Contributions to the work function of crystals

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We consider a simple model of the work function based on the overlapping spherical atomic charge-density approximation to the potential (the so-called Mattheiss construct). We show analytically that the dipole barrier of nonpolar crystals is simply related to a moment of the spherical densities, and hence there is no face dependence of the work function in this model. For the polar faces of polar crystals there is an additional face-dependent term that was found previously by different means. We calculate the bulk contributions to the work function for the metals with atomic number less than 50. The dipole barriers obtained from free-atomic densities result in work functions which are on the average ~80% too large. The use of contracted atomic densities, while leaving the bulk density virtually unchanged, decreases the dipole barriers and yields work functions in reasonable agreement with experiment. Some implications for surface calculations, electronegativity scales, and charge-transfer and bonding trends are briefly discussed.

I. INTRODUCTION

One of the most important physical properties of a crystal surface is its work function, ϕ. Defined as the work necessary to remove a Fermi-level electron from the crystal to infinity,[1,2] ϕ not only controls the ability of electrons to escape the crystal but it correlates with the chemical properties of both the surface and the bulk. For example, Gordy,[3] and more recently Miedema and co-workers,[4] have equated the ϕ of the elemental crystals to their electronegativities, an electronegativity being the ability of one element to compete with others for the valence electron charge when a compound is formed. In this paper, we consider a very simple model of the work function which relies on the so-called Mattheiss construct[5] for the crystal potential. This potential yields surprisingly good band structures; in fact, self-consistent calculations must be done with some care if they are to improve on these initial results. Although not universally recognized, this construct has crystal surfaces implicitly built in. The work function is then simply the (negative of the) Fermi energy of the energy bands calculated with this potential. Having the virtue of being well defined, the construct offers a benchmark with respect to which the results of

more detailed calculations may be measured.

For metals, ϕ is of the order[6] of 3 to 6 eV, and the variation from fact to face of the crystal is typically a few tenths of an eV. There are two types of contributions[1,2] to the work function. First there is the bulk chemical potential $\bar{\mu}$ which is the Fermi level measured with respect to some suitable reference potential or "zero" of the crystal potential and, secondly, there is the dipole barrier D associated with the surface of the crystal. The work function is then[2] (cf. Fig. 1)

$$\phi = D - \bar{\mu} , \tag{1}$$

where D and $\bar{\mu}$ must, of course, be defined with respect to the same reference potential, V_0. The potential outside the crystal is the vacuum zero. The dipole barrier depends upon the charge distribution at the surface, in particular on how the electronic charge decays into the vacuum. Other factors may contribute to D. There will be seen, for example, a term intrinsic[7,8] to polar surfaces of polar crystals associated with the alternating layers of $+$ and $-$ charges.

The Mattheiss construct[5] assumes that the crystal density is a superposition of spherical (atomic) densities. This approximation has been very successful in non—self-consistent bulk calculations and has even been used in self-consistent surface calculations[9] in which the spherical densities were modified. If we assume that the surface, as well as the bulk, of a perfect crystal is created by summing over these spherical densities, then the charge-density falloff in the vacuum is atomiclike, which is intuitively reasonable. The situation for a monatomic system is depicted in Fig. 2: There is a surface (in fact a set of crystal faces) implicit in a Mattheiss construct and each surface has a dipole charge distribution associated with it. There is no net dipole in the crystal because of the opposing faces. This must be, given that the crystal has been constructed by a superposition of spherical charge densities. Granted that different crystal faces have different atomic densities within atomic layers and different spacing between layers, it is reasonable to ask whether the di-
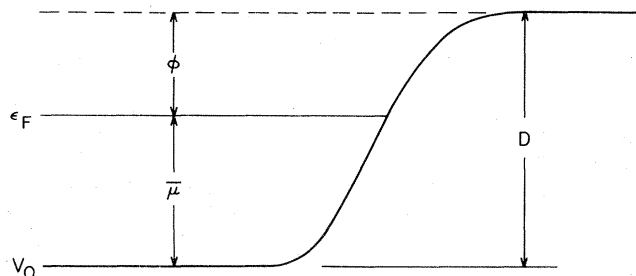

FIG. 1. Schematic representation of the energies relevant to the work function ϕ. The dipole barrier D is the difference between the vacuum zero and the bulk zero V_0. The chemical potential $\bar{\mu}$ is given by the Fermi level ϵ_F relative to V_0.
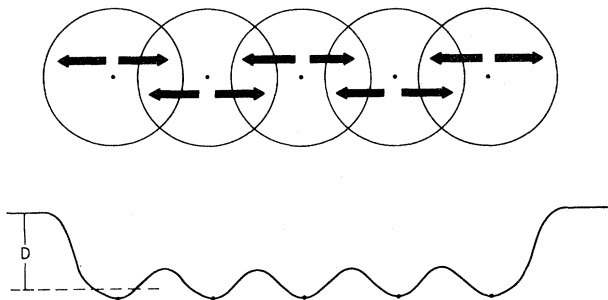

FIG. 2. Schematic representation of a superposition of objects with no net dipole moments (arrows crudely represent the dipole moments of each half of the atom) and the resulting potential. The dipole barrier D is the difference between the average potential inside and that outside the film.

pole barrier within the Mattheiss construct varies with the face involved. It will be shown analytically that the sum is, in fact, independent of the face for a nonpolar crystal. If it were otherwise, the calculated crystal potentials, used by so many workers, would depend on how the individual charge densities were summed. This would be unfortunate. The known variations in work function from face to face on monatomic crystals thus involve factors outside the Mattheiss construct such as reconstruction and valence charge reorganization specific to specific surfaces. Previous workers have used[10,11] the Mattheiss construct to obtain face-dependent dipole barriers but this was because screening terms were introduced into the sums and these terms were the source of the face dependencies.

In the next section we consider the overlapping spherical atomic charge-density approximation and derive some exact relationships between the spherical densities and the dipole barrier. In particular, we find that there is no face dependence of the work function within this model if the system is nonpolar as is the case for the elemental metals. There is, however, an additional face-dependent term[7] when the crystal is polar. We then apply our results to the problem of obtaining dipole barriers and work functions of the metals with an atomic number less than 50. Whereas the dipole barrier is a purely electrostatic term, the chemical potential implies a quantum-mechanical treatment; we obtain $\bar{\mu}$ from the band-structure results of Moruzzi, Janak, and Williams.[12]

While necessary for the calculation of the work functions, the $\bar{\mu}$, when defined with respect to a common reference potential V_0, are of interest by themselves. It will be shown, in Sec. V, that the $\bar{\mu}$ of the transition metals do *not* correlate with known electronegativity trends; hence the relative position of the chemical potentials does not control the bonding and charge transfer associated with transition-metal compound formation.

II. GENERAL CONSIDERATIONS

Consider a slab of M layers normal to z and partially filling the half-space $z < 0$, where each layer consists of one, or if computationally necessary, several planes of atomic sites such that there is neither a net charge nor a normal dipole moment associated with the layer[13] (the

charge of the atoms, making up the layer, may extend outside its boundary). These requirements imply that there are no long-range Coulomb interactions between the layer and a charge at some distance from it.

Consider the average Coulomb potential at some position z, where the average has been taken over a plane normal to z (and parallel to the boundaries of the layers). This potential may be written as a superposition of potentials $v(z)$, each one derived from the periodic array of atomiclike densities associated with a single layer. Note that we can use $v(z)$ instead of the full position-dependent $v(\vec{r})$ without loss of generality since the dipole barrier by symmetry can depend only on z. In order to ensure convergence of sums as we let M (the number of layers) go to infinity, we must require that

$$\lim_{|z| \to \infty} zv(z) = 0 . \tag{2}$$

If the interlayer spacing is d, then we can write the total (averaged) potential $V(z)$ as

$$V(z) = \sum_{n=0}^{M} v(z + nd) , \tag{3}$$

where the sum starts with $n = 0$ since the crystal surface has been defined to be at $z = 0$.

Now let us define the dipole barrier as the difference in the Coulomb potentials averaged over a layer on going from far inside the slab to far outside, i.e., the average electrostatic work a unit test charge must do to leave the slab:

$$D = \langle V(z) \rangle_N - \langle V(z) \rangle_{-N'} \tag{4}$$

where $\langle \cdots \rangle_N$ denotes the average over a unit cell of the layer at $z = Nd$. For a semi-infinite crystal, we will let $M, N, N' \to \infty$ subject to having $N' \ll M$ and that Nd and $N'd$ be small compared with the transverse dimensions of this slab. It should be noted that our definition of the reference potential is not the only possible one: other definitions are possible, such as using a reference level inside the crystal, which is zero in the same sense that the vacuum zero is zero, i.e., which is defined for a crystal where the surface as well as the bulk atomic sites are constrained to have the charge-density distribution of bulk Wigner-Seitz cells with no charge leaking outside the surface layer of cells. This choice of a "renormalized-atom" potential would shift the second term in Eq. (4) by a constant amount. Since, however, we are interested in the work function given by Eq. (1), a constant shift in D *and in* $\bar{\mu}$ will cancel out and ϕ will be independent of the choice of zero. The first of the above choices of zero, which corresponds to the Ewald convention for the bulk,[14] is of the same form as that used in many jellium calculations,[2,15] and has the advantage of being both a well-defined quantity and the natural reference to work within the present derivations. The disadvantage associated with this choice is that taking the averge of the potential samples deep into the core of an atomic-charge distribution, causing D and $\bar{\mu}$ to be separately large in magnitude and to depend strongly on the element involved. This serves to mask the trends in dipole behavior associated specifically with the charge at the surfaces of the crystals. The second choice is less defi-

cient in this respect, so one reference will be employed in the calculations and the other when inspecting the results.

Let us now determine the averages of the potential. First consider $z = Nd$ in the vacuum; we will average over the region $(N - \frac{1}{2})d \le z \le (N + \frac{1}{2})d$ [it is easy to verify that the final results will be unchanged if instead we averaged over $(N - \delta)d \le z \le (N + 1 - \delta)d$, where δ is any finite number]:

$$\langle V(z) \rangle_N = \frac{1}{d} \int_{(N-1/2)d}^{(N+1/2)d} dz \, V(z)$$

$$= \frac{1}{d} \sum_{n=0}^{M} \int_{(N-1/2)d}^{(N+1/2)d} dz \, v(z + nd) \; .$$

After rearranging sums and integrals, we arrive at

$$\langle V(z) \rangle_N = \frac{1}{d} \int_{(N-1/2)d}^{(M+N+1/2)d} dz \, v(z) \; . \tag{5}$$

For N tending to infinity, this average vanishes since the individual $v(z)$ vanish [cf. Eq. (2)]. $\langle V(z) \rangle_N$ is then the vacuum zero.

Now consider the case for $z = -N'd$:

$$\langle V(z) \rangle_{-N'} = \frac{1}{d} \int_{(-N'-1/2)d}^{(-N'+1/2)d} dz \, V(z)$$

$$= \frac{1}{d} \sum_{n=0}^{M} \int_{(-N'-1/2)d}^{(-N'+1/2)d} dz \, v(z + nd)$$

$$= \frac{1}{d} \int_{-(N'+1/2)d}^{(M-N'+1/2)d} dz \, v(z) \; . \tag{6}$$

Using Eqs. (5) and (6), we obtain an expression for the dipole barrier:

$$D = \frac{1}{d} \int_{(N-1/2)d}^{(M+N+1/2)d} dz \, v(z) - \frac{1}{d} \int_{-(N'+1/2)d}^{(M-N'+1/2)d} dz \, v(z)$$

$$= \frac{1}{d} \int_{(M-N'+1/2)d}^{(M+N+1/2)d} dz \, v(z) - \frac{1}{d} \int_{-(N'+1/2)d}^{(N-1/2)d} dz \, v(z) \; . \tag{7}$$

For a finite slab ($M < \infty$), the net dipole barrier will vanish as $N, N' \to \infty$. This result is in accord with Fig. 2, that the total dipole moment must vanish.

In order to obtain the dipole barrier between the inside of the crystal and the vacuum, we must have $M \sim 2N'$. Then letting N, N' go to infinity, the first term in the second line of Eq. (7) goes to zero and we are left with

$$D = -\frac{1}{d} \int_{-\infty}^{\infty} dz \, v(z) \; . \tag{8}$$

At this point we observe that adding a layer of different atoms or molecules to the crystal surface will not affect the dipole barrier (and hence the work function) unless the adsorbate has a net dipole moment. (If the adsorbate does not have a permanent dipole moment, and does not induce a dipole in the substrate, then for $|z|$ large enough, the adsorbate potential will not contribute to the average potential inside or outside.) This simple result demonstrates the quite general feature that the adsorption of atoms on a surface which causes a change in the work function (e.g., cesiation of the surface[16]) must be accompanied by polarization and/or charge transfer at the interface.

Let us express this result in terms of the charge density

of the layer. Again without loss of generality, we need consider only the z-averaged density $\rho(z)$, i.e., the first component of the two-dimensional Fourier representation. The z-averaged potential and density are related by Poisson's equation

$$\frac{\partial^2}{\partial z^2} v(z) = -4\pi \rho(z) \; .$$

With the boundary conditions that the potential and electric field vanish at $z = +\infty$, the potential is given by

$$v(z) = -4\pi \int_z^{\infty} dz' \int_{z'}^{\infty} dz'' \rho(z'') \; .$$

Interchanging the order of integration leads to the standard (but less familiar) form

$$v(z) = -4\pi \int_z^{\infty} dz'' \rho(z'') \int_z^{z''} dz'$$

or

$$v(z) = -4\pi \int_z^{\infty} dz' z' \rho(z') + 4\pi z \int_z^{\infty} dz' \rho(z') \; . \tag{9}$$

It is easy to verify that Eq. (9) satisfies Poisson's equation. From Eq. (2), we see that we must deal with layers that are (i) neutral, (ii) have no net dipole moments, and (iii) have a charge density that vanishes at infinity faster than z^{-3}. The first two conditions ensure that the potential and electric fields vanish at $z = -\infty$, while the third condition guarantees the convergence of the infinite summations and integrals. This last condition is satisfied for all realistic models of the surface since the wave functions (and hence the density) have exponential falloff.

Using Eq. (9), the dipole barrier of Eq. (8) is given by

$$D = \frac{4\pi}{d} \int_{-\infty}^{+\infty} dz \left[\int_z^{\infty} dz' z' \rho(z') - z \int_z^{\infty} dz' \rho(z') \right] \; . \tag{10}$$

If the charge density of a layer is given as a superposition of spherical charge densities $\rho^\alpha(\vec{r})$,

$$\rho^\alpha(\vec{r}) = n_\alpha(r) - Z_\alpha \delta(\vec{r})$$

centered at $\vec{\gamma}_\alpha$, the site of the αth atom in one of the unit cells [$n_\alpha(r)$ is the radial charge density and Z_α is the nuclear charge], then the average density $\rho(z)$ is given by

$$\rho(z) = \frac{1}{A} \int d\vec{r}_{||} \sum_\alpha \rho^\alpha(\vec{r} - \vec{\gamma}_\alpha) \; ,$$

where the integration is in the plane normal to z (A being the area of a layer unit cell in that plane) and the sum is over sites in the layer. Then

$$\rho(z) = \frac{1}{A} \sum_\alpha \left[2\pi \int_{|z - \gamma_z^\alpha|}^{\infty} dr \, r n_\alpha(r) - Z_\alpha \delta(z - \gamma_z^\alpha) \right]$$

$$\equiv \sum_\alpha \rho_0^\alpha(z - \gamma_z^\alpha) \; , \tag{11}$$

where

$$\rho_0^\alpha(z) = \frac{2\pi}{A} \int_{|z|}^{\infty} dr \, r n_\alpha(r) - \frac{Z_\alpha}{A} \delta(z) \; . \tag{12}$$

For the case of neutral entities, for which the potential associated with ρ_0^α is zero at large distance, substitution of Eq. (11) into (10) yields a dipole barrier

$$D = \frac{4\pi}{d} \sum_\alpha \int_0^\infty dz \, z^2 \rho_0^\alpha(z) \, . \tag{13}$$

In order to obtain Eq. (13), we have made use of the relation $\rho^\alpha(-z) = \rho^\alpha(z)$. We can write this in terms of the radial density as

$$D = \frac{2\pi}{3\Omega} \sum_\alpha 4\pi \int_0^\infty dr \, r^4 n_\alpha(r) \, , \tag{14}$$

where we have made use of the fact that the volume of a unit cell in a layer making up the crystal is just $\Omega = Ad$. Note that the sum over α is over atoms within the volume Ω. We see that the barrier, in this model, is a property of the bulk and hence this construction cannot give any face dependence to the work functions of the monatomic metals.

Equations (13) and (14) were obtained for neutrally charged entities. Their extension to the case of a polar crystal adds a term yielding

$$D = \frac{4\pi}{d} \sum_\alpha \int_0^\infty dz \, z^2 \rho_0^\alpha(z) + \frac{4\pi}{Ad} \frac{1}{2} \sum_\alpha q_\alpha (\gamma_z^\alpha)^2$$

$$= \frac{2\pi}{3\Omega} \sum_\alpha 4\pi \int_0^\infty dr \, r^4 n_\alpha(r) + \frac{2\pi}{\Omega} \sum_\alpha q_\alpha (\gamma_z^\alpha)^2 \, , \tag{15}$$

where q_α is the net charge associated with the spherical distribution centered at the αth site, i.e.,

$$q_\alpha \equiv -Z_\alpha + 4\pi \int_0^\infty dr \, r^2 n_\alpha(r)$$

$$= A \int_{-\infty}^\infty dz \, \rho_0^\alpha(z) \, . \tag{16}$$

Consider, for example, a polar surface with alternate layers of $+q$ and $-q$ charges, one pair of charges per area A, separated by $d/2$. Then, the second term of (15) becomes

$$\frac{2\pi}{\Omega} \sum_\alpha q_\alpha \gamma_\alpha^2 = \frac{2\pi}{A} (\tfrac{1}{2} q) \left[\frac{d}{2} \right] \equiv 2\pi\sigma(\tfrac{1}{2}) \, , \tag{17}$$

where $\sigma(\tfrac{1}{2})$ is the dipole moment density for charges $\pm q/2$ (not q), $d/2$ apart, per area A. This result has been obtained by a quite different method elsewhere.[8] Clearly the Mattheiss construct for polar crystals does yield a dipole term which depends on the crystal face involved. The variation from face to face is substantial;[7,8] for example, for an ionic charge, $q = 0.25e$, and a spacing $d = 3$ Å (and assuming $A = d^2$) the resulting polar dipole term of Eq. (17) is almost 2 eV. This is large compared with the variations in Φ which are actually encountered suggesting the importance of screening at polar surfaces.

The q_α, as defined by Eq. (16), are associated with spherical charge distributions centered on, but *not* necessarily localized within, the atomic cells in question. Thus, to the extent to which the actual valence charge density in a polar crystal can be described as a superposition of such spherical charge distributions, the q associated with these distributions provide a physically meaningful definition of the ionic character of the system. These q are relevant to the crystal fields within, as well as to the dipole terms at the surface of, the crystal in question. [Any asphericities in the valence charge density that cannot be accounted for within this construct will, of course, also contribute to the

spherical (and higher l) component(s) of the potential at an atomic site. These can be obtained with the bipolar expansion.[17,18]]

Once obtained, the simple form of the dipole barrier given by Eq. (14) is obvious: The Mattheiss construct yields a surface dipole which is independent of the crystal surface involved unless that surface is a polar one. [In such a case there is the extra term given by Eqs. (15)–(17).] The known variations in the work functions of monatomic crystals comes from reconstruction and valence charge redistribution and screening. The Smoluchowski rules[19] are associated with such terms and, as has already been discussed, recent worker's imposed[10,11] local charge neutrality on their Mattheiss constructs in a way which introduced face-dependent results.

III. THE CALCULATIONS AND THE EXPERIMENTAL WORK-FUNCTION DATA

Although the dipole barrier is strictly an electrostatic property, the work function requires knowledge of the bulk chemical potential which may be obtained from band-structure calculations. For this we have utilized the work of Moruzzi, Janak, and Williams who published[12] self-consistent local-density calculations for the elemental metals with an atomic number less than 50. To obtain $\bar{\mu}$ of Eq. (1), we use their value of the Fermi level relative to the muffin-tin zero (V_{MTZ}) plus the calculated difference between the average Coulomb potential and V_{MTZ} for a muffin-tin density created by overlapping spherical atoms in a manner consistent with their work; i.e., the same lattice constants and crystal structures were assumed and the atomic calculations, yielding the spherical charge densities, employed the same exchange-correlation potential. Moruzzi et al. chose the room-temperature crystal structures (e.g., calculations were done for the bcc, rather than the lower-temperature hcp, structure for Li and Na), and they substituted fcc calculations for the hcp structures when they occurred. In addition, they determined the lattice constants variationally, obtaining results in reasonable accord with experiment. The structure and lattice constant enter the dipole term, defined by Eq. (14), only through the volume Ω. These factors are of more importance, however, when defining the dipole and chemical potential terms with respect to a common reference potential.

The atomic calculations were done for free atoms which, for the case of transition elements, were taken to be in $d^n s^1$ configurations. This is the closest atomic configuration, with integral d and non-d counts, to what is appropriate in the metals. Other choices were investigated and one example of the effect of changing the d count will be reported in the next section. As will be seen, free-atom charge densities lead to surface dipole terms which are too large, as already noted[20] by Taut et al., and results for free atoms in stabilizing potential wells will also be considered. The potentials associated with these wells were taken to be constant out to the Wigner-Seitz radius, to rise linearly by a value of 0.25 Ry at twice this radius, and then to be constant outside. This proved computationally convenient though one could as well have taken the potential associated with a suitably chosen positive charge dis-

tributed over a spherical shell at the Wigner-Seitz radius. The point of using such a potential is that it leaves the atomic-wave-function shape untouched within the Wigner-Seitz cell while reducing the tail outside. Employing the resulting charge density in a Mattheiss construct makes a negligible change in the charge density within the crystal while significantly affecting the surface dipole.

As noted earlier, the use of the average Coulomb potential as the zero of energy, while convenient for calculations, has the disadvantage of masking the trends in dipole behavior. Instead of presenting the dipole barriers given by Eq. (14) with respect to this zero, we instead will define $\bar{\mu}$ and D with respect to the "crystal zero" which will be taken to be equal to the vacuum zero when the crystal sites, up to and including the surface sites, are taken to be bulk Wigner-Seitz cells *with* the bulk charge density inside them. The chemical potential with respect to this "crystal zero" can be obtained given the calculated Coulomb potential of Moruzzi *et al.*[12] and an assumed distribution for the charge density in the interstitial region. This chemical

potential and the correspondingly shifted dipole barriers (assuming spherical Wigner-Seitz cells and a constant density between the muffin-tin and Wigner-Seitz radii) will be termed $\bar{\mu}'$ and D', respectively. The work functions, of course, do not change. Bounds will be given for $\bar{\mu}'$ which are obtained by placing the charge of the muffin-tin region entirely at the muffin-tin radius on one hand and placing it at the Wigner-Seitz radius on the other. This range of $\bar{\mu}'$ values should encompass the effects associated with properly accounting for the fact that Wigner-Seitz cells are polyhedra rather than spheres.

In comparing with experiment, we must keep in mind that there is significant scatter in the experimental work-function values available in the literature. This is due, in part, to questions of sample preparation and, in part, to the use of different measurement techniques. We will employ the "preferred polycrystalline" values tabulated by Michaelson.[6] There are undoubtedly some inconsistencies in the tabulated experimental numbers, on going from one metal to another, but these are not important here.

TABLE I. Calculated values of the work-function contributions in eV. The chemical potentials $\bar{\mu},\bar{\mu}'$ are given with respect to the average electrostatic potential and the "crystal zero," respectively. The calculated work functions and corresponding dipole barriers relative to the "crystal zero" are obtained from free-atomic densities (ϕ_0,D_0') and for atoms in a well ($\tilde{\phi},\tilde{D}'$). These are compared with the D' deduced from experimental values of the work function ϕ_{expt}.

Element	$\bar{\mu}$	$\bar{\mu}'$	ϕ_0	D_0'	$\tilde{\phi}$	$\tilde{D}'$	$(\phi_{expt})^a$	D'
H	3.7	−0.2	7.2	7.0	4.0	3.8		
Li	0.8	−2.2	7.5	5.3	4.3	2.1	2.9	0.7
Be	9.1	1.6	9.2	10.8	4.8	6.4	5.0	6.6
Na	1.8	−2.2	4.8	2.6	3.1	0.9	2.8	0.6
Mg	5.5	−1.4	5.3	3.9	3.5	2.1	3.7	2.3
Al	9.7	−0.2	7.5	7.3	4.2	4.0	4.3	4.1
K	2.5	−2.1	4.0	1.9	2.8	0.7	2.3	0.2
Ca	6.0	−2.0	5.9	3.9	4.0	2.0	2.9	0.9
Sc	10.1	−1.3	7.6	6.3	3.9	2.6	3.5	2.2
Ti	14.4	−0.3	8.9	8.6	4.4	4.1	4.3	4.0
V	17.8	0.2	10.0	10.2	5.1	5.3	4.3	4.5
Cr	20.3	1.1	9.7	10.8	4.8	5.9	4.5	5.6
Mn	20.7	0.8	9.7	10.5	5.1	5.9	4.1	4.9
Fe	20.8	0.7	8.9	9.6	4.8	5.5	4.5	5.2
Co	20.3	0.3	8.7	9.0	5.0	5.3	5.0	5.3
Ni	18.4	−0.6	8.1	7.5	5.1	4.5	5.2	4.6
Cu	16.6	−0.8	6.6	5.8	4.2	3.4	4.7	4.1
Zn	14.9	−0.4	4.9	4.5	3.2	2.8	4.3	3.9
Ga	12.4	−1.1	6.6	5.5	4.1	3.0	4.2	3.1
Rb	3.1	−2.1	3.6	1.5	2.7	0.6	2.2	0.1
Sr	7.0	−2.0	5.4	3.0	3.7	1.7	2.6	0.6
Y	12.1	−1.3	7.0	5.7	3.8	2.5	3.1	1.8
Zr	16.9	−0.4	7.9	7.5	4.3	3.9	4.1	3.7
Nb	20.0	−0.3	8.7	8.4	5.0	4.7	4.3	4.0
Mo	23.8	0.8	8.4	9.2	4.6	5.4	4.6	5.4
Tc	24.2	0.2	8.7	8.9	5.2	5.4		
Ru	24.5	−0.1	8.3	8.2	5.1	4.9	4.7	4.6
Rh	23.2	−0.8	8.0	7.2	5.3	4.5	5.0	4.2
Pd	20.2	−2.1	7.9	5.8	5.7	3.6	5.1	3.0
Ag	17.9	−1.7	5.7	4.0	4.1	2.4	4.3	2.6
Cd	15.3	−1.4	4.6	3.2	3.4	2.0	4.2	2.8
In	13.2	−1.8	5.7	3.9	4.0	1.2	4.1	1.3

[a]Reference 6.

IV. WORK-FUNCTION RESULTS

Results appear in Table I. First displayed are $\bar{\mu}$ and $\bar{\mu}'$, the chemical potentials defined with respect to the average and the "zero" of the crystal potentials, respectively. Then listed are the dipole terms D_0', obtained with free-atom charge densities and, with them, the resulting work-function values. These are, on average, 80% larger than experiment. Some of the error may be associated with details of the band calculations and with the class of crystal potentials used, but this probably contributes less than 0.5 eV to the error. It would appear that the surface dipole terms are simply too large. This can, in part, be associated with a wrong choice of atomic configurations employed in the atomic densities or with densities simply being too diffuse. Consider the former: $d^n s^1$ configurations were assumed for the transition elements which for Pd is $d^9 s$ with a resulting ϕ of 7.9 eV. Going to the self-consistent charge density for a $d^{9.5} s^{0.5}$ Pd atom and in turn $d^{10} s^0$, yield ϕ of 6.6 and 4.9 eV, respectively. The latter is in fair accord with experiment. However, sp-d hybridization in transition metals tends to increase the non-d electron count to above one, implying that the $d^n s^1$ ϕ of Table I are, if anything, underestimates. Of course, the atomic configuration would differ somewhat at the surface. An elementary estimate for Ni indicates[21] an increase in d count and would suggest a decrease for transition metals with under half-filled bands. More recently there have been detailed band calculations for a number of surfaces. Any detailed accounting of charge character must apportion the valence charge outside the muffin-tin spheres. Neglecting this, calculations[22] for V, W, Fe, Ni, Pd, and Pt all indicate that the *fraction* of valence charge which is d-like within the muffin-tin sphere increases at the surface in all cases. The effect is small, being equivalent to an increase of 0.1 d electrons or less at a surface site. However, using the Pd results cited above, this could yield a 0.25- to 0.5-eV reduction in the surface dipole as compared with a construct employing the atomic configuration appropriate to bulk sites. (The most pronounced feature of the surface calculations is the reduction of p-like character at surface sites.)

It would appear that free-atom charge densities simply yield too large surface dipoles in the Mattheiss construct. Consider an alternative: The $\tilde{D}'$ and the associated $\tilde{\phi}'$ of Table I were derived with the densities obtained for the atoms in the stabilizing wells described in the preceding section. These work functions are in semiquantitative agreement with experiment; two thirds of the ϕ are within 0.5 eV of experiment and only Li, Ca, Sr, and Zn have results in error by greater than 1 eV. The results tend to be a few tenths of an eV greater than experiment. A somewhat deeper stabilizing well would "correct" for this and would allow for going to atomic configurations with more realistic nonintegral electron counts. This will not be done here. The point is that the Mattheiss construct with free-atom functions yields too large a surface dipole but that the construct with stabilized atomic wave functions, which are arguably a good linear combination of atomic orbitals (LCAO) basis set for bulk calculations, yields surface dipoles of the right magnitude. This observation has been made by Taut et al. previously.[20]

V. THE CHEMICAL POTENTIAL AND ELECTRONEGATIVITY SCALES

If the chemical potentials of two different regions in a solid are not the same, one expects charge to flow from the one which is higher to the one which is lower so as to equilibrate them. This leads to the idea of attributing a chemical potential or electronegativity to an atomic species which upon compound formation measures the charge transfer between it and other species. Lacking a measure of the chemical potentials *within* crystals, Gordy and Thomas[23] early on introduced the usage of work functions as an electronegativity scale, i.e., they employed the two terms of Eq. (1) rather than $\bar{\mu}$ alone. More recently, Miedema and co-workers[24] employed the same type scale in their model Hamiltonian for the heats of compound formation. There are many other electronegativity scales[25] based on atomic ionization energies and electron affinities, on hyperfine effects, on pseudopotentials, and on fitting thermochemical or dielectric properties or force constants. Involving different measures of bonding effects these scales are not the same but generally, starting with the alkalis, they increase (i.e., the chemical potentials drop) monatomically until they peak somewhere at the upper end of a transition-metal row.

The chemical potentials obtained in the band calculations of Moruzzi et al. display a quite different trend. These are plotted in Fig. 3. The solid line is the $\bar{\mu}'$ of Table I where the chemical potential is measured with respect to the crystal zero and a constant valence charge density is assumed in the muffin-tin region (see Sec. III). The upper bound of the shaded region is associated with placing all the charge of the interstitial region on the surface of the muffin-tin sphere while the lower bound has the charge at the Wigner-Seitz radius. A careful accounting of the charge distribution within the muffin-tin region and of the shapes of the Wigner-Seitz cells would likely lead to results between the line and the upper bound. Some of the jaggedness of the plot is associated with alternating between bcc and fcc structures (the two structures assumed in the band calculations[12]).

The $\bar{\mu}'$ for the 3d and 4d rows peak[26] at Cr and Mo, respectively. This is readily understood since these metals have half-filled d bands where the "bonding" levels are occupied and the "antibonding" levels are not. Maximum cohesion is obtained by compressing the atoms so as to gain the bonding energy associated with having a large bandwidth. This is done at the cost of raising the band center of gravity so that $\bar{\mu}'$ lies shallower than it does in the metals of the neighboring elements. Assuming that charge transfer is controlled by the relative positions of the elemental metal chemical potentials would then have Cr and Mo donating electrons to elements to both their left and their right. This is contrary to bonding trends and to conventional wisdom concerning charge transfer. The dominant factor involved in transition-metal bonding and electron transfer is d-band hybridization. While the relative position of the d bands is not insignificant in this, the strength of hybridization is largely controlled by the relative availability of occupied and unoccupied d-band levels and by the bandwidths. It has been shown[27] that the d transfer associated with d-band hybridization is con-
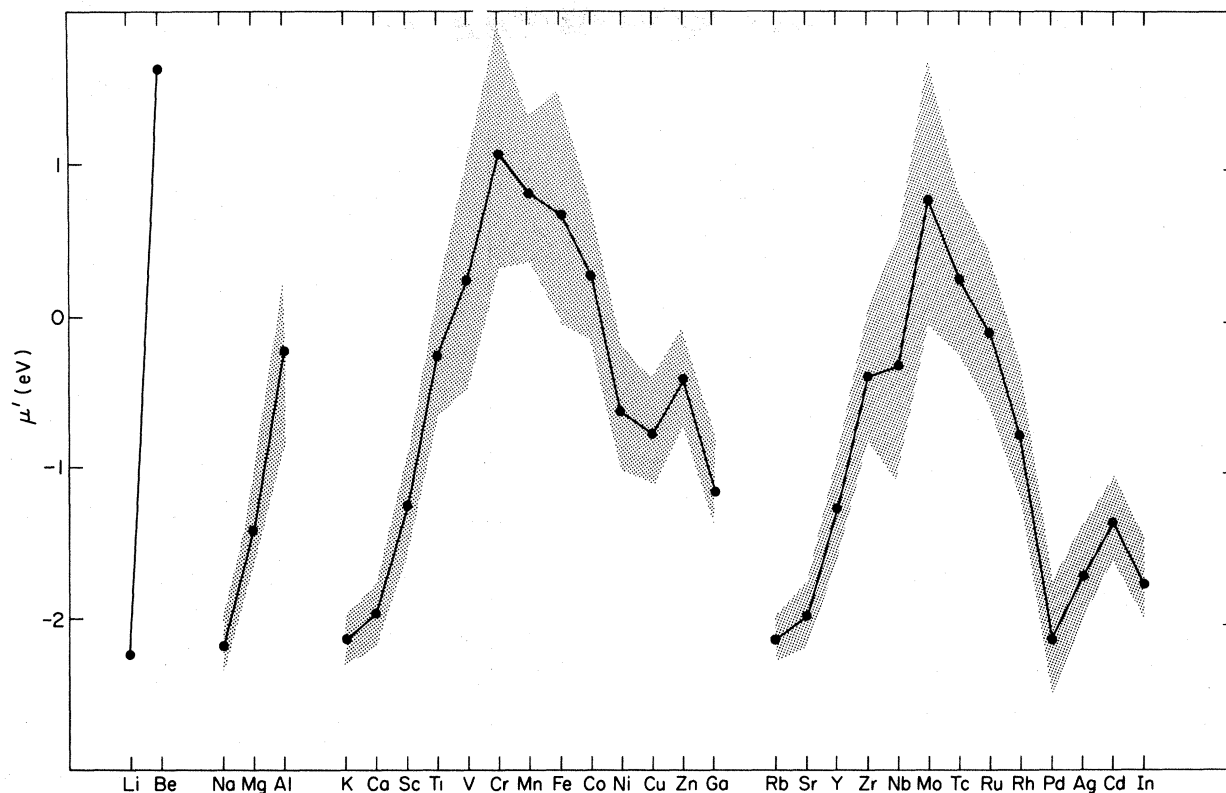
FIG. 3. Chemical potentials relative to the "crystal zero."

sistent with the conventional view of electronegativity trends.

VI. DISCUSSION

In this paper it has been shown analytically that the Mattheiss construct leads to a surface dipole term which is independent of the crystal surface involved unless that surface is a polar one. The form of the dipole barrier given by Eq. (14) is exactly the difference in the average potentials between the Ewald[14] and Bethe-Frenkel[28] conventions for nonionic infinite bulk crystals. (The difference between these conventions for the bulk zero arises mathematically from the interchange of limits and integrals in a conditionally convergent integral and corresponds physically to how the crystal is made infinite.) From our results, it is clear that the Bethe-Frenkel convention must have implicitly the same construct for the surface as discussed here. Hence although the results which we have presented have not, to our knowledge, been previously derived in the context of surfaces, they are intuitively obvious. Moreover, there is an extra face-dependent term associated with polar surfaces which has been derived in a quite different way elsewhere[7,8] and whose presence does not seem to be generally appreciated.

The nonpolar surface dipole, associated with the Mattheiss construct, involves a sum over the lattice sites of the crystal but here it has been shown that this can be rewritten, Eq. (14), as a sum of an atomic moment over the one or several atoms comprising a unit cell in the crystal. This result was then used, along with the band-theory calculations[12] of Moruzzi et al., to calculate the work

functions of the lighter metals ($Z < 50$). As was already noted[20] by Taut et al., the utilization of free-atom charge densities yields surface dipole terms, and in turn work functions, which are too large. The present investigation introduced a simple stabilizing well which, when used, contracted the tails of the atomic densities and led to work functions in semiquantitativie agreement with experiment. The very agreement suggests that these contracted atomic densities would provide a good starting potential for self-consistent surface band calculations though, of course, such contractions are not the only way valence charge redistributes itself at a crystal surface.

The extra dipole term associated with polar surfaces involves an ionic charge defined by Eq. (16). This follows from having limited consideration to only the spherical term in a multipole expansion and suggests a mathematically and physically sensible, but computationally inconvenient, measure of ionic character: namely, to the extent that the charge distribution within a crystal or at its surface is describable as a superposition of spherical charge densities (which may extend well outside of the atomic sites in question), let the charge associated with those distributions [i.e., Eq. (16)] define the site ionicities. A quite different picture of bonding effects might arise than that from the approach of counting charge just within muffin-tin (or Wigner-Seitz) spheres as is often done.

Calculations of the work functions required estimates of the Fermi levels inside the crystals and for this purpose we employed the band-theory results of Moruzzi and co-workers.[12] These chemical potentials are plotted with respect to a common crystal "zero" in Fig. 3 correspond-

ing to having peeled-off surface dipole terms. If one attributes these chemical potentials to individual atomic sites within an alloy or compound, one might ask whether charge transfers from the site with the higher chemical potential to the one that is lower. This is not the case for transition-element systems as was discussed in the preceding section. This is because d-band hybridization, which depends only weakly on the positions of the chemical potentials, is primarily responsible for changes in site d counts and hence in the net change in valence charge at a site. Work functions have been used[23,24] as a measure of electronegativity or bonding tendencies and thanks to the surface dipole terms which contribute to them, they are not indicative of the relative positions of local chemical potentials of atoms within a crystal. Instead, and it would seem by accident, they mimic the combination of bonding effects important to compound formation.

ACKNOWLEDGMENT

[1]E. Wigner and J. Bardeen, Phys. Rev. 48, 84 (1935).

[2]N. D. Lang, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 225.

[3]W. Gordy, Phys. Rev. 69, 604 (1946).

[4]For example, A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica (Utrecht) 100, 1 (1980) or A. K. Niessen, F. R. de Boer, R. Boom, P. F. de Chatel, W. C. M. Mattens, and A. R. Miedema, Calphad 7, 51 (1983).

[5]L. F. Mattheiss, Phys. Rev. 134, 970 (1964).

[6]For example, H. B. Michaelson, J. Appl. Phys. 48, 4729 (1977).

[7]R. E. Watson, M. L. Perlman, and J. W. Davenport, Surf. Sci. 115, 117 (1982).

[8]R. E. Watson and M. L. Perlman, Surf. Sci. 122, 371 (1982).

[9]C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 793 (1979).

[10]L. Fritsche, H. Gollisch, and J. Noffke, Phys. Status Solidi B 89, 367 (1978).

[11]M. Taut and M. Schubert, Phys. Status Solidi B 107, K139 (1981).

[12]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[13]On occasion it proves necessary to apportion an atom, lying on a layer boundary, between the two adjacent layers. If divided, say, half and half, then half the nuclear charge and half of the spherical electron charge density would be assigned to each of the layers. Such a construct is necessary when dealing with a polar surface if one is to have layers which are electrically neutral and have no normal dipole moment and, hence, no long-range Coulomb interactions (see Refs. 7 and 8). The implication, then, is that the outermost layer of a polar surface tends to be fractionally charged.

[14]P. P. Ewald, Ann. Phys. (Leipzig) 64, 253 (1921).

[15]N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

[16]E. Wimmer, A. J. Freeman, M. Weinert, H. Krakauer, J. R. Hiskes, and A. M. Karo, Phys. Rev. Lett. 48, 1128 (1982).

[17]M. E. Rose, J. Math. Phys. (Cambridge, Mass.) 37, 215 (1958).

[18]As an example, see L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972) where aspherical charge-density contributions to the spherical potentials were estimated for the monatomic transition metals. In this case, the contributions are very small.

[19]R. Smoluchowski, Phys. Rev. 60, 661 (1941).

[20]M. Taut, H. Eschrig, and M. Schubert, Phys. Status Solidi B 100, 243 (1980).

[21]P. Fulde, A. Luther, and R. E. Watson, Phys. Rev. B 8, 440 (1973).

[22]The population counts necessary to make this observation are not, in general, available in the literature. Here we have relied on unpublished self-consistent results obtained by M. Weinert, E. Wimmer, S. Ohnishi, and A. J. Freeman for the different surfaces.

[23]W. Gordy and W. J. O. Thomas, J. Chem. Phys. 24, 439 (1958).

[24]For example, A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica (Utrecht) 100B, 1 (1980).

[25]For a review see L. H. Bennett and R. E. Watson, in *Theory of Alloy Phase Formation*, edited by L. H. Bennett (The Metallurgical Soc. of AIME, Warrendale, Pennsylvania, 1980), p. 390.

[26]The observation that $\bar{\mu}$ rises at the start of a row is not an artifact of the chosen reference potential. Inspection of Table I shows that a similar peaking, though sharper and displaced farther to the right (i.e., to heavier transition metals), occurs if the average potential is used as the reference level.

[27]R. E. Watson and L. H. Bennett, Phys. Rev. B 18, 6439 (1978).

[28]H. Bethe, Ann. Phys. (Leipzig) 87, 55 (1928); J. Frenkel, Z. Phys. 59, 649 (1930).