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Total Energy of Copper, Silver, and Gold[†]

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The pseudopotential theory of d-band metals discussed by the author in a previous paper is used to consider the total energy of the noble metals. The theoretical total-energy calculation is completed by adding to the total electronic energy the direct electrostatic repulsion between ions and subtracting from it an energy equal to the electron-electron interaction. The result is expressed as a sum of four quantities: a free-electron energy, a band-structure energy, an electrostatic (or Ewald) energy, and an overlap energy. The first three are directly analogous to the usual quantities found in the simple-metal total energy. The fourth contribution enters as a result of overlapping atomic d states and is most conveniently expressed in terms of a repulsive pair potential. Energy–wave-number characteristics are evaluated for copper, silver, and gold by the numerical procedures previously used to calculate the form factors of these metals. Two improvements relating to exchange approximations are introduced, however. The most important of these involves a modification of the Kohn-Sham conduction-core, d exchange potential in a manner suggested by Lindgren. This removes the spurious behavior otherwise obtained at long wavelengths in both the form factor and the energy–wave-number characteristic. The overlap potential for each metal is evaluated as a function of the separation between two ions in the metal and then fitted to a simple analytic form. Applications to the calculation of the binding energies, the low-temperature stable phases, and the phonon spectra of the noble metals are described. All three metals are calculated to be most stable in an hcp structure, rather than in the observed fcc structure. Reasonable phonon spectra are obtained, although large Kohn anomalies, which have not been reported experimentally, are seen in copper.

I. INTRODUCTION

One of the more appealing features of the pseudopotential theory of metals is that it permits calculation of the total energy as an analytic function of the configuration of the individual ions. This greatly facilitates the study of the many physical properties which depend upon the change in the total energy when the ions are rearranged at constant volume. In the past ten years or so, there has been steady progress in understanding such things as the lattice dynamics and phase stability of simple (free-electron-like) metals through use of the pseudopotential method.[1,2] Recent advances in pseudopotential theory[3–5] have permitted analytic calculation of the total energy for d-band metals as well. In the generalized pseudopotential method, it is recognized that the atomic d states φ_d are not good eigenstates of the crystal Hamiltonian of a d-band metal and that they give rise to bands which hybridize with the free-electron-like conduction band. This hybridization is taken into account through a potential Δ, which is a simple linear function of the extra potential $-\delta V$, seen by a d electron in the metal. The total energy is then calculable as a systematic expansion in both Δ and an ordinary pseudopotential w_0.

In the category of d-band metals we include the alkaline earths, the transition metals, and the noble metals, which have empty, partially filled, and filled d bands, respectively. In this paper we shall focus our attention on the total energy of the noble metals. Numerical calculations of the pseudopotential form factors for copper, silver, and gold have already been discussed in a previous paper[6] (hereafter referred to as Paper I). These calculations provide the necessary foundation we shall need to quantitatively evaluate the total energy. The extension of the numerical procedures used in Paper I to the total energy calculation is discussed in Sec. III.

Our total energy calculation is based on the self-consistent-field approximation. In such a calculation there are always two main steps. The first is to sum the one-electron energies of the occupied states. This sum is the total electronic energy, and the general result for a metal with a filled d band has been given in another previous paper[5] (hereafter referred to as Paper II). The second part of the total energy calculation involves addition of the direct electrostatic repulsion between ions and subtraction of an energy equal to the electron-electron interaction, which has been counted twice in the total electronic energy. We first discuss these amendments in Sec. II before proceeding to a quantitative evaluation of the total energy in Sec. III, and various applications in Sec. IV.

II. TOTAL ENERGY OF A d-BAND METAL

The total energy to be considered is that of the valence electrons in the presence of compensating nuclear charges. The energy associated with the core electrons is assumed to add only a constant to the total energy of the metal and need not be considered. The total electronic energy $E_{\rm el}$ of the valence electrons of a d-band metal can be written

$$E_{\rm el} = E_{\rm fe}^{\rm el} + E_{\rm bs}^{\rm el} + E_{\rm ol}^{\rm el} \ , \tag{1}$$

where $E_{\rm fe}^{\rm el}$, $E_{\rm bs}^{\rm el}$, and $E_{\rm ol}^{\rm el}$ are the free-electron energy, band-structure energy, and overlap energy, respectively, as defined in Paper II. The quantities $E_{\rm fe}^{\rm el}$ and $E_{\rm bs}^{\rm el}$ are directly analogous to the free-electron-energy and band-structure-energy terms found in simple-metal pseudopotential theory. The energy $E_{\rm ol}^{\rm el}$, on the other hand, enters as a result of the overlap of the φ_d centered on neighboring ion sites in the metal. The calculation of $E_{\rm el}$ was carried out in Paper II to second order in both the pseudopotential w_0 and the square of the hybridization parameter Δ. As emphasized there, the dependence of $E_{\rm el}$ on the ion configuration first appears in that order. For the same reason, the electrostatic corrections to the total energy will be included to second order in these variables.

In order to incorporate the two electrostatic terms into the total energy, it is necessary to do some bookkeeping with respect to charge densities and potentials. We identify seven charge densities of interest: the charge density of the ions, the valence charge density of the nuclei, the uniform electron density, the orthogonalization hole density, the screening electron density, the electron density of filled core (or d) states, and the electron density of filled d states. The charge density of the ions includes the electron density of filled core and d states plus the nuclear density of all the protons. The valence charge density corresponds to Z protons centered on each ion site. (For the noble metals $Z=1$.) Within the small-core approximation, it is not necessary to distinguish between these two densities. However, in the present case we do not wish to apply this approximation to the d states, so we shall retain the distinction. The uniform electron density is Z^*/Ω_0, where Z^* is the usual effective valence and Ω_0 is the atomic volume of the metal. The orthogonalization hole density depletes (Z^*-Z) electrons from around each ion site, while the total screening charge in the metal is exactly zero. The sum of the uniform, orthogonalization hole, and screening densities corresponds to Z electrons per ion.

The electrostatic energy of a given charge distribution is just equal to one-half the integral of the charge density times the potential arising from that charge distribution. The potentials arising from the above charge densities we write as $V^{\rm ion}$, $V^{\rm val}$, $V^{\rm unif}$, $V^{\rm oh}$, $V^{\rm sc}$, V^{α}, and V^{d}, respectively. If we denote the single-ion contributions to our seven charge densities as $n_{\rm ion}$, $n_{\rm val}$, $n_{\rm unif}$, $n_{\rm oh}$, $n_{\rm sc}$, n_α, and n_d, respectively, then the total energy per ion of a metal with N ions can be written

$$\begin{aligned} E_{\rm total} = {} & N^{-1}E_{\rm el} + \tfrac{1}{2}(n_{\rm ion} - n_d)(V^{\rm ion} - V^d)' \\ & - \tfrac{1}{2}(n_{\rm unif} + n_{\rm oh} + n_{\rm sc} + n_d)(V^{\rm unif} + V^{\rm oh} + V^{\rm sc} + V^d) \ , \end{aligned} \tag{2}$$

where the volume integrations are implicitly understood and where the prime means that the self-energy term involving the interaction of a given ion with itself is to be excluded. Note that n_d has been subtracted from $n_{\rm ion}$ because the electrostatic interaction between d electrons has already been included in the total electronic energy.

The final two electrostatic terms in Eq. (2) can be combined in a simple way in terms in $E_{\rm fe}^{\rm el}$. Using Eq. (78) of Paper II, one can write $(1/N)E_{\rm fe}^{\rm el}$ in the form

$$\begin{aligned} \frac{1}{N} E_{\rm fe}^{\rm el} = {} & \sum_{k<k_F} (\mathcal{E}_{\vec{k}} + \langle \vec{k} | w_0 | \vec{k} \rangle) + \sum_d E_d \\ & - \sum_{k>k_F} \sum_d \frac{\langle \varphi_d | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | \varphi_d \rangle}{\mathcal{E}_{\vec{k}} - E_d} \\ & \times \left(1 + \langle \vec{k} | P | \vec{k} \rangle - \sum_{d'} \frac{\langle \varphi_{d'} | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | \varphi_{d'} \rangle}{\mathcal{E}_{\vec{k}} - E_{d'}} \right) \ , \end{aligned} \tag{3}$$

where the pseudopotential w_0 has been taken in the optimized form used in Paper I:

$$\begin{aligned} \langle \vec{k}+\vec{q} | w_0 | \vec{k} \rangle = {} & \langle \vec{k}+\vec{q} | v | \vec{k} \rangle \\ & + \sum_{\alpha=c,d} (\mathcal{E}_{\vec{k}} + \langle \vec{k} | w_0 | \vec{k} \rangle - E_\alpha) \langle \vec{k}+\vec{q} | \varphi_\alpha \rangle \langle \varphi_\alpha | \vec{k} \rangle \\ & + \sum_d (\langle \vec{k}+\vec{q} | \Delta | \varphi_d \rangle \langle \varphi_d | \vec{k} \rangle + \text{c.c.}) \end{aligned} \tag{4}$$

and

$$\mathcal{E}_{\vec{k}} = \hbar^2 k^2 / 2m \ , \tag{5}$$

$$E_\alpha = \langle \varphi_\alpha | T + V | \varphi_\alpha \rangle \ , \tag{6}$$

$$P = \sum_{\alpha=c,d} | \varphi_\alpha \rangle \langle \varphi_\alpha | \ . \tag{7}$$

The notation is exactly the same as that used in Paper I. The plane waves $|\vec{k}+\vec{q}\rangle$ and $|\vec{k}\rangle$ are normalized in the atomic volume Ω_0; k_F is the free-electron Fermi wave number. The quantity T is the kinetic energy operator, while v is the contribution to the total self-consistent potential (V) associated with a single ion site. The φ_c are localized core states and the sums in the above equations run over states on a single ion site.

One can write out the terms $\langle \vec{k} | v | \vec{k} \rangle$, E_d, and E_α exactly. The quantity $\langle \vec{k} | v | \vec{k} \rangle$ is just the average potential in the metal:

$$\langle \vec{k} | v | \vec{k} \rangle = \bar{v}^{\,\rm core,\it d} + (n_{\rm unif}/Z^*)(V^{\rm val} + V^{\rm unif} + V^{\rm oh}) \ , \tag{8}$$

where $\bar{v}^{\,\rm core,\it d}$ is the average potential arising from the filled core and d states of a single ion and compensating nuclear charges. In writing the last series of terms in Eq. (8), we have used the fact that the uniform electron density is just a constant. Also, we have noted that $n_{\text{unif}} V^{\text{sc}}$ vanishes identically, since the total screening charge in the metal is zero.

The quantity E_d may be written

$$E_d = \langle \varphi_d | T + (V^{\text{ion}} + V^{\text{unif}} + V^{\text{oh}} + V^{\text{sc}}) | \varphi_d \rangle$$
$$= E_d^{\text{ion}} + (n_d V^{\text{ion}})' + n_d (V^{\text{unif}} + V^{\text{oh}} + V^{\text{sc}}) , \qquad (9)$$

where

$$E_d^{\text{ion}} = \langle \varphi_d | T + v^{\text{ion}} | \varphi_d \rangle . \qquad (10)$$

The potential v^{ion} is that arising from the single ion on which φ_{d} is centered. Similarly, we have

$$E_\alpha = E_\alpha^{\text{ion}} + (n_\alpha V^{\text{ion}})' + n_\alpha (V^{\text{unif}} + V^{\text{oh}} + V^{\text{sc}})$$
$$= E_\alpha^{\text{ion}} + n_\alpha (v^{\text{oh}} + v^{\text{sc}}) - (n_{\text{val}}/Z) V^{\text{unif}}$$
$$- [n_{\text{oh}}/(Z^* - Z)](V^{\text{ion}} + V^{\text{oh}} + V^{\text{sc}})' + C_\alpha , \quad (11)$$

where

$$C_\alpha = [n_\alpha + (n_{\text{val}}/Z)]\, V^{\text{unif}} + (n_\alpha + n_{\text{oh}})(V^{\text{ion}} + V^{\text{oh}} + V^{\text{sc}})' . \qquad (12)$$

The quantities v^{oh} and v^{sc} are, respectively, the potentials arising from the n_{oh} and n_{sc} associated with the ion on which φ_α is centered. We have written E_α in the form (11) so as to take advantage of the fact that this quantity need be computed only to first order in calculating the total energy to second order. The second term in C_α is essentially negligible since $n_\alpha \sim -n_{\text{oh}}/(Z^* - Z)$ outside any given core region.

Using Eqs. (3), (8), (9), and (11) and the formal definition of the magnitude of the orthogonalization hole to second order,

$$Z^* - Z = \sum_{k<k_F} \frac{\langle \vec{k} | P | \vec{k} \rangle}{1 - \langle \vec{k} | P | \vec{k} \rangle} , \qquad (13)$$

one can recombine the various terms in the total energy and obtain

$$E_{\text{total}} = \tfrac{3}{5} Z \mathcal{E}_{\vec{k}_F} + Z^* \overline{v}^{\text{core}, d} - \tfrac{1}{2} n_{\text{oh}} v^{\text{oh}} - n_{\text{oh}} v^{\text{sc}} + \sum_{k<k_F} \Big[\sum_{\alpha = c, d} (\mathcal{E}_{\vec{k}} - E_\alpha^{\text{ion}} - n_\alpha v^{\text{oh}} - n_\alpha v^{\text{sc}} - C_\alpha) \langle \varphi_\alpha | \vec{k} \rangle \langle \vec{k} | \varphi_\alpha \rangle$$
$$+ \sum_d (\langle \varphi_d | \Delta | \vec{k} \rangle \langle \vec{k} | \varphi_d \rangle + \text{c.c.}) \Big] (1 - \langle \vec{k} | P | \vec{k} \rangle)^{-1} - \sum_{k>k_F} \sum_d \frac{\langle \varphi_d | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | \varphi_d \rangle}{\mathcal{E}_{\vec{k}} - E_d}$$
$$\times \left(1 + \langle \vec{k} | P | \vec{k} \rangle - \sum_{d'} \frac{\langle \varphi_{d'} | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | \varphi_{d'} \rangle}{\mathcal{E}_{\vec{k}} - E_{d'}} \right) + \{ \tfrac{1}{2} (n_{\text{ion}} + n_{\text{oh}})(V^{\text{ion}} + V^{\text{oh}})' + (Z^*/Z) n_{\text{unif}} V^{\text{val}}$$
$$+ \tfrac{1}{2} n_{\text{unif}} V^{\text{unif}} - \tfrac{1}{2} n_{\text{sc}} V^{\text{sc}} \} + (1/N)(E_{\text{bs}}^{\text{el}} + E_{\text{ol}}^{\text{el}}) + E^{\text{ion}} , \qquad (14)$$

where we have set

$$E^{\text{ion}} = \sum_d E_d^{\text{ion}} - \tfrac{1}{2} n_d v^d . \qquad (15)$$

In arriving at the quantity in curly brackets in Eq. (14), one uses the fact that any one part of the charge density can be formally interchanged with the potential arising from another part and still provide the same answer. Also note that the term E^{ion} is essentially just the contribution of the d electrons to the total energy of the free ion (or atom). Since such a term contributes only a constant to the total energy of the metal, it may be dropped from future considerations.

The last step is to redivide E_{total} into its four separate contributions:

$$E_{\text{total}} = E_{\text{fe}} + E_{\text{bs}} + E_{\text{es}} + E_{\text{ol}} . \qquad (16)$$

It is convenient to define the components on the right-hand side of Eq. (16) in such a way that they are analogous to those which make up the simple-metal total energy. To do this, it is first necessary to point out that the effects of exchange and correlation among the conduction electrons (n_{unif}, n_{oh}, and n_{sc}), as calculated in the spirit of the Hubbard-Sham method,[7] can be inserted directly into E_{total} if proper interpretations of the various terms are made. This has been demonstrated in detail by Shaw[8] for the case of simple metals, and the generalization to the present case is direct. Specifically, a term like $n_{\text{oh}} V^{\text{oh}}$ can be broken up into a Hartree or Coulomb (Coul) term and an exchange-correlation (xc) term. If the $n_{\text{sc}} V^{\text{sc}}$ term and the exchange-correlation part of the $n_{\text{oh}} V^{\text{oh}}$ term are added to $E_{\text{bs}}^{\text{el}}$, one obtains the generalized band-structure energy per ion:

$$E_{\text{bs}} = (1/N) E_{\text{bs}}^{\text{el}} - \tfrac{1}{2} n_{\text{sc}} V^{\text{sc}} + \tfrac{1}{2} (n_{\text{oh}} V^{\text{oh}})_{\text{xc}} . \qquad (17)$$

In the limit $\Delta \to 0$, Eq. (17) reduces to Shaw's simple-metal result.[8]

If one now replaces n_{oh} by $[(Z^* - Z)/Z] n_{\text{val}}$ for the remaining term in E_{total} and, further, sets

$$n_{\text{ion}} = n_{\text{val}} + n_D , \qquad (18)$$

where n_D represents the electron density n_d plus compensating positive charges at the nuclei, the electrostatic or Ewald energy per ion of N point ions of charge $Z^* e$ immersed in a compensating uniform background can be extracted from Eq. (14):

$$E_{\mathrm{es}}=\tfrac{1}{2}(Z^*/Z)^2(n_{\mathrm{val}}V^{\mathrm{val}})'+(Z^*/Z)n_{\mathrm{val}}V^{\mathrm{unif}}+\tfrac{1}{2}(n_{\mathrm{unif}}V^{\mathrm{unif}})_{\mathrm{Coul}}\;. \qquad (19)$$

The extra terms involving n_D and V^D can be absorbed into a generalized overlap energy per ion:

$$E_{\mathrm{ol}}=N^{-1}E_{\mathrm{ol}}^{\mathrm{el}}+(Z^*/Z)(n_{\mathrm{val}}V^D)'+\tfrac{1}{2}(n_DV^D)'\;. \qquad (20)$$

The term $(Z^*/Z)(n_{\mathrm{val}}V^D)'$ represents the electrostatic energy per ion of the two-body interactions between the n_D from one ion and a point charge Z^*e on another ion site. The quantity $\frac{1}{2}(n_DV^D)'$ is the electrostatic energy per ion of all pairs of overlapping d shells. In the limit that the φ_d become (nonoverlapping) core states, E_{ol} vanishes identically.

Finally, the remaining terms in E_{total} can be combined to form a generalized free-electron energy per ion:

$$E_{\mathrm{fe}}=\tfrac{3}{5}Z\mathcal{E}_{\vec{k}_F}+Z^*\overline{v}^{\mathrm{core},d}-\tfrac{1}{2}(n_{\mathrm{oh}}v^{\mathrm{oh}})_{\mathrm{Coul}}+\sum_{k<k_F}\Big[\sum_{\alpha=c,d}T_\alpha(\vec{k})\langle\varphi_\alpha|\vec{k}\rangle\langle\vec{k}|\varphi_\alpha\rangle+\sum_d(\langle\varphi_d|\Delta|\vec{k}\rangle\langle\vec{k}|\varphi_d\rangle+\mathrm{c.c.})\Big]$$

$$\times[1+\langle\vec{k}|P|\vec{k}\rangle]^{-1}-\sum_{k>k_F}\sum_d\frac{\langle\varphi_d|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_d\rangle}{\mathcal{E}_{\vec{k}}-E_d}\left(1+\langle\vec{k}|P|\vec{k}\rangle-\sum_{d'}\frac{\langle\varphi_{d'}|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_{d'}\rangle}{\mathcal{E}_{\vec{k}}-E_{d'}}\right)+\tfrac{1}{2}(n_{\mathrm{unif}}V^{\mathrm{unif}})_{\mathrm{xc}}\;, \qquad (21)$$

where

$$T_\alpha(\vec{k})=\mathcal{E}_{\vec{k}}-E_\alpha^{\mathrm{ion}}-(n_\alpha v^{\mathrm{oh}})_{\mathrm{Coul}}-\{[n_\alpha+n^{\mathrm{oh}}/(Z^*-Z)]v^{\mathrm{oh}}\}_{\mathrm{xc}}-[n_\alpha+n^{\mathrm{oh}}/(Z^*-Z)]v^{\mathrm{sc}}-C_\alpha\;. \qquad (22)$$

The free-electron energy is unique in that it does not depend on the ion configuration (to second order) but only on the atomic volume Ω_0.

III. STRUCTURE-INDEPENDENT QUANTITIES IN E_{total}

As we have divided up the total energy, it consists of three contributions which depend explicitly on the ion configuration and one which does not. Our principal concern is with the structure-dependent terms, although we shall also discuss an approximate evaluation of the structure-independent free-electron energy. As for simple metals, the configuration dependence of the band-structure energy is easily isolated in reciprocal space in the form of a structure factor,

$$S(\vec{q})=(1/N)\textstyle\sum_j e^{-i\vec{q}\cdot\vec{r}_j}\;, \qquad (23)$$

where the sum is over all ion sites $\vec{r}_j$. The additional energy-wave-number characteristic $F(q)$ is a function of only the atomic volume. The overlap energy, on the other hand, is most conveniently written as a double sum over a pair potential v_{ol}, which also may be calculated as a function of Ω_0. Below we consider the evaluation of E_{fe}, $F(q)$, and v_{ol} for the noble metals. The evaluation of the remaining electrostatic energy is a standard problem and is adequately discussed elsewhere.[1,2]

A. Free-Electron Energy

It is a reasonably straightforward matter to compute E_{fe} as given by Eq. (21). One can reduce the computational effort required, however, by introducing some simplifying approximations. To do this, we first gather up all the exchange-correlation terms in E_{fe} and approximate them by the standard uniform gas result[9]

$$E_{\mathrm{xc}}=-Z(0.916/r_s+0.115-0.031\ln r_s)\;, \qquad (24)$$

where $r_s=(3\Omega_0/4\pi Z)^{1/3}$. Equation (24) is written in the atomic units $\hbar=2m=\frac{1}{2}e^2=1$, which will be used in the remainder of this paper. In these units energies are in rydbergs and distances are in Bohr radii. Also, we neglect the difference between n_α and $-n_{\mathrm{oh}}/(Z^*-Z)$ and write Eq. (22) as

$$T_\alpha(\vec{k})=k^2-E_\alpha^{\mathrm{ion}}-\langle\varphi_\alpha|v^{\mathrm{unif}}+v^{\mathrm{oh}}|\varphi_\alpha\rangle$$

$$=k^2-E_\alpha^{\mathrm{atom}}+\langle\varphi_\alpha|v^s-v^{\mathrm{unif}}-v^{\mathrm{oh}}|\varphi_\alpha\rangle\;. \qquad (25)$$

The second form of Eq. (25) is appropriate to our evaluation procedure, in which we take the φ_α's and the term values E_α^{atom} from the Herman-Skillman tables for the free atom.[10] The potential v^s is calculated as that arising from the valence s-electron density in the free atom. The final three potential terms on the right-hand side of Eq. (25) are equal to δV as calculated in Paper I. This form of δV is used to compute the matrix element $\langle\vec{k}|\Delta|\varphi_d\rangle$.

The particular advantage in making the above approximations is that all the quantities now needed to evaluate E_{fe} are necessarily computed in evaluating the energy-wave-number characteristic. Numerical values of E_{fe} for the noble metals are given in Sec. IV in connection with the binding energy.

B. Energy-Wave-Number Characteristic

We now turn to the evaluation of Eq. (17) for the band-structure energy. First note that one can write

$$\begin{aligned}\tfrac{1}{2}n_{\mathrm{sc}}V^{\mathrm{sc}}&=\frac{1}{2N}\int\Big[{\sum_{\vec{q}}}'\,S(\vec{q})n_{\vec{q}}^{\mathrm{sc}}e^{i\vec{q}\cdot\vec{r}}\Big]\Big[{\sum_{\vec{q}\,'}}'\,S(\vec{q}\,')\,v_{\vec{q}\,'}^{\mathrm{sc}}e^{i\vec{q}\,'\cdot\vec{r}}\Big]d^3\vec{r}\\&=\tfrac{1}{2}\Omega_0{\sum_{\vec{q}}}'\,|S(\vec{q})|^2\,n_{\vec{q}}^{\mathrm{sc}}\,v_{\vec{q}}^{\mathrm{sc}}\\&={\sum_{\vec{q}}}'\,|S(\vec{q})|^2\,(4\pi\Omega_0/q^2)\,[1-G(q)]\,|n_{\vec{q}}^{\mathrm{sc}}|^2\,,\end{aligned}\tag{26}$$

where the prime on the summations means that the $\vec{q}=0$ term is to be omitted. The Fourier transform of the screening electron density $n_{\vec{q}}^{\mathrm{sc}}$ is given by Eq. (12) of Paper I. The quantity $G(q)$ is the exchange-correlation function, which is also discussed in Paper I.

The term $\frac{1}{2}(n_{\mathrm{oh}}V^{\mathrm{oh}})_{\mathrm{xc}}$ in Eq. (17) can be handled similarly, so that by using Eq. (85) of Paper II for $E_{\mathrm{bs}}^{\mathrm{el}}$, one can finally write

$$E_{\mathrm{bs}}={\sum_{\vec{q}}}'\,|S(\vec{q})|^2F(q)\,,\tag{27}$$

where the energy–wave-number characteristic is given by

$$\begin{aligned}F(q)=\frac{2\Omega_0}{(2\pi)^3}\int_{k<k_F}d^3\vec{k}\,\frac{|\langle\vec{k}+\vec{q}\,|w_0|\vec{k}\rangle|^2}{k^2-|\vec{k}+\vec{q}\,|^2}-\frac{2\Omega_0}{(2\pi)^3}\int_{k>k_F}d^3\vec{k}\,\frac{1}{k^2-|\vec{k}+\vec{q}\,|^2}\\\times\left(\sum_d\frac{\langle\vec{k}|\Delta|\varphi_d\rangle\langle\varphi_d|\Delta|\vec{k}+\vec{q}\,\rangle\langle\vec{k}+\vec{q}\,|w_0|\vec{k}\rangle+\mathrm{c.c.}}{k^2-E_d}+\left|\sum_d\frac{\langle\vec{k}|\Delta|\varphi_d\rangle\langle\varphi_d|\Delta|\vec{k}+\vec{q}\,\rangle}{k^2-E_d}\right|^2\right)\\-\frac{4\pi\Omega_0}{q^2}\,[(1-G(q))\,|n_{\vec{q}}^{\mathrm{sc}}|^2+G(q)|n_{\vec{q}}^{\mathrm{oh}}|^2]\,.\end{aligned}\tag{28}$$

The quantity $n_{\vec{q}}^{\mathrm{oh}}$ is the Fourier transform of orthogonalization hole density [Eq. (10) of Paper I].

All the quantities needed to evaluate $F(q)$ for the noble metals have already been discussed in detail in Paper I. We have found it desirable, however, to reconsider the calculation of $\langle\vec{k}+\vec{q}\,|w_0|\vec{k}\rangle$. Specifically, the Kohn-Sham free-electron-exchange approximation used in Paper I to calculate the conduction-core, d exchange contribution to w_0 does very poorly at long wavelengths $(q<k_F)$. The reason why is now fairly clear. The free-electron-exchange potential, as applied to a single ion, is only reasonable where the electron density $(n_{\mathrm{core},d})$ is large, i.e., well inside the core region. Outside the core region, where $n_{\mathrm{core},d}$ is small, the free-electron-exchange approximation considerably overestimates the potential because of the $(n_{\mathrm{core},d})^{1/3}$ dependence. We have found a simple way to correct this problem. Lindgren has pointed out that the free-electron-exchange approximation really applies to the *total* electron density in a system.[11] If we isolate the self-exchange among conduction electrons [as we do through $G(q)$], the remaining part of the potential is more properly given by

$$-4\{[(3/8\pi)(n_{\mathrm{core},d}+n_s)]^{1/3}-[(3/8\pi)n_s]^{1/3}\}\,,\tag{29}$$

where n_s is just $(n_{\mathrm{unif}}+n_{\mathrm{oh}}+n_{\mathrm{sc}})$. In pseudopotential jargon, n_s is the pseudoatom electron density, and we approximate it in Eq. (29) by the valence s-electron density from the free atom. Note that inside the core region $n_{\mathrm{core},d}\gg n_s$ and the Kohn-Sham potential is recovered; outside the core $n_s\gg n_{\mathrm{core},d}$ and the potential goes rapidly to zero, as desired.

The quantitative significance of the new exchange approximation (29) can be appreciated by examining its effect on the form factor,

$$\langle\vec{k}+\vec{q}\,|w|\vec{k}\rangle=\langle\vec{k}+\vec{q}\,|w_0|\vec{k}\rangle+\sum_d\frac{\langle\vec{k}+\vec{q}\,|\Delta|\varphi_d\rangle\langle\varphi_d|\Delta|\vec{k}\rangle}{k^2-E_d}\,,\tag{30}$$

where $|\vec{k}+\vec{q}\,|=|\vec{k}|=k_F$. In Fig. 1 we have plotted the form factor for copper calculated both with the Kohn-Sham potential and with the Lindgren potential, Eq. (29). Note that the difference is fairly large at small q, but by the time $q=2k_F$ the difference has almost disappeared. This is in line with our qualitative reasoning above. Figure 1 also serves to resolve a puzzle with regard to the calculation of physical properties. Specifically, it was previously noted,[4] in using the Kohn-Sham potential, that reasonable results could be obtained in any calculation which did not depend sensitively on either $\langle\vec{k}+\vec{q}\,|w|\vec{k}\rangle$ or $F(q)$ at small q. For this reason, the resistivity of the liquid metal (which was considered in Paper I) is affected at most by only a few percent by use of the Lindgren exchange potential. On the other hand, for the longitudinal modes of the phonon spectrum, which do depend sensitively on $F(q)$ at small q, the correct behavior is critical. In fact, the Kohn-Sham potential leads to imaginary longitudinal phonon frequencies for copper.[4]

In calculating the energy–wave-number characteristics for the noble metals, we have introduced one further refinement. This involves the exchange-correlation function $G(q)$, which has received a considerable amount of attention in the literature in the past few years.[8,12,13] Instead of the exchange-only form used in Paper I, we now employ the most recent interpolation formula of Singwi *et al*[13]:

$$G(q)=A(1-e^{-B(q/k_F)^2})\,, \qquad (31)$$

where A and B are functions of r_s. At metallic densities, $G(q)$ goes approximately to 1 as $q\to\infty$ to properly account for correlation effects among the electrons.

Using Eqs. (29) and (31), we have calculated the normalized energy–wave-number characteristic $F_N(q)$, defined by the equation

$$F(q)=-(4\pi Z^{*2}/\Omega_0 q^2)F_N(q)\,, \qquad (32)$$

for copper, silver, and gold from $q=0$ to $q=5k_F$ at intervals of $0.1k_F$. The results are listed in Table I together with the appropriate values of Ω_0 and Z^*. Also listed in Table I are new values of the form factors for the noble metals. In Fig. 2 we have plotted $F_N(q)$ for copper, silver, and gold.

C. Overlap Potential

As indicated above, the overlap energy can be written in the general form

$$E_{01}=(1/2N){\sum_{i,j}}'\, v_{01}(\vec{r}_i-\vec{r}_j)\,, \qquad (33)$$

where the sums on i and j are over all ion positions $\vec{r}_i$ and $\vec{r}_j$. Using Eq. (86) of Paper II for E_{01}^{el} and Eq. (20), one obtains

$$\begin{aligned} v_{01}(\vec{r}_i-\vec{r}_j)=\sum_{d,d'}\Bigg\{&\langle\varphi_d|\varphi_{d'}\rangle\langle\varphi_{d'}|\Delta|\varphi_d\rangle-\langle\varphi_d|\varphi_{d'}\rangle\Bigg(\sum_{k<k_F}[(k^2-E_d)\langle\varphi_{d'}|\vec{k}\rangle\langle\vec{k}|\varphi_d\rangle+(\langle\varphi_{d'}|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_d\rangle+\text{c.c.})]\\ &-\sum_{k>k_F}\frac{\langle\varphi_{d'}|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_d\rangle}{k^2-E_d}\Bigg)+\langle\varphi_d|\Delta|\varphi_{d'}\rangle\Bigg[\sum_{k<k_F}\langle\varphi_{d'}|\vec{k}\rangle\langle\vec{k}|\varphi_d\rangle-\sum_{k>k_F}\Bigg(\frac{\langle\varphi_{d'}|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_d\rangle+\text{c.c.}}{k^2-E_d}\\ &+\frac{\langle\varphi_{d'}|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|\varphi_d\rangle}{(k^2-E_d)^2}\Bigg)\Bigg]+\text{c.c.}\Bigg\}-2Z^*v^D(\vec{r}_i-\vec{r}_j)+\int d^3\vec{r}\,n_D(\vec{r}-\vec{r}_i)v^D(\vec{r}-\vec{r}_j)\,, \end{aligned} \qquad (34)$$

where φ_d is centered on $\vec{r}_i$ and $\varphi_{d'}$ on $\vec{r}_j$, and where v^D is the potential arising from the electron density n_D. Since the d states are localized, it is clear that the magnitude of v_{01} must decrease rapidly as $|\vec{r}_i-\vec{r}_j|$ increases. The sign of the potential, however, is not obvious from Eq. (34). It turns out that for the noble metals E_{01}^{el} is positive and dominates the negative electrostatic terms. Hence v_{01} is a repulsive potential.

In principle, it is a straightforward matter to evaluate Eq. (34) as a function of $(\vec{r}_i-\vec{r}_j)$. In practice, however, the problem is very greatly complicated by the two-center geometry involved. Especially difficult is an accurate evaluation of the matrix element $\langle\varphi_{d'}|\Delta|\varphi_d\rangle$, where the correct variation in potential in the interstitial region between the two ion centers i and j is needed. The spherical average for δV used in calculating $\langle\vec{k}|\Delta|\varphi_d\rangle$ is no longer appropriate. An approximate but adequate improvement in δV can be made by replacing the constant potential contribution from the neighboring ion in question by the actual potential associated with that ion. Also, note that in a noble-metal free-atom v^s is exactly cancelled at large distances from the nucleus, since the potential must go as e^2/r. If the coordinates are centered on ion i, one can thus write a new $\delta V'$ as follows:

$$\delta V'(\vec{r})=\delta V(\vec{r})-v^s(\vec{r})-v^{\text{ion}}(\vec{r}-\vec{r}_j)-v^{\text{oh}}(\vec{r}-\vec{r}_j)+\text{const}\,. \qquad (35)$$

We have chosen the constant in Eq. (35) such that $\delta V'(0)=\delta V(0)$ and have calculated $\langle\varphi_{d'}|\Delta|\varphi_d\rangle$ according to the formula

$$\langle\varphi_{d'}|\Delta|\varphi_d\rangle=\langle\varphi_{d'}|\delta V'-\langle\varphi_d|\delta V|\varphi_d\rangle|\varphi_d\rangle\,. \qquad (36)$$

Note that the approximations (35) and (36) make v_{01} a function of $|\vec{r}_i-\vec{r}_j|$ only.

Even using Eqs. (35) and (36), it is a difficult computational problem to evaluate v_{01} from Eq. (34), and considerable computer time is needed. We have found it desirable, therefore, to fit v_{01} to a simplified analytic form. In the region of the nearest-neighbor distance r_{nn} in the metal, Eq. (34) is adequately represented by

$$v_{01}(r)=\alpha[1+l(\rho-1)+\beta l^2(\rho-1)^2]\,e^{-\gamma(\rho-1)}\,, \qquad (37)$$

where $\rho=r/r_{\text{nn}}$. The constants α, β, γ, and l are determined by calculating v_{01} and its first and second derivatives at r_{nn} and v_{01} at the second-nearest-neighbor distance with Eq. (34). The values so determined for the noble metals are given in Table II.

D. Effective Interaction between Ions

In calculating physical properties, the reciprocal-space treatment of the band-structure energy and the real-space treatment of the overlap energy are the most useful for reasons of convergence.

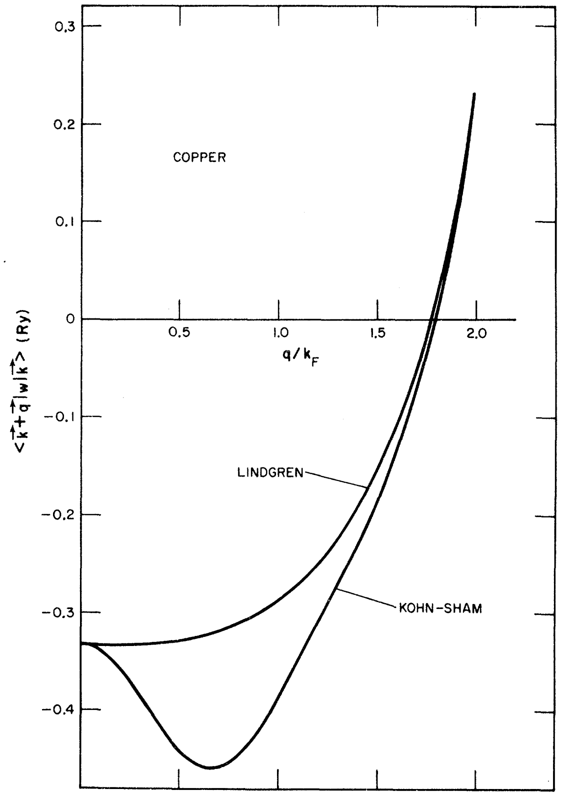

FIG. 1. Form factor for copper computed both with the Kohn-Sham exchange potential and with the Lindgren exchange potential, Eq. (29).

It is worth noting, however, that just as in simple-metal pseudopotential theory, one can formally write the total energy in terms of a two-body effective interaction potential between ions:

$$E_{\text{total}} = E_0(\Omega_0) + \tfrac{1}{2}\sum_{i,j}{}' v_{\text{eff}}(|\vec{r}_i - \vec{r}_j|) , \qquad (38)$$

where E_0 depends only on the atomic volume Ω_0. There are three contributions to the effective interaction potential v_{eff}. One contribution comes from the electrostatic energy and is simply the direct Coulomb repulsion between ions of charge Z^*e. The band-structure-energy contribution is just the Fourier transform of the energy-wave-number characteristic. The final contribution is, of course, the overlap potential discussed above. One thus has

$$v_{\text{eff}}(r) = \frac{2Z^*}{r} - \frac{4Z^*}{\pi}\int_0^\infty F_N(q)\,\frac{\sin qr}{qr}\,dq + v_{01}(r) . \qquad (39)$$

Using Eqs. (37) and (39), we have calculated v_{eff} for copper, silver, and gold and have plotted the results in Fig. 3. The curves show several interesting features. Note that the first distinct minimum in v_{eff} for each metal lies between the position of the first and second nearest neighbors. (As discussed in Sec. V, the minimum for copper should probably be deep, like that for silver and gold.) This qualitative feature is also observed[14] in the simple metals lithium, sodium, and potassium, which, like the noble metals, are all monovalent. The position and strength of this minimum are inevitably related to the structural stability of the metal.

Note also that v_{eff} oscillates about zero. At large r these are just the familiar Friedel oscillations, which result from the sharp cutoff of the electron distribution function at k_F. The inclusion of hybridization here has modified the amplitude but not the form of the oscillations.

E. Quantitative Effect of Hybridization

The quantitative effect of hybridization on the above quantities can be exemplified by computing the form factor and the energy-wave-number characteristic with Δ set equal to zero. We have done this for copper, and in Figs. 4 and 5 we have plotted, respectively, $\langle \vec{k}+\vec{q}|w|\vec{k}\rangle$ and $F_N(q)$ both with and without hybridization. The effect of hybridization is clearly most pronounced in the intermediate q region ($1 < q/k_F < 3$). This region of $\vec{q}$ space is extremely important in many calculations. For example, neglecting hybridization reduces the calculated resistivity of liquid copper by a factor of 4.

It is quite interesting to move one step to the right in the Periodic Table and to repeat the above calculation for zinc. In Fig. 6 we have plotted the form factor for zinc computed both with and without hybridization. Note that the effect of hybridization has been dramatically reduced. On the surface, this result would support the usual practice of treating zinc as a simple metal in pseudopotential calculations. The calculational evidence,[15] however, suggests that hybridization may still be important in understanding many of the physical properties of zinc, as well as of cadmium and

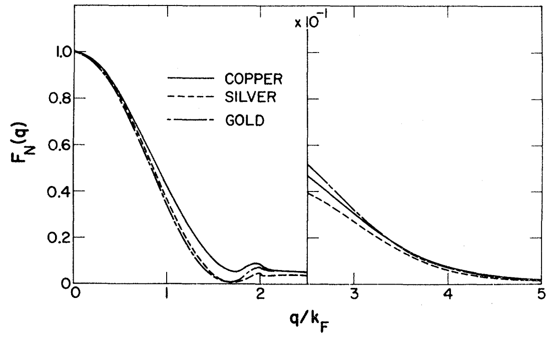

FIG. 2. Normalized energy–wave-number characteristics for copper, silver, and gold.

mercury.

The magnitude of the hybridization terms in the total energy is determined by the quantities E_d and Δ. It is of direct interest then to ask how well we calculate these quantities for the noble metals. In band-theory language E_d is (to lowest order) the position of the d resonance in the metal and, as calculated in Paper I, it corresponds to the mean

TABLE I. Form factors and normalized energy–wave-number characteristics for the noble metals in a.u. (For $q \le 2k_F$ in $\langle \vec{k}+\vec{q}|w|\vec{k}\rangle$, $\vec{k}$ and $\vec{k}+\vec{q}$ are on the free-electron Fermi sphere. For $q > 2k_F$, $\vec{k}$ is on the Fermi sphere and $\vec{k}$ and $\vec{q}$ are antiparallel.)

	Cu		Ag		Au	
	(Ω_0=79.68, Z^*=1.1937)		(Ω_0=115.1, Z^*=1.2345)		(Ω_0=114.4, Z^*=1.2971)	
q/k_F	$\langle \vec{k}+\vec{q}\|w\|\vec{k}\rangle$	$F_N(q)$	$\langle \vec{k}+\vec{q}\|w\|\vec{k}\rangle$	$F_N(q)$	$\langle \vec{k}+\vec{q}\|w\|\vec{k}\rangle$	$F_N(q)$
0.00	−0.3316	1.000 00	−0.2540	1.000 00	−0.2380	1.000 00
0.10	−0.3317	0.992 32	−0.2535	0.991 85	−0.2378	0.991 34
0.20	−0.3306	0.969 59	−0.2507	0.967 68	−0.2352	0.965 77
0.30	−0.3311	0.932 12	−0.2486	0.927 64	−0.2354	0.923 24
0.40	−0.3290	0.881 68	−0.2427	0.873 49	−0.2304	0.866 29
0.50	−0.3275	0.818 89	−0.2369	0.805 38	−0.2273	0.794 25
0.60	−0.3229	0.747 77	−0.2274	0.727 52	−0.2193	0.713 31
0.70	−0.3178	0.668 99	−0.2171	0.640 31	−0.2115	0.622 71
0.80	−0.3095	0.588 01	−0.2035	0.549 63	−0.1999	0.530 30
0.90	−0.2994	0.505 24	−0.1888	0.456 14	−0.1878	0.435 35
1.00	−0.2861	0.425 07	−0.1717	0.365 30	−0.1733	0.343 77
1.10	−0.2696	0.348 34	−0.1528	0.279 56	−0.1567	0.258 92
1.20	−0.2493	0.276 08	−0.1318	0.202 52	−0.1373	0.183 83
1.30	−0.2238	0.211 40	−0.1090	0.135 83	−0.1155	0.119 31
1.40	−0.1926	0.152 86	−0.0843	0.081 31	−0.0906	0.067 26
1.50	−0.1528	0.106 24	−0.0568	0.041 41	−0.0608	0.030 78
1.60	−0.1035	0.071 51	−0.0263	0.016 35	−0.0258	0.010 41
1.70	−0.0413	0.054 68	+0.0086	0.007 02	+0.0167	0.007 47
1.80	+0.0357	0.059 85	0.0483	0.013 85	0.0681	0.024 83
1.90	0.1311	0.085 97	0.0948	0.031 95	0.1309	0.055 60
2.00	0.2492	0.088 52	0.1499	0.043 56	0.2083	0.072 13
2.10	0.2545	0.062 47	0.1586	0.038 31	0.2157	0.059 32
2.20	0.2493	0.058 04	0.1624	0.039 63	0.2170	0.058 34
2.30	0.2374	0.053 52	0.1629	0.040 24	0.2143	0.056 76
2.40	0.2218	0.049 89	0.1608	0.040 05	0.2086	0.054 51
2.50	0.2049	0.046 75	0.1568	0.039 09	0.2007	0.051 61
2.60	0.1889	0.043 58	0.1514	0.037 37	0.1912	0.048 08
2.70	0.1749	0.040 55	0.1447	0.035 21	0.1805	0.044 30
2.80	0.1634	0.037 25	0.1372	0.032 62	0.1693	0.040 23
2.90	0.1540	0.034 00	0.1291	0.029 86	0.1576	0.036 20
3.00	0.1462	0.030 64	0.1207	0.027 00	0.1460	0.032 25
3.10	0.1391	0.027 30	0.1121	0.024 15	0.1345	0.028 48
3.20	0.1319	0.024 18	0.1036	0.021 42	0.1233	0.024 97
3.30	0.1240	0.021 22	0.0953	0.018 81	0.1125	0.021 71
3.40	0.1152	0.018 53	0.0872	0.016 39	0.1021	0.018 77
3.50	0.1055	0.016 12	0.0793	0.014 18	0.0922	0.016 12
3.60	0.0953	0.013 96	0.0718	0.012 18	0.0829	0.013 78
3.70	0.0850	0.012 10	0.0645	0.010 41	0.0740	0.011 74
3.80	0.0753	0.010 45	0.0576	0.008 85	0.0657	0.009 96
3.90	0.0664	0.008 98	0.0511	0.007 49	0.0581	0.008 43
4.00	0.0587	0.007 74	0.0450	0.006 32	0.0510	0.007 13
4.10	0.0521	0.006 62	0.0393	0.005 32	0.0445	0.006 02
4.20	0.0465	0.005 65	0.0341	0.004 48	0.0385	0.005 09
4.30	0.0417	0.004 83	0.0293	0.003 77	0.0331	0.004 31
4.40	0.0371	0.004 13	0.0249	0.003 18	0.0282	0.003 65
4.50	0.0327	0.003 53	0.0209	0.002 68	0.0238	0.003 10
4.60	0.0281	0.003 04	0.0172	0.002 28	0.0200	0.002 65
4.70	0.0234	0.002 65	0.0139	0.001 95	0.0165	0.002 27
4.80	0.0186	0.002 31	0.0109	0.001 67	0.0135	0.001 96
4.90	0.0139	0.002 03	0.0083	0.001 45	0.0109	0.001 69
5.00	0.0096	0.001 81	0.0059	0.001 26	0.0086	0.001 47

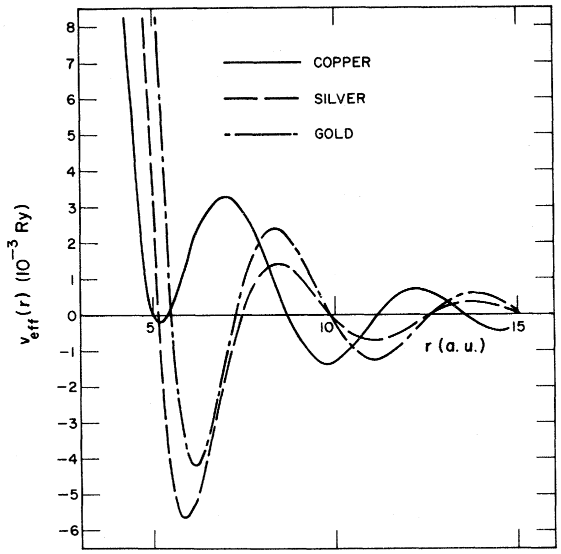

FIG. 3. Effective interaction potentials for copper, silver, and gold.

position of the d band. In Table III we have listed our values of $E_F - E_d$ and also those estimated directly from band-structure calculations. Note that there is fairly good agreement for copper and silver. Our value for gold, however, is undoubtedly too large. The color of the noble metals suggests (from elementary optical absorption considerations) that $E_F - E_d$ for gold lies between the values for copper and silver, as is found in the band-structure calculations.

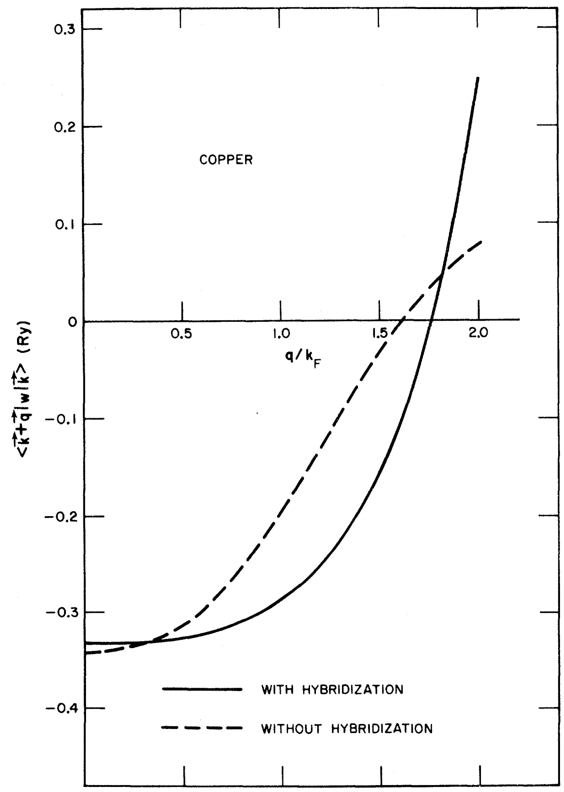

FIG. 4. Form factor for copper computed both with and without hybridization.

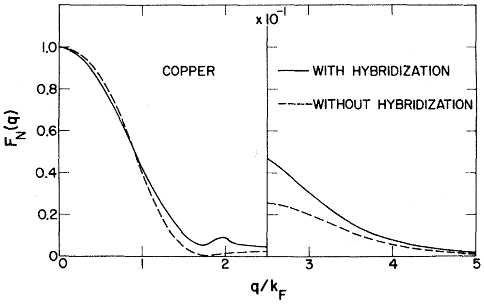

FIG. 5. Normalized energy-wave-number characteristic for copper computed both with and without hybridization.

The corresponding width of the resonance W_d is calculable from the one-electron potential used to generate a band structure. This quantity is also related to $\langle \vec{k}|\Delta|\varphi_d\rangle$ by the simple equation[4,5]

$$W_d = 2\Omega_0 k_d \Delta_d^2 \ , \tag{40}$$

where $E_d = k_d^2$ and

$$\langle \vec{k}_d | \Delta | \varphi_d \rangle = -4\pi Y_{2m}(\vec{k}_d)\, \Delta_d \ . \tag{41}$$

In Table III the value of W_d obtained from Eq. (40) for copper may be compared with that calculated directly from the Chodorow potential and also with that found in fitting the band structure generated by this potential with a model Hamiltonian. The agreement is quite satisfying since it is generally accepted that the Chodorow potential gives a good band structure for copper.

IV. APPLICATIONS

A. Binding Energy

As defined in Sec. II, E_{total} is just the binding energy of the metal. The value of E_{total} for a noble metal in its observed fcc lattice structure is rather easily determined. The structure factor is unity at reciprocal-lattice vectors $\vec{q}_0$ and zero otherwise, so the band-structure energy, Eq. (27), reduces to

TABLE II. Parameters in $v_{01}(r)$ [Eq. (37)] for the noble metals in a.u.

Element	α	γ	β	l	r_{nn}
Cu	0.00670	8.43	0.750	6.20	4.83
Ag	0.00516	10.95	0.772	4.90	5.46
Au	0.01109	9.80	0.741	3.73	5.45

TABLE III. Position and width of the d resonance for the noble metals in Ry.

	Cu	Ag	Au
	$E_F - E_d$		
Present work	0.188	0.429	0.452
Estimate from band calculations	0.2[a]	0.4[b]	0.3[c]
	W_d		
Present work	0.0276	...	...
Other work	0.024[d] 0.0284[e]	...	...

[a] G. A. Burdick, Phys. Rev. 129, 138 (1968); B. Segall, *ibid.* 125, 109 (1962); and E. C. Snow, *ibid.* 171, 785 (1968).

[b] B. Segall (unpublished); and E. C. Snow, Phys. Rev. 172, 708 (1968).

[c] H. Schlosser, Phys. Rev. B 1, 491 (1970).

[d] V. Heine, Phys. Rev. 153, 673 (1967). This value was calculated directly from the Chodorow potential.

[e] D. G. Pettifor, Phys. Rev. B 2, 3025 (1970). This value was obtained by fitting Burdick's band structure (which was generated from the Chodorow potential) with a model Hamiltonian.

$$E_{\text{bs}} = -\sum_{\vec{q}_0}{}' (4\pi Z^{*2}/q_0^2\Omega_0) F_N(q_0) , \qquad (42)$$

where the $\vec{q}_0 = 0$ term is to be omitted from the sum. We have found it necessary to sum over approximately 500 reciprocal-lattice vectors in Eq. (42) to obtain adequate convergence for the noble metals. For values of q_0 greater than $5k_F$, we have extrapolated $F_N(q)$ with a decaying exponential.

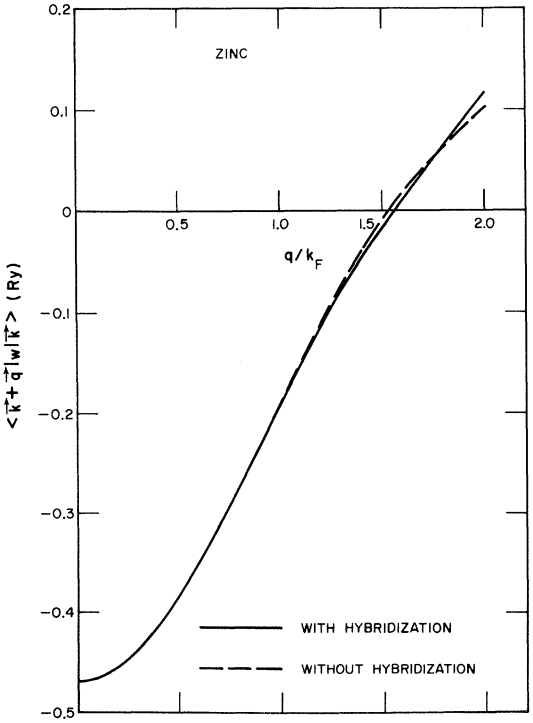

FIG. 6. Form factor for zinc computed both with and without hybridization.

The overlap energy is computed with Eqs. (33) and (37):

$$E_{\text{ol}} = \tfrac{1}{2} \sum_i{}' v_{\text{ol}}(r_i) , \qquad (43)$$

where the $r_i = 0$ term is to be excluded from the sum. Convergence is very rapid for the noble metals; we have carried the sum in Eq. (43) over approximately the 50 closest neighbors in our calculations.

The evaluation of the electrostatic energy for simple crystalline structures is well known. One can write Eq. (19) in the form

$$E_{\text{es}} = -\alpha_{\text{es}} Z^{*2}/[(3/4\pi)\Omega_0]^{1/3} , \qquad (44)$$

where α_{es} is a dimensionless geometrical coefficient. The values of α_{es} for various structures are tabulated elsewhere.[1,4]

The values of the binding energy and its four components for the noble metals are listed in Table IV. Also given there are the experimental binding energies and the theoretical values of E_{fe}, E_{bs}, and E_{ol} calculated in the simple-metal limit of no hybridization (i.e., $\Delta = 0$ and $\varphi_d =$ core state). There are several points which should be made about these results. Note that the agreement between theory and experiment is good for copper but rather poor for silver and gold. The disagreement for silver and gold is not necessarily serious, however. As we have divided up the total energy, the calculation of the free-electron energy is the most crucial in obtaining the correct binding energy. But E_{fe} is a quantity we have treated quite approximately since it is independent of structure and is of secondary interest. Moreover, E_{fe} is somewhat sensitive to the details of its calculation.

Also, note from Table IV that hybridization decreases the magnitude of the calculated binding energy in each case. This finding can be explained

TABLE IV. Binding energy of the noble metals in Ry. Values in parentheses are those calculated in the simple-metal limit of no hybridization.

	Cu	Ag	Au
Experiment[a]	−0.826	−0.775	−0.957
Theory	−0.800(−0.812)	−0.649(−0.691)	−0.652(−0.741)
E_{fe}	0.176(0.177)	0.273(0.254)	0.351(0.316)
E_{bs}	−0.069(−0.033)	−0.049(−0.040)	−0.074(−0.056)
E_{ol}	0.049(0.0)	0.032(0.0)	0.070(0.0)
E_{es}	−0.956	−0.905	−1.001

[a] Experimental binding energy is equal in magnitude to the cohesive energy plus the first ionization energy of the free atom.

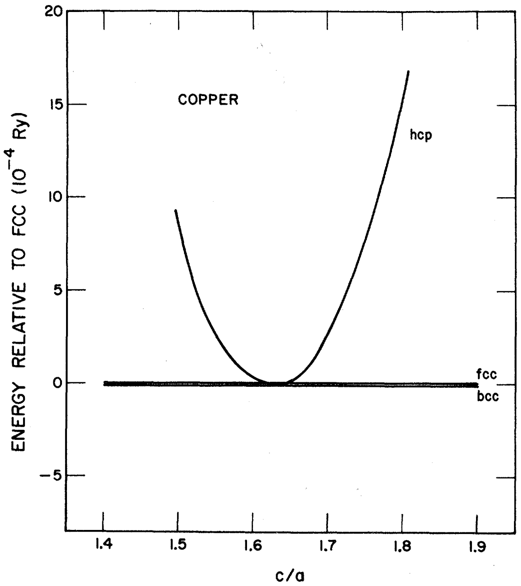

FIG. 7. Total energy of copper as a function of lattice structure computed without hybridization.

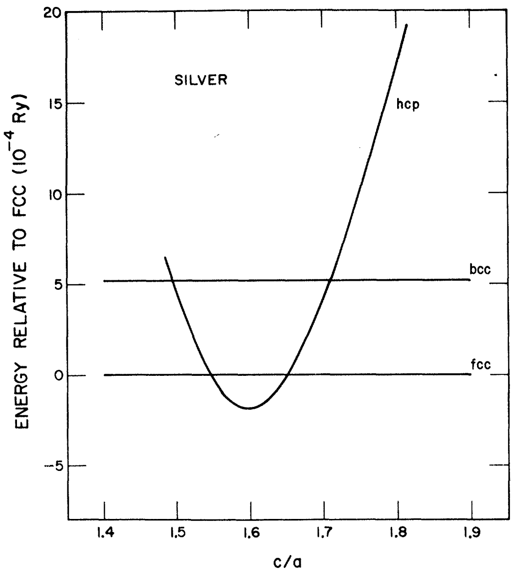

FIG. 9. Total energy of silver as a function of lattice structure.

as follows. The quantities $E_F - E_\alpha$, and hence the repulsive part of the pseudopotential, decrease when one sets $\Delta = 0$; in silver and gold, at least, this effect seems to govern the sign and magnitude of the change in E_{fe} rather than the vanishing of the hybridization terms involving matrix elements of Δ. Furthermore, note that hybridization always increases the magnitude of the (negative) band-structure energy, as would be expected from Fig. 5, but that this is more than offset by the appearance of the overlap energy.

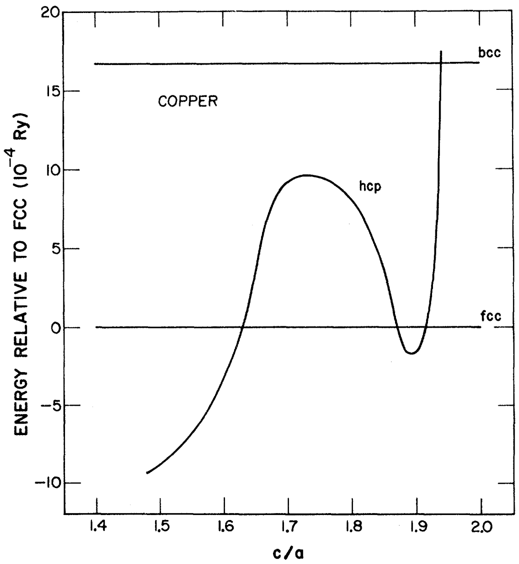

FIG. 8. Total energy of copper as a function of lattice structure.

B. Phase Stability

One of the more interesting calculations that the pseudopotential method facilitates is that of the total energy of a metal as a function of crystal structure. Comparisons can be made at a fixed volume by considering only the structure-dependent terms in the total energy. In principle, the lattice structure which leads to the lowest total energy should be the one which is most stable at a given volume (at zero temperature).

We have sought to predict the stable structures of the noble metals by calculating E_{bs}, E_{ol}, and E_{es} for nine different structures: face-centered cubic (fcc); body-centered cubic (bcc); and hexagonal close-packed (hcp) at c/a axial ratios of 1.5, 1.6, 1.63 (ideal), 1.7, 1.8, 1.9, and 2.0. Figure 7 shows graphically the result obtained for copper in the simple-metal limit of no hybridization. We see that the fcc, bcc, and ideal hcp structures are almost degenerate. The same qualitative results are obtained for silver and gold. When we include hybridization, the degeneracy is lifted for all three metals, as is shown in Figs. 8–10. The experimentally observed fcc structure is now clearly favored over the bcc structure in each case, but there is always at least one range of axial ratio for which the hcp structure has the lowest total energy of all.

Let us account for these findings in more detail. The electrostatic energy favors the fcc structure over the others, but only slightly over the bcc and ideal hcp structure. The band-structure energy,

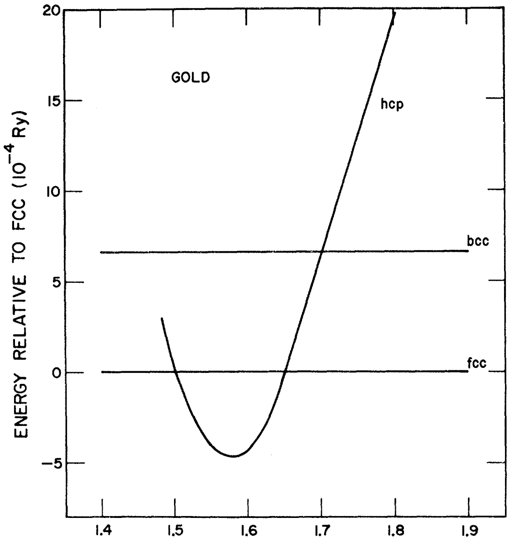

FIG. 10. Total energy of gold as a function of lattice structure.

on the other hand, tends to favor hcp structures because their first few reciprocal-lattice vectors are shorter than those of either the fcc or bcc structures. The energy differences, however, are clearly dependent on the exact shape of the energy-wave-number characteristic. Finally, the overlap energy again favors the fcc structure because of the short-range nature of v_{01}. But the energy difference between the fcc and ideal hcp structures is small because the number and distance of the first and second nearest neighbors are the same in each case. These tendencies qualitatively explain what we see in Figs. 7–10. If we neglect hybridization, the electrostatic energy predominates over the band-structure energy and a result like that shown in Fig. 7 emerges. Including hybridization increases the magnitude of the band-structure energy and adds the overlap energy. The overlap energy separates the bcc from the fcc structure, but the band-structure energy now dominates (at least at certain axial ratios) and lowers the hcp energy below that of the fcc structure.

It is not obvious why this calculation fails, but there are a number of possible explanations. The calculation is certainly a demanding one in that the scale of energy differences among the various structures is 10^{-4} Ry. It is possible that improvements in our calculational techniques might alter the result, but we do not consider this likely. We have found for copper that the qualitative picture is not changed by increasing or decreasing the atomic volume at which the calculation is made nor by altering the energy-wave-number characteristic through the exchange-correlation function $G(q)$ or the position of the resonance E_d. A more probable explanation is that our method does not adequately describe the hybridization. Specifically, we have not included the effects of crystal-field splitting in computing $\langle \vec{k}+\vec{q}\,|w|\,\vec{k}\rangle$, $F(q)$, or $v_{01}(r)$. As pointed out in Paper I, this is a good approximation for the noble metals, affecting these quantities by a few percent at most. However, the crystal-field splitting does make these quantities structure dependent, and on the energy scale of 10^{-4} Ry this is probably not negligible.

C. Phonon Spectrum

Another interesting application of the pseudopotential method is the calculation of the phonon spectrum. What is needed here is the change in the total energy of the metal in the presence of a lattice vibration of wave number $\vec{q}$. This again requires only a consideration of the structure-dependent terms in E_{total}. Harrison[1] has derived the appropriate formulas for the band-structure and electrostatic energy contributions to the phonon spectrum. The former involves summations of $F_N(q)$ over reciprocal-lattice vectors, which can be carried out as above. The overlap energy contribution to the phonon spectrum is again most conveniently handled in real space; the necessary formula has been given by Squires[16] in terms of atomic force constants. The force constants are easily calculable from Eq. (37). For the noble metals one needs only to consider nearest- and next-nearest-neighbor interactions.

We have calculated phonon frequencies $\nu(q)$ for the noble metals along the three principal symmetry directions. The results are plotted in Figs. 11–13 for copper, silver, and gold, respectively. For copper and silver a direct comparison with the experimentally measured frequencies is possible. Note that the agreement is fairly good for silver and, except for the strong Kohn anomalies, is reasonable for copper. An experimental phonon

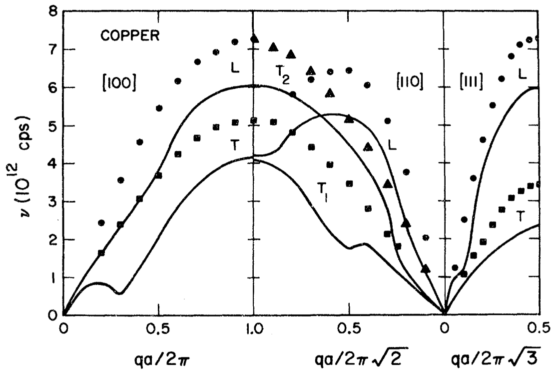

FIG. 11. Phonon frequencies of copper along principal symmetry directions. The experimental points are from Ref. 19.

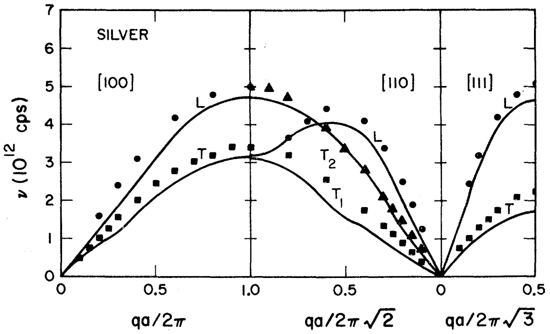

FIG. 12. Phonon frequencies of silver along principal symmetry directions. Experimental points are from W. A. Kamitakahara and B. N. Brockhouse, Phys. Letters 29A, 639 (1969).

spectrum for gold has not been measured.

Figure 14 illustrates the effect of hybridization on the phonon frequencies. The general trend is for the hybridization to increase the frequencies (except at the positions of the Kohn anomalies), which for copper and silver improves agreement with experiment.

The Kohn anomalies in copper deserve a few additional comments. Figure 14 shows that hybridization is responsible for the strong anomalous behavior we find in that metal. The origin of our Kohn anomalies can be traced to the hybridization terms in $F_N(q)$ which result from principal-values integrations over quantities like $(k^2 - |\vec{k}+q|^2)^{-1}$ $(k^2 - E_d)^{-1}$. The first factor provides the necessary singular behavior at $q = 2k_F$, while the second apparently acts as an enhancement factor. Presumably, the almost complete disappearance of the anomalies in silver and gold occurs because of the larger values of $E_F - E_d$ we find in those metals.

No Kohn anomalies have been reported experimentally in copper, although the phonon frequencies have been measured by several groups[17–19] with consistent results. To our knowledge, however, only Svensson *et al.*[18] have searched for anomalous behavior in the phonon spectrum. It is interesting to note that they speculated on the existence of a Kohn anomaly in the lower transverse branch in the [110] direction at the very spot where we find it. (This anomaly corresponds to electronic transitions across the "belly" of the Fermi surface.) They had previously seen such an anomaly in the phonon spectrum of palladium, but found no evidence of one in copper. Svensson *et al.* apparently did not investigate the transverse branch in the [100] direction nor the longitudinal branch in the [111] direction, where we see the other Kohn anomalies.

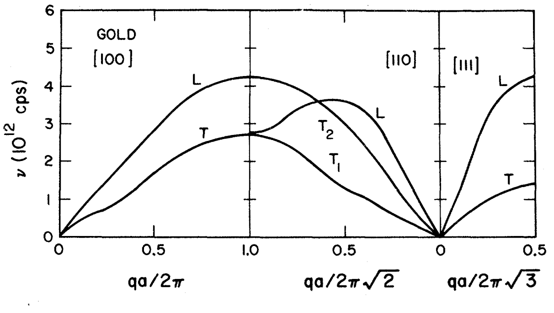

FIG. 13. Phonon frequencies of gold along principal symmetry directions.

V. CONCLUSIONS

Just as for simple metals, there are many additional physical properties one can conceivable calculate by using the energy–wave-number characteristics and overlap potentials given in Sec. III. We anticipate that our results will be useful in this regard. Weaver and DuCharme[20] have already used our $F_N(q)$ and v_{01} to calculate the activation energies for motion of vacancies and divacancies in copper, obtaining reasonably good agreement with experiment. On the other hand, the phase stability calculation in Sec. IV indicates that there is a limit on the success we can expect in those calculations involving very small energy differences (10^{-4} Ry or smaller).

We have made a reasonable attempt here to minimize the approximations used in evaluating our theoretical expressions, but uncertainties do exist in several places nevertheless. Exchange and correlation, for example, are incompletely understood in the noble metals. Our use of the Lindgren conduction-core, *d* exchange represents an improvement over the Kohn-Sham exchange, but it still must be considered a somewhat uncertain approximation.

As indicated in Sec. III, there is reason to believe that we have calculated the hybridization contribution to $F_N(q)$ reasonably well through the matrix element $\langle \vec{k} | \Delta | \varphi_d \rangle$. On the other hand, the reliability of our calculation of $\langle \varphi_d | \Delta | \varphi_{d'} \rangle$, and

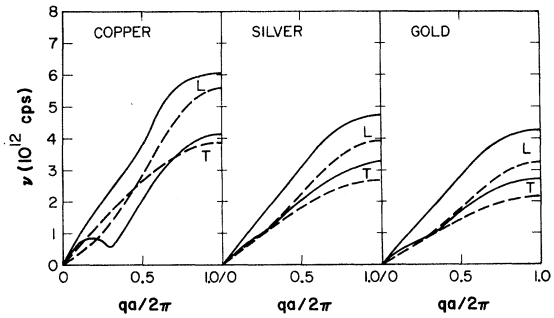

FIG. 14. Phonon frequencies of copper, silver, and gold along the (100) direction. The solid lines are the results obtained with hybridization and the dashed lines are those obtained without hybridization.

hence $v_{01}(r)$, is unknown. We have found, in fact, that agreement with the experimental phonon spectrum of copper is improved if the parameter γ in Eq. (37) is increased from 8.43 to 13.4. This corresponds to increasing the magnitude of dv_{01}/dr and has the effect of deepening the first minimum in $v_{\text{eff}}(r)$ in Fig. 3. It also moves the calculated binding energy closer to the experimental value and moves the fcc curve in Fig. 8 downward with respect to the hcp curve, although not significantly in either case.

We finally point out that the separation of overlap energy from the band-structure energy here is really an artifact of the overlapping atomic d states. In the general theory given in Paper II, the d states are arbitrary as long as they are orthogonal to the core states. The need to calculate $v_{01}(r)$ could be eliminated by artifically constructing nonoverlapping d states. This is an attractive idea, but it does introduce a whole new series of problems related to the construction of such states. It remains to be seen whether or not such an approach can lead to simplified pseudopotential calculations of the total energy for d-band metals.

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Many-Site Interactions and Correlations in Disordered Binary Alloys

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An approximate method for obtaining the pair and higher-order correlation functions specifying the site-occupancy correlations in disordered substitutional binary alloys of arbitrary composition is described. The method is easily generalized from the usual pairwise interaction model to alloys with multi-site interactions. The value of $1/z$, where z is the number of sites interacting with a given site, is used as a parameter of smallness to obtain a set of quasilinear equations which may be solved numerically for the correlation functions. The long range of the interatomic interactions found in many alloys would make $1/z$ seem a good expansion parameter. The validity of the solution is discussed. We use the method in a numerical analysis to investigate the effect of three-site interactions in a disordered face-centered-cubic binary alloy with a nearest-neighbor pair interaction and a "nearest-neighbor-triangle" triplet interaction. A simple analytic solution for a corresponding idealized mean-field situation is also carried out. An enlightening result is that the mean-field solution and the more realistic computer solution have similar general features. We also compare our solution with others for a choice of parameters in which comparison is possible.

I. INTRODUCTION

The equilibrium arrangement of the atoms in a substitutional binary alloy at a given temperature depends on the part of the Hamiltonian which changes when the atoms of the alloy are rearranged on the crystal lattice, which in this paper is taken to be rigid. The most commonly used model