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Elastic constants of the transition metals from a uniform electron gas

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The trends in the elastic constants of the simple and transition elemental cubic metals are explained in terms of a uniform electron-gas theory. Recently, the bonding energetics of elemental metals were systematized using a new uniform electron-gas model. Dubbed the "ideal metal," this model stems from a physical interpretation of the process of cleaving the positive background, and posits that no forces act on the background in the uniform state. Previously, this new model was used to show that the cohesive energies of the elemental transition metals depend primarily on the bonding valence and the average electron density at the boundary of the unit cell. Here, we use a slight modification of the same model to show that the elastic constants of the elemental cubic metals depend primarily on the bonding valence, the density at the cell boundary, and the symmetry of the lattice.

I. INTRODUCTION

The last two decades have seen a great advance in our ability to compute the energetics and ground-state structures of the elemental metals. The digital computer combined with density-functional theory and the local-density approximation now allow not only the computation of the cohesive energy of the elemental metals, but also the very small differences in energies that determine the particular symmetry of the ground-state lattice. Our ability to compute such detailed properties continues to expand rapidly and is paying great dividends. However, as remarked by Wigner and Seitz[1] in their famous quote concerning a great calculating machine, "It would be preferable instead to have a vivid picture of the behavior of the wave functions, a simple description of the essence of the factors which determine cohesion and an understanding of the origins of variation in properties from metal to metal." It is the purpose of this paper to contribute to the qualitative picture envisioned in the quote. Previously it has been shown that a model based on the electron gas explains the trends in the cohesive energies of the elemental metals.[2] In this paper we show that a simple extension of this uniform electron-gas model also explains the trends in the elastic constants of the simple and transition metals.

The jellium model of the electron gas has long been used to understand the qualitative trends in the plasmon[3] and electron-hole excitation spectra of elemental metals. The calculated spectra agree semiquantitatively with experiment for simple metals, and are qualitatively useful for the transition metals. One is used to thinking that the excitations of quantum systems are harder to predict than ground-state properties. From this point of view, it is surprising that the jellium model has not provided a similarly simple explanation for the trends in the ground-state energetics (e.g., the cohesive and surface energies) of the elemental metals. Recently, this conundrum has been cleared up and two closely related uniform-electron-gas models have been introduced that explain the systematics of the ground-state energetics of the elemental metals. These models were dubbed the "ideal metal" by the present authors,[2,4,5] and "pressure stabilized jellium" by Perdew, Tran, and Smith.[6] Both models modify jellium so zero force acts on the positive background in the uniform state. Trends for the ground-state energetics of the elemental metals then follow. For example, the theory of ideal metals reproduces, semiquantitatively, the cohesive energies, work functions, and chemical potentials of both the transition and simple metals.[2] It also explains the trends in the surface energies and bulk moduli of the simple metals.[4,5]

The theory of ideal metals was constructed by considering the cleavage of the electron gas and insisting that no forces act on the positive background in the uniform state. Cleavage is defined as splitting the positive background into pieces that can be separated or overlapped, each piece having the original constant density. The condition of zero force is not satisfied when the conventional electron gas is cleaved. For $r_s < 4.0$, the background pieces would spontaneously move apart, since the electrons in jellium are under pressure. Here, $4\pi a^3 r_s^3/3 = 1/\bar{n}$, where a is the radius of the Bohr orbit and $\bar{n}$ is the uniform equilibrium electron density. The theory of ideal metals introduces an *ad hoc* interaction between the electrons and the background, in addition to the conventional electrostatic interaction. The strength of this interaction is chosen so that the condition of zero force is satisfied. The *ad hoc* interaction is described by an additional electron potential, which is proportional to the background density, $n_b(\mathbf{r})$. In the uniform state, the background density is constant and so, consequently, is the *ad hoc* interaction potential. For nonuniform (inhomogeneous) systems the background density varies with position and the new potential gives rise to forces. The total external electron potential $v_{\text{ext}}(\mathbf{r})$ is given explicitly by

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$$v_{\text{ext}}(\mathbf{r})=\phi(\mathbf{r})+v_0 n_b(\mathbf{r})/\bar{n}\ , \tag{1}$$

where $\phi(\mathbf{r})$ is the usual electrostatic potential. The strength of the *ad hoc* interaction v_0 is uniquely fixed by the condition of zero forces for the uniform state, and is given explicitly (below) in terms of the energy of bulk jellium. The additional potential can be interpreted in terms of an electrostatic model that associates a δ-function dipole barrier of uniform strength with the cleaved surface of the background.[2,4]

The ideal metal has a simple, known, many-body Hamiltonian, since all interactions between the electrons and the positive background are specified by the external potential of Eq. (1). Consequently, many-body calculations for adsorbate line shapes, surface plasmons, etc., can be defined in terms of this Hamiltonian. For example, Ainsworth and Krotscheck[7] have recently used this model Hamiltonian to estimate the surface energies of the simple metals beyond the local-density approximation, using the Fermi hypernetted-chain method.

Several works have related the electron gas to the bulk moduli of the metals. Morruzzi, Janak, and Williams[8] computed the electronic ground-state densities of the elemental metals through the 4*d* series using the local-density approximation to density-functional theory. They noted that the bulk modulus of jellium, calculated for the electron density at the cell boundary, roughly predicted (within a factor of 2) the bulk moduli of these metals (except for the alkali metals). Perdew, Tran, and Smith[6] estimated the bulk moduli for "pressure stabilized jellium" as follows. They retained a uniform positive background whose density varied as the metal was compressed, ignored the effects of cleavage, and set the effective charge per atom equal to one for all metals. This procedure provided a systematic correlation with the experimental bulk moduli. Finally, the present authors presented preliminary results for the bulk moduli of the simple metals.[5] We used the ideal metal model, which systematically incorporates cleavage, and obtained semiquantitative agreement with experiment.

In this paper, we use electron-gas theory to calculate the elastic constants of the elemental cubic metals through the 5*d* transition series and compare them to experiment. The theory of ideal metals provides reasonable agreement for the simple metals. It predicts the overall size of the elastic constants, the relative ordering of the elastic constants $C_{11}>C_{12}>C_{44}$, as well as the dependence of the elastic constants on the electron density and the bonding valence.

Elastic constants calculated from the theory of ideal metals, as presently formulated, are too small for transition metals by up to a factor of 5. However, it is possible to modify the theory in such a way that semiquantitative agreement is obtained for the transition metals, as well as the simple metals. This modification redefines the *ad hoc* additional potential, so that it depends on the electron density, as well as the background density. On the one hand, this change has the following costs. First, the modification to the theory of ideal metals is not forced by any internal considerations of the model. Consequently, it requires an undetermined parameter β (a single number), which is chosen to provide the best overall fit between the model and experiment. Second, the new model is defined in terms of an energy-density functional, and the corresponding many-body Hamiltonian is unavailable. On the other hand, the new model has the following benefits. The revised model provides semiquantitative estimates for the elastic constants of the cubic elemental metals, and provides an elementary method for understanding the trends in these quantities.

The structure of this paper is as follows. In Sec. II, we do the following: Review the theory of ideal metals; modify it for transition metals, and detail the calculation of the elastic constants. In Sec. III, we present and discuss the results. The paper is concluded with a summary.

II. IDEAL METAL AND ELASTIC CONSTANTS

We review the theory of ideal metals and calculate the elastic constants of cubic elemental metals. In Sec. II A, we first describe the many-body Hamiltonian appropriate to the unmodified theory of ideal metals, in the Born-Oppenheimer approximation. Next, we describe the theory of ideal metals in terms of an energy-density functional, which we modify to improve agreement for the transition metals. In Sec. II B, we calculate the energy change due to a specified lattice strain using second-order perturbation theory and the electronic potential-density response function of the uniform system. The energy evaluation is similar to the widely used pseudopotential perturbation method. Finally, in Sec. II C, we describe the extraction of the elastic constants from the change in the energy.

A. Hamiltonian, energy functional and response function

The theory of ideal metals can be understood by starting with an electron gas that has a uniform electron and background density $\bar{n}$, cleaving the background into pieces with density $\bar{n}$, and requiring that no net forces act on the pieces of positive background in the uniform state. The zero-force condition is achieved by introducing an additional *ad hoc* "electron-ion" potential, which at a point $\mathbf{r}$ is proportional to the background density at that point, and is defined in Eq. (1). The strength of the additional potential is determined by the zero-force condition, and is given by[2,4]

$$v_0=-\bar{n}\left.\frac{\partial e_{\text{jell}}}{\partial n}\right|_{\bar{n}}\ . \tag{2}$$

Here, e_{jell} is the energy per electron in uniform jellium of density n.

The Born-Oppenheimer approximation yields the following many-body Hamiltonian for the unmodified theory of ideal metals:

$$\begin{aligned}H=&-\frac{\hbar^2}{2m}\sum_i \nabla_i^2+\frac{e^2}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\\&+\frac{e^2}{2}\int\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{n_b(\mathbf{r})n_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\&-e^2\sum_i\int d^3\mathbf{r}\frac{n_b(\mathbf{r})}{|\mathbf{r}_i-\mathbf{r}|}+v_0\sum_i\frac{n_b(\mathbf{r}_i)}{\bar{n}}\ .\end{aligned} \tag{3}$$

Here, m and e and $\mathbf{r}_i$ are the mass, charge and coordinates of the electrons. From here on, we will use Rydberg units with $e^2=2$, $\hbar=1$, and $m=1$.

The *ad hoc* potential v_0 has the following electrostatic interpretation. We assume that cleavage not only splits the positive background into pieces of uniform positive charge, but also causes an *ad hoc* δ-function dipole barrier of uniform strength at the surface. The δ-function dipole causes a constant potential change v_0 for electrons inside an isolated piece of background, and zero potential change for electrons outside. Now, imagine overlapping or separating the pieces of background charge. The background density $n_b(\mathbf{r})$ is obtained by summing the background density of the pieces that overlap at $\mathbf{r}$. Some consideration shows that the total potential change at a point $\mathbf{r}$ due to the dipole barriers is proportional to $n_b(\mathbf{r})$ in this electrostatic model. Finally, the strength of the dipole barrier is determined by the zero-force condition, Eq. (2).

A density functional for the energy can also be used to describe the theory of ideal metals in the Born-Oppenheimer approximation. Formally,

$$E[n_e,n_b]=T_s[n_e]+\int\int d^3\mathbf{r}'d^3\mathbf{r}\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{xc}}[n_e]+E_{\mathrm{ei}}[n_e,n_b]\ . \tag{4}$$

Here, $\rho=n_e-n_b$ denotes the net charge. E_{xc} denotes the exchange-correlation energy, while T_s denotes the kinetic energy of noninteracting electrons. The second term on the right-hand-side denotes the classical electrostatic energy and is the only contribution to the electron-ion interaction in jellium. Finally, the last term on the right-hand side models electron-ion interactions beyond the classical electrostatic interaction. It is given, for the unmodified ideal metal by

$$E_{\mathrm{ei}}[n_e,n_b]=\frac{v_0}{\bar{n}}\int d^3\mathbf{r}\,n_b(\mathbf{r})n_e(\mathbf{r})\ . \tag{5}$$

We modify the theory of ideal metals by introducing the following, more general form for the electron-ion interaction

$$E_{\mathrm{ei}}[n_e,n_b]\approx\int d^3\mathbf{r}\,n_e(\mathbf{r})\left\{v_0\frac{n_b(\mathbf{r})}{\bar{n}}\left[1-\frac{1}{2}\beta^2\frac{[n_e(\mathbf{r})-\bar{n}]^2}{\bar{n}^2}\right]\right\}\ . \tag{6}$$

Here, β is an *ad hoc* parameter that is chosen once to give agreement with experiment for all metals. The approximate energy functional was obtained by considering infinitesimal strains about the uniform state, and by assuming that the additional interaction depended linearly on the background density n_b and nonlinearly but locally on the electron density. We expanded the resulting function in a Taylor series and set the linear term equal to zero so that no additional force would be generated on the background. Equation (6) is the general result of this procedure.

Solutions for the energy can be obtained from the energy-density functional by following the procedure of Kohn and Sham. The energy functional is minimized with respect to a set of single-particle orbitals of a fixed number of noninteracting electrons in a fixed external potential. The result is the standard set of Kohn-Sham[9] self-consistent equations with an effective potential that is given by

$$v_{\mathrm{eff}}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[n_e]}{\delta n_e}+\frac{\delta E_{\mathrm{ei}}[n_e,n_b]}{\delta n_e}\ . \tag{7}$$

Density-functional theory can also be used to compute the response of the electron gas to a perturbation. The screened potential-density linear response function can be obtained in the random-phase approximation following Shore *et al.*[10] One finds

$$\tilde{\chi}^{\mathrm{sc}}(\mathbf{q})\approx\frac{\tilde{\chi}^0(\mathbf{q})}{1-(8\pi/q^2+\delta^2E_{\mathrm{xc}}/\delta n_e^2|_{\bar{n}}+\delta^2E_{\mathrm{ei}}/\delta n_e^2|_{\bar{n}})\tilde{\chi}^0(\mathbf{q})}\ . \tag{8}$$

Here, $\tilde{\chi}^0$ is the Lindhard function. In the above equation, the functional derivative of the exchange-correlation energy can be evaluated in the local-density approximation, and is given by

$$\left.\frac{\delta^2E_{\mathrm{xc}}}{\delta n_e^2}\right|_{\bar{n}}=\frac{d^2}{dn_e^2}(n_e e_{\mathrm{xc}}(n_e))|_{\bar{n}}\ . \tag{9}$$

Here, e_{xc} denotes the exchange-correlation energy of jellium per unit volume. The functional derivative for the electron-ion interaction can be evaluated from (6)

$$\left.\frac{\delta^2E_{e-i}}{\delta n_e^2}\right|_{\bar{n}}=v_0\frac{n_b}{\bar{n}}\frac{d^2}{dn_e^2}\left.\left\{n_e\left[1-\frac{1}{2}\beta^2\frac{(n_e-\bar{n})^2}{\bar{n}^2}\right]\right\}\right|_{\bar{n}}=-v_0\frac{\beta^2}{\bar{n}}\ . \tag{10}$$

B. Perturbation calculation of the elastic constants

The energy-density functional, Eq. (4), provides the basis for modeling the energy changes of metals via the theory of ideal metals and its extension for transition metals. We model a uniform single crystal of an elemental metal in equilibrium at zero temperature, introduce infinitesimal uniform strains, evaluate the changes in the energy, and infer the elastic constants. The procedure is general. However, we restrict ourselves to fcc and bcc lattices for simplicity.

The elastic constant calculation requires three inputs. These are the density of the uniform state $\bar{n}$, the bonding valence, and the symmetry of the lattice being modeled. The definition of the appropriate valences (and electron densities) for the transition metals has been an important output of our earlier work. In principle, we define the electron density of the ideal metal $\bar{n}$ to be equal to the average electron density at the boundary of the unit cell in the elemental metal. We have used the muffin-tin, local-density-functional calculations of Moruzzi, Janak, and Williams[8] and Sigalas, Papaconstantopolous, and Bacalis,[11] for the elemental metals to approximate the average density at the cell boundary.[12] These authors reported the number of interstitial electrons between the surface of the muffin-tin sphere and the cell boundary of an fcc and/or bcc unit cell. We divided the number of interstitial electrons by the actual interstitial volume to estimate $\bar{n}$.

The ideal metal's second key input is the bonding valence, i.e., the number of electrons that each atom contributes to the ideal metal. It is defined as the product of the electron density $\bar{n}$ and the volume per atom at zero temperature in the metal. The bonding valence Z_B and the density parameter r_s are repeated for convenience in Table I. Note that the bonding valences of the transition metals range from somewhat less than 3 to nearly 5. Bonding valences of simple metals are reasonably close to the nominal valences, with the striking exception of nominally tetravalent lead, which has a bonding valence of only 2.35.

Figure 1 shows schematically how the electron gas is partitioned to simulate a metal's ground state. The positive background is divided into Wigner-Seitz cells centered about the position of each atom. The positive background is assumed to be rigid and uniform within each cell and to be equal to the equilibrium electron density $\bar{n}$. At equilibrium, the result is a uniform electron gas. If the metal is compressed (or expanded), the rigid positive backgrounds of the various Wigner-Seitz cells overlap (or separate) and the background becomes inhomogeneous. Consider an isolated Wigner-Seitz cell centered about the origin of coordinates and define the characteristic function $\gamma(\mathbf{r})$ as follows:

$$\gamma(\mathbf{r})=1 \quad \mathbf{r}\in\text{Wigner-Seitz cell}$$

and

$$\gamma(\mathbf{r})=0 \quad \mathbf{r}\notin\text{Wigner-Seitz cell}\ . \tag{11}$$

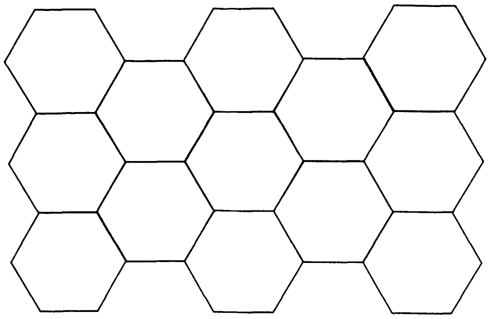

FIG. 1. Schematic representation of the division of the electron gas into Wigner-Seitz cells. The background density is assumed to remain uniform within each cell. However, as the metal is strained the cells of positive background can be overlapped (with twice the background density) or separated.

In the following, we will consider background densities that can be formed as follows:

$$n_b(\mathbf{r})=\bar{n}\sum_{\{\mathbf{R}_i\}}\gamma(\mathbf{r}-\mathbf{R}_i)\ , \tag{12}$$

where $\{\mathbf{R}_i\}$ denotes the set of vectors that define the centers of the "atoms" in the uniformly strained system. The lattice vectors used to model the metal's uniform ground state are denoted by $\{\mathbf{R}_i\}_{\text{eq}}$.

The elastic constants are computed from second-order changes in the energy due to infinitesimal strains. This computation requires (1) the specification of the changes in the background density due to the imposed strain (and the overlap or separation of the various Wigner-Seitz cells); (2) the change in the potential seen by the electrons; (3) the change in the electrons density computed using χ^{sc} and (4) the resulting change in the energy. The strains are introduced by specifying the lattice vectors $\{\mathbf{R}_i\}$. For example, a uniform expansion or contraction of the lattice is given by $\{\mathbf{R}_i\}=(1+\alpha)\{\mathbf{R}_i\}_{\text{eq}}$.

The change in energy to second order $E^{(2)}$ is obtained by comparing three states. The first state is defined to be the uniform ideal metal at the equilibrium density; its energy is given by

TABLE I. Bonding valences and density parameters recommended for the theory of ideal metals. Most values are taken from Ref. (11); those in parentheses are taken from Ref. (8), while the value for Cs was extrapolated from K and Rb.

Li (1.09) (3.15)	Be 1.99 1.88				ELEMENT BONDING VALENCE DENSITY PARAMETER								
Na (1.11) (3.80)	Mg 2.08 2.65											Al (2.76) (2.12)	
K (1.21) (4.57)	Ca 2.22 3.16	Sc 2.85 2.37	Ti 3.20 2.07	V 3.45 1.86	Cr 3.53 1.76	Mn 3.41 1.79	Fe 3.32 1.79	Co 3.09 1.80	Ni 2.83 1.84	Cu 2.57 1.95	Zn 2.40 2.17	Ga (2.43) (2.35)	Ge
Rb (1.24) (4.87)	Sr 2.32 3.39	Y 3.21 2.55	Zr 3.75 2.16	Nb 4.14 1.91	Mo 4.42 1.79	Tc 4.24 1.76	Ru 4.05 1.76	Rh 3.67 1.82	Pd 3.15 1.96	Ag 2.70 2.17	Cd 2.48 2.41	In (2.51) (2.57)	Sn
Cs (1.28) (5.18)	Ba 2.51 3.42	La 3.50 2.58	Hf 3.97 2.08	Ta 4.51 1.86	W 4.79 1.75	Re 4.79 1.70	Os 4.72 1.69	Ir 4.36 1.74	Pt 3.90 1.84	Au 3.26 2.03	Hg 2.53 2.46	Tl 2.38 2.68	Pb 2.35 2.75

$$E_{\rm eq}(\bar{n})=N[e_{\rm jell}(\bar{n})+v_0]\ , \tag{13}$$

where N is the total number of electrons. The second state is defined to account for the overall change in the system's volume (and average electron density). In this hypothetical state the electron and background densities are uniform with density $\bar{n}'$. The difference in the energy $E^{(2)}_{\rm vol}$ of the second state and the first state follows by evaluating Eq. (4) for uniform densities and is

$$E^{(2)}_{\rm vol}=N\left\{e_{\rm jell}(\bar{n}')-e_{\rm jell}(\bar{n})+v_0\left[\frac{\bar{n}'}{\bar{n}}-1\right]\right.$$
$$\left.-v_0\frac{1}{2}\beta^2\frac{(\bar{n}'-\bar{n})^2}{\bar{n}^2}\right\}\ . \tag{14}$$

The third and final state is obtained by allowing the electrons to relax to the nonuniform background induced by the overlapping Wigner-Seitz cells. The change in energy due to electron relaxation, $E^{(2)}_{\rm relax}$, is calculated via perturbation theory (and is called the band-structure energy in pseudopotential perturbation theory). The difference in energy $E^{(2)}$ between energy state three and state one is given by the sum of $E^{(2)}_{\rm relax}+E^{(2)}_{\rm vol}$.

$$E^{(2)}(\bar{n})=E^{(2)}_{\rm vol}+\int\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{\delta n_B(\mathbf{r})\delta n_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\frac{1}{2}\int\int d^3\mathbf{r}\,d^3\mathbf{r}'\chi^{\rm sc}(\bar{n},\mathbf{r}-\mathbf{r}')\delta v(\mathbf{r})\delta v(\mathbf{r}')\ . \tag{15}$$

The second term on the right-hand side denotes the electrostatic interaction of the positive background with itself. The deviation in the background charge from uniformity is written as

$$\delta n_B(\mathbf{r})=n_B(\mathbf{r})-\bar{n}'\ . \tag{16}$$

The third term on the right-hand side of (15) describes the energy change due to the rearrangement of the electrons. Here, $\chi^{\rm sc}$ denotes the screened potential-density response function of the electron gas, Eq. (8), while δv denotes the change in the electron's potential due to the nonuniformity of the background. The change in the electron's potential is given explicitly to second order in δn by

$$\delta v(\mathbf{r})=v_0\left\{1-\frac{1}{2}\beta^2\frac{(\bar{n}-\bar{n}')^2}{\bar{n}^2}\right\}(n_b(\mathbf{r})-\bar{n}')$$
$$-2\int d^3\mathbf{r}'\frac{(n_b(\mathbf{r}')-\bar{n}')}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{17}$$

The bulk moduli of metals that have a high density of bonding electrons depends primarily on the volume contribution to the energy change, which can be evaluated to second-order by expanding Eq. (14) to second order in $\bar{n}-n$. Note that the first-order term is zero due to the choice of v_0. Upon expanding $E^{(2)}_{\rm vol}$ to second order in the change δV in the volume per atom V, we find

$$E^{(2)}_{\rm vol}=N\left[\frac{\delta V}{V}\right]^2\left[\beta^2\bar{n}\left.\frac{\partial e_{\rm jell}}{\partial n}\right|_{\bar{n}}+\bar{n}\left.\frac{\partial^2 e_{\rm jell}}{\partial n^2}\right|_{\bar{n}}\right]\ . \tag{18}$$

The change in energy due to the change in average volume is determined from the parameter β and the energy per electron of the uniform electron gas $e_{\rm jell}$, which is approximated by

$$e_{\rm jell}(n)=\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+e_c(n)\ . \tag{19}$$

The first term on the right-hand side denotes the kinetic energy, the second term the exchange energy and the last term the correlation energy. We use the parametrization of Gunnarson and Lundquist for the correlation contribution.[13]

The evaluation of the relaxation term is more elaborate. Since the kernels in (15) are translationally invariant, it is convenient to Fourier transform this equation with respect to $\mathbf{r}$. The numerical evaluation of the relaxation energy requires a specification of the potential-density response function, the inhomogeneous background charge, and the change in the electron's potential.

Our Fourier transform conventions for L_2 functions of $\mathbf{r}$ are

$$\tilde{f}(\mathbf{q})=\int_{\text{all-space}}d^3\mathbf{r}\exp(i\mathbf{q}\cdot\mathbf{r})f(\mathbf{r})\ , \tag{20}$$

and

$$f(\mathbf{r})=\frac{1}{(2\pi)^3}\int_{\text{all q}}d^3\mathbf{q}\exp(-i\mathbf{q}\cdot\mathbf{r})\tilde{f}(\mathbf{q})\ . \tag{21}$$

For a function $g(\mathbf{r})$ that is periodic on a lattice with unit-cell volume Ω, we define

$$\hat{g}(\mathbf{G})=\int_{\Omega}d^3\mathbf{r}\exp(i\mathbf{G}\cdot\mathbf{r})g(\mathbf{r})\ . \tag{22}$$

$\mathbf{G}$ denotes a reciprocal-lattice vector. The inverse transform for a periodic function is

$$g(\mathbf{r})=\frac{1}{\Omega}\sum_{\{\mathbf{G}\}}\hat{g}(\mathbf{G})\exp(-i\mathbf{G}\cdot\mathbf{r})\ , \tag{23}$$

where $\{\mathbf{G}\}$ denotes the sum over the set of reciprocal-lattice vectors.

The Fourier transform of the background density [Eq. (12)], which is periodic with respect to the unit cell of the lattice, is determined by the Fourier transform of the characteristic function [Eq. (11)] over all space,

$$\hat{n}_B(\mathbf{G})=\bar{n}\tilde{\gamma}(\mathbf{G})\ . \tag{24}$$

The analytic Fourier transforms of the characteristic functions of fcc and bcc unit cells were determined as part of this work. The result for the bcc lattice is reported in the Appendix.

The second-order relaxation energy is

$$E^{(2)}_{\rm relax}=\frac{N_{\rm cells}\bar{n}^2}{\Omega}\sum_{G\neq 0}\frac{4\pi}{G^2}\tilde{\gamma}(\mathbf{G})\tilde{\gamma}(-\mathbf{G})$$
$$+\frac{N_{\rm cells}}{2\Omega}\sum_{G\neq 0}\tilde{\chi}^{\rm sc}(\mathbf{G})\delta\hat{v}(\mathbf{G})\delta\hat{v}(-\mathbf{G})\ , \tag{25}$$

where $\delta\hat{v}(\mathbf{G})$ is obtained from the Fourier transform of

(17) and is given by

$$\delta\hat{v}(\mathbf{G})=\left\{\frac{v_0}{\bar{n}}\left[1-\beta^2\left[\frac{\bar{n}'-n'}{\bar{n}}\right]^2\right]-\frac{8\pi}{G^2}\right\}\delta\hat{n}_B(\mathbf{G})\ . \tag{26}$$

This completes the formal description of the method for evaluating the energy changes.

C. Extraction of elastic constants

The extraction of the elastic constants is straightforward once the energy changes have been calculated. The change in energy is related to the strain ε_{ij} and the elastic constants c_{ijkl}, via

$$\delta E=\tfrac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl}\ . \tag{27}$$

We computed the energy changes for the fcc and bcc cubic metals using the following strains:

$$\begin{bmatrix}\delta&0&0\\0&0&0\\0&0&0\end{bmatrix},\quad\begin{bmatrix}\delta&0&0\\0&\delta&0\\0&0&0\end{bmatrix},\quad\begin{bmatrix}\delta&0&0\\0&\delta&0\\0&0&\delta\end{bmatrix},\ \text{and}\ \begin{bmatrix}0&\delta&0\\0&0&0\\0&0&0\end{bmatrix}. \tag{28}$$

The axes of the strain tensor are aligned with the set of (100) directions of the cubic crystal. These strains overdetermine C_{11}, C_{12}, and C_{44}, since we have three unknowns and four equations. The extra equation was used to check the consistency of the calculation.

III. CALCULATED ELASTIC CONSTANTS: THEORY OF IDEAL METALS

The elastic constants were calculated from the theory of ideal metals, our extension of the electron gas, and are reported and discussed in this section. We briefly discuss the heuristics of our model in Sec. III A. We point out the weakness in the unmodified theory of ideal metals ($\beta=0$) that makes it unsuited for the calculation of transition-metal elastic constants. We then discuss the choice of β and relate its size to certain questions concerning the stability of the lattice in our model. In Sec. III B, we report good agreement with experiment for the elastic constants of the simple metals for $\beta=0$, and show that calculations of the elastic constants of the transition metals result in small unphysical values. In Sec. III C, we report the calculated elastic constants of the simple and transition metals for $\beta=1$. Finally, in Sec. III D, we explain the trends in the elastic constants that have been uncovered by our calculation.

We remind the reader that it is not our intention to provide precise results for the elastic properties of the metals. Rather, we wish to show that simple considerations of stability, combined with the electron-gas model, lead to an understanding of the trends in the elastic properties of metals. Further, these simple considerations lead to reasonable estimates for the velocity of sound in metals. We chose the name "ideal metal" for the new model, since one of the major triumphs of the theory of ideal gases was the prediction of the velocity of sound.

We carried out the calculations described in Sec. II using lattices of Wigner-Seitz cells with bcc and fcc symmetry. Bulk moduli of metals that have other lattice symmetries were computed for a hypothetical fcc lattice. The calculated results are compared with experimental values taken from the tabulations in Refs. (3, 14, and 15). The lowest-temperature elastic constants in Simmons and Wang[14] were preferred, if available; the room-temperature elastic constants reported by Landolt and Borstein[15] were secondarily preferred. Finally, if no results were available in the other compendia, we used the room-temperature experimental bulk moduli reported by Kittel.[3]

A. Heuristics

The energy calculation is divided into two terms, the relaxation (or band-structure) energy and the volume energy. For the moment we focus on the volume-energy contribution to the bulk modulus, which dominates for transition metals and can be calculated from Eq. (18). This volume energy makes the following contribution to the bulk modulus

$$B_{\mathrm{vol}}=\bar{n}^3\frac{\partial^2 e_{\mathrm{jell}}}{\partial n^2}\bigg|_{\bar{n}}+\beta^2\bar{n}^2\frac{\partial e_{\mathrm{jell}}}{\partial n}\bigg|_{\bar{n}}\ . \tag{29}$$

This can be compared with the bulk modulus of jellium (under a fixed external pressure), which, as found by Moruzzi, Janak, and Williams,[8] reproduces the trends for the bulk moduli of the polyvalent metals;

$$B_{\mathrm{jell}}=\bar{n}^3\frac{\partial^2 e_{\mathrm{jell}}}{\partial n^2}\bigg|_{\bar{n}}+2\bar{n}^2\frac{\partial e_{\mathrm{jell}}}{\partial n}\bigg|_{\bar{n}}\ . \tag{30}$$

If $\beta=\sqrt{2}$, the volume contribution B_{vol} would equal the bulk modulus predicted for jellium under external pressure. However, it turns out that such a large value of β would lead to substantial overestimates of the bulk moduli of metals, since the band-structure term makes a substantial positive contribution to the bulk modulus. Consequently, we expect that β will be less than $\sqrt{2}$.

Further insight into the appropriate value of β can be obtained by considering the stability of the ideal metal. The original motivation for constructing the theory of ideal metals was to insure that the uniform electron gas is mechanically stable. As a first step we required the condition of equilibrium for the uniform state, i.e., zero forces act on the positive background. This led to the theory with $\beta=0$. However, for $\beta=0$, the uniform state is not the global ground state,[2,16] and for sufficiently high electron densities the equilibrium is unstable.[16] This instability is removed for $\beta>\sqrt{3}/3$ as we discuss immediately below. One can roughly analyze the high-density instability by neglecting the correlation energy of jellium. The energy per electron in jellium is then approximated by

$$e_{\mathrm{jell}}\approx\frac{2.21}{r_s^2}-\frac{0.916}{r_s}\ . \tag{31}$$

The volume contribution to the bulk modulus can be roughly evaluated by substituting (31) in (29). This volume contribution to the bulk modulus becomes negative for sufficiently high electron densities if $\beta<\sqrt{3}/3$, and it becomes negative for sufficiently low-electron densities if $\beta>\sqrt{2/3}$. The lower bound, $\sqrt{3}/3$, is the more important since the volume term makes the largest contribution to the bulk moduli of the transition metals. Probably, $\sqrt{2/3}$ does not serve as an upper bound on β since the band-structure term dominates at low densities and the behavior of the volume term is relatively insignificant. Consequently, we propose that β should be chosen to be greater than $\sqrt{3}/3$, i.e., 0.577. The exact value will be determined by fitting the calculation to the data.

B. Elastic constants, $\beta=0$

The trends for the elastic constants of the cubic simple metals are well reproduced by the theory of ideal metals with $\beta=0$ despite the instability of the theory at high densities. This is not too surprising since the electron densities of the simple metals are relatively low. The calculated elastic constants of the transition metals, on the other hand, are up to five times smaller than experiment. We associate this discrepancy with the high-density instability mentioned above, since the transition metals typically have high electron densities.

The calculated bulk moduli of the alkali metals ($\beta=0$) are shown in Fig. 2; the bulk moduli of the other simple metals are shown in Fig. 3. The bulk moduli of the alkali metals are in good quantitative agreement with experiment. This is satisfying since the alkalis are often used as examples of "free-electron" metals. The trends in the bulk moduli of the other simple metals are surprisingly well reproduced, considering that the theory has no content beyond the electron gas and the "zero-force" condition. The largest discrepancies, roughly 50%, occur for Al, Be, and Pb. On the average, the theory of ideal metals ($\beta=0$) underestimates the bulk moduli slightly, with the largest discrepancies (30–50 %) occurring for metals with high electron densities. We believe that the discrepancies for Al and Be are related to the negative volume energy contribution to the bulk modulus for $\beta=0$, as discussed above.

The bulk moduli of the 5*d* transition metals were calculated for $\beta=0$, and are compared with experiment in Fig. 4. The bulk moduli increase as one crosses the series, with the maximum value occurring for a half-filled *d* shell. This trend is reproduced by the $\beta=0$ calculation. However, the calculated bulk moduli are too small by a factor of 3–5. The elements with the largest electron densities have the largest discrepancies, in agreement with the negative contribution of the volume term to the bulk modulus.

Calculated values of C_{11}, C_{12}, and C_{44} for the alkali metals are shown in Fig. 5 and compared with experiment. The results are in semiquantitative agreement with experiment. Typically, the calculated values for C_{11} are somewhat (10–30 %) too large, while the values for C_{44} are somewhat (10–15 %) too small.

The elastic constants were also calculated for the polyvalent cubic metals Sr, Ba, Ca, Al, and Pb. Experimental elastic constants are not available for Sr, Ba, and Ca. The agreement for Al and Pb is less good than for the alkali metals. Nonetheless, reasonable results are obtained from this simple model, whose only inputs are the electron gas and the zero-force condition.

C. Transition-metal elastic constants, $\beta=1$.

The calculated bulk moduli of the elemental metals through the 5*d* series are shown in Figs. 6(a)–6(d) for $\beta=1$. This choice for β was made to obtain the best agreement between the calculations and experiment and because it is a round number. Since β is larger than $\sqrt{3}/3$ mechanical stability at high electron density is assured. Very importantly the calculated bulk moduli of the alkali metals remain in good agreement with experiment despite the several-fold changes in the calculated bulk moduli of the transition metals. The trends in the

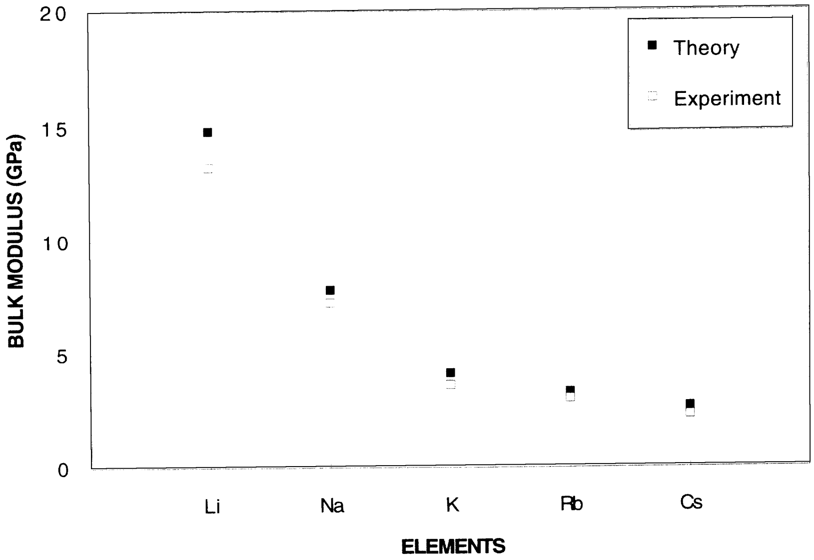

FIG. 2. Calculated bulk moduli of the alkali metals, $\beta=0$, compared with experiment.

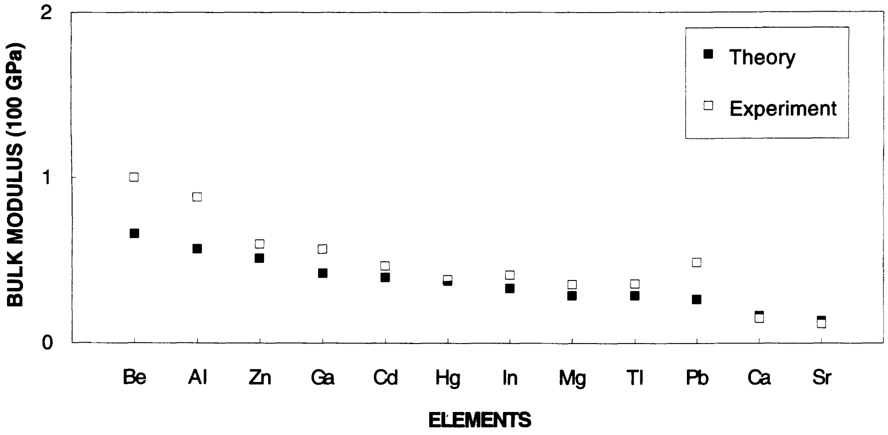

FIG. 3. Calculated bulk moduli of the other simple metals, $\beta=0$, compared with experiment.

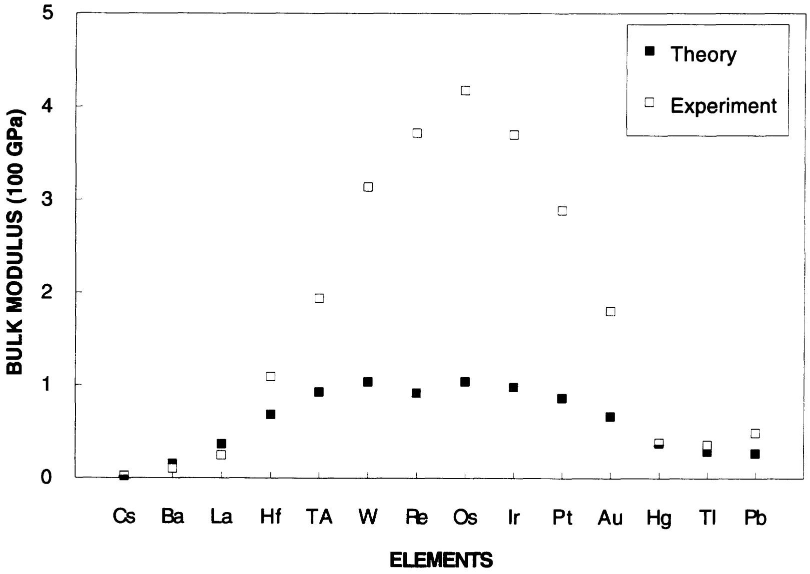

FIG. 4. Calculated bulk moduli of the 5*d* series elements, $\beta=0$, compared with experiment.

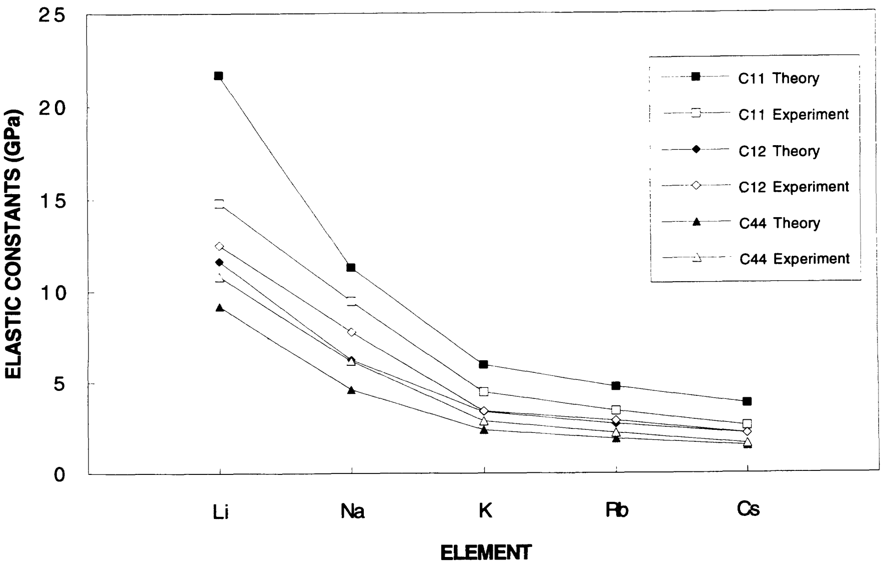

FIG. 5. Calculated C_{11}, C_{12}, and C_{44} for the alkali metals, $\beta=0$, compared with experiment.

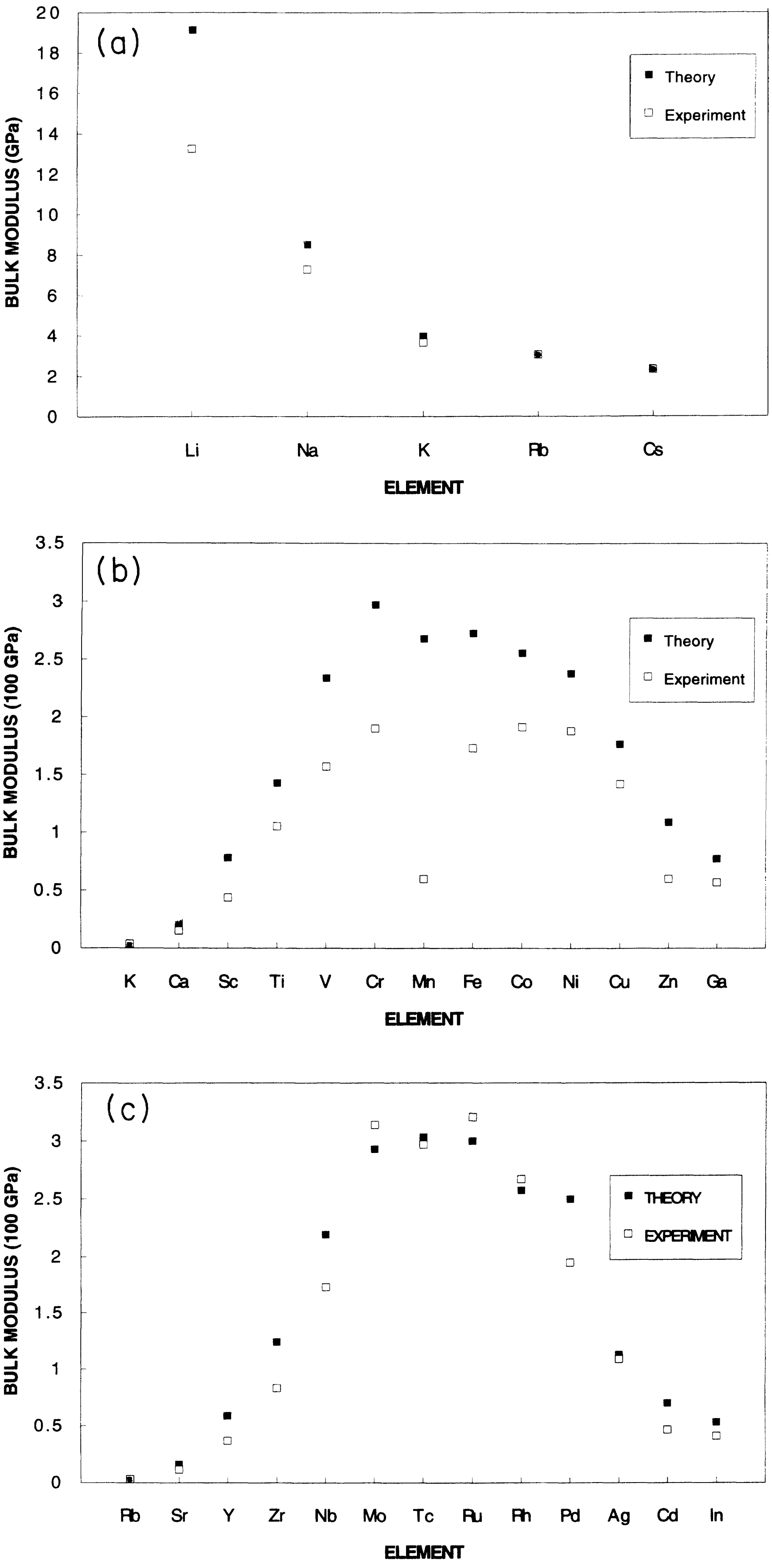

FIG. 6. (a) Calculated bulk moduli for the alkali metals, $\beta=1$, compared with experiment. (b) Calculated bulk moduli for the $3d$ series elements, $\beta=1$, compared with experiment. (c) Calculated bulk moduli for the $4d$ series elements, $\beta=1$, compared with experiment. (d) Calculated bulk moduli for the $5d$ series elements, $\beta=1$, compared with experiment.

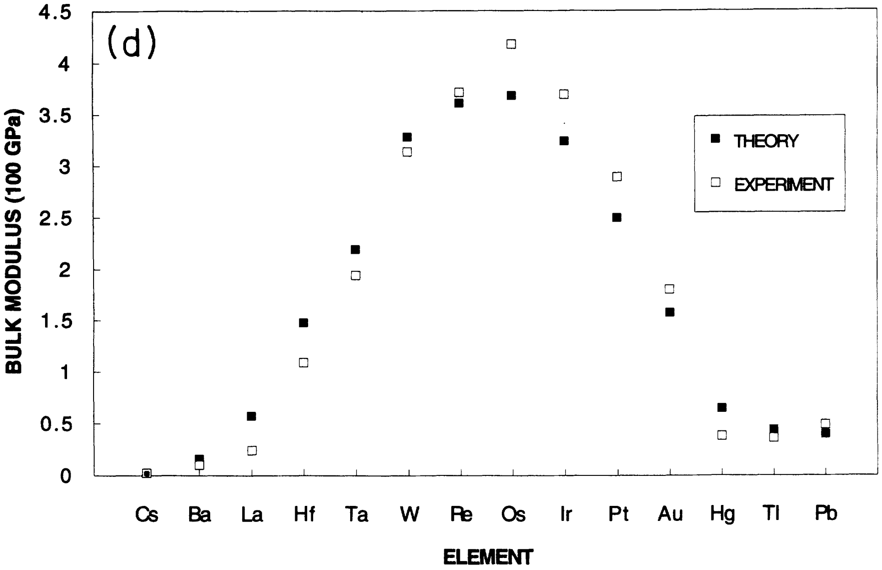

FIG. 6. (*Continued*).

bulk moduli of the elemental metals are well reproduced. Note that the bulk modulus of the stiffest transition metals and the softest alkali metals differ by more than a factor of 200. The modified theory of ideal metals with $\beta=1$ spans this entire range.

The elastic constants of the elemental cubic metals were computed from the modified theory of ideal metals with $\beta=1$. The calculated constants are compared with experiment as follows: fcc metals, Figs. 7(a)–7(c), bcc transition metals, Figs. 8(a)–8(c), and alkali metals, Fig. 9. For the alkali metals, Na, K, Rb, and Cs, agreement between theory and experiment is good for all three elastic constants. C_{11} is substantially overestimated for Li. For the fcc metals the agreement for C_{11} and C_{12} is surprisingly good with the largest errors occurring for Al. The agreement is also good for C_{44} except that the values for Rh and Ir are substantially underestimated. For the bcc metals the agreement is quite good for C_{11}. However, C_{12} is underestimated for all the elements. C_{44} is in good agreement except for V and Nb. In sum, the trends in the elastic constants of the elemental cubic metals are surprisingly well reproduced by calculations based on a simple electron-gas picture.

D. Trends

The most important result is that the modified theory of ideal metals reproduces the magnitude of the elastic constants of metals ranging from cesium to tungsten and platinum. The magnitude of the calculated elastic constants invariably ordered as $C_{11} > C_{12} > C_{44}$. This ordering is experimentally observed for the cubic metals considered with the exception of Ir (C_{44} and C_{12} are nearly the same size for Ir). The results of Moruzzi, Janak, and Williams[8] suggested that the bulk modulus depends primarily on the electron density; other factors such as the atomic size are of secondary importance. The calculated elastic constants also showed this trend. In Fig. 10 we show the computed elastic constants for a series of hypothetical transition metals with $r_s = 1.85$ and valences Z_B ranging from one to five, which corresponds to a change in the radius of a factor of slightly more than 2. As can be seen, both C_{11} and C_{12}, which together determine the bulk modulus, are only weakly dependent on the valence and are primarily determined by r_s. C_{44}, on the other hand, varies by almost a factor of 2 as Z_B increases from one to five.

We were particularly encouraged that reasonably good agreement between theory and experiment was obtained for C_{44}, since C_{44} is calculated from the energy change due to a pure shear strain. In this case, the change in energy is solely due to the overlap of Wigner-Seitz cells; there is no volume contribution. Consequently, C_{44} depends weakly on the value of β, which primarily controls the volume contribution to the energy. C_{44} cannot be adjusted easily by varying β. Wigner-Seitz cells of uniform charge are far from describing the actual ions, and it is encouraging, as well as puzzling, that such an idealized model can reproduce the trends in C_{44}.

IV. SUMMARY AND CONCLUSION

The trends in the elastic constants of the elemental simple and transition metals have been reproduced from a slightly modified version of the theory of ideal metals. For this theory, the elastic properties of the elemental metals depend primarily on two parameters: the average electron density at the cell boundary and less importantly the bonding valence.

The average elastic properties have been determined from a uniform electron-gas model. Deviations from these properties should be taken as a sign that something exceptional is occurring in the bonding. The question remains, "Why is it possible to calculate the elastic properties of the metals, especially C_{44}, from a uniform electron gas model?" We do not have a complete answer. We assume that the gross features of the bonding energy is dominated by the interstitial electrons at the cell boundary. Calculations based on these interstitial bonding electrons do describe the cohesive energies and trends

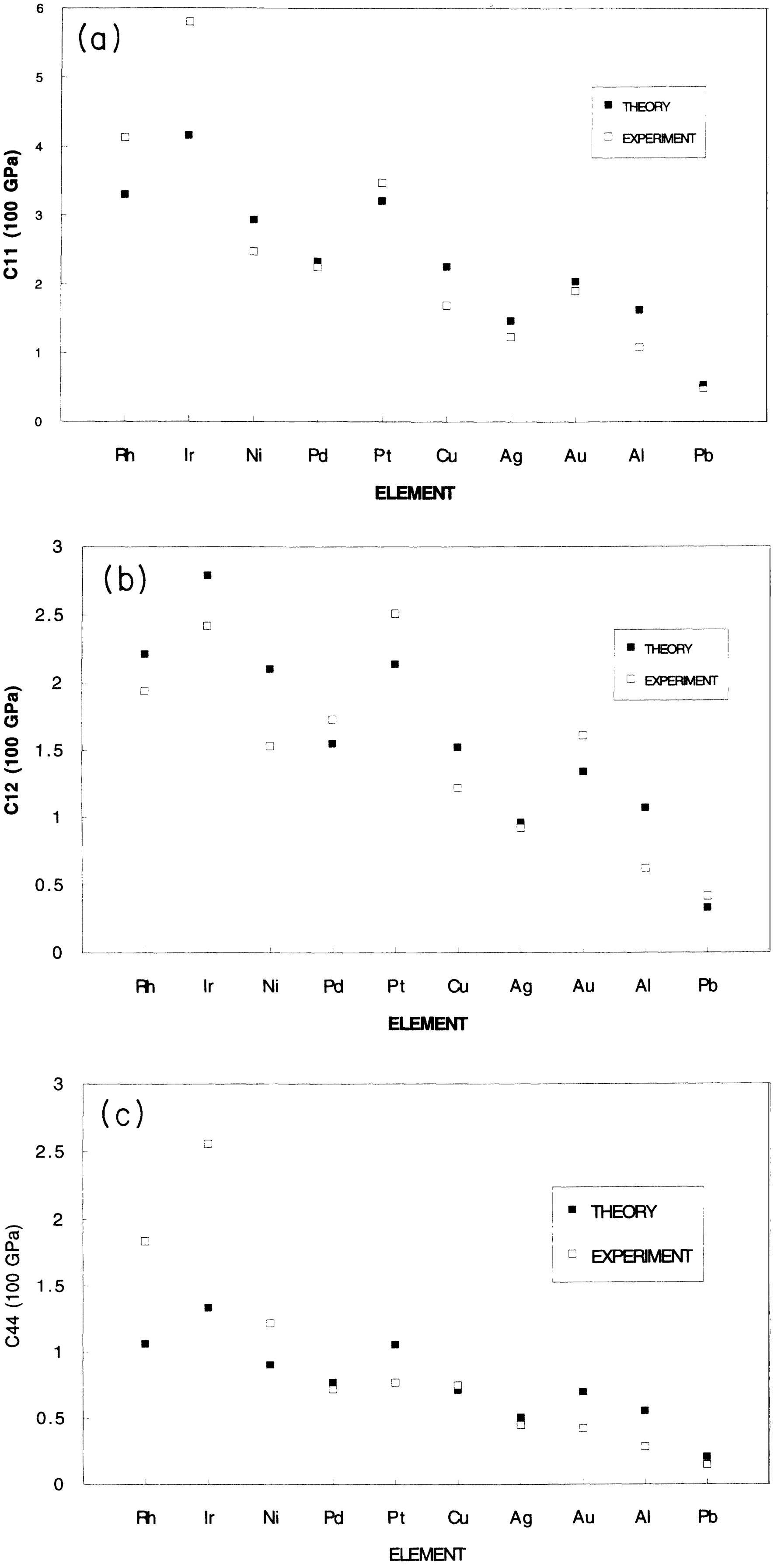

FIG. 7. (a) Calculated C_{11} for fcc metals, $\beta=1$, compared with experiment. (b) Calculated C_{12} for fcc metals, $\beta=1$, compared with experiment. (c) Calculated C_{44} for fcc metals, $\beta=1$, compared with experiment.

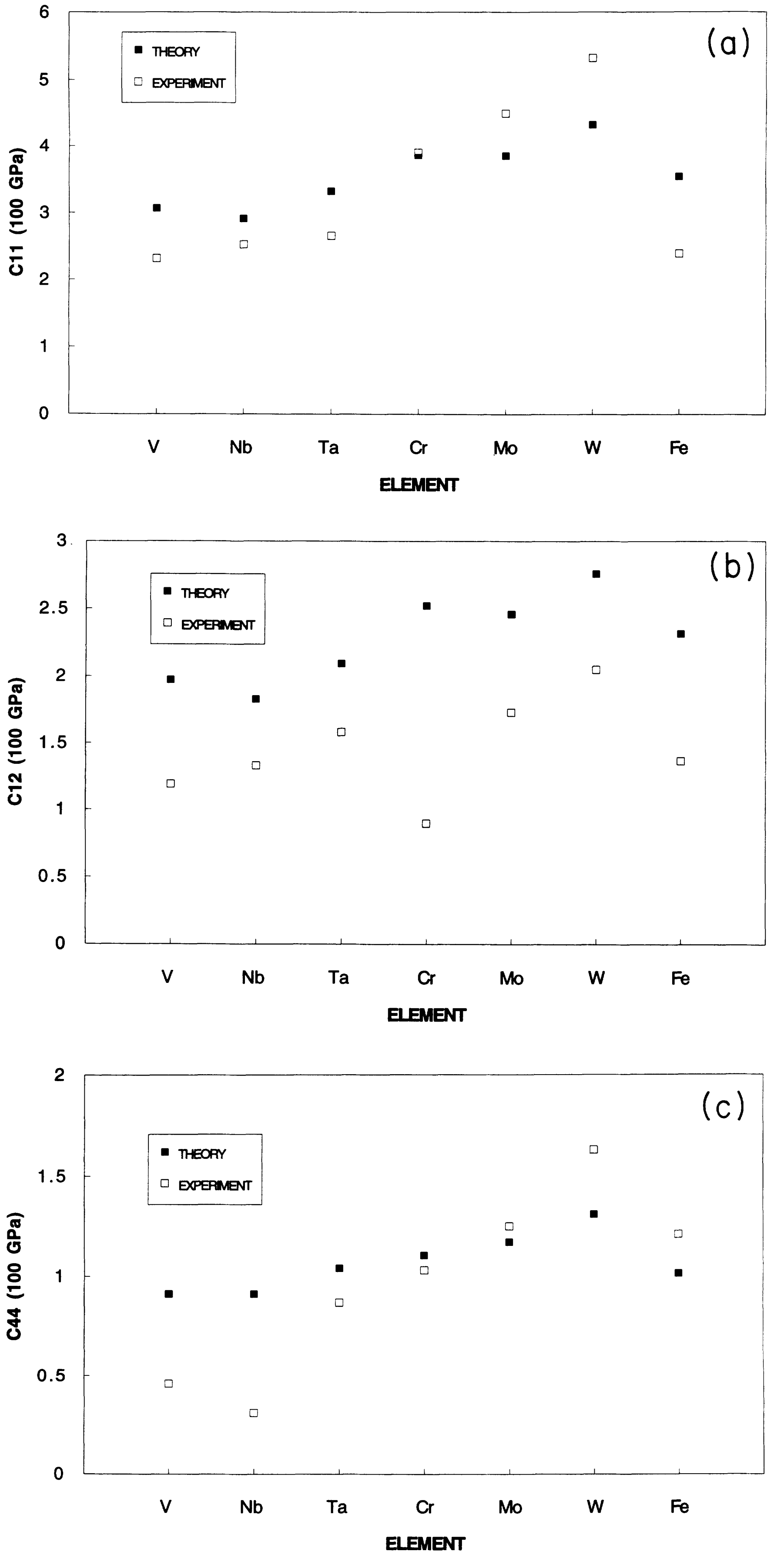

FIG. 8. (a) Calculated C_{11} for bcc transition metals, $\beta=1$, compared with experiment. (b) Calculated C_{12} for bcc transition metals, $\beta=1$, compared with experiment. (c) Calculated C_{44} for bcc transition metals, $\beta=1$, compared with experiment.

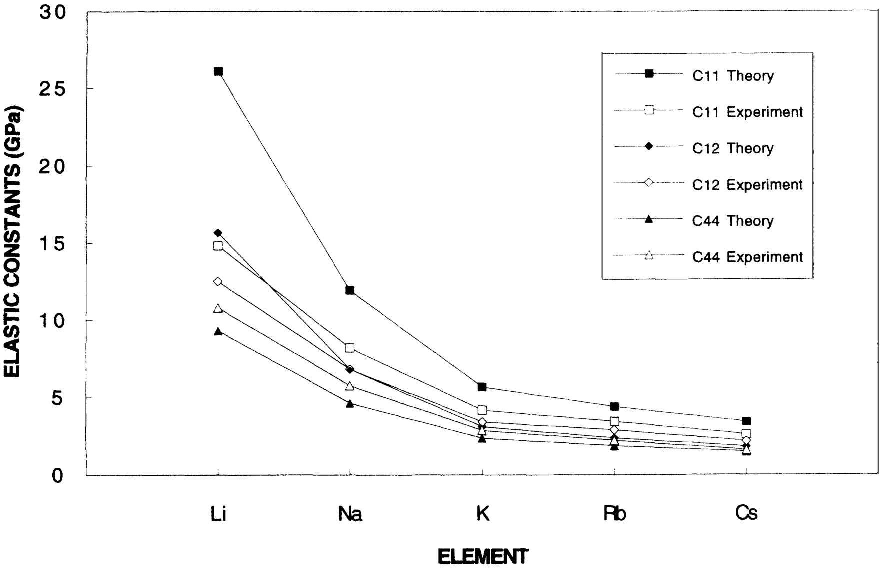

FIG. 9. Calculated C_{11}, C_{12}, and C_{44} for alkali metals, $\beta=1$, compared with experiment.

in the elastic constants of the transition metals adequately. Subtle features of the bonding, such as structural energies, are not expected to be described by the present approach.

The electron gas is used to simulate metals for a variety of important calculations. The ideal metal is no more complicated than the jellium model. However, the ideal metal provides a substantially and qualitatively improved picture of the basic energetics of the inhomogeneous electron gas. Consequently, we believe that the ideal metal should be preferred to jellium in all calculations.

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APPENDIX

The Fourier transform of the background density is determined from the Fourier transform of the characteristic function $\gamma(\mathbf{r})$, which is defined to be unity inside a Wigner-Seitz cell centered at the origin of coordinates and zero otherwise. We define

$$\tilde{\gamma}(\mathbf{q}) \equiv \int_{\text{all-space}} d^3\mathbf{r}\,\exp(i\mathbf{q}\cdot\mathbf{r})\gamma(\mathbf{r}) \ . \tag{A1}$$

For the bcc lattice, with conventional cube edge a and $\mathbf{q}=(q_x,q_y,q_z)$ we find

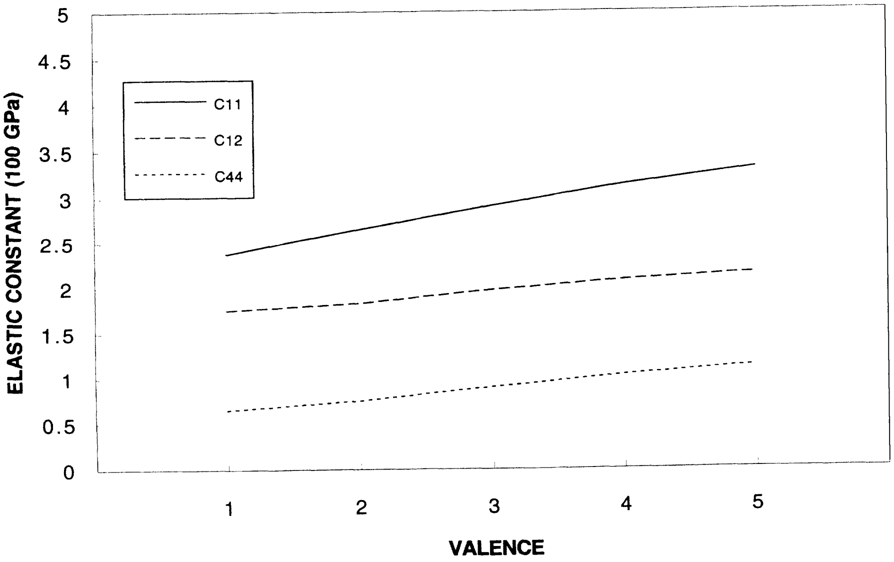

FIG. 10. Shows the dependence of the elastic constants on the valence of a hypothetical bcc element with $r_s=1.85$ and bonding valences ranging from one to five.

$$\tilde{\gamma}(\mathbf{q})=\frac{8\left[\left\{q_x\sin\left[\frac{q_xa}{4}\right]\left[\cos\left[\frac{q_za}{2}\right]+\cos\left[\frac{q_ya}{2}\right]\right]\right\}+\left\{\cos\left[\frac{q_xa}{4}\right]\left[q_y\sin\left[\frac{q_ya}{2}\right]+q_z\sin\left[\frac{q_za}{2}\right]\right]\right\}\right]}{(q_x^2-q_z^2)(q_x^2-q_y^2)}$$
$$+\{q_x\to q_y,q_y\to q_z,q_z\to q_x\}+\{q_x\to q_z,q_y\to q_z\to q_y\} \tag{A2}$$

In the evaluation of the lattice sums it sometimes happens that two of the components of a reciprocal-lattice vector are the same ($G_x=G_y$) and/or are zero. In these cases, the evaluation of (A2) is complicated by a vanishing denominator. Explicit expressions for the Fourier transform can be obtained as limits of (A2).

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