart;" negative values for P_{vol} in Table I thus imply repulsive interactions between the nearest-neighbor atoms.] Among the noble metals, the quantities κ_{vol}, P_{vol}, and $\kappa_{\text{vol}}/\kappa$ all increase with increasing atomic number; this behavior can be incorporated in the "core correction" to the electrostatic attraction between the ionic cores and the valence electrons, as is discussed in the following section. Likewise, the quantities κ_{vol}, P_{vol}, and $\kappa_{\text{vol}}/\kappa$ also increase with increasing atomic number among Ni, Pd, and Pt, which respectively, are the $3d$, $4d$, and $5d$ transition metals constituting the column of the Periodic Table adjacent to that of the noble metals. The fact that such monotonic behavior is not observed among the elastic moduli themselves (in both columns of the Period Table) lends support to the contention that the quantities κ_{vol} and P_{vol}, as specified by Eqs. (20) and (21) [or (22) and (23)], represent fundamental elastic properties of the metals. (Note, e.g., that C_{11} decreases from Cu to Ag but increases from Ag to Au or that μ decreases from Ni to Pd but increases from Pd to Pt.) Interpretation of the P_{vol} values for Ni, Pd, and Pt is more complicated owing to additional attractive interactions between what are evidently nearly filled d shells. However, it may be presumed that, for each of these metals, these interactions cause increased attraction between ion cores (relative to the respective noble metal, in the same row of the Periodic Table). Thus, one would expect P_{str} (which is positive algebraically and therefore repulsive for the noble metals) to be less for Ni than for Cu, less for Pd than for Ag, and

TABLE I. Elastic moduli and properties calculated from Eqs. (10), (20), and (21) at atmospheric pressure (i.e., $P=0$) for fcc metals. The moduli are from Refs. 31 and 32 and are in units of 10^{12} dyn/cm^2.

Crystal	Temperature (K)	C_{11}	C_{12}	$\mu'=C_{44}$	μ	κ	$\kappa_{\text{vol}}-2P_{\text{vol}}$	κ_{vol}	P_{vol}	$\kappa_{\text{vol}}/\kappa$
Cu	0	1.762	1.249	0.818	0.2565	1.420	0.431	−0.179	−0.305	−0.126
	300	1.684	1.214	0.754	0.235	1.371	0.460	−0.108	−0.284	−0.079
Ag	0	1.315	0.973	0.511	0.171	1.087	0.462	0.124	−0.169	0.114
	300	1.240	0.937	0.461	0.1515	1.038	0.476	0.160	−0.158	0.154
Au	0	2.016	1.697	0.454	0.1595	1.803	1.243	0.973	−0.135	0.540
	300	1.923	1.631	0.420	0.146	1.728	1.211	0.955	−0.128	0.553
Ni	0	2.612	1.508	1.317	0.552	1.876	0.191	−0.235	−0.213	−0.125
	300	2.508	1.500	1.235	0.504	1.836	0.265	−0.189	−0.227	−0.103
Pd	0	2.341	1.761	0.712	0.290	1.954	1.049	0.785	−0.132	0.402
	300	2.271	1.760	0.717	0.2555	1.930	1.043	0.631	−0.206	0.327
Pt	0	3.580	2.536	0.774	0.522	2.884	1.762	2.302	0.270	0.798
	300	3.467	2.507	0.765	0.480	2.827	1.742	2.132	0.195	0.754
Al	0	1.143	0.619	0.316	0.262	0.794	0.303	0.719	0.208	0.906
	300	1.068	0.607	0.282	0.2305	0.761	0.325	0.683	0.179	0.898
Pb	0	0.555	0.454	0.194	0.0505	0.488	0.260	0.074	−0.093	0.152
	300	0.495	0.423	0.149	0.036	0.447	0.274	0.120	−0.077	0.268

less for Pt than for Au; the converse would be true for P_{vol}, since $P_{\text{vol}}=-P_{\text{str}}$ at zero external pressure. For the 0-K data, this is indeed the case, as is seen in Table I (i.e., P_{vol} is greater for Ni than for Cu, etc.).

The element Al presents a particularly interesting case; Al is known to be highly isotropic, i.e., $\mu/\mu'\approx 1.0$. However, in view of Table I, perhaps a more fundamental statement of aluminum's elastic properties is that $\kappa_{\text{vol}}\approx\kappa$, or [from Eq. (20)] $\mu/\mu'\approx 0.9$. (For Al at 0 and 300 K, respectively, $\mu/\mu'=0.83$ and 0.82.) The large contribution of κ_{vol} to κ and the positive value of P_{vol} in Al can be understood qualitatively from aluminum's relatively high valence and small, closed-shell ionic core (i.e., that of the Ne configuration), which evidently result in a zero-pressure equilibrium volume in which the nearest-neighbor ionic cores are well separated. Thus, the bulk modulus of Al is mainly determined, not by the repulsive interactions between neighboring ion cores, but by the distribution of the valence electrons which are scattered by the lattice of ion cores in the crystal. This evidently causes the elastic behavior of Al to be anomalous (when compared with most other fcc crystals); for example, most fcc crystals exhibit a negative Poisson ratio in [110] uniaxial loading,[23] whereas Al does not; and most fcc crystals exhibit upward concavity of the initial stress-strain curve in [100] uniaxial loading, but Al does not.[24] In view of the above considerations, presumably the fcc metals Ca and Sr would behave elastically similarly to Al. (Elastic constant data for Sr and Ca could not be found in any of our "usual" handbooks.) It is also interesting to note in Table I that the behavior of P_{vol} and $\kappa_{\text{vol}}/\kappa$ for the noble metals tends toward that of Al as the atomic number of the metals increases; this behavior occurs even more markedly in the group Ni, Pd, and Pt. This tendency (toward the elastic behavior of Al) evidently is also reflected in other elastic properties; e.g., consider the aforementioned Poisson ratio, which is given by[23]

$$\nu_{1\bar{1}0}=(R-2C_{44})/(R+2C_{44})\ ,$$

where

$$R=C_{11}+C_{12}(1-2C_{12}/C_{11})$$

($\nu_{1\bar{1}0}$ is the negative of the ratio of strain in the $[1\bar{1}0]$ direction to the strain in the [110] direction under [110] uniaxial load); for Cu, Ag, and Au at 0 K, $\nu_{1\bar{1}0}=-0.138$, -0.093, and -0.029, respectively; for Ni, Pd, and Pt at 0 K, $\nu_{1\bar{1}0}=-0.051$, 0.010, and 0.240, respectively ($\nu_{1\bar{1}0}=-0.048$ for Pd at 300 K); for Al at 0 K, $\nu_{1\bar{1}0}=0.267$.

Finally, it is noted that the behavior of Pb is most like that of Cu, Ag, and Ni (and to a lesser extent Au and Pd) in that P_{vol} is negative and $\kappa_{\text{vol}}/\kappa$ is relatively small. For these metals, neglect of κ_{vol} in Eq. (20) gives $\kappa=\frac{1}{3}(9\mu'-10\mu)$ or from Eq. (21), $C_{44}=\frac{1}{3}(2C_{11}-C_{12})$; this condition is more accurately fulfilled for fcc crystals, in general, than is the well-known Cauchy relation $C_{44}=C_{12}$.[18]

For bcc crystals, computations[15–17] with a variety of potential functions ϕ have shown that next-nearest neighbors make relatively large contributions to the moduli (especially to μ); thus, for bcc, it is necessary to include at least second-nearest neighbors to determine κ_{vol} and P_{vol}. The leading terms in the expansions for the structure-dependent part of the bcc crystal's moduli are[15,16]

$$3\kappa_{\text{str}}=4\sqrt{3}r_1[\phi''(r_1^2)+\tfrac{4}{3}\phi''(\tfrac{4}{3}r_1^2)]+P_{\text{str}}\ , \tag{24}$$

$$\mu_{\text{str}}=\frac{8r_1}{\sqrt{3}}[0\phi''(r_1^2)+\phi''(\tfrac{4}{3}r_1^2)]-P_{\text{str}}\ , \tag{25}$$

$$\mu'_{\text{str}}=\frac{4r_1}{\sqrt{3}}[\phi''(r_1^2)+0\phi''(\tfrac{4}{3}r_1^2)]-P_{\text{str}}\ . \tag{26}$$

However, here we are unable to eliminate P_{str} and the ϕ'' terms without assuming a particular form for ϕ (e.g., Born-Meyer, Morse, Lennard-Jones, etc.), and thus, for the bcc crystals, we do not attempt to formulate separate equations for κ_{vol} and P_{vol}, independent of the form of ϕ, as was done for the fcc crystals [Eqs. (20)—(23)].

INTERATOMIC POTENTIALS FOR THE NOBLE METALS

Work by Harrison[25] and Moriarty[26] has allowed pseudopotential theory to be applied to d-band metals. The binding energy per atom E_{bind} is written as

$$E_{\text{bind}}=E_{\text{FE}}+E_{\text{es}}+E_{\text{BS}}+E_{\text{ol}}\ , \tag{27}$$

where the four terms on the right-hand side of Eq. (27) are, respectively, the free-electron energy, the electrostatic energy, the band-structure energy, and the overlap energy. Thomas[27] employed such a model in his computations of the third-order elastic moduli of copper and silver; he used five model adjusting constants to fit experimental values of the binding energy, lattice parameter, and the three second-order elastic constants C_{ij} of these metals. (An attempt to apply the five-parameter fitting procedure to gold was unsuccessful; in view of the preceding section of the present paper, this difficulty seems to be connected with the relatively large value of $\kappa_{\text{vol}}/\kappa$ for Au.) Thomas found good agreement between computed and experimental third-order elastic constants. He also found that the E_{ol} term (which he approximated as a nearest-neighbor summation of Born-Mayer repulsive interactions) made the dominant contributions to the elastic moduli; this is consonant with our findings in Table I that P_{vol} is negative and $\kappa_{\text{vol}}/\kappa$ is small for these metals. Similarly, Hiki and Granato,[28] in their explanation of their higher-order elastic constant experimental data, suggested that the closed-shell repulsive interaction between nearest-neighbor atoms makes the dominant contribution to the higher-order constants in the noble metals (particularly in Cu). Thomas's pseudopotential calculations and the discussion of Hiki and Granato of the fitting of elastic constant data to interatomic potentials led Johnson[29] to model the elastic properties of Cu using Born-Mayer repulsion between atoms plus a single volume-dependent energy term of the form $C\Omega^n$, where C and n are constants; using a value of $n=\frac{1}{2}$, he was able to obtain reasonably good fits to experimental values of the second-order elastic constants C_{ij} and to three combinations of third-order elastic constants C_{ijk} for Cu. (Johnson did not mention whether or not he had attempted to describe Ag and/or Au in this manner.)

The above discussion suggests that simplified interatomic potentials that have a basis in pseudopotential theory can be developed for the noble metals. First, consider the volumetric parts of the binding energy. The electrostatic energy of interaction of a lattice of positive ion cores (treated as point ions) with the valence electrons (treated as a uniform negative background) is written as

$$E_{\mathrm{es}}^{*}=-\frac{\beta z^{2}}{\Omega^{1/3}}\ , \tag{28}$$

where z is the valence and β is a constant that depends upon the specific crystal structure. The effect of the finite-ion core size on the electrostatic attraction between the ion cores and valence electrons can be taken into account using a Heine-Abarenkov bare ion potential.[30] If the ionic core is assumed to have a radius R_m, outside of the core a valence electron is attracted to the core through Coulombic attraction, giving an interaction energy of $-2z/r$. Inside the core, however, owing to the repulsion from the core electrons, the magnitude of the interaction energy between the valence electron and the ion core is reduced to a constant value $-A_0$. This reduction in electrostatic energy can be accounted for by a core correction term of the form

$$E_{\mathrm{CC}}=\frac{\alpha z^{2}}{\Omega}\ , \tag{29}$$

where α is a constant given by

$$\alpha=(4\pi/3)R_m^2(2u+3)$$

with $u=-A_0R_m/2z$.

In addition to correcting for the finite size of the ion cores, it would appear, as mentioned in the preceding section, to be important to correct the electrostatic energy to account for valence-electron scattering by the ion core lattice, which leads to the "piling up" of valence-electron charge. The energy contribution resulting from this scattering is typically called the band-structure energy, and its computation generally requires summations in reciprocal space, owing to the long-range nature of the interaction. Such calculations involve analytic and computational complexities that we seek to avoid in the present model. That this is a reasonable goal, at least for Cu and Ag, is indicated by Thomas's computations, which included the band-structure corrections and showed that the dominant contributions to the elastic constants comes from the overlap energy, while the contributions from the band-structure energy tended to cancel with the structure-dependent contributions from the electrostatic energy. This would suggest that the band-structure energy contribution might be neglected, if at the same time the structure-dependent contributions to the electrostatic energy are also neglected; that is, if E_{es} is treated as a completely volume-dependent term, with the structure coefficient β being considered an adjustable constant. This procedure would thus eliminate the computational complexities associated with calculating the band-structure energy contribution and the structure-dependent part of the electrostatic energy. (Of course, this is not to say that the band-structure contributions are unimportant; for example, owing to small differences between the energies of the fcc and hcp structures, band structure is no doubt crucial to determining crystal structures.)

The volume-dependent part of the binding energy can then be written as

$$E_{\mathrm{vol}}=E_{\mathrm{FE}}+E_{\mathrm{es}}^{*}+E_{\mathrm{CC}}\ , \tag{30}$$

where E_{FE} (which includes the kinetic, exchange, and correlation contributions to the energy of the free-electron gas) is given by a standard form, i.e.,

$$E_{\mathrm{FE}}=z[\,5.742(z/\Omega)^{2/3}-1.477(z/\Omega)^{1/3}-0.031\ln(z/\Omega)^{1/2}-0.130]\ . \tag{31}$$

(The units are rydbergs and Bohr radii a_0 for energies and lengths, respectively.)

Finally, the overlap energy, expressed (as usual) as a summation over Born-Mayer repulsive interactions, is taken to be synonymous with the structural part of the binding energy, i.e.,

$$E_{\mathrm{str}}=E_{\mathrm{ol}}=\tfrac{1}{2}\sum_{r}Ae^{-B(r/r_1-1)}\ , \tag{32}$$

where the r values are the distances between the origin atom and its neighbors, A and B are adjustable parameters, and r_1 is the nearest-neighbor distance. [Although three constants A, B, and r_1 appear in the Born-Mayer interaction (as it is normally written), there are of course only two "real" adjustable parameters, $A'\equiv Ae^{B}$ and $B'\equiv B/r_1$.] The total binding energy per atom is then

$$E_{\mathrm{bind}}=E_{\mathrm{FE}}+E_{\mathrm{es}}^{*}+E_{\mathrm{CC}}+E_{\mathrm{ol}}\ , \tag{33}$$

where the asterisk on the electrostatic term indicates that it is treated as completely volume dependent.

TABLE II. Values of the model-adjusting constants for the noble metals in the present simplified model [Eqs. (28)—(33)]. For comparison, three of the five model-adjusting constants are also listed for Cu and Ag for the full pseudopotential model (Ref. 27).

Element	α (Ry a_0^3)	β (Ry a_0)	A (10^{-3} Ry)	B	Reference
Cu	5.3344	4.1859	6.6397	13.167	present work
Ag	36.823	7.4018	4.6598	14.697	present work
Au	144.26	20.638	3.2660	16.297	present work
Cu	2.92		4.62	14.95	27
Ag	22.41		4.21	15.26	27

The binding energy per atom, as given by Eqs. (28)–(33), contains four adjustable constant, i.e., α, β, A, and B. We matched these four constants to the experimental values of the three 0-K elastic moduli given in Table I and lattice parameters (3.6153, 4.0856, and 4.0783 Å, respectively) for Cu, Ag, and Au; the values of these model adjusting constants are given in Table II, together with the "comparable values" based upon the full pseudopotential fit.[27] The parameters α, β, and B increase while A decreases with increasing atomic number. Table III shows the contributions of the individual energy terms to the total pressure P and bulk modulus κ of these metals in the framework of the present model; these terms are

$$P_{\mathrm{FE}}=-\frac{dE_{\mathrm{FE}}}{d\Omega},\quad P_{\mathrm{CC}}=-\frac{dE_{\mathrm{CC}}}{d\Omega},\quad P_{\mathrm{es}}^{*}=-\frac{dE_{\mathrm{es}}^{*}}{d\Omega},$$

$$P_{\mathrm{vol}}=P_{\mathrm{FE}}+P_{\mathrm{CC}}+P_{\mathrm{es}}^{*},\quad P_{\mathrm{str}}=-\frac{dE_{\mathrm{ol}}}{d\Omega},$$

$$P=P_{\mathrm{vol}}+P_{\mathrm{str}},\quad \kappa_{\mathrm{FE}}=-\Omega\frac{dP_{\mathrm{FE}}}{d\Omega},\quad \kappa_{\mathrm{CC}}=-\Omega\frac{dP_{\mathrm{CC}}}{d\Omega},$$

$$\kappa_{\mathrm{es}}^{*}=-\Omega\frac{dP_{\mathrm{es}}^{*}}{d\Omega},\quad \kappa_{\mathrm{vol}}=\kappa_{\mathrm{FE}}+\kappa_{\mathrm{CC}}+\kappa_{\mathrm{es}}^{*},$$

$$\kappa_{\mathrm{str}}=-\Omega\frac{dP_{\mathrm{str}}}{d\Omega},\quad \text{and } \kappa=\kappa_{\mathrm{vol}}+\kappa_{\mathrm{str}},$$

the derivatives are all taken at $\Omega=\Omega_0$ (for the values listed in Table III). The values of P_{vol} and κ_{vol} are slightly different in Table I from those in Table III; this is because for Table III the summation in Eq. (32) was summed to convergence, rather than just over nearest neighbors [that this difference is very small somewhat supports the use of the nearest-neighbor approximation in determining Eqs. (20)–(23) in the preceding section]. Values of $\kappa_{\mathrm{vol}}-2P_{\mathrm{vol}}$ based upon Table III of course agree with those in Table I, since the derivation of Eq. (10) did not limit E_{str} to nearest-neighbor interactions only. The approximate canceling of the net contributions of κ_{FE}, κ_{CC}, and κ_{es}^{*} is seen for Cu and Ag, but not for Au (as, of course, was expected from the values of $\kappa_{\mathrm{vol}}/\kappa$ in Table I).

TABLE III. Contributions of the individual energy terms to the pressure and bulk modulus of the noble metals at zero pressure and temperature; the units are 10^{12} dyn/cm^2.

	Cu	Ag	Au
P_{FE}	0.151	0.064	0.065
P_{CC}	0.123	0.408	1.616
P_{es}^{*}	-0.597	-0.647	-1.818
P_{vol}	-0.323	-0.175	-0.137
P_{str}	0.323	0.175	0.137
P	0	0	0
κ_{FE}	0.334	0.159	0.160
κ_{CC}	0.246	0.816	3.233
κ_{es}^{*}	-0.796	-0.863	-2.424
κ_{vol}	-0.216	0.112	0.969
κ_{str}	1.636	0.975	0.834
κ	1.420	1.087	1.803

As a further test of the efficacy of the simplified potentials for the noble metals, we used the potentials to compute theoretical pressure-volume relations and the first

TABLE IV. Pressure derivatives of the bulk and shear moduli κ, μ, and μ' of the noble metals.

Element	$d\kappa/dP$	$d\mu/dP$	$d\mu'/dP$	$d^2\kappa/dP^2$	$d^2\mu/dP^2$ (10^{-12} dyn/cm^2)	$d^2\mu'/dP^2$	Footnote
Cu	5.57	0.80	2.66	-4.1	-0.85	-2.4	a
	5.80	0.92	2.58	-3.6	-0.69	-1.3	b
	5.44	0.38	2.63				c
	8.07	0.70	2.43				d
	5.3						e
Ag	5.48	0.78	2.42	-4.0	-0.62	-1.5	a
	5.73	0.80	2.07	-4.9	-0.61	-0.84	b
	4.11	0.76	3.04				c
	5.96	0.64	2.27				f
	5.1						e
Au	4.66	0.49	1.43	-1.0	0.14	0.56	a
	5.21	0.38	1.52				c
	6.43	0.44	1.79				g
	4.6						e

[a] Computed in the present study using Eqs. (28)–(33).

[b] Computed in the present study using the pseudopotential model developed by Thomas (Ref. 27).

[c] Experimental at 300 K, Ref. 28.

[d] Experimental at 4.2 K, determined in Ref. 27 from data in Ref. 33.

[e] Experimental at 300 K, Ref. 34.

[f] Experimental at 77 K, Ref. 35.

[g] Experimental at 300 K, Ref. 36.

and second pressure derivatives of the elastic moduli κ, μ, and μ', and compared the results with available experimental data and with the results of analogous computations using the full pseudopotential model. These comparisons are summarized in Table IV and Figs. 1(a), 1(b), and 1(c). The theoretical values of the pressure derivatives of the elastic moduli (i.e., the first two rows for the elements Cu and Ag and the first row for Au in Table IV) were determined by computing the moduli themselves as a function of pressure and taking numerical derivatives of the data in the neighborhood of the zero-pressure state; this was done for both the simplified model and the full pseudopotential model. (Numerical accuracy was such that the number of significant figures far exceeded those listed in Table IV.) The values computed for the first derivatives with the full pseudopotential model agree well with those reported by Thomas;[27] small differences occur, evidently because we summed E_{0l} to converge and Thomas used nearest neighbors only (e.g., for $d\kappa/dP$ of Ag, we obtained 5.73 for the full pseudopotential result whereas Thomas reported 5.72).

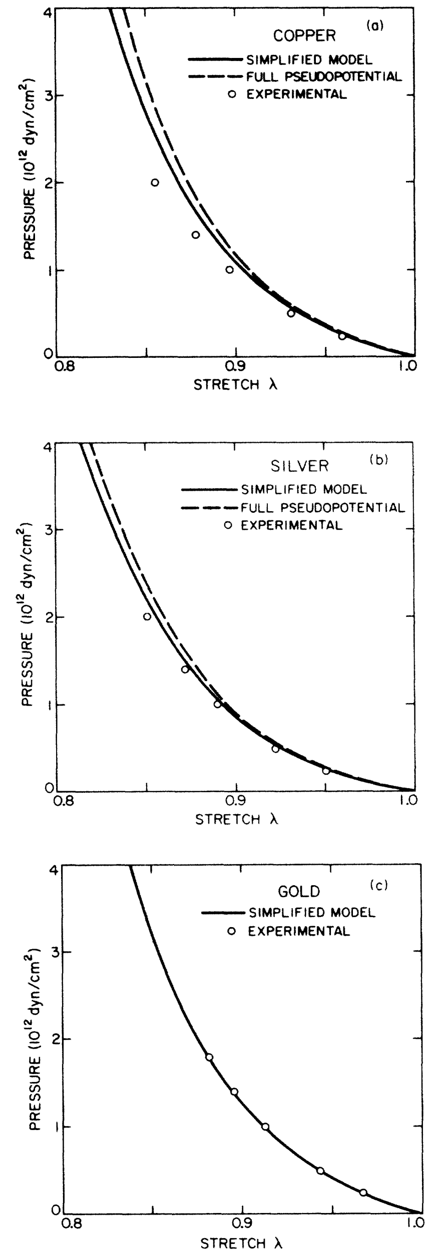

FIG. 1. Theoretical and experimental pressure versus stretch $[\lambda=(\Omega/\Omega_0)^{1/3}]$ relations; the theoretical results were computed in the present study using Eqs. (28)—(33) ("simplified model") and using the pseudopotential model presented in Ref. 27 ("full pseudopotential"); the experimental data are from Refs. 37 and 38. (a) copper; (b) silver; (c) gold.

In recent years, a variety of investigators have employed various simplified models and theoretical techniques to study bonding and related properties of metals. Rose *et al.*[39] studied "universal features of the equation of state of metals," and obtained a scaling relation from which zero-temperature equations of state and first derivatives of bulk modulus with respect to pressure were calculated. For Cu, Ag, and Au, respectively, they obtained $d\kappa/dP=4.99$, 5.55, and 6.18. For Cu and Ag, there is reasonably good agreement with our values in Table IV, but for Au, there is about a 30% discrepancy. Barnett *et al.*[40] modeled multilayer relaxation at metal surfaces using a model in which the total energy is expressed as a sum of the ground-state electron-gas energy, the Madelung electrostatic energy of point ions in the presence of a semi-infinite negative neutralizing background, the interaction of point ions with the surface dipole layer, and the Hartree and band-structure contributions. In the evaluation of the latter contributions, they used the local form of the Heine-Abarenkov model pseudopotential. They compared their computational results with those of simpler models (e.g., the PITB model, consisting of point ions in the presence of a truncated bulk electron density), and concluded that the multilayer relaxation phenomena predicted by the simple electrostatic models do occur when electron response is included properly. For bcc metals, Finnis and Sinclair[41] constructed an empirical model consisting of a bonding term, which is the square root of a site density, summed over atoms, and a summation over repulsive, pairwise terms. They defined their potential by fitting to experimental data for a perfect crystal, taking into account first- and second-neighbor atoms. The model successfully accounted for experimental vacancy-formation energies. Daw and Baskes[42] developed an embedded-atom method, based upon density-functional theory, as a means of calculating ground-state properties of metals. They obtained the embedding energy and associated pair potentials semiempirically for Ni and Pd, and found that a simple embedding energy and a short-ranged pair potential (nearest neighbors only) were sufficient to give reasonable fits to several properties of the bulk crystals (e.g., lattice parameter and elastic constants) and to calculate energies and geometries of defects. They emphasized problems with hydrogen and with surfaces which could not be treated with pair potentials alone. They concluded that the embedded-atom method gives a reasonable description of metallic cohesion and ground-state impurity energies.

In this section of the present paper we proposed to formulate simplified models (for the noble metals) that can provide accurate descriptions of elastic properties (both harmonic and anharmonic). The specific format for the models is suggested by pseudopotential theory; four empirical parameters were adjusted so that the theoretical values of the second-order elastic constants and lattice parameters fit the respective 0-K experimental values. The models were then used to compute various anharmonic properties [Table IV and Figs. 1(a), 1(b), and 1(c)]; the computed values are fairly close to experimental values and to those computed using the full pseudopotential model (in some respect the simplified model computations are in better agreement with experiment than those made with the full pseudopotentials). Finally, in addition to the increased computational simplicity, there is the "added bonus" of having obtained an interatomic potential model for gold, which was unfittable in the pseudopotential scheme of Ref. 27.

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