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Bonding energetics of metals: Explanation of trends

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Bonding energetics of elemental metals are explained by a uniform electron-gas model that has been modified to be in mechanical equilibrium. The trends in the work functions, cohesive energies, and chemical potentials are explained semiquantitatively. The same model explains the surface energies of the simple metals; however, it fails qualitatively for the surface energies of the transition metals. The approach retains the simplicity of the uniform electron gas; its only input parameter is the average electron density. Basically, we change the definition of the uniform electron gas slightly, so that the electron gas is in mechanical equilibrium at any particular specified density. The change is a rule for splitting the constant background charge when jellium is cleaved. The trends in the energetics of metals result. The concept of a bonding valence will be defined in order to treat the transition metals in terms of a uniform electron gas. Further, the model, due to its simplicity, may serve as a theoretical laboratory for the study of bonding in metals. For example, it presents the possibility of a nonperturbative calculation of the surface energy of the simple metals beyond the local-density approximation. It is also expected to be a better starting point than jellium for modeling the dynamical surface excitations of metals.

I. INTRODUCTION

The uniform electron-gas model (jellium) has proven to be an important intuitive and pedagogical guide to understanding the electronic excitations of metals. For example, both the plasmon and the particle-hole excitation spectra are qualitatively described by jellium. These results become semiquantitative when restricted to the simple metals, e.g., see Ref. 1. Further, the electron-gas model is used in current calculations of electronic excitations at bare and adsorbate-covered metal surfaces.

Jellium, on the other hand, does not provide a useful guide to the energetics of bonding in metals. From one point of view, this failure is inherent since the jellium model, as it stands, gives no prescriptions for dividing the positive uniform background into pieces. From another, complementary point of view, the failure to predict the bonding energetics is due to the inadequate treatment of the electron-ion interaction. The electron-ion interaction has been directly included in the calculation of metal properties for the past two decades, primarily through the use of density-functional and pseudopotential theory. However, these calculations all sacrifice one of the most attractive features of the electron gas, its uniform ground state.

The uniform electron gas fails qualitatively as a model for the energetics of metals. For example, it predicts negative surface energies for $r_s < 2.5$ (where r_s is the density parameter, $4\pi r_s^3/3 = 1/n_0$, and n_0 is the electron density).[2] This pathology will be shown to arise from the fact that the uniform electron gas is under external pressure. The electrons have their minimum energy at $r_s \simeq 4$. At other densities the positive background, which is kept rigid by external forces, imposes a pressure on the electrons to keep them at the specified r_s.

Utreras-Diaz and Shore[3,4] have included the effects of the ion core in a uniform electron-gas model by modifying the interaction of the electrons and the positive background. They model the additional electron-ion interaction (i.e., that part not accounted for by jellium) by adding an electron potential that is constant inside pseudojellium and zero outside. As in the present work, this additional potential can be thought of as incorporating the electron-ion interaction via a pseudopotential that is constant inside the unit cell and zero outside. Pseudojellium requires an adjustable parameter (fixed by the chemical potential) and gives reasonably good agreement for the surface properties and cohesive energies of the simple metals. However, external forces are still required to maintain equilibrium. The work presented here results from understanding how these external forces may be removed from the pseudojellium model. This understanding allows us to predict the electron-ion interaction in an average way from the condition of mechanical equilibrium, and thus to fix the additional potential. Since the work in this paper has been completed, Perdew *et al.*[5] have presented somewhat similar results. Their work is an extension of the pseudopotential point of view. Also, there exist some unpublished results for simple metals.[6]

In this paper, a simple prescription is given for cleaving the electron gas. This prescription removes the need for external forces. It ensures that the *uniform* electron gas is in mechanical equilibrium at any specified electron density. The result is a uniform electron-gas picture (christened the "ideal metal") that is capable of predicting the trends in the bonding energetics of elemental metals. The only input parameter is the average electron density.

Our motivation in studying the ideal metal is threefold. First, a substantially improved version of the electron gas is introduced, which allows a more realistic treatment of bonding in metals. Second, we determine those properties that depend only on the average electron density, and thus distinguish them from properties that depend on the electron's nonuniformity. This identifies the crucial variables that determine the bonding energies of the metals (the size of the atom and the electron density at the cell boundary). Finally, the new model, due to its simplicity, may be used in a variety of practical calculations. For example, it provides a better starting point than jellium (due to the more realistic treatment of the electron falloff) for calculations of bimetallic adhesion, and for the calculation of plasmons at the surfaces of metals.

This paper is structured as follows. A rule for cleaving the positive background, which leads to the theory of ideal metals, is presented in Sec. II. Transition metals are related to the theory in Sec. III. In Sec. IV we show that (1) the model leads to a simple analytic formula for the chemical potential that is in semiquantitative agreement with experiment, and (2) that it explains (again semiquantitatively) the trends in the experimental cohesive energies of metals. Surface energies and work functions are dealt with in Sec. V. The paper is concluded by a discussion and summary.

II. CLEAVING THE IDEAL METAL

A consistent picture for the cleavage of the ideal metal into pieces should satisfy the following conditions: (1) it should be possible to reassemble the pieces to yield the uniform electron gas, (2) the reassembled uniform system should be in mechanical equilibrium, and (3) only Coulomb interactions should be introduced in the model (that is, arbitrary external forces should not be invoked to explain the interactions between pieces of the background). As discussed above, mechanical stability is not achieved by simply splitting the background into pieces of otherwise unmodified positive charge.

The conditions given above can, however, be satisfied in the following way. (The method we are about to present seems intuitively reasonable; we note that it probably is not unique and that other conditions can probably be chosen that also satisfy mechanical equilibrium.) Imagine that the background (which has density n_0 in the equilibrium state) has been split into pieces. For each piece the positive charge density is chosen to be uniform and to have the value n_0 within the boundaries of the piece and zero outside. In addition we require a δ-*function dipole barrier* at the surface of each piece of the background density. This surface dipole barrier is chosen to have the same value for all pieces and for all points on their surfaces.

The effect of the dipole barrier can be seen by considering the interaction of a single electron with one particular piece of background that is otherwise isolated in free space. The electron potential is given by

$$v_e(\mathbf{r})=n_0\int d\mathbf{r}'\frac{\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+v_0\gamma(\mathbf{r}) \; . \qquad (1)$$

Here, $\gamma(\mathbf{r})$ is the characteristic function, defined to be one within the piece and zero outside. The first term on the right-hand-side represents the electron's interaction with the charge interior to the piece. The second term represents the interaction of the electron with the constant, δ-function, surface dipole barrier. The effect of the dipole barrier is to cause the electron to see an additional constant potential v_0 inside the piece and zero additional potential outside the piece. As can be seen from the discussion below, for $r_s<4$, v_0 is negative and thus increases the bonding.

Now imagine reassembling the system. When the pieces of background are brought into contact, their dipole barriers cancel and one is left with the background of the uniform electron gas. As will be shown below, the value of the dipole barrier can be chosen, i.e., v_0 can be chosen, so that the reassembled system is, for the uniform state, in mechanical equilibrium.

An arbitrary cleavage of the ideal metal may result in many pieces of positive background. The question arises, how do these pieces interact when they are overlapped? The rule is that the additional potentials add as do the positive background charges. Thus, if the local positive background density is $2n_0$, then the additional local potential is $2v_0$.

The following example (see Fig. 1) illustrates the rule for cleavage, gives an idea of its origin, and sets the stage for the numerical results that follow. Consider cleaving the ideal metal into two half spaces of positive background, and separating the two pieces along a line that is normal to the half-space surface. In this case, the additional electron potential (by the definition just given) is v_0 inside the charged half spaces, but it is zero between them. The two half spaces may, also, be overlapped. In this case, the potential is equal to twice v_0 in the overlap region and v_0 elsewhere.

The additional potential changes the force between the two half spaces. We *choose the value of the potential so that the force is zero when the separation is zero.* That is, the ideal metal is in mechanical equilibrium for the specified r_s. In the present example, this is the same as requiring that there be zero forces between the half spaces when they are aligned and have zero separation.

The fact that there is one value of v_0 that allows one to

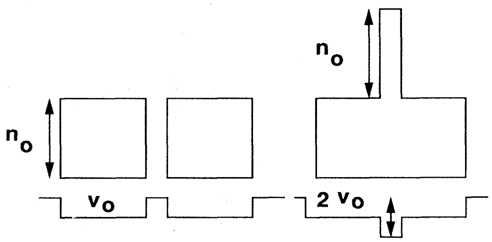

FIG. 1. Schematic representation of the positive background and additional potential for the cleaved ideal metal. The half spaces are shown separated and overlapped.

split the uniform metal into arbitrary pieces and to maintain mechanical stability may be somewhat surprising. Here, we analyze the stability of the ideal metal by dividing it into an arbitrary number of pieces and then shifting these pieces infinitesimally with respect to each other. The change in energy can be computed up to second order in perturbation theory given the linear response function of the electron gas.

The mechanical stability of the system requires that the first-order term in the energy be zero. First-order perturbation theory evaluates the change in the energy due to the change in the potential while the electron density is kept uniform. We consider two states: (1) the uniform state at the equilibrium density, and (2) the state with the background and potentials overlapped but with a constant electron density at the new average electron density $\bar{n}$. E_1 is defined to be the difference in energy between these two states and is given explicitly by

$$E_1 = N[e_{\text{jell}}(\bar{n}) - e_{\text{jell}}(n_0) + v_0(\bar{n} - n_0)/n_0] \ . \qquad (2)$$

Here, n_0 is the average electron density at equilibrium while $\bar{n}$ is the average electron density after the various pieces are shifted. Finally, the energy per electron in the standard uniform electron gas is denoted by $e_{\text{jell}}(n)$. Upon expanding $e_{\text{jell}}(\bar{n})$ about the equilibrium density and setting $E_1 = 0$, to first order in $(\bar{n} - n_0)$, we find

$$v_0 = -n_0 \left[\frac{\partial e_{\text{jell}}}{\partial n} \right]_{n_0} \ . \qquad (3)$$

Equation (3) yields the additional potential required to keep the electron gas in mechanical equilibrium at the specified density.

The ideal metal is a very substantial idealization of the structure of metals. As a result, it has the following defective feature. Namely, the uniform ground state is only a relative minimum in the energy. This can be seen by imagining that we overlap many pieces (say N) of the background in the same place. The additional potential increases as Nv_0. This contribution to the energy increases more rapidly than the buildup in kinetic energy. Hence, the true ground-state results when all of the ions and electrons have been compressed into a single point. This "catastrophe" arises due to our inadequate treatment of the ion cores. It implies that calculations of the *compressed* ideal metal must be treated cautiously.

III. BONDING VALENCES OF THE METALS

Specification of an average electron density is needed to relate the properties of actual metals to the properties of the ideal metal, since the ideal metal is itself a *uniform* electron-gas model. For simple metals, the electron density is nearly uniform throughout the unit cell. Consequently, the electron density that is used as an input to electron-gas models has typically been computed by dividing the nominal valence by the volume per atom. However, for transition metals the number of electrons that participate in metallic bonding does not correlate with the nominal valence. Consequently, one needs a definition of an average electron density (and valence) that correlates with bonding properties.

The electron charge density that builds up in the spaces between the atoms is the focus of most heuristic explanations of bonding in molecules and solids. That is, one focuses on the electrons at the boundaries of the unit cell, which, it is assumed, control the bonding. We will take this view and define the input density for the ideal metal to be the average electron density at the cell boundary. Combined with the specific volume per atom V_{atom} and the ideal metal model, this leads to a definition of a nonintegral bonding valence.

The bonding properties of the elemental metals through the second row of transition elements have been computed from density functional theory[7,8] by Moruzzi, Janak, and Williams (MJW).[9] MJW used the Korringa,

TABLE I. Density parameter r_s and bonding valence.

ELEMENT
BONDING VALENCE
r_s - DENSITY PARAMETER

H												
Li 1.09 3.15	**Be** 1.99 1.87											
Na 1.11 3.80	**Mg** 2.07 2.60											**Al** 2.76 2.12
K 1.21 4.57	**Ca** 2.31 3.11	**Sc** 2.41 2.88	**Ti** 3.25 2.07	**V** 3.46 1.86	**Cr** 3.55 1.76	**Mn** 3.34 1.81	**Fe** 3.26 1.79	**Co** 3.03 1.81	**Ni** 2.76 1.85	**Cu** 2.49 1.96	**Zn** 2.44 2.13	**Ga** 2.43 2.35
Rb 1.24 4.87	**Sr** 2.44 3.32	**Y** 3.25 2.43	**Zr** 3.82 2.06	**Nb** 4.11 1.91	**Mo** 4.37 1.78	**Tc** 4.14 1.78	**Ru** 3.91 1.78	**Rh** 3.51 1.85	**Pd** 2.96 2.00	**Ag** 2.55 2.19	**Cd** 2.42 2.42	**In** 2.51 2.57

Kohn, and Rostoker[10,11] (KKR) method with a muffin-tin approximation for the metallic state. They reported the density both at the muffin-tin boundary, and the number of electrons interstitial between the muffin tins. In this paper we will assume that the input electron density n_0 for the ideal metal is the average interstitial electron density. For simple metals, the values of r_s determined from n in this way are fairly close (within 10%) of those determined from the nominal valence. The values determined for the transition metals are also physically reasonable. The values of r_s used in this paper are shown in Table I.

A bonding valence Z_B for elemental metals is implied by the specific volume per atom in the metal and by the definition of the average electron density in the last paragraph. We define the bonding valence to be

$$Z_B = n_0 V_{\text{atom}} = V_{\text{atom}} / (4\pi r_s^3/3) \ . \tag{4}$$

That is, the bonding valence is the number of electrons of a uniform electron gas with density n_0 that would be contained in the specific volume V_{atom}. Table I contains the values of the bonding valence.

IV. CHEMICAL POTENTIAL AND COHESIVE ENERGY

We show that the ideal metal models the chemical potentials and cohesive energies of the elemental metals. The chemical potential is predicted by a simple analytic formula. The cohesive energy for the ideal metal is computed using density functional theory. For most elements the ideal metal values of the cohesive energy and chemical potential are in semiquantitative agreement with known values, although there are substantial deviations for a number of elements. This is much the same situation that one finds when the electron gas is used to explain electronic excitations such as plasmons.

The chemical potential is the energy required to remove an electron to infinity, neglecting the surface. The chemical potential μ_{ideal} of the ideal metal is shifted from the jellium value by v_0, i.e.,

$$\mu_{\text{ideal}} = \left[\frac{\partial [n e_{\text{jell}}(n)]}{\partial n} \right]_{n_0} + v_0 \ . \tag{5}$$

Using Eq. (3) for v_0, we get the remarkably simple result

$$\mu_{\text{ideal}}(n_0) = e_{\text{jell}}(n_0) \ . \tag{6}$$

Thus for any r_s, $v_0 = e_{\text{jell}} - \mu_{\text{jell}}$, where μ_{jell} is the chemical potential of the uniform electron gas. The idea that the chemical potential of the metals could be predicted by the energy per electron of the electron gas has been previously suggested by Hodges.[12] His work was based on a Wigner-Sietz model for the cohesion of metals and a gradient expansion of the kinetic energy. Note that for metals with $r_s \approx 4.0$, such as sodium, v_0 is close to zero and the jellium model is itself "ideal." There is also a simple formula for the energy per electron in the uniform state of the ideal metal:

$$e_{\text{ideal}} = e_{\text{jell}} - \Omega p_{\text{jell}} \ . \tag{7}$$

Here, Ω represents the volume per electron and p_{jell} denotes the electron pressure in jellium, $p_{\text{jell}} = -\partial e_{\text{jell}} / \partial \Omega$.

The chemical potentials predicted by Eq. (6) for the ideal metal are shown in Fig. 2. The parametrization of Gunnarson and Lundqvist[13] was used to estimate the exchange-correlation energy here and in the density-functional calculations that follow. Weinert and Watson[14] have estimated the chemical potentials for most of the metallic elements based on a combination of first-principles band-structure calculations, model estimates of the dipole barrier, and experimental evaluations of the work functions. These values are compared with the ideal metal in Fig. 2 for the simple metals. As can be seen, Eq. (6) accurately explains the trends for the simple metals. The chemical potentials of the first two rows of transition metals (as well as the simple metals up through the second transition series) are also shown in Fig. 2. For these elements the agreement is somewhat rougher, with a few substantial outliers such as Ag and Pd.

The cohesive energy E_{coh} is the energy needed to disassemble a solid into its constituent neutral atoms. In order to estimate the cohesive energy from the ideal metal model, we need a description for atoms within the ideal metal model. Basically, we imagine the uniform ideal metal being divided into a lattice of "atoms." Each "atom" is represented by the electrons and positive background contained in a Wigner-Seitz cell having a volume equal to V_{atom}. Thus, as shown schematically in Fig. 3, the uniform ideal metal is divided into an array of Wigner-Seitz cells, each modeling an "atom." The cohesive energy is modeled as the difference in energy (per Wigner-Seitz cell) of two states. The first state is the uniform ideal metal. The second state has the ("atoms") Wigner-Seitz cells separated to infinity.

The energy in the first, uniform state can be determined trivially, and the energy per Wigner-Seitz cell is

$$E_u = Z_B [e(n_0) + v_0] \ , \tag{8}$$

where the subscript u refers to the uniform state.

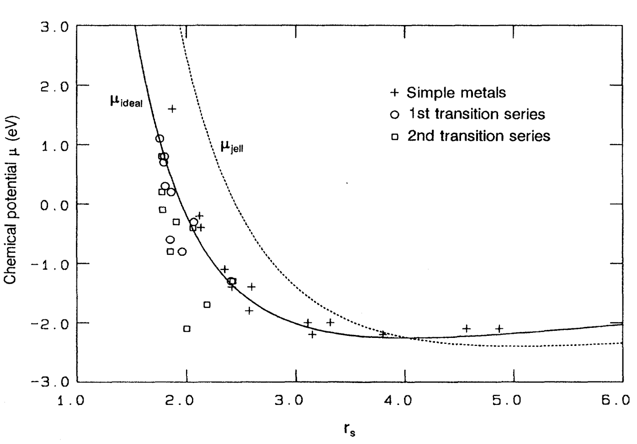

FIG. 2. Chemical potentials predicted for the ideal metal and jellium. They are compared with experimental values for the metals through the second row of transition elements. The element can be identified by comparing its r_s with Table I.

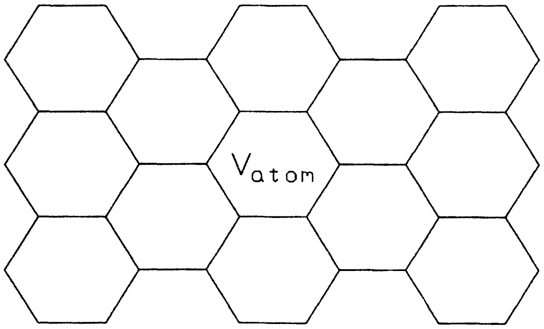

FIG. 3. Schematic representation of the bulk ideal metal divided into "atoms" as indicated by the Wigner-Seitz cells.

The energy $E_{\rm WS}$ of the second state is determined by calculating the energy of a single Wigner-Seitz cell with its compensating electrons in free space. This calculation models the binding energy of the atom in the ideal metal model. The evaluation of $E_{\rm WS}$ is nontrivial, and has been carried out using density-functional theory, with a local approximation for the exchange-correlation energy (as summarized below).

The cohesive energy, as described above, is the difference between an atom in the metal and in free space. For the ideal metal model, it is given by

$$E_{\rm coh}=E_u-E_{\rm WS}\ . \tag{9}$$

The energy of the isolated Wigner-Seitz cell $E_{\rm WS}$ is computed from density-functional theory.[7] The energy functional for our case can be written as

$$E[n_e]=T_s[n_e]+E_{\rm xc}[n_e]+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\int d\mathbf{r}\,n_e(\mathbf{r})v_0\frac{n_b(\mathbf{r})}{n_0}\ . \tag{10}$$

Here $n_e(\mathbf{r})$ denotes the electron density while $n_b(\mathbf{r})$ denotes the positive background density at $\mathbf{r}$. T_s denotes the kinetic energy and $E_{\rm xc}$ denotes the exchange-correlation energy. The net charge density is denoted by ρ and is given by

$$\rho(\mathbf{r})=n_e(\mathbf{r})-n_b(\mathbf{r})\ . \tag{11}$$

Finally, the exchange-correlation energy is inferred from the local-density approximation

$$E_{\rm xc}[n_e]=\int d\mathbf{r}\,n_e(\mathbf{r})e_{\rm xc}(n_e(\mathbf{r}))\ . \tag{12}$$

Here, $e_{\rm xc}(n_e)$ denotes the exchange-correlation energy of a uniform electron gas with density n_e.

The ground state is obtained by solving the Kohn-Sham equations,[8] which are given by

$$-\frac{h^2}{2m}\nabla^2\Psi_k+v_{\rm eff}\Psi_k=\varepsilon_k\Psi_k\ . \tag{13}$$

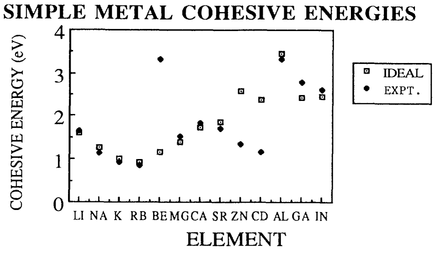

FIG. 4. Cohesive energies of the simple metals compared with ideal metal results.

Here,

$$v_{\rm eff}(\mathbf{r})=v_0\frac{n_b(\mathbf{r})}{n_0}+v_{\rm xc}+e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ , \tag{14}$$

and in the local-density approximation

$$v_{\rm xc}(n_e(\mathbf{r}))=\frac{d}{dn_e}[n_e e_{\rm xc}(n_e(\mathbf{r}))]\ . \tag{15}$$

Finally,

$$n_e(\mathbf{r})=\sum_{\mathbf{k}}|\Psi_{\mathbf{k}}(\mathbf{r})|^2\ . \tag{16}$$

The simultaneous solution of Eqs. (12)–(16) determines the total ground-state energy and density.

The calculation of the ground state energy of an "atom," i.e., an isolated Wigner-Seitz cell with its compensating electrons proceeds as follows. First, in order to simplify the calculation, we replace the Wigner-Seitz cell by a sphere with volume $v_{\rm atom}$. Equations (12)–(16) are then solved iteratively. Consistent with the bonding valence defined above, we fractionally occupy the single-particle electron states. It is assumed that the isolated "atom" is spin neutral; spin-dependent energies are small for the ideal metal. The atom is replaced by a small sphere of the ideal metal. Consequently, the order of filling of the electron states differs from that of a real atom. Minimizing the total energy fills the 1*s* and 2*p* states in order. The single-particle wave functions were calculated numerically using the Numerov technique.

The calculated cohesive energies are compared with ex-

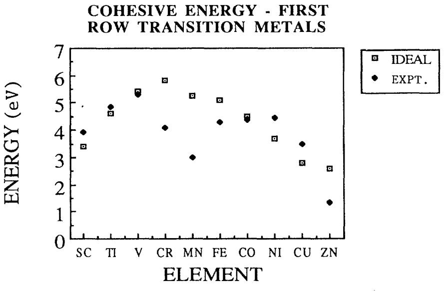

FIG. 5. Cohesive energies of the first row of transition metals compared with ideal metal results.

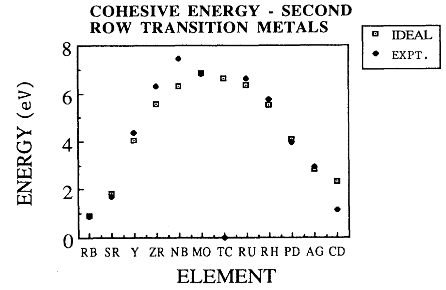

FIG. 6. Cohesive energies of the second row of transition metals compared with ideal metal results.

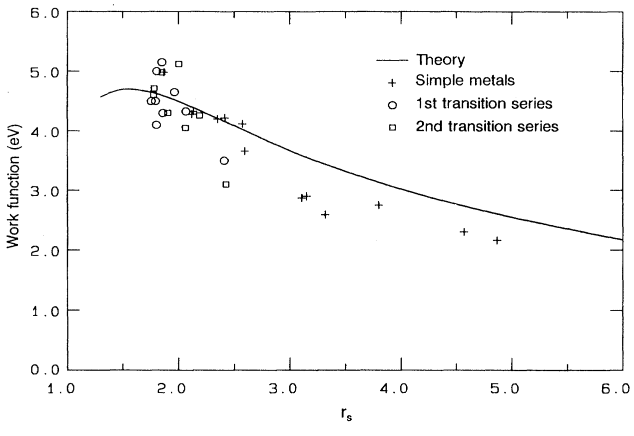

FIG. 7. Work function of the elemental metals compared with ideal metal results. The elements can be identified by comparing their r_s with Table I.

periment[1] in Figs. 4–6. The overall trends in the cohesive energy of the metals are well represented by the ideal metal model. This is particularly surprising for the transition metals, where the details of the core and the d electrons were expected to be critically important. Instead, it appears that all of these effects can be roughly accounted for by the specific volume per atom in the metal and by the input density for the ideal metal model, i.e., the average electron density at the cell boundary.

V. SURFACE PROPERTIES OF THE IDEAL METAL

We calculate the surface properties of the ideal metal using the local-density approximation (LDA) to density-functional theory. The calculation follows along the lines of the work of Lang and Kohn.[2] The ideal metal fills all space for $z<0$; the rest of space, $z>0$, is vacuum. The additional potential is chosen to be v_0 in the ideal metal ($z<0$) and zero otherwise. A similar calculation was reported in Ref. 3, except that v_0 was fit to the experimental chemical potential rather than being determined by Eq. (3).

Work functions of the ideal metal are shown in Fig. 7 and compared with experiment[15] for the densest face of the crystal. The ideal metal clearly explains the trends in the work functions of the elemental metals. The d electrons of the transition metals seem to influence the work functions only through the average electron density.

Surface energetics depend on the particular face of the crystal that is exposed. The approximate calculations reported in this paper do not allow for this dependence. This is not an intrinsic restriction of the ideal metal. Rather, it results from the fact that we cleaved the ideal metal about a plane. In a more realistic calculation, one would account for the atomicity of the metal by splitting it along the boundaries of the Winger-Seitz cells, which represent the atoms in this model. Face dependence for surface quantities would then appear in a natural way. In comparing the results of the ideal metal with experiment, we have always taken experiments on the most densely packed face of the metallic crystal.

Surface energies of the ideal metals are shown in Fig. 8, and compared with the experimental estimates of Tyson and Miller.[16] Agreement for the simple metals is good. The general shape of the surface energy curve is physically reasonable for $r_s>2$. However, the predicted surface energies of the simple metals are systematically too small (compared to Tyson and Miller's estimates) by about 25%, which is consistent with other density-functional calculations. The agreement between theory and experiment might be considered startling since the only input to the theory is the average valence electron density of the given metal. There is no detailed input and there is no attempt to model the atomic core at all. The surface energy of a simple metal is determined by the theory of the electron gas, once it has been modified to be in mechanical equilibrium at the density of that metal.

The ideal metal model fails systematically, however, when used to estimate the surface energies of the transition metals. Surface energies of the ideal metal are typically too low by a factor of 2 or 3. For $r_s<2$, which is characteristic of most transition metals, the surface energy curve behaves unphysically. The curve reaches a max-

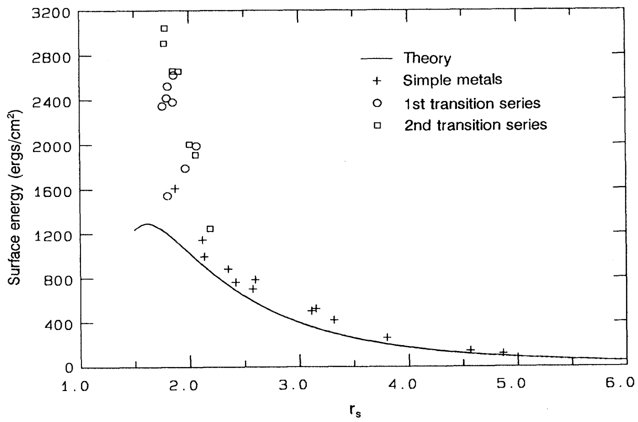

FIG. 8. Surface energies predicted for the ideal metal, and compared with the experimental estimates of Tyson and Miller. The elements can be identified by comparing their r_s with Table I.

imum of 1400 ergs/cm^2 at $r_s = 1.6$, and then becomes negative for r_s even smaller. This qualitative failure of the model is unexplained.

VI. DISCUSSION AND SUMMARY

The theory of ideal metals simplifies our understanding of the origin of the metallic bond. The electron density at the cell boundary was revealed to be a key variable. In particular, the trends in the chemical potentials and work functions (as well as the surface energy of the simple metals) depend primarily on this density. The trends in the cohesive energy of the elemental metals can be computed if one knows, in addition, the size of the "atom," which is the second key variable.

A widely successful empirical formulation for the energetic of metals was introduced by Miedema.[17] His key idea was that the atoms of a metal might be usefully approximated as small uniform pieces of the macroscopic metal. The theory of ideal metals is a microscopic realization of this idea. In this present case the "atoms" are just the Wigner-Seitz cells with their uniform positive background.

One advantage of the present model is that it is so simple that calculations beyond the local-density approximation appear to be feasible. For example, the ideal metal yields the surface energies of the simple metals fairly accurately within a strictly one-dimensional framework. This presents an opportunity for calculating the surface energy of the ideal metal nearly exactly, using either Jastrow function methods[18] or perhaps the variational Monte Carlo approach.[19] Consequently, one would be able to estimate the reliability of the local-density approximation for more complicated surface calculations.

The ideal metal provides a good starting point for any calculation that uses the jellium model as its starting point. For example, the dynamical properties of metal surfaces[20] (and of adsorbates at metal surfaces) are generally calculated using the jellium model. The ideal metal, however, should be preferred, since it is just as simple as jellium and since it models, in a more accurate fashion, the falloff of the surface's electron density.

In summary, a simple model has been constructed for the energetics of the metals. The only ideas used are those of the electron gas and mechanical equilibrium. The ideal metal predicts the surface energies of the simple metals. Finally, there is good agreement with experiment for the trends in the cohesive energies, the work functions, and the chemical potentials of the elemental metals.

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