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Static quantum-size effects in thin crystalline, simple-metal films

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Surface-energy and work-function quantum-size fluctuations are predicted for thin Al(111) and Mg(0001) films. The work-function results follow the jellium behavior found by Schulte. For Al(111), a 0.3-eV drop in work function occurs between a two- and three-layer film. For Mg(0001), predicted work-function changes versus layer number are slight because the interlayer spacing is close to $\lambda_F/2$ where λ_F is the Fermi wavelength. The surface energy for Al(111) is also found to vary significantly with layer thickness. This result can be expected to affect the way in which Al grows epitaxially. Generally, one expects static quantum-size effects to be smaller in the transition metals, because the Fermi wavelength is strongly anisotropic.

I. INTRODUCTION

In 1976, Schulte reported that self-consistent calculations of the electronic structure of thin jellium slabs result in static quantum size effects (QSE), and most importantly, oscillations in the work function ϕ as a function of slab thickness.[1] It is generally of interest to know how surface electronic properties depend on atomic geometry—for example, if the local work function of a thin-film electrode is different depending on the film thickness, its performance could be greatly affected. So, it is surprising that there has been no follow-up to Schulte's paper. Here I remedy that situation, presenting calculated work functions and surface energies for few-layer, crystalline Al(111) and Mg(0001) slabs.

There are several reasons why one needs to go beyond jellium-model calculations to predict static QSE with confidence. The most obvious is that the thickness of a crystalline film cannot be varied infinitesimally. One can control the crystal orientation (the Miller indices of the surface) and the number of atomic layers, but the thickness of the film is specified uniquely by minimizing the total energy. In the jellium calculations, the wavelength of the oscillations in surface properties is roughly $\lambda_F/2$, where λ_F is the Fermi wavelength. Therefore, one would expect to see virtually no oscillations with layer number for a crystal oriented such that the layer spacing d equals $n\lambda_F/2$, and maximal oscillations for $d=(2n-1)\lambda_F/4$, where n is a positive integer. An immediate question posed by this prediction is whether λ_F calculated for the jellium density appropriate to the metal in question adequately represents the behavior of the crystalline metal. In a crystal the electron density is anisotropic, and it is not *a priori* obvious what average or "effective" λ_F one should use to predict the static QSE. A reasonable guess might be to use the jellium value that corresponds to the interstitial electron density in an augmented-plane-wave (APW) calculation (which, according to the results of Moruzzi *et al.*,[2] can be either greater or less than the average valence-electron density). The interstitial wave functions control phase changes from layer to layer and thus should play a role in determining QSE. This guess is apparently approximately right for Al, for which I find, by comparison to Schulte's results for the electron-gas radius $r_s=2$, that the effective Fermi wavelength $\lambda_F^{\text{eff}}=1.05\lambda_F^{\text{jellium}}$; while using the results of Moruzzi *et al.*[2] the interstitial Fermi wavelength $\lambda_F^{\text{int}}=1.03\lambda_F^{\text{jellium}}$. For Mg, I have not confirmed this result, because Schulte has not published work functions for $r_s=2.65$ jellium films, and because hcp APW calculations for Mg have not been published (for fcc Mg, $\lambda_p^{\text{int}}=0.99\lambda_F^{\text{jellium}}$, according to Ref. 2).

A second question left open by Schulte's work concerns surface relaxation. As I review in the next section, the source of the oscillations he found with slab thickness is changes in the electron-density profile in the region where it drops off to zero. One cannot, of course, change this profile without incurring a cost in energy. In the jellium model one does not vary the spatial distribution of the positive background charge in an attempt to determine a total-energy minimum—such a calculation would be doomed to failure. For a crystalline slab, however, one can allow the nuclear positions to relax, and it is of interest to see whether in doing so they counteract the electronically induced QSE.

Quite apart from the question of whether outer-layer relaxation affects the QSE in a crystal calculation, the result of minimizing the total film energy with regard to layer spacings is a calculation of the surface energy per exposed atom E_S. This thermodynamic parameter is important in predicting, for example, how epitaxial layers will grow. In the usual macroscopic picture, the surface energy is assumed to have a certain value for each crystal plane, related roughly to the bond breakage energy necessary to expose it. However, the present calculations show that surface energies, like work functions, manifest quantum size effects—E_S for a two-layer Al(111) film, for example, turns out to be about $\frac{1}{2}$ that for the three layer case. This result is of obvious significance in determining the geometry of Al(111) films in the earlier stages of growth.

A final reason for interest in calculating QSE for crystalline films concerns the convergence of slab calculations with film thickness. In a recent publication, for example, Mednick and Kleinman[3] report "perfect agreement" between E_S calculated for a six-layer Al(111) film and experiment. Although Schulte's QSE are quite small for a film this thick, variations of as much as 0.2 eV in ϕ are still possible. Thus only by accounting for QSE and by making a proper extrapolation to a semi-infinite crystal is it possible to claim perfect agreement with single-crystal measurements.

II. THE PHYSICS OF STATIC QSE

That QSE are measurable in thin metal films was first shown by Jaklevic and Lambe,[4] who found resonances in the I-V curves for tunneling through thin Mg, Pb, Ag, and Au films which correspond to the resonances predicted for a particle traversing a square-well potential of an appropriate thickness. Schulte's static QSE, of course, concern the nature of ground- rather than excited-state properties of a film. They are due to the effects on the Fermi sea of the quantization of the electron states normal to the thin-film surfaces, in much the same way as de Haas–van Alphen oscillations are brought about by the imposition of a magnetic field.

Schulte's oscillations in the work function have a period of close to $\lambda_F/2$ as a function of film thickness, where λ_F is the Fermi wavelength of the bulk jellium metal. This result can be understood if it is assumed that the Fermi wave vector of a film rapidly approaches its bulk value, which is determined only by the electron density. In this case the Fermi energy (in a.u.) is given by

$$\epsilon_F = 2\pi^2/\lambda_F^2 \ . \tag{1}$$

Let us now neglect the details of the surface potential barrier and consider the spectrum of levels appropriate to a film bounded by infinite square walls a distance D apart. The spectrum of such a film is

$$\epsilon_{j,k_{\|}} = \tfrac{1}{2}[k_{\|}^2 + (\pi j/D)^2] \ , \tag{2}$$

where the integer j corresponds to the jth level normal to the surfaces and $k_{\|}$ is the parallel wave vector. Schulte's oscillations occur because as D increases, new levels normal to the film become occupied. Comparing Eqs. (1) and (2), one sees that such a new level falls below E every time D increases by $\lambda_F/2$. It remains to understand why the film work function should *oscillate* as a result of energy levels periodically dropping below E_F as D increases. Schulte's explanation is that when a wave function is only weakly bound in the film potential, its exponentially decaying tail in the vacuum region is long. So when a new level is pulled below E_F, electron charge is thrown out into the vacuum region, causing an increase in the work function. If D increases a little further, this effect is enhanced because the parallel Fermi sea built upon the newly occupied level acquires more electrons. But eventually this effect is overcome by the fact that all the levels normal to the film get deeper with increasing film thickness. As a consequence, their vacuum tails become shorter, the surface dipole shortens, and the work function decreases. When D has increased by $\lambda_F/2$, a new level arrives at E_F and the cycle begins anew.

An important feature of Schulte's work-function QSE prediction is that the oscillations should be bigger for higher-electron-density metals, because the normal level spacing is bigger if k_F is. This means that Schulte's effect is easily distinguishable from a Friedel-oscillation-related phenomenon. Friedel oscillations diminish in importance as the electron density increases.

Finally, it should be noted that although the arguments through which the period $\lambda_F/2$ was derived for Schulte's QSE was based on non-self-consistent description of a jellium film and an asymptotic (bulk) value of k_F, this periodicity describes Schulte's self-consistent calculations very well, as he demonstrates.

III. CRYSTALLINE-SLAB CALCULATIONS

In order to investigate static QSE for crystalline films, I have performed self-consistent linear combination of atomic orbitals (LCAO) calculations for Al(111) and Mg(0001) slabs. The methods used in the calculation have been described earlier, in detail.[5] For the present results two features of the method are important. First, the only physical approximation made is the use of a local potential to represent the effects of exchange and correlation. Specifically, I have used the Wigner interpolation formula[6] to obtain V_{xc}. The same xc potential was used by Schulte. It is known to predict the structural properties of metals accurately[2] and their work functions rather well. Apart from the necessity of using a finite, and therefore incomplete, LCAO basis to represent the metal's occupied bands, the most important numerical approximation in the calculation is the representation of the charge and potential as a linear combination of s-like Gaussian functions. This representation, originally introduced by Sambe and Felton,[7] greatly reduces the labor involved in calculating multicenter integrals to obtain the Hamiltonian matrix. But, if one is to obtain reasonable values for work functions and surface energies, one is required to find (generally by trial and error) a suitable Gaussian basis. For Al(111) I have succeeded in finding a charge-potential fit basis such that in the region where the fit is the most difficult, namely where the density falls off to zero into the vacuum, Gibbs oscillations do not set in till the density has fallen to about $\frac{1}{40}$ of the average bulk valence charge density. The appearance of Gibbs oscillations is, of course, a sign that the charge-density fit is fit-basis dependent.[5,8] For Mg(0001) I found a still better basis. In this case, Gibbs phenomena do not appear in the charge-density contour plots till the density has fallen to $\frac{1}{125}$ of the bulk average electron density. By changing the charge-potential fit basis, I judge that the accuracy of my final choices were such that errors induced in the calculated work functions were no more than 0.1 eV. No doubt the results will soon be checked via linear APW (LAPW) calculations, for which there is no need for a charge-potential fit basis. [Five- and nine-layer Al(111)-film LAPW results have already been reported.[9] The work functions found were, respectively, 4.4 and 4.7 eV, which is evidence in itself of QSE in LAPW work functions. Unfortunately, these results were obtained using the Hedin-Lundqvist rather than the Wigner interpolation formula form of V_{xc}, which prevents a meaningful comparison with the present results. Generally, the latter potential gives more accurate work functions.[9]]

Since a reasonably accurate determination of work functions is the desired output of the present calculations, I supplemented the "double-zeta" basis of atomic orbitals (i.e., two s and two p orbitals per metal atom) by a set of "floating" s and p orbitals, at a distance of 1.3 a.u. outside the outer layers of nuclei. For each surface metal atom I introduced three sets of floating orbitals centered, respectively, on the three symmetry lines of the fcc(111) or hcp(0001) surface unit cell. (Recall that these two surfaces have the identical rotation symmetries, and that the three symmetry axes are normal to the surface, one through a surface atom and the other two through the two inequivalent threefold coordination sites in the surface unit cell.)

In order to carry out the surface Brillouin-zone integrations necessary to evaluate the charge density after each iteration of the self-consistent calculations I used 10 special points, according to the scheme of Pack and Monkhorst.[10] Using 19 points, in a spot check, made a difference of about 0.03 eV in the calculated work function and about the same difference in the calculated surface energy.

IV. CALCULATED RESULTS

Calculated work functions and per-surface-atom surface energies are presented for Al(111) in Table I. Work functions for unrelaxed Mg(0001) films are given in Table II. The surface energies were calculated for the n-layer Al(111) films via the formula

$$E_S=\tfrac{1}{2}[E^{\text{tot}}(n\text{-layer film})-nE_b^{\text{tot}}] ,$$

where E_b^{tot} is the total energy[11] per atom of bulk Al, and E^{tot} (n-layer film) is the total energy per surface unit cell of the film. The factor $\frac{1}{2}$ represents the fact that the film has two surfaces. In the one-layer case this definition has the consequence that each atom is treated as *two* surface atoms.

For the multilayer films, the total energy was calculated for several different outer layer separations (e.g., "ideal," 7.5% expansion and 7.5% contraction), and the values of E_S and ϕ that are quoted in Table I correspond to the separation which minimizes the surface energy according to a parabolic fit. Also given are the values of ϕ for the unrelaxed films.

Several aspects of the results in the tables are interesting. For Al(111) there are significant QSE which are somewhat diminished by relaxation of the outer-layer separation. The work function of three- and four-layer Al(111) films are calculated to be 0.3—0.4 eV lower than that for one and two layers and ~0.2 eV lower than that for six layers. The surface energy of the two-layer film is less than half

TABLE I. Calculated work functions and surface energies for Al(111) films. ϕ^{ideal} is the work function computed when the outer-layer separation is unrelaxed from its bulk value. E_S and ϕ are the surface energy calculated at the equilibrium outer-layer separation, which is quoted in the column labeled "percent expansion."

No. of layers Al(111)	% expansion	E_S	ϕ	ϕ^{ideal}
1		0.40	4.2	4.2
2	6.1%	0.18	4.1	4.1
3	2.4%	0.39	3.8	3.7
4	4.3%	0.48	3.8	3.8
6	3.8%	0.52	3.8	4.0

TABLE II. Work functions calculated for Mg(0001) films. Outer-layer separation here has been taken to equal its "ideal" bulk value.

No. of layers Mg(0001)	ϕ^{ideal}
2	3.2
3	3.2
4	3.3
5	3.4
7	3.3

that for one, three, four, or six layers. For Mg(0001), the calculated QSE are slight. In what follows, I attempt to establish the credibility of these results, and explain them by comparison to Schulte's work.

To begin, note that the calculated surface energies agree roughly with values calculated for Al(111) by Lang and Kohn[12] and Sahni *et al.*,[13] both about 0.3 eV and with the experimental value for liquid Al, 0.44 eV/surface atom. The slight surface expansions found agree with what one would expect on the basis of (some, though not all[3]) low-energy-electron diffraction analyses for single-crystal Al(111). For example, Jepsen *et al.*[14] determine that the outer-layer separation relative to its ideal bulk value is expanded by 2.5%. The work functions for both Al and Mg seem somewhat low compared to experiment and other calculations. For Mg(0001), the experimental $\phi = 3.84$ eV according to the ultraviolet photoemission spectroscopy data of Hayden *et al.*,[15] while for single-crystal Al(111), $\phi = 4.26$ eV.[16] Finally, for a six-layer film, Mednick and Kleinman[3] obtain $\phi = 4.28$ eV, while, as noted above, Wang *et al.*,[9] using a different xc potential, find 4.4 and 4.7 eV, respectively, for five- and nine-layer films. For an *ideal* six-layer film I find $\phi = 4.0$ eV, which (cf. Fig. 1) represents an excellent extrapolation of the results I obtain for one, two, three, and four layers, using Schulte's jellium results. However, this value of ϕ is 0.26 eV or 6% lower than Mednick and Kleinman's. It is difficult to be certain about what is responsible for this discrepancy. Their set of charge-potential-fit Gaussians is somewhat more extensive than that which I use, and it is true that in the vacuum region, when the fit to the charge begins to fail, it generally occurs that the electron number density goes (unphysically) negative. This means that as a consequence of fit inaccuracies, unphysical *positive* charge can effectively be placed in the vacuum, which, of course, would lower the calculated work function. Mednick and Kleinman only have published charge-density contours out to $\frac{1}{20}$ the average bulk valence electron density. So it is difficult to say how accurate their charge fit was. In my calculations I tried many different charge-fit bases, and by comparing better and worse bases, do not expect that the work functions given in the tables are inaccurate by more than about 0.1 eV due to fit errors. Moreover, as shown below, the values I calculate agree well with the jellium results of Schulte, which lends them some credence.

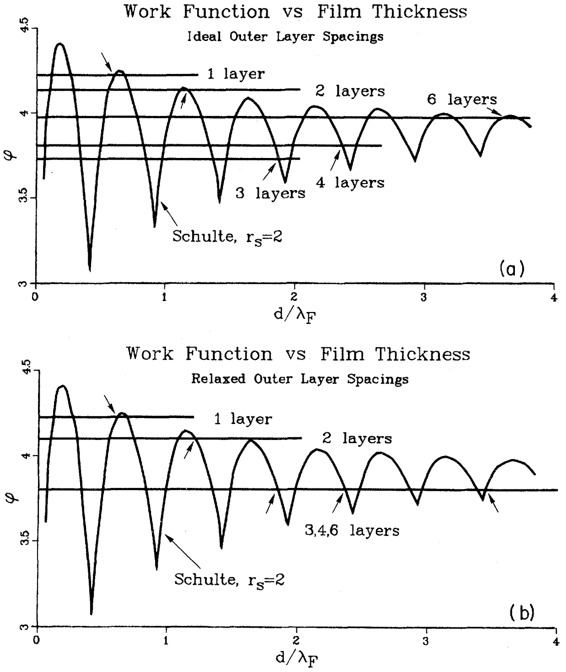

FIG. 1. Schulte's results for work function ϕ as a function of jellium positive background thickness d, divided by the Fermi wavelength, for $r_s = 2$. (a) Horizontal lines indicate calculated values of ϕ for n-layer crystalline films with ideal outer-layer spacing and $n = 1$, 2, 3, 4, and 6. Note that the spacing of the intersections at roughly $d/\lambda_F \approx 0.6$, 1.2, 1.9, 2.4, and 3.6 corresponds to an approximately equal increase in the effective jellium-film thickness each time a new atomic layer is added. (b) Here the horizontal lines correspond to ϕ for one-, two-, three-, four-, and six-layer films with equilibrium outer-layer separations. Intersections with Schulte's curves lie at $d/\lambda_F \approx 0.6$, 1.2, 1.9, 2.4, and 3.5.

Again in the case of Mg, my calculated work functions are about 0.5 eV lower than experiment. This fits a trend which appears to be fairly general—that calculated ϕ's for reactive metals are several tenths of an eV too low.[17] Whether this means that because of their reactivity they are generally coated with submonolayer quantities of oxygen or some other impurity (F?), or that Gaussian fit bases are never adequate, will soon be known.

LAPW computer codes, in which fit bases are avoided, should settle the theoretical question.

Let us now compare the results obtained here for ϕ with Schulte's jellium values. In his calculations, he introduced, "by hand," a potential contribution to represent the image force on an electron well outside the film. The image force is not correctly included when a strictly local description of exchange and correlation is used in a surface electronic calculation.[6] Nevertheless, since the electron density is very small by the time image force becomes important, the fact that Schulte introduced an "image-potential tail" and I did not should have little effect on the comparison of results.

In Figs. 1(a) and 1(b), I compare Schulte's results for the electron-gas radius $r_s = 2$ to my calculations of ϕ for Al(111). Note at the outset that Schulte's curve for $r_s = 2$ intersects the calculated ϕ^{ideal}'s for one-, two-, three-, four-, and six-layer films spaced at approximately regular intervals, $\Delta(d/\lambda_F) \approx 0.60$. Moreover, the calculated ϕ^{ideal} for the six-layer film crosses Schulte's curve at a value of d/λ_F that is ~ 1.2 greater than for four layers. The results for films at equilibrium outer-layer separations are only slightly different. This set of results is *necessary* if the crystal and jellium calculations are to correspond: Each time a new layer is added, the film gets thicker by about one bulk interlayer spacing.

Let us now use the results of Fig. 1(a) to obtain a value of λ_F^{eff}, the "effective" Fermi wavelength. Correcting for the fact that the oscillations of Schulte would be a factor of $2.07/2 = 1.035$ farther apart for the actual Al electron-gas radius $r_s = 2.07$ than for $r_s = 2$, the spacing of the intersections of my calculated ϕ's with the jellium curve is $0.60(1.035) = 0.62$. The interlayer spacing for Al(111) is 4.42 a.u. Consequently, $\lambda_F^{\text{eff}} = 4.42/0.62 = 7.12$ a.u. On the other hand, for $r_s = 2.07$ jellium, one has $\lambda_F^{\text{jellium}} = 6.77$ a.u. Thus for Al(111), $\lambda_F^{\text{eff}} = 1.05\lambda_F^{\text{jellium}}$. As noted in the Introduction, this is satisfyingly close to the interstitial λ_F of Moruzzi *et al.*[2]

For Mg(0001) it is not possible to draw such a definitive conclusion. The results given in Table II show that variations in ϕ are slight for unrelaxed films. This is understandable, in that the interlayer spacing of 4.92 a.u. is only 14% greater than $\lambda_F^{\text{jellium}}/2 = 4.33$ a.u. Thus the addition of a layer of Mg(0001) does not represent a large phase advance on a Schulte oscillatory curve. A more detailed interpretation of the Mg results awaits a jellium-film calculation for $r_s = 2.65$.

V. DISCUSSION

The results presented here show persuasively that static QSE should be observable in simple metal films cut along crystal planes whose separation is not the effective $\lambda_F/2$. They should appear as oscillations not only in work function but also in surface energy as a function of layer number. Although the appropriate calculations have not been done, there is no reason to believe that similar results would not be seen for thin metal overlayers on semiconducting or insulating substrates, for which experiments might actually be carried out. The work of Tracy indicates that very uniform growth of Al overlayers is possible under carefully controlled experimental conditions.[18]

As noted in the Introduction, the predicted QSE should be important in the performance of electrodes, as well as in determining the geometry of epitaxial layers, and possibly the direction of certain surface chemical reactions. For this reason it is important to consider whether QSE will be important for thin transition-metal films. The answer is that they are probably not: Since the "wavelength" of the QSE is one-half the effective Fermi wavelength, and since d-band metals have complicated Fermi surfaces, one can anticipate that the QSE will be smeared out by the greatly increased Fermi-wavelength anisotropy. It would be of interest to check this result theoretically.

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