

DEPENDENCE OF THE WORK FUNCTION ON THE DEGREE OF COVERAGE OF ALKALINE METALS ADSORBED ON TUNGSTEN*

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In the paper difficulties are presented encountered when explaining the experimentally found dependence of the work function on the degree of coverage for alkaline metals adsorbed on the planes of a tungsten monocrystal by means of the existing theoretical models.

For low coverages ($\theta < 0.5$) a simple model is proposed which allows to calculate the dependence of the adion charge on the degree of coverage. A decrease of this charge with increasing coverage has been obtained in agreement with experiment. For higher coverages ($0.6 \leq \theta < 1$) it has been assumed basing on numerous experimental facts that the adsorbed layer shows properties of the solid metal with varying lattice constants. The band model allows to obtain a formula describing the dependence of the work function on the degree of coverage which is in good agreement with experiment.

1. Introduction

Recently a number of experimental studies were carried out on the adsorption of potassium (Schmidt and Gomer 1966) and caesium (Gavrilyuk *et al.* 1966, Swanson and Strayer 1968, and Sidorski *et al.* 1969) on tungsten. These studies were performed using a field emission microscope which allowed for taking measurements on the single crystal planes. Earlier works on the adsorption of alkaline metals on a metallic substrate were performed on polycrystalline samples or referred (as, for instance, in the case of a field emission microscope of traditional construction) to the whole monocrystal. In both cases the results obtained were an average of a large number of complicated processes, and hence it was impossible to compare them with theoretical models. In this respect the results of the studies cited above show a significant progress, since they refer to the single crystal planes and may therefore be compared with simple theoretical models. However, the attempts of comparing the experimental results with theoretical models described in the above cited works cannot

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be regarded as successful. The measurements taken on the single planes, which were carried out under very clean conditions and were experimentally difficult, contributed to the explanation of the adsorption phenomenon much less than it might be expected. It seems that this was due to the fact that the theoretical models are too rough and inadequate to the progress achieved in experimental techniques.

In the present paper we shall discuss critically the theoretical adsorption models used at present, and propose a different approach to this phenomenon. It seems that such a treatment of the problem is in better accordance with the precision of experimental data and allows to make better use of these data to obtain new information on the adsorption phenomenon.

2. Dependence of the work function on the degree of coverage

a. Experimental facts

The basic experimental results, given in the works quoted above, are the dependences of the work function φ for the single crystal planes on the concentration n (or degree of coverage θ) of the adsorbate on these planes. As it could be expected, the character of this dependence for the particular planes is similar to the dependence of the average work function for the whole crystal on the average concentration. A distinct relation was found to exist between adsorption and the crystallographic orientation, especially for low coverages. This relation, $\varphi = \varphi(n)$, is similar for all the planes. For small concentrations the work function decreases rapidly (initially almost linearly). For coverages approximating a monolayer the relation passes through a distinct minimum, to attain saturation at a coverage equal to unity. The value of the work function at the minimum is lower than that for the substrate and lower than that of the bulk adsorbate. This fact has not found as yet sufficient theoretical support. There is no doubt, however, that we encounter here a phenomenon characteristic of an alkaline metal-tungsten system. The attempts of explaining the minimum of $\varphi(\theta)$ by the presence of contaminations must be discarded in the light of experimental facts. At saturation the values of the work function are practically equal to that of the bulk adsorbate independently of the kind of metallic substrate. This is supported by the measurements carried out by Swanson and Strayer (1968), where the dependences of the work function on the degree of coverage for caesium on tungsten, molybdenum and rhenium are given.

b. Existing interpretations

If the adsorbed layer consists of ions, we shall obtain on the surface a double layer formed of ions with a charge q distant by l_0 from the surface, and their images. We then have

$$\Delta\varphi = 2\pi\mu n = 2\pi\mu n_0\theta \quad (1)$$

where: μ is the dipole moment ($2l_0q$), and n and n_0 are the surface density, and surface density at monatomic coverage, respectively.

Assuming a constant dipole moment μ , relation (1) gives a linear dependence of $\Delta\varphi$ on μ , which is in agreement with experiment only for small densities.

For higher coverages it should be assumed that the dipole moment μ is a function of the degree of coverage. Boudart (1952) tried to explain the dependence of μ on θ by mutual depolarization of the ions adsorbed. Making use of the results of Topping (1927) and Miller (1949) he obtained the equation:

$$\Delta\varphi(\theta) = \frac{4\pi n_0 \mu_0}{1 + \frac{9\alpha\theta}{r^3}} \quad (2)$$

where: $\mu_0 = \mu(\theta = 0)$, α is the polarizability, and r is the distance between adions for $\theta = 1$.

Equation (2) gives only the saturation of the $\Delta\varphi$ versus θ curve for $\theta \rightarrow \infty$, but the minimum observed experimentally is not obtained. In this equation $r = \text{constant}$, whereas Macdonald and Barlow (1963) claim that the distance d between the atoms should vary with θ . These authors, assuming that in the case of a mobile adsorption layer the adatoms are distributed for every θ in a regular lattice, found¹ that

$$d \approx \theta^{-1/2} \quad (3)$$

for a square lattice with a lattice constant a

$$d = a\theta^{-1/2}. \quad (3a)$$

By (3) we can obtain the relation (Schmidt and Gomer 1966):

$$\frac{\theta}{\Delta\varphi} = \frac{1}{C_1} + \frac{C_2}{C_1} \theta^{3/2} \quad (4)$$

where:

$$C_1 = 2\pi\mu_0 n_0 \quad (5)$$

$$C_2 = 9\alpha n_0^3 d^3.$$

This relation already gives the minimum of $\Delta\varphi(\theta)$. Hence, if we plot the $\theta/\Delta\varphi$ ratio found experimentally versus $\theta^{3/2}$ we should obtain a straight line. The experimental data for $\theta < 0.5$ are in good agreement with this model (Schmidt and Gomer 1966, Sidorski *et al.* 1969). Also the value of μ_0 found from Eqs (5) does not depart very much from the values obtained from Eq. (7). Of course for $\theta \rightarrow 0$ Eq. (4) becomes Eq. (1). Depolarization comes into prominence for higher coverages, for which the relation between $\Delta\varphi$ and θ ceases to be linear. The results of Swanson and Strayer (1968) indicate that for higher coverages the model of Miller and Topping disagree with experiment. This is a sufficient proof that the depolarization model does not describe adequately the phenomena occurring during adsorption at higher coverage.

¹ It is worth mentioning that Macdonald and Barlow obtained for an immobile layer $d = \text{constant}$. They characterized the immobile layer as follows: the atoms are immobile, distributed at random in the short range, and uniformly with a density θ in the long range. The result referring to d for such a layer obtained by these authors is doubtful, what may be seen from the considerations forwarded in Appendix I, where it is shown that $d \approx \theta^{-1/2}$ also in the case of an immobile layer.

If we introduce into Eq. (1) the experimental values of $\Delta\varphi$ and $n > 0$, we can find the relation $\mu = \mu(n)$:

$$\mu = \frac{\Delta\varphi(n)}{2\pi n}. \quad (6)$$

For $n = 0$ we have

$$\mu_0 = \frac{1}{2\pi} \left. \frac{d(\Delta\varphi)}{dn} \right|_{n=0}. \quad (7)$$

Such plots are given in the above cited experimental works. It seems, however, that the density range for which the Helmholtz formula (Eq. (1)) holds is small and difficult to determine. Surely, substitution of the discrete dipole distribution by the double layer (what means that the charge is spread uniformly over the whole surface) is rather rough approximation. Also for high coverages, where metallization of the layer commences (what will be discussed below), the use of the double layer as approximation finds no justification. May be it is worth emphasizing that the determination of the dipole moment on the basis of the above scheme provides but little information allowing for drawing a comparison between experiment and the theory of adsorption, since it does not permit to calculate unequivocally the charge of the adion and its distance from the substrate.

Topping's formulae, which served as a basis for Miller, were derived for elastic dipoles, whose charge is constant but their length is variable; this is the reason for the polarizability α appearing in these formulae. In the adsorption phenomenon we have to do with dipoles consisting of an adion and its image. The fact that the values of the work function obtained by applying small external electric fields (*e.g.* thermal emission) and very strong fields (field emission) are practically equal would indicate that adsorbed dipoles are very rigid, *i.e.* their length, $2l_0$, is practically constant. Theoretical considerations given below lead to a similar conclusion. The values of α obtained from the relations (5) are very high (several dozen \AA^3). This would indicate that the dipoles are very soft. Generally speaking, a physical interpretation of polarizability is very difficult. The variation of the work function is surely connected with electron processes taking place as the coverage increases, and the depolarization model cannot account for them.

Gyftopoulos and Levine (1962) advanced a tentative theory of the dependence of the work function on the degree of coverage covering the range from $\theta = 0$ to $\theta = 1$ for adsorption of alkaline metals and alkaline earth metals on tungsten. They derived the following equation:

$$\varphi(\theta) = \varphi_f + G(\theta) \left[\varphi_0 - \varphi_f - \frac{n_0 \mu_0 \theta}{1 + 9\alpha n_0^{3/2} \theta^{3/2}} \right] \quad (8)$$

where φ_f is the work function of the adsorbate, and φ_0 that of clean tungsten. $G(\theta) = 1 - 3\theta^2 + 2\theta^3$ is an arbitrarily chosen polynomial. For $\theta = 1$ we obtain $\varphi = \varphi_f$, what is in agreement with experiment. Equation (8) describes quite well experimental data, but the physical meaning of the model is still obscure.

c. Low coverages

It follows from the above considered experimental facts as well as from theoretical works (Gadzuk 1968, Wojciechowski 1968) that for very low coverages it may be expected with a high certainty that the valency electron of the adatom is transferred to the metal increasing the density of the conduction electrons. Hence, on the surface of the adsorbent we have positive adions distributed far apart whose equilibrium distance l_0 from the metallic surface determines the minimum of the total energy of interaction. In the first approximation it may be considered that this energy consists of a quantum part corresponding to the repulsion forces and the classical part corresponding to the electrostatic interaction between the adions and between adions and their images in the metal. Generally speaking, the variation of the work function with coverage (for low coverage) may be caused by two factors: (1) variation of the density of conduction electrons due to the transfer of the charge from the adatoms to the substrate, and hence variation of the Fermi energy E_F , or (2) depolarization of the dipoles of the layer adsorbed. From what was said in the preceding section we may conclude that the effect of depolarization should be eliminated. This is further supported by the fact that, as it will be shown below, the length of the image dipole does not change with increasing coverage. Hence the variation of $\Delta\varphi(\theta)$ for small θ should be related to the change of the electron density. This allows us to refer to the results obtained for alloys with a low concentration of the admixture. The calculations carried out by Gurov and Pekarev (1964) show that

$$\Delta\varphi(\theta) = \frac{\theta}{N(E_F)} \quad (9)$$

where $N(E_F)$ is the density of energy states in vicinity of the Fermi level per one atom.

In the light of such a mechanism the linear decrease of $\varphi(\theta)$ for small θ seems comprehensible.

d. High coverages

When θ increases significantly we observe a distinct lowering of the adion charge which may be interpreted as a progressing metallization of the adsorbed layer with increasing coverage. The metallization of the adsorbed layer at coverage close to 1 is further supported by experimental facts. The work function at saturation, which occurs at $\theta = 1$, is equal to that for the bulk adsorbate irrespective of the kind of adsorbent involved. The binding energy of the adsorbate approximates the sublimation energy of the solid adsorbate at θ tending to unity (Gavrilyuk *et al.* 1967). The dependence of the work function on the degree of coverage at coverage $\theta \geq 0.6$ cannot be described by the depolarization model (Swanson and Strayer 1968). Fedorus and Naumovets (1970) studied the structure of a caesium layer adsorbed on the (011) tungsten plane. They found that starting from the coverage corresponding to the minimum work function the structure of the layer and its orientation with respect to the substrate do not change. For higher coverages we have a layer with a constant structure and continuously decreasing lattice constant. Measurements of flicker noises for adsorption of potassium on single planes of a tungsten monocrystal showed that no noises are observed when the tungsten surface is clean. However, as the coverage grows

the noise power increases reaching a maximum at a coverage of about $\theta = 0.5$, after which it decreases to reach zero when the coverage is $\theta = 1$ (Błaszczyszyn, Kleint and Męclewski 1970). All these facts prove that in the case of thick coverage, when properties of an adsorption layer are revealed, it is rather the forces between the adatoms than the interaction with the substrate that are decisive.

3. Dependence of the charge localized in the vicinity of the adion on the degree of coverage (low coverage)

The answer to the question how does the charge q of the adion depend on θ is of great importance for understanding the course of the layer metallization process, explaining the relation $\varphi = \varphi(\theta)$, and the relation $E = E(\theta)$, where E is the adsorption energy. As yet the only quantum calculus pertaining to the variation of alkaline adatom charges with coverage

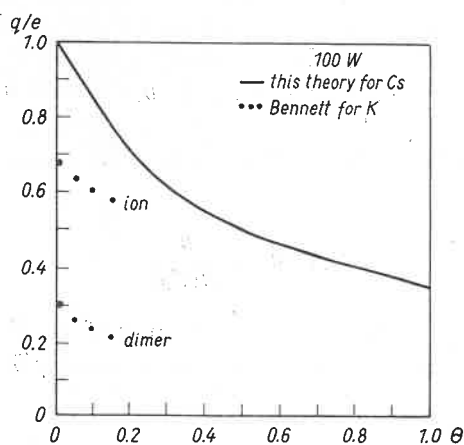


Fig. 1. Variation of the charge $q(\theta)$ accumulated around the adion with the degree of coverage found by the present authors for caesium adsorbed on the (100) tungsten plane (solid line). The points denote the values of $q(\theta)$ calculated by Bennett for the K-W system.

was carried out by Bennett (1968). This study concerned very low coverage: $0 \leq \theta \leq 0.15$, and although one may have some reservations as to the mathematical and physical simplifications involved it brings two interesting results. First of all Bennett found that the charge localized at the adatom decreases with increasing θ , and secondly that the charge localized at the ion dimer decreases as compared with that localized at the isolated adion. In Fig. 1 the points calculated by Bennett for these two situations in the case of a K-W system for the (100) plane are marked by black dots. Both these results provide a theoretical proof that the process of metallization discussed above proceeds with increasing coverage.

Bennett's calculations were performed numerically under the assumption that the equilibrium distance of an adsorbed ion does not vary with increasing coverage. In order to find whether the increase of θ produces only the variation of the charge or also that of the distance of the adion from the metallic surface, we propose below a simplified theoretical

model. The latter will allow us to obtain at least a qualitative analytical dependence $q(\theta)$ (for low θ), and interpret some experimental results.

The potential energy of the adion consists of the repulsion energy $U_R(l)$ between the adion and the surface ions of the metal, and of the electrostatic attractive energy $U_e(l)$. If we assume a square lattice of the substrate plane (e.g. tungsten (100) plane) with a lattice constant $a = a(\theta = 1)$, and that the atoms of the successive metallic layers do not contribute to the repulsion, we have

$$U_R(l) = A \sum_{m,n=0}^{\infty} e^{-Ba \sqrt{(m+\frac{1}{2})^2 + (n+\frac{1}{2})^2 + (\frac{l}{a})^2}} \quad (10)$$

where A and B are constants, and l is the distance of the adion from the metallic surface.

Assuming that the number of grid points (m, n) in a circle of radius ρ is $\pi\rho^2$, we may write

$$\sum_{m,n=0}^{\infty} e^{-Ba \sqrt{(m+\frac{1}{2})^2 + (n+\frac{1}{2})^2 + (\frac{l}{a})^2}} = 2\pi \int_0^{\infty} \rho e^{-Ba \sqrt{\rho^2 + (\frac{l}{a})^2}} d\rho$$

and hence

$$U_R(l) = 2\pi A \left[(Ba)^{-2} + (Ba)^{-1} \sqrt{\frac{1}{2} + \left(\frac{l}{a}\right)^2} \right] e^{-Ba \sqrt{\frac{1}{2} + \left(\frac{l}{a}\right)^2}} \quad (11)$$

The electrostatic energy consists of the contribution from the positive adion layer and their negative images. We may, therefore, present it as follows (assuming the distance between the adions $d = \frac{a}{\sqrt{\theta}}$):

$$U_e(l) = -\frac{q^2}{4l} + \frac{q^2\theta^{1/2}}{a} \sum_{m,n=\pm 1} \left\{ \frac{1}{\rho_{mn}} - \frac{1}{\left[\rho_{mn}^2 + \left(\frac{2l}{a}\right)^2\right]^{1/2}} \right\} \quad (12)$$

where $\rho_{mn}^2 = m^2 + n^2$.

Expanding into a series we have

$$\left[1 + \left(\frac{2l}{a}\right)^2 \frac{\theta}{\rho_{mn}^2} \right]^{-1/2} = 1 - \frac{1}{2} \left(\frac{2l}{a}\right)^2 \theta \frac{1}{\rho_{mn}^2} + \dots$$

and replacing, as above, the sum by the integral we finally obtain

$$U_e(l) = q^2 \left[-\frac{1}{4l} + \frac{\pi}{a} \left(\frac{2l}{a}\right)^2 \theta^{1/2} \right] \quad (13)$$

In the general case both q and l may vary with increasing coverage. If the distance of adions from the metal changed with increasing θ , mechanical work connected with this variation would be performed which would contribute to the lowering of the adsorption

energy $E(\theta)$ with increasing θ . Hence we would have

$$\Delta E(\theta) = U_R(0) - U_R(\Delta l) = 2\pi A \left[\alpha e^{-Ba\sqrt{1/2}} - \beta e^{-Ba\sqrt{1/2 + \left(\frac{\Delta l}{2a}\right)^2}} \right] \quad (14)$$

where

$$\alpha = (Ba)^{-2} + (Ba\sqrt{1/2})^{-1}, \quad \beta = (Ba)^{-2} + (Ba)^{-1} \sqrt{\frac{1}{2} + \left(\frac{\Delta l}{2a}\right)^2}.$$

From Eq. (14) we obtain

$$\alpha = \frac{\Delta E(\theta)}{2\pi A} = \beta e^{-Ba\sqrt{\frac{1}{2} + \left(\frac{\Delta l}{2a}\right)^2}}$$

and since $\Delta E \ll A$ (*cf.* the experimental values of ΔE , for example given by Schmidt and Gomer (1966), and the value of constant A given by Abrahamson (1969)), we have

$$\frac{\alpha}{\beta} = e^{-Ba} \left[\sqrt{\frac{1}{2} + \left(\frac{\Delta l}{2a}\right)^2} - \frac{1}{\sqrt{2}} \right]$$

however, since $\alpha \approx \beta$, $\Delta l \approx 0$. It follows therefrom that the work performed in the course of the adsorption process with changing θ is not connected with a variation of the adsorbed dipole length, but is used for the redistribution of the charge around the adions. A change

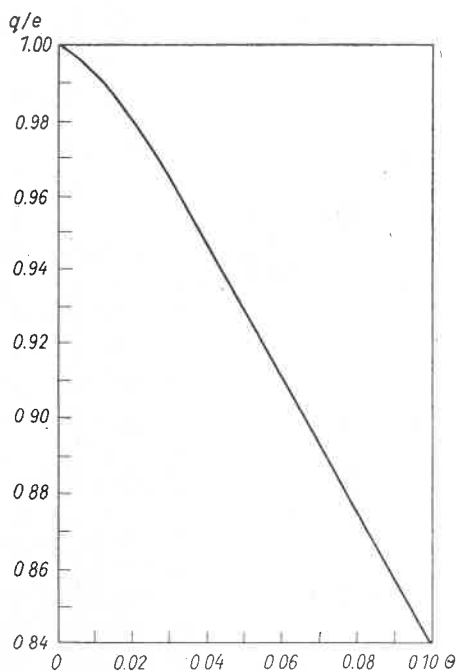


Fig. 2. The $q(\theta)$ plot calculated by the present authors for caesium adsorbed on the (100) tungsten plane for very low coverage

should therefore be expected of $q = q(\theta)$ at constant l . The function $q(\theta)$ may be found from the minimum condition for $U = U_R + U_e$, viz.

$$\frac{\partial U}{\partial l} = 0.$$

The result thus obtained is presented by the solid curves in Figs 1 and 2. These curves have been plotted for caesium adsorbed on the tungsten (100) plane with $l = 3.6 \text{ \AA}$, and the constants $A_{\text{Xe-W}}$ and $R_{\text{Xe-W}}$ calculated according to the scheme advanced by Abrahamson (1969) under the assumption that the charge of the adion for $\theta = 0$ is equal to that of the electron e . In Fig. 2 the relation $q(\theta)$ is presented for $0 \leq \theta \leq 0.1$. It is worth noting that the shape of the $q(\theta)$ curve for $0 \leq \theta \leq 0.3$ shows a character similar to that of the corresponding parts of the experimental curves derived from the Helmholtz formula for small θ .

The result obtained supports the experimental conclusions and theoretical suggestions already presented that the charge localized at the adions decreases with increasing θ , what points to the gradual metallization of the adsorbed layer with increasing coverage. Of course the relation $q(\theta)$ obtained may be true only for low coverage, when the above adopted model of the discrete layer composed of adsorbed dipoles is truthful. With increasing coverage the charge originating from the transfer of the valency electrons from the adatoms to the metal-adatom system is gradually localized in the adsorbed layer, and we can no more consider image dipoles. Instead, complicated quantum processes come into prominence, when a theoretical approach for the coverage range from $\theta \approx 0.2$ to $\theta = 1$ encounters great computational difficulties.

4. Dependence of the work function on the degree of coverage for high coverages

We shall start with an experimentally established fact that a monomolecular layer of an alkaline metal adsorbed on the surface of tungsten shows the properties of the bulk metal. This allows us to apply the band theory to such a layer. We assume that

$$\varphi = |E_A| - E_F \quad (15)$$

where E_A is the energy (negative) of bottom of the conduction band measured from the vacuum level, and E_F is the Fermi energy measured from the bottom of the conduction band. Let us assume further that the metallic character of the layer is preserved when the degree of coverage decreases insignificantly. The decrease of θ causes solely an increase of the lattice constant of the two-dimensional metal, which in our case is the adsorption layer. Both E_A and E_F are functions of the lattice constant, and hence of the degree of coverage. Therefore for $\theta \lesssim 1$ we may write

$$\varphi(\theta) = |E_A(\theta)| - E_F(\theta). \quad (15a)$$

Our considerations have the character of a first approximation, we shall adopt the free electron model. We then have

$$E_F = \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \left(\frac{N}{V} \right)^{2/3}$$

where $\frac{N}{V}$ is the density of the electron gas dependent on the lattice constant. Introducing the volume of the elementary cell $V = da$ where d is the constant "thickness" of the layer, and a is the lattice constant dependent on the degree of coverage, $a = a_0\theta^{-1/2}$ (3a), we obtain

$$E_F(\theta) = E_F^0\theta^{2/3}$$

where E_F^0 is the Fermi energy for $\theta = 1$, i.e. for the bulk metal.

It is much more difficult to determine the dependence of E_A on the lattice constant. Making use of the Hartree-Fock approximation (Kittel 1963; Callaway 1964) we may assume $E_A \approx -r_s^{-1}$, where r_s is the radius of the Wigner-Seitz sphere. Placing $r_s \approx a \approx \theta^{-1/2}$ we obtain

$$E_A(\theta) = E_A^0\theta^{1/2}$$

where E_A^0 is the energy of the conduction band bottom for the solid metal. After substituting the values obtained into Eq. (15a) we have

$$\varphi(\theta) = |E_A^0\theta^{1/2} - E_F^0\theta^{2/3}| \quad (16)$$

The relations $E_A = E_A(\theta)$ and $E_F = E_F(\theta)$ are presented schematically in Fig. 3. Equation (16) is true for $\theta_m \leq \theta \leq 1$, where θ_m is the degree of coverage corresponding to the minimum work function. For $\theta < \theta_m$ coverages the distances between atoms become so large that the metallic character of the layer disappears, and the interaction between the adatom and

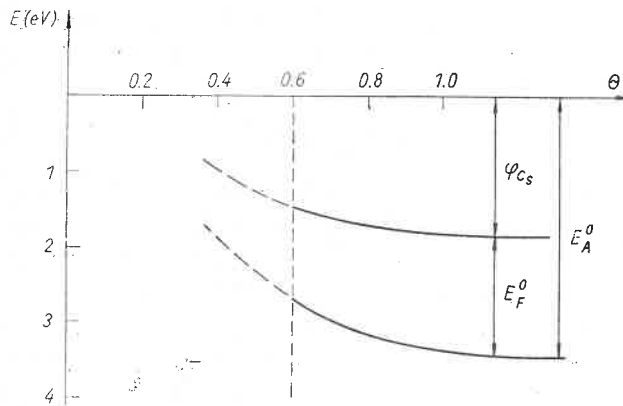


Fig. 3. Dependence of the Fermi energy and the energy of the bottom of conduction band on the degree of coverage for caesium on tungsten

substrate comes into prominence. The picture proposed explains the decrease of work function below the value characteristic for the bulk metal when the coverage is monomolecular. Since in this range of coverages ($\theta_m \leq \theta \leq 1$) the variations of

function with θ are due to changes taking place in the metallic adsorbate layer, they should be independent of the substrate, what is in agreement with experiment (Swanson and Strayer 1968). If for bulk caesium we assume $E_F^0 = 1.5$ eV and $E_A^0 = 3.3$ eV, we shall obtain $\theta_m = 0.64$, $\varphi(\theta_m) = 1.35$ eV what is in good agreement with experiment.

5. Final remarks and conclusions

The considerations presented in this paper indicate that the hitherto interpretation of the variation of the work function with increasing coverage of metallic substrates with alkaline metal atoms is not fully justified. The progressing process of metallization of the adsorbed layer, which finds confirmation both in experimental facts and in the theoretical considerations presented above, indicates that the Helmholtz formula, used so far very commonly, does not describe the phenomenon adequately. For low coverage it cannot be used since the layer is distinctly discrete. In the case of high coverage, we have in fact a metallic layer, which may have only an insignificant electric moment due to the existence of a crystal surface, which is not, as it was shown by Smoluchowski (1941), different from zero for all planes. For similar reasons it is not possible to use Topping's model, which has an additional drawback consisting in that it applies to elastic dipoles with polarizability $\alpha \neq 0$. As we have shown at low coverage the dipoles are inelastic, and at high coverages the notion of a dipole has no more its simple classical sense. Therefore, $\mu(\theta)$ plots given in experimental works not only provide no information which would have a physical meaning, but furthermore obliterate the already complicated picture of the adsorption process. It seems therefore that in the present situation only the $q(\theta)$ relation may be given, calculated in accordance with the proposed scheme, use being made of the adsorption energy measured for low coverage. In the case of high coverages, $\theta \approx 1$, the considerations given in the present work afford certain new possibilities. For instance, in the case of the caesium-tungsten system it is worth emphasizing that caesium like tungsten crystallizes yielding a body centred cubic lattice. The lattice constant for caesium (6.05 Å) is approximately twice that for tungsten (3.16 Å). Only in the (110) and (100) planes the structure of the caesium layer is similar to that of the corresponding planes in the caesium crystal. In the (210) and (111) planes the packing of the monomolecular layer is higher than in solid caesium, what corresponds to the decrease of the lattice constant (Gavrilyuk *et al.* 1966). The values of the work function observed for the monomolecular layer are different for different crystallographic orientation. This may be due both to the different values of the work function for caesium in different crystallographic orientations and differences in the packing of the adsorption layer as compared with solid caesium. Accurate measurement of the work function for monomolecular layers of alkaline metals adsorbed on a metallic substrate may be interesting from the point of view of metal physics. Since the adsorbed layers have the structure of different planes of a monocrystal it is possible to find the variation of the work function with the crystallographic orientation. As a result of interaction with the substrate we may obtain metallic layers showing properties of the solid metal and with a lattice constant differing significantly from that corresponding to equilibrium. Using Eq. (16) it is possible to establish by comparison with experiment the parameters determining such band structures

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of the metal as E_A and E_F in dependence on the lattice constant, varying within comparatively wide limits. It is impossible to obtain such variations of the lattice constant by any other way, *e.g.* by deformation.

APPENDIX

In order to find the relation $\bar{d}(\theta)$ for an immobile layer let us consider the following probabilistic problem. Let us draw a circle ω from a given point 0 with radius $\varrho = \bar{d}/a(1)$, where $a(1)$ is the distance between neighbouring adsorption centres of the substrate. In a large area Ω enclosing the circle ω we distribute arbitrarily N_a points. We are to find the probability that no point lies inside the circle ω . We denote this probability as $1 - P(\varrho)$, where $P(\varrho)$ is the probability that the distance from the nearest point is less than ϱ . The probability of a single point finding its way into the circle is $\frac{\omega}{\Omega}$. The probability that N_a points will remain outside the circle ω is hence $\left(1 - \frac{\omega}{\Omega}\right)^{N_a}$, and since $\omega = \pi\varrho^2$ we have

$$1 - P(\varrho) = \left(1 - \frac{\pi\varrho^2}{\Omega}\right)^{N_a}$$

Assuming that $\Omega \approx N$, where N is the number of adsorption centres in the Ω area, we may write the above equation in the form

$$1 - P(\varrho) = \left(1 - \frac{\pi\varrho^2}{N}\right)^N$$

Since we want to find the mean distance between the neighbouring points we may assume that $N \rightarrow \infty$. Hence

$$1 - P(\varrho) = \lim_{N \rightarrow \infty} \left(1 - \frac{\pi\varrho^2}{N}\right)^N = e^{-\pi\theta\varrho^2}$$

therefore

$$P(\theta) = 1 - e^{-\pi\theta\varrho^2}$$

and

$$\bar{\varrho}(\theta) = \int_0^\infty \varrho dP(\varrho) = \frac{\pi}{2} \frac{1}{\sqrt{\theta}}$$

finally

$$\bar{d} = \frac{\pi a(1)}{2\sqrt{\theta}}$$

Hence in the case of an immobile layer as in the case of a mobile layer \bar{d} depends on θ .

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