

SUMMARY AND CONCLUSIONS

The formation of anticlastic kinks along the corners of ionic single crystals deformed by bending has been described. Kinks are generated to accommodate the lateral contraction of the beam. They form in rock-salt crystals by the interaction of families of glide dislocations moving on intersecting planes. The kink boundaries developed at low temperatures consist of diffuse arrays of $\{121\}\langle 110\rangle$ edge dislocations which cannot move in their slip plane. At high temperatures the dislocations become more mobile and the kinks correspondingly sharper.

At low temperatures the anticlastic kinks are observed to initiate fracture. It is proposed that the immobile dislocations in the kink boundary act as barriers to slip causing dislocations to pile up, coalesce, and nucleate a crack. At high temperatures the dislocations in the kink boundary are no longer effective as barriers and the crystals remain ductile.

At very low temperatures the lateral contraction of the beam cannot be accommodated by anticlastic kinking, instead the crystal fractures rather than kinks to relieve the lateral stress.

It is possible to regard these transitions in fracture behavior as contributing to the ductile brittle transition observed on ionic solids under impact bending.

Constraints developed in beams of any solid, single, or polycrystalline undergoing plastic bending can have important consequences on their mechanical behavior.

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Work Function Variation of Metals Coated by Metallic Films

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A theoretical correlation is derived to account for the variation of the work function of refractory metals coated by metallic films for all degrees of coverage. This correlation is based on an extension of the concept of electronegativity to composite surfaces and use of Pauling's rule about electronegativity and dipole moment of complex molecules. A series of theoretical curves is given for different crystallographically ideal surfaces of refractory metals such as W, Mo, and Ta coated by Cs, Sr, Ba, and Th.

The derived correlation is compared with available experimental data for which the experimenters specify the exact conditions under which the experiment is performed and excellent agreement between theory and experiment is established.

It is shown for the first time that the maximum work function variation does not necessarily always occur either when a full monolayer is reached or at a definite fractional coverage. The exact position of the maximum variation is a function of the adsorbate and substrate materials and the type of the substrate surfaces. It is also shown that it is erroneous to characterize a monolayer as the point at which maximum emission (or maximum work function variation) is achieved because such a maximum may be flat and extend from half a monolayer to one monolayer.

I. INTRODUCTION

THE adsorption of a metallic film on the surface of a refractory metal induces a change of the work function. This fact has been investigated by many authors¹⁻⁶ and plays an important role in the field of surface physics.

The most extensive experimental study of the phe-

nomenon has been performed by Langmuir¹ who investigated the variation of the work function of tungsten immersed in a cesium vapor. Langmuir also proposed a semi-empirical correlation between the degree of coverage θ , the temperatures of the metal and the vapor, and the resulting work function variation. This correlation predicts approximately the observed work function variation only for small degrees of coverage ($\theta < 0.5$).

The purpose of this communication is to present a theoretical correlation between the work function and all degrees of coverage. The correlation is based on present concepts about metals and is in good agreement

¹ I. Langmuir and J. Taylor, *Phys. Rev.* **44**, 423 (1933).

² J. Becker, *Trans. Am. Electrochem. Soc.* **55**, 153 (1929).

³ W. Brattain and J. Becker, *Phys. Rev.* **43**, 428 (1933).

⁴ S. T. Martin, *Phys. Rev.* **56**, 947 (1939).

⁵ M. Nichols, *Phys. Rev.* **57**, 297 (1940).

⁶ G. E. Moore and H. W. Allison, *J. Chem. Phys.* **23**, 1609 (1955).

with reported experimental results. No attempt is made to correlate the variation of coverage with the temperature of the coated metal or the temperature of the vapor bath. Dynamic equilibrium is presumed for all degrees of coverage.

The paper is arranged as follows. First, a brief review of the relationship between work function and electronegativity is given. Second, the concepts of electronegativity and unsaturated bonding between metallic atoms are used to elucidate the mechanism which leads to the variation of the work function of a film coated metal. A theoretical correlation between work function variation and degree of coverage ($0 < \theta < 1$) is derived. Third, the available experimental data of work function variation of tungsten covered by cesium, strontium, and thorium are discussed and compared with the derived theoretical correlation. Very good agreement is established between theory and experiment.

The emphasis of the paper is on refractory metals because of their usefulness in thermionic converters.

II. WORK FUNCTION OF METALS

The work function of a metallic surface is defined as the minimum amount of energy required to remove an electron from the surface of the metal at 0°K . This is called the true work function in distinction from the effective and Richardson work functions⁷ which are derived via thermionic emission measurements.

For the purposes of this communication, the effective work function is considered⁸ defined as

$$\phi_e = kT \ln(AT^2/J), \quad (1)$$

where k is the Boltzmann constant ($\text{ev}/^\circ\text{K}$), T is the temperature ($^\circ\text{K}$), A is a constant [$120(A/(m^2 - (^\circ\text{K})^2))$], and J is the current density (A/m^2). This choice is made because the experimental data that are discussed later are based on thermionic emission measurements.

The effective work function of a pure metallic surface can be related to the electronegativity of its constituent element. More precisely, Gordy and Thomas⁹ found, semiempirically, that

$$\phi_e = 2.27x + 0.34 \text{ ev}, \quad (2)$$

where x = relative electronegativity. Using the concept of absolute electronegativity, as defined by Pauling¹⁰ and Mulliken,¹¹ Eq. (2) reduces to

$$\phi_e = 0.817x_a + 0.34 \text{ ev}, \quad (3)$$

where x_a = absolute electronegativity. Equation (3) affords a simple physical interpretation. The absolute electronegativity characterizes the energy required to

⁷ E. B. Hensley, *J. Appl. Phys.* **32**, 301 (1961).

⁸ The Richardson work function could also be considered. However, to a first approximation, this would not alter the subsequently derived results.

⁹ W. Gordy and W. Thomas, *J. Chem. Phys.* **24**, 439 (1956).

¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd edition.

¹¹ R. Mulliken, *J. Chem. Phys.* **2**, 782 (1934); **3**, 573 (1935).

remove an electron from an atom or molecule. However, the energy necessary to remove an electron from the surface of a lattice is different from the absolute electronegativity for at least two reasons. First, electrons in a lattice are shared by more than one lattice site and therefore they are more loosely attached to the lattice atoms. Only $\sim 80\%$ of the electronegativity energy is necessary to detach them from the lattice. Second, the lattice surface gives rise to image electrostatic forces as the electrons are removed. The energy required to overcome image forces is the same for all metals and equal to 0.34 ev.

It should be pointed out that the correlation between work function and electronegativity is approximate but it proves very useful in the elucidation of work function variation of composite surfaces.

III. WORK FUNCTION OF COMPOSITE SURFACES

General Remarks

Langmuir¹ finds that for a cesium film on tungsten, the effective work function of the composite surface decreases from that of pure tungsten for $\theta=0$ to a minimum at $\theta=0.67$ and then increases slightly for $\theta=0.8 \div 1$. Also, when there are many monolayers of cesium on tungsten, the effective work function is that of pure cesium (1.81 ev) and almost equal to the value for $\theta=0.8$. Other experimenters find similar results for different composite surfaces.

Langmuir attributes the work function variation to a contact potential due to a surface double layer. However, this cannot be the only reason because, for one or more monolayers, experimental and theoretical data show that there are practically no dipoles in the adsorbate and yet the work function of the composite surface is that of the adsorbate rather than that of the substrate.

A microscopic theoretical correlation of the experimental results is extremely difficult. This fact may be appreciated on the grounds of the following considerations. When a refractory metal is partially covered ($\theta < 1$) by a metallic film, the surface is heterogeneous, the heterogeneity being only quasi-static. The effective work function, which from the experimental standpoint represents the entire surface, is an appropriate average over the work function of sites covered by the film and others that are uncovered. Due to cooperative phenomena between sites of different types, each site cannot be considered independently. Thus, the task of deriving the appropriate averaging procedure is beyond detailed analysis.

Another approach to the problem is to use a phenomenological model based on well established physical arguments and arrive at an averaging procedure which incorporates at least the gross features of the experimental results. To this purpose, consider the following:

Visualize the composite surface as completely homogenized and characterized by an over-all effective

work function $\phi_e(\theta)$, a function of the degree of coverage θ . In other words, assume that the adsorbate is uniformly distributed over the substrate. The effective work function consists of at least two superimposed barriers.

(a) Electronegativity Barrier

The individual sites of the homogenized surface exhibit a relative electronegativity $x(\theta)$ which determines an electronegativity barrier $e(\theta)$, according to the Gordy-Thomas correlation [Eq. (2)]. The electronegativity barrier would be the only contribution to the effective work function $\phi_e(\theta)$ if the molecules made of the adsorbate and substrate atoms were not polarized. Actually, this is not the case.¹² There is adequate experimental evidence which indicates that the adsorbate is held on the substrate by strong intermetallic bonds.¹³ Intermetallic bonds are partially covalent and partially ionic and give rise to dipole moments. Therefore, there is a second contribution to the work function.

(b) Dipole Barrier

The polarized adatom-substrate molecules result in a double layer at the surface which determines a dipole barrier $d(\theta)$. Thus, the effective work function is

$$\phi_e(\theta) = e(\theta) + d(\theta). \quad (4)$$

The implication of Eq. (4) is that the concept of electronegativity is extended to composite surfaces and corrected to account for the presence of the surface double layer. This approach to the problem of work function variation versus coverage is different from that of all previous authors who dealt with the subject.

The next task is the derivation of the explicit functional dependence of $e(\theta)$ and $d(\theta)$ on θ .

Electronegativity Barrier

Notice that when the coverage is zero, the electronegativity of the surface is that of the pure substrate metal. Furthermore, for zero coverage the addition of a few more adatoms does not change appreciably the electronegativity of the homogenized surface.¹³ The analytical expressions for these two assertions are

$$e(0) = \phi_m, \quad de(\theta)/d\theta|_{\theta=0} = 0, \quad (5)$$

where ϕ_m is the effective work function of the substrate. Also notice that it is experimentally observed that when the surface is covered by one or more monolayers, the effective work function is that of the adsorbate. This observation implies two things. First, the electronegativity of the fully covered surface is that of the pure adsorbate and second the addition of extra adatoms beyond full coverage ($\theta=1$) does not

change the work function. The analytical statements for these two experimental facts are

$$e(1) = \phi_f, \quad de(\theta)/d\theta|_{\theta=1} = 0, \quad (6)$$

where ϕ_f is the effective work function of the adsorbate.

As already mentioned, the exact analytical expression for $e(\theta)$ in the range $0 < \theta < 1$ is difficult to derive from first principles. However, whatever this expression is, it must satisfy boundary conditions (5) and (6). To this effect, expand $e(\theta)$ into a power series in θ and choose the simplest polynomial consistent with Eqs. (5) and (6). Thus find

$$e(\theta) = \phi_m - (\phi_m - \phi_f)(3\theta^2 - 2\theta^3) = \phi_f + (\phi_m - \phi_f)G(\theta). \quad (7)$$

Of course, the choice of the shape factor $G(\theta) = 1 - 3\theta^2 + 2\theta^3$ is somewhat arbitrary but proves very satisfactory for the purposes of this communication. In Langmuir's approach to the problem, it can be deduced that $G(\theta)$ is taken equal to unity. However, this is erroneous because it does not account for the redistribution of the electronic structures of the adsorbate and substrate with coverage, a fact which is evident both in work function and heat of adsorption measurements.¹⁴

Dipole Barrier

Regarding the dipole barrier, notice that it can be derived directly from the electronegativity barrier. Indeed, according to Pauling¹⁰ and Malone,¹⁵ a molecule made of two dissimilar atoms, of relative electronegativities x_1 and x_2 , exhibits a dipole moment proportional to the difference in electronegativities ($x_1 - x_2$). If it is assumed that Pauling's statement is also applicable in the case of molecules made between a lattice site of a partially covered surface and an adatom, then the dipole moment is

$$M(\theta) = M_0(x(\theta) - x_f)/(x_m - x_f) = M_0G(\theta), \quad (8)$$

where M_0 is the dipole moment of a single adsorbate-substrate dipole at zero coverage,¹⁶ and $x(\theta)$, x_f , x_m the electronegativities of the partially covered surface sites, the film atoms, and the pure metal atoms, respectively. The important implication of Eq. (8) is that the dipole moment is a function of coverage, a fact that is well supported by many experiments.

Of course, Pauling's correlation between electronegativity and dipole moment does not account for dipole-dipole interactions. If the uniformly distributed surface dipoles are assumed to be arranged on a square array, the depolarizing field is¹⁷

$$E(\theta) = 9\sigma_f^2\theta^2 M(\theta)/4\pi\epsilon_0, \quad (9)$$

where σ_f is the number of sites available for adatom

¹² R. T. Sanderson, *Chemical Periodicity* (Reinhold Publishing Corporation, New York, 1960).

¹³ G. Ehrlich in *Structure and Properties of Thin Films*, edited by C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea (John Wiley & Sons, Inc., New York, 1959).

¹⁴ J. H. deBoer in *Chemisorption*, edited by W. E. Garner (Butterworths Scientific Publications Ltd., London, 1957).

¹⁵ J. G. Malone, *J. Chem. Phys.* **1**, 197 (1933).

¹⁶ In deriving Eq. (8), use has been made of the proportionality between electronegativity and work function.

¹⁷ J. Topping, *Proc. Roy. Soc. (London)* **A114**, 67 (1927).

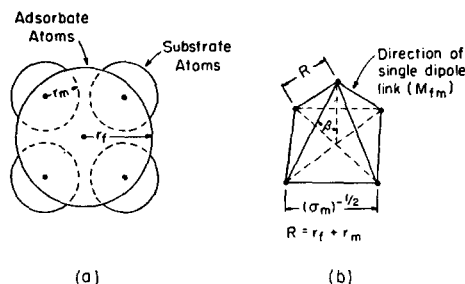


FIG. 1. Idealized arrangement of adsorbate and substrate atoms for calculation of dipole moment M_0 at zero coverage. (a) Substrate atoms are on a square array. Four substrate atoms are in contact with one adsorbate atom. (b) M_0 is the vector sum of the four dipole links M_{fm} .

occupancy per unit substrate area to form a monolayer. Therefore, the effective dipole moment is¹⁸

$$M_e(\theta) = M(\theta) / [1 + 9\alpha\sigma_f^3\theta^3 / 4\pi\epsilon_0], \quad (10)$$

where α is the polarizability of the adsorbate-substrate molecules.

The dipole barrier is

$$d(\theta) = -M_e(\theta)\sigma_f\theta/\epsilon_0 \\ = -\theta G(\theta)\sigma_f M_0/\epsilon_0 [1 + 9\alpha\sigma_f^3\theta^3 / 4\pi\epsilon_0]. \quad (11)$$

Equation (11) proves the statement that the dipole barrier can be derived directly from the electronegativity barrier.

Evaluation of the Dipole Moment M_0

The value of the dipole moment M_0 at zero coverage depends on the adsorbate and substrate materials as well as on the crystallographic structure of the surface. In the case of refractory metals as substrates, each adsorbate-substrate molecule can be visualized as shown in Fig. 1.

The substrate atoms are assumed arranged on a square lattice so that the surface density is equal to the actual average density. The adsorbate atom occupies a position of maximum binding energy and is in contact with four substrate atoms.¹² All atoms are assumed hard spheres with constant radius¹⁹ equal to their covalent radius [Fig. 1(a)].

The dipole moment M_0 is the component along the vertical axis of the vector sum of the dipole moments along the four edges of the pentahedron [Fig. 1(b)]:

$$M_0 = 4M_{fm} \cos\beta, \quad \cos\beta = (1 - 1/2\sigma_m R^2)^{1/2}, \quad (12)$$

where M_{fm} is the dipole moment per link of the complex adsorbate-substrate molecule and σ_m the surface density of the substrate.

The dipole moment M_{fm} can be evaluated by again invoking Pauling's observation about the proportionality between dipole moment and difference in electro-

negativity. More precisely,

$$M_{fm} = k(x_m - x_f) = k(\phi_m - \phi_f)/2.27, \quad (13)$$

where $k = 3.83 \times 10^{-30}$ coul-m/v. The value of k is deduced from existing data on the relationship between electronegativities and molecular dipole moments.¹⁰ Again, as pointed out by several authors,^{20,21} it is necessary to notice that Pauling's rule does not account for self depolarization. A more correct expression for the dipole moment per link is

$$M_{fm} = k(x_m - x_f) / (1 + \alpha/4\pi\epsilon_0 R^3), \quad (14)$$

where R is the sum of the adsorbate and substrate covalent radii. Equation (14) is derived by assuming that the interatomic distances remain constant and that depolarization leads to a charge redistribution.

A Note on the Value of Polarizability α

There are not many data on polarizability of metallic surface dipoles. Some quantum mechanical calculations of heats of adsorption²² suggest that this polarizability may be taken equal to the electronic polarizability of the adsorbate. But even so, the exact value of the electronic polarizability of the alkali, alkaline earth, and transition metal atoms is not well known.

To have an estimate of α , assume that

$$\alpha = 4\pi\epsilon_0 n r_f^3, \quad (15)$$

where r_f is the covalent radius of the adsorbate and n a number to account for the electronic shell structure effects on polarizability. Such effects have been observed by several authors. In particular: for alkali metals $n=1$; for alkaline earth metals $n=1.65$ because there are two valence electrons and one valence electron shields the other by an amount which is usually taken to be 0.35²³; for transition metals $n=1.65$ because there are two valence electrons in the outer shell and it is expected that the "d" electrons of the inner shell, which sometimes participate in chemical bonding, do not contribute appreciably to the polarizability.

Summary

The combination of Eqs. (7) and (11) yields (in mks units)

$$\Delta\phi/(\phi_m - \phi_f) = [\phi_m - \phi_e(\theta)]/(\phi_m - \phi_f) \\ = 1 - G(\theta) \left[1 - \frac{0.765 \times 10^{-18} \sigma_f \theta \cos\beta}{\left(1 + \frac{\alpha}{4\pi\epsilon_0 R^3}\right) \left(1 + \frac{9\alpha\sigma_f^3\theta^3}{4\pi\epsilon_0}\right)} \right]. \quad (16)$$

Notice that the normalized variation of the work func-

²⁰ K. Fajans, *Ceram. Age* **54**, 288 (1949).

²¹ E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).

²² E. J. R. Prosen and R. G. Sachs, *Phys. Rev.* **61**, 65 (1942).

²³ J. W. Smith, *Electric Dipole Moments* (Butterworths Scientific Publications Ltd., London, 1955).

¹⁸ Equation (10) is derived by assuming that the dipoles are mobile and feeding back the depolarizing effect of $E(\theta)$ on $M(\theta)$.

¹⁹ J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939).

tion is independent of electronegativities and depends only on the lattice parameters of the adsorbate and substrate such as covalent radii, surface densities, and polarizability.

In the next section, the derived theoretical correlation, Eq. (16), is compared with reported experimental data.

IV. COMPARISON OF THEORY WITH REPORTED EXPERIMENTAL RESULTS

General Remarks

The comparison of experimental results with the derived formula (16) requires knowledge of the covalent radii r_f and r_m , the electronic polarizability of the adsorbate α , the surface densities σ_f and σ_m and that the experimental results be plotted as a function of coverage θ .

The covalent radii present no difficulty because they are tabulated. The polarizability can be estimated from Eq. (15).

The surface densities can be calculated when the substrate surface is monocrystalline or of known structure. In particular, for bcc crystals, knowledge of the density of the [100] face is adequate to calculate other densities. More precisely,

$$\sigma_m[110] = \sqrt{2}\sigma_m[100], \quad \sigma_m[B]^{24} = \sqrt{3}\sigma_m[100].$$

$$\sigma_f:\sigma_m = 1:4 \quad \text{for Cs on W, Mo, Ta.}$$

$$\sigma_f:\sigma_m = 1:2 \quad \text{for Ba, Sr, Th on W etc.}$$

For other surfaces, either σ_m or σ_f must be measured and the given ideal ratios be used to calculate the other.²⁵

The presentation of the data in terms of the coverage θ is more involved. Many authors report their results in terms of the fraction covered f and there is some

ambiguity about the exact relationship between θ and f . To a first approximation, it may be assumed that θ and f are linearly related and the data normalized so that $\theta=1$ corresponds to the value of f at which one monolayer is completed.

Calculated constants for different crystallographically ideal substrates and different adsorbates are tabulated in Tables I and II. These constants are used to plot the theoretical curves (solid lines) of Figs. 2-7 which are self-explanatory.

Experimental Data for Cesium on Tungsten

The best data on the variation of the work function of tungsten coated by cesium are reported by Langmuir.¹ Langmuir presents his data as a function of coverage θ . However, he does not specify the exact type of tungsten surface that is used in the experiments. He only reports a measured value of the cesium surface density

$$\sigma_f = 4.8 \times 10^{18} \text{Cs atoms/m}^2.$$

On the basis of this measured density and the data of Table I, it is found that

$$\sigma_m = 19.2 \times 10^{18} \text{W atoms/m}^2, \quad \cos\beta = 0.896, \\ \Delta\phi/(\phi_m - \phi_f) = 1 - G(\theta)[1 - 2.6\theta/(1 + 1.22\theta^3)]. \quad (17)$$

Equation (17) is the theoretical correlation for the experimental conditions reported by Langmuir and is plotted in Fig. 2 (dashed line). Superimposed on this curve are the experimental points normalized over the measured value $\phi_m - \phi_f = 2.8$ ev. The agreement between theory and experiment is very good.

Experimental Data for Strontium on Tungsten

Moore and Allison investigated the variation of work function of tungsten as a function of strontium coverage.⁶ Their experimental results normalized over the measured value $\phi_m - \phi_f = 2.2$ ev are given on Fig. 5 (crosses). Notice that the experimental points fall on the [100] theoretical curve. This is to be expected because Moore and Allison used an extensively rolled tungsten ribbon which they believed presented a [100]

TABLE II. Calculated values of the constants k_1 and k_2 for different ideal surfaces and adsorbates. $k_1 = 0.765 \times 10^{-18} \sigma_f \cos\beta / (1 + \alpha/4\pi\epsilon_0 R^3)$. $k_2 = 9\alpha\sigma_f^3/4\pi\epsilon_0$.

	100		110		B	
	k_1	k_2	k_1	k_2	k_1	k_2
Cs on W	1.2	0.47	1.85	0.78	2.29	1.05
Cs on Mo	1.23	0.48	1.87	0.80	2.37	1.10
Cs on Ta	1.1	0.4	1.68	0.69	2.14	0.94
Sr on W	2.04	1.17	3.24	1.95	4.17	2.6
Ba on W	2.04	1.29	3.24	2.16	4.17	2.94
Th on W	1.93	0.76	3.22	1.24	4.18	1.7

TABLE I. Lattice constants for different ideal surfaces and adsorbates.

Substrate:	<i>Tungsten</i>		[100]		[110]		[B]	
Density	$\sigma_m \times 10^{-18}$ (No./m ²)		10		14.1		17.3	
Covalent radius $r_m(m)$					1.3 $\times 10^{-10}$			
Adsorbate	Covalent radius $\times 10^9 m$	Polarizability $\times 10^{40} f \cdot m^2$	$\sigma_f \times 10^{-18}$			$\cos\beta$		
			100	110	B	100	110	B
Cs	2.35	14.4	2.5	3.53	4.33	0.79	0.86	0.88
Sr	1.91	12.7	5.0	7.05	8.65	0.72	0.81	0.85
Ba	1.98	14.3	5.0	7.05	8.65	0.73	0.82	0.86
Th	1.65	8.2	5.0	7.05	8.65	0.65	0.77	0.82
<i>Molybdenum</i>			10.2			14.4		
Cs	2.35	14.4	2.55	3.6	4.42	0.8	0.86	0.89
<i>Tantalum</i>			9.2			13.0		
Cs	2.35	14.4	2.3	3.25	4.0	0.78	0.85	0.88

²⁴ $\sigma_m[B]$ refers to a fictitious bumpy surface. It is included for comparison since many experiments are performed using bumpy surfaces.

²⁵ Integer ratios are not necessarily true for all coated surfaces. In such cases, σ_f and σ_m have to be measured individually.

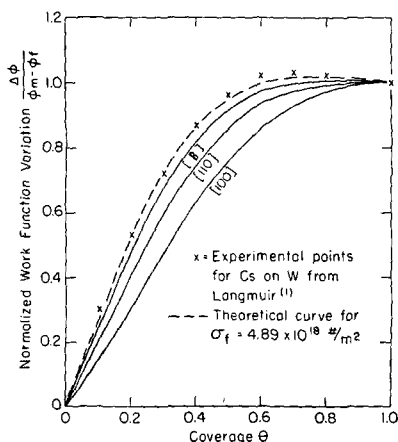


FIG. 2. Theoretical curves and experimental data for Cs on W.

surface. In fact, they measured the average cesium surface density and found it to be 4.89×10^{18} Cs atoms/ m^2 , which is very close to the theoretical density (5×10^{18}).

The agreement between theory and experiment is again excellent.

Experimental Data for Thorium on Tungsten

Brattain and Becker³ investigated the variation of work function of tungsten covered with thorium. The results are difficult to correlate with the derived formula because the authors did not measure any surface densities and they report their data in terms of the fraction covered f . However, the data suggest that a monolayer is reached at $f=2$ and therefore, to a first approximation, it may be assumed that $\theta=0.5f$ for all values of f . On the basis of this transformation and using the value $\phi_m - \phi_f = 1.2$ ev, measured by Brattain and Becker, their experimental data are normalized and depicted on Fig. 7. The only reasonable conclusion that can be drawn from the data is that the tungsten surface used was bumpy and therefore denser than [110]. In fact, a theoretical curve for $\sigma_m = 2\sigma_m[100]$

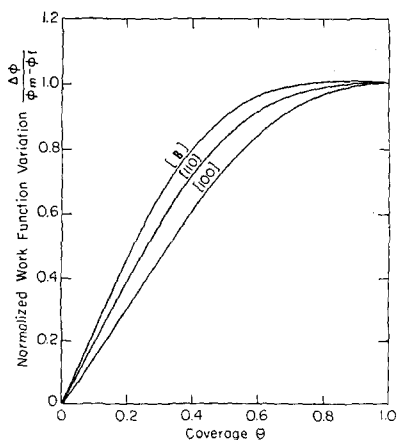


FIG. 3. Theoretical curves for Cs on Mo.

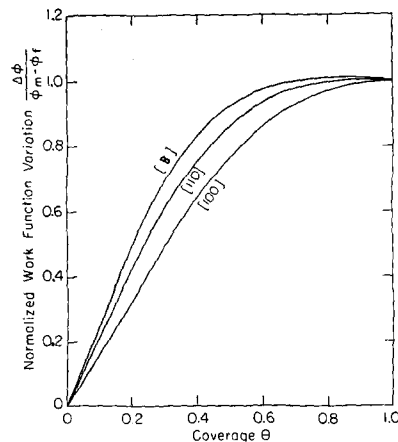


FIG. 4. Theoretical curves for Cs on Ta.

(dashed line) is in very good agreement with the experimental results.

The interesting qualitative point about the data on Th on W is the large value of the work function variation around $\theta \sim 0.5$ (or $f \sim 1$). This large variation is also predicted by the theory for ideal surfaces with high surface densities (see Fig. 7, solid curves).

V. DISCUSSION AND CONCLUSIONS

By extending the concept of electronegativity to composite surfaces and using Pauling's rule about the relationship between electronegativity and dipole moment, a theoretical correlation is derived for the variation of work function of refractory metals coated by metallic films.

The basic physical idea behind the present derivation is that both the electronegativity and the dipole moment of the surface double layer (which is directly related to electronegativity) are continuous functions of coverage. This functional dependence stems from the fact that when the coverage is low the adsorbate-substrate molecules are so far away from each other

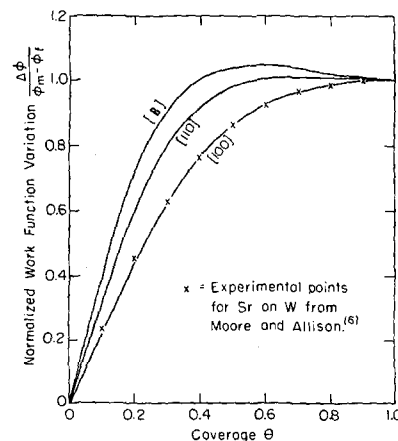


FIG. 5. Theoretical curves and experimental data for Sr on W. Notice that the [110] surface has a flat maximum for $\theta = 0.6 \div 1$.

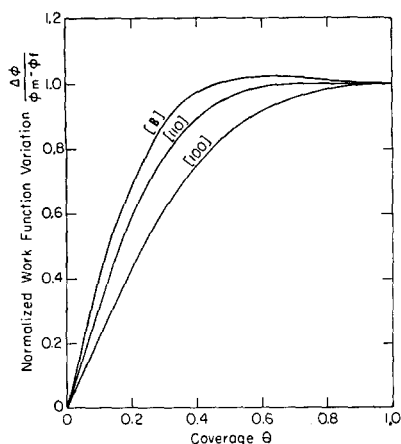


FIG. 6. Theoretical curves for Ba on W. Notice that the [110] surface has a flat maximum for $\theta = 0.65 \div 1$.

that they behave as isolated molecules. Then the electronegativity of the homogenized surface is almost that of the substrate but the dipole moment is high, contributing appreciably to the effective work function. On the other hand, when the coverage is high, the adsorbate-substrate molecules are so close to each other that the surface looks almost like that of the adsorbate. The electron clouds of the adatoms are no longer shared only with the substrate but also with adatoms. The sharing of electrons with adatoms reduces the surface dipole moments and their contribution to the dipole barrier. All these physically sound properties are incorporated in the derived correlation and it is felt that this is the reason for the favorable comparison between theory and experiment in spite of the somewhat arbitrary character of $G(\theta)$.

The theoretical curves of Figs. 2-7 bring out some interesting points which so far have been controversial or ambiguous. First, the maximum work function variation does not necessarily occur always either at a fractional coverage as some authors suggested¹ or at a coverage of one monolayer as some others supported.^{3,6} The coverage for maximum variation is a function of the adsorbate and substrate materials and the crystallographic character of the substrate surface. Second, the definition of a monolayer as the point at which the work function variation reaches a maximum (or thermionic emission from a coated surface reaches a maximum) is sometimes erroneous (see, for example, Fig. 7, curves [110] and [B]). In other cases, it may be misleading as the [110] curve for Ba on W indicates. Of course it may be argued that the derived curves are not absolutely correct. However, the previous conclusions are still valid because it is conceivable that

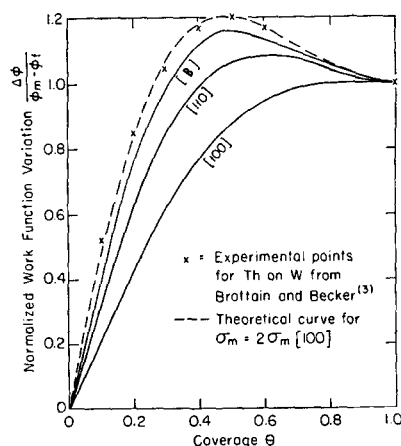


FIG. 7. Theoretical curves and experimental data for Th on W. Notice that a pronounced maximum variation occurs for a fractional coverage both in the theoretical and experimental results.

the surface is of such a nonideal character that the average electronegativity and dipole barriers result in an almost constant work function over a broad range of coverage. In fact, this is the reason why it is not possible to intelligently correlate Moore and Allison's experimental data⁶ on barium on tungsten with the theory. No surface specifications are given and the results present a plateau over such a broad range that any attempt to normalize would be mere guesswork. Third, the higher the surface density of the substrate, the higher the work function change for small coverages.²⁶ This is important for thermionic converters operating with a partially covered emitter. It is evident that for this purpose, [B] or bumpy high density emitter surfaces should be used. Finally, for Cs on identical W, Mo, and Ta surfaces and a given small coverage, the largest work function variation is achieved by Cs on Mo. This is also of some interest in thermionic conversion.

Even though the emphasis of this paper has been on refractory metals and metallic adsorbates, it is felt that the concepts involved are directly applicable to other composite surfaces. This application will be discussed in a future communication.

The important problem of coverage dependence on surface and vapor bath temperatures has admittedly not been discussed in this paper. Work on this topic is currently in progress and will also be reported later.

²⁶ Note added in proof. This theoretical prediction has been recently verified experimentally by H. F. Webster of General Electric. His experiments done with Cs or Rb on W, Mo, Ta, Nb, Ni, and Re all confirm this prediction (private communication).