# THE TRANSITION FROM THE NON-METALLIC TO THE METALLIC STATE IN ADSORBED LAYERS OF ALKALI METALS

BY Z. SIDORSKI

Institute of Experimental Physics, Wrocław University*

Basing on experimental results recently obtained concerning the adsorption of alkali metals on metallic substrate the view is advanced that the minimum appearing at $\theta_m$ on the work function *versus* coverage curve is caused by non-metal to metal transition (Mott transition) in the adsorbed layer. Sharp changes of many properties of the adlayer occuring at this coverage indicate that the electron structure of the layer may change at $\theta_m$.

## 1. Introduction

New experimental methods were recently used for studying the adsorption of alkali metals on metallic substrates. Low energy electron diffraction (LEED) measurements were performed for cesium adsorbed on (100) and (110) faces of tungsten (Mac Rae *et al.* 1969, Fedorus and Naumovets 1970), for sodium adsorbed on (100), (110) and (111) faces of nickel (Gerlach and Rhodin 1969, 1970) and for sodium adsorbed on the (211) face of tungsten (Chen and Papageorgopoulos 1970). Lander and Morrison (1969) measured spectra of inelastic scattering of electrons for the (100) tungsten face covered with a cesium layer. Fehrs and Stickney (1971) measured the contact potential for cesium and potassium adsorbed on the (110) face of tantalum and the (100) face of tungsten. In the light of results obtained by these new methods existing views on adsorption of alkali metals on metallic substrates have to be changed considerably, particulary as far as the structure of the adsorbed layer is concerned. Mac Rae *et al.* (1969) basing on LEED measurements put forward the hypothesis that by adsorption of cesium on the W (100) face initialy the layer of Cs$^+$ ions is formed with a c $(2 \times 2)$ structure. This ionic layer is completed before the minimum of the work function is reached (see Fig. 1, solid curve). On top of this ionic layer the second atomic layer is formed with a $(2 \times 2)$ structure which changes into a close-packed hexagonal arrangement when the work function passes through its mini-

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* Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Wrocław, Cybulskiego 36, Poland.

mum. The loss peak at 1.5 eV was found in scattered electrons for the Cs-W system only in the range from the minimum of the work function to its saturation (Lander and Morrison 1969). The loss peak was described as due to the surface plasmon (SP) excitation. Ngai, Economou and Cohen (1970) tried to explain the absence of SP losses in the adsorbed second layer with (2×2) structure by the occurence of Mott transition in this layer. This explanation does not seem to be satisfactory. The electron gas density changes in the second (atomic) layer continuously and SP losses should be comparable in a complete (2×2) structure and a hexagonal array. There were no losses found in the (2×2) layer. It is also not clear why the work function decreases while the atomic layer begins to form and increases when the (2×2) structure changes into a close-packed one. The presented above "duo-layer" model of Mac Rae *et al*. contradicts numerous data concerning the values of atom density of cesium adsorbed on tungsten (see for example: Gavrilik *et al*. 1966, Swanson and Strayer 1968, Sidorski *et al*. 1969, Fehrs *et al*. 1970, Fehrs and Stickney 1971) and was not confirmed by other LEED measurements performed for the Cs-W system (Fedorus and Naumovets 1970).

In this paper we will base on the commonly accepted view that physical processes of the greatest interest occur during the formation of the first layer of the adsorbed atoms. This opinion is strongly supported by numerous precise measurements of the dependence
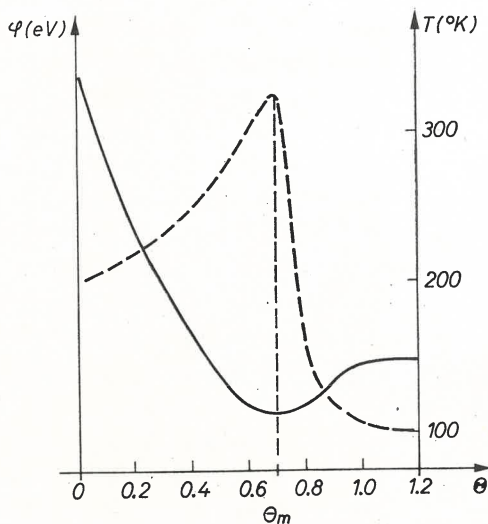


Fig. 1. The dependence of the work function on the degree of coverage (schematic). Dashed curve represents the temperature required for equilibration of small doses of potassium over the field-emission tip in 60 sec as a function of potassium coverage (after Schmidt and Gomer 1965)

of the work function on the degree of coverage. This relationship has the same character for various alkali metals adsorbed on different substrates (Fig. 1, solid curve). The shape of the curve allows one to distinguish two different coverage ranges. In the low coverage range $0 < \theta < \theta_m$ the work function decreases steeply with increasing coverage. At $\theta_m$

which divides the two coverage ranges, the work function passes through a distinct minimum. In the second region of high coverage $\theta_m < \theta \leqslant 1$ the work function increases and saturates when the first layer is completed. Adding of further layers does not change the work function any more. It remains constant and equal to that of the bulk adsorbate. In the high coverage range the work function variation does not depend on the character of the substrate. This shows that in this coverage range the adlayer screens the substrate almost completely and the properties of the adlayer are determined by processes taking place within the layer. It is reasonable to assume that the adlayer in this coverage range forms a two-dimensional ($2D$) metal with lattice constant decreasing continuously with increasing coverage. When the degree of coverage reaches unity the properties of adlayer are the same as those for the bulk metal. On applying to this $2D$ metal the energy band theory one can derive the formula describing fairly well the dependence of the work function on the degree of coverage in the high coverage range (Sidorski and Wojciechowski 1971). In the low coverage range the variation of the work function is influenced markedly by the substrate (Swanson and Strayer 1968) which shows that the character of adlayer is different.

Recently Moss and Blott (1969) measured the work function for copper adsorbed on the (111) face of tungsten. The shape of the work function *versus* coverage curve is very similar to that of an alkali metal adsorbed on a metallic substrate. The conclusion can be drawn that the relationship between the work function and the coverage described above is characteristic for adsorption of one valence electron metals.

In 1961 Mott put forward the hypothesis that as the lattice parameter of the crystalline array of atoms with one valence electron decreases there will be a sharp transition from the non-metallic to the metallic state at a critical lattice constant $d_0$. In such an array a pair of carries is formed when an electron is removed from one atom and placed on another. The electron and hole made in this way attract each other due to Coulomb interaction and form a bound state which does not allow conduction. When the lattice constant decreases the density of carriers increases and the Coulomb interaction is to be replaced by screened Coulomb interaction. For a critical lattice constant $d_0$ the interaction becomes too weak to keep the electron and hole bound and a sharp transition from no free carriers to a large number of carriers takes place. The hypothesis is proved theoretically. Basing on theoretical models the prediction can be made that it may be very difficult to observe the Mott transition in a crystalline lattice because of lattice instability associated with metal-insulator transition (Mott 1968). In fact so far the Mott transition was observed in heavily doped solid semiconductors *i.e.* in two or more component systems. In this case the covalent forces holding the atoms in position are stronger than forces exterted by the electron gas. The impurity centres form a rigid lattice distributed at random, not in a crystalline array. Not all metal-instulator transitions are due to electron-electron interaction. The observed metal-insulator transitions in dense mercury vapor, in concentrated solutions of alkali metals in liquid ammonia and in transition-metal oxides and sulfides are most probably transitions of different type.

The aim of this paper is to discuss the possibility of the Mott transition in an adsorbed layer of alkali metal atoms. The variation of the work function with increasing thickness

of adsorbed layer of alkali metals gives evidence that properties of the adlayer at low coverage differ significantly from those at high coverage. Basing on experimental results concerning the structure and behaviour of the adlayer it will be shown that the change of properties is sharp and occurs at $\theta_m$. An opinion is advanced that at this coverage the transition from the non-metallic to the metallic state takes place.

## 2. The structure of adsorbed layer

The investigations of alkali metals adsorption using theormoionic or field emission did not enable the determination of the adsorbed layer structure to be achieved. Some hypothetical models concerning this problem were proposed. Usualy the interaction between adsorbed atoms (or ions) and the substrate was considered to be the most important. It was assumed that on the substrate crystal surface adsites with high binding energy exist where adsorption occurs. The arrangement of adsites is regular and closely connected with the structure of substrate surface. With increasing coverage more and more adsites get randomly occupied. The adsorbed layer forms by intermediate coverage, two-dimensional gas with the density increasing, with increasing coverage. Only when the adlayer is completed the arrangement gets regular and corresponds to the structure of the substrate (coherent adsorption). Knowing the structure of substrate and the radius of the adatom (usualy two alkali atoms cannot sit on adjacent adsites) the atom density corresponding monolayer can be calculated. Another way of occupying of adsites can also be taken into account. In the intermediate range of coverage, two-dimensional "islands" with monolayer structure can be formed. With increasing coverage the number and/or size of islands increases. Finally the monolayer with coherent structure is formed.

LEED measurements recently performed made it possible to determine the structure of adsorbed layer precisely. They showed that the views on adsorption mechanism must be changed. It was found that at least on smooth crystal faces like (110) in *bcc* or (111) in *fcc* structures the adsorbed layer is incoherent (Fedorus and Naumovets 1970, Gerlach and Rhodin 1969). Beginning from very low coverages the adsorbed atoms form regular structures not necessarily of the same type as the structure of substrate surface. For instance the cesium layer on the $W$ (110) face is hexagonal (Fedorus and Naumovets 1970). This statement indicates that even at very low coverage the mutual interaction of adatoms is of great importance. Thus newest experimental results show that when an alkali metal is adsorbed on a metallic substrate beginning from very low coverage, a two-dimensional ctystal is formed by the adsorbed atoms. The structure of this $2D$ crystal does not depend on the substrate structure. With increasing coverage the lattice constant of the $2D$ crystal decreases continuously.

## 3. The properties of adsorbed layer at $\theta_m$

The common opinion that there is no significant change in the electronic structure of the adlayer at $\theta_m$ is based on the fact that the dipole moment *versus* coverage curves show no discontinuity at this coverage (see for example: Sidorski *et al.* 1969, Gerlach

and Rhodin 1970). The dipole moments are calculated from experimental data using the Helmholtz formula. In our previous work (Sidorski and Wojciechowski 1971) we advanced the opinion that the Helmholtz equation is a very rough approximation and cannot be used for the evaluation of the dipole moment (at least not in the antire coverage range). Thus the statement that at $\theta_m$ no change in electron structure occurs cannot be considered as well founded. Basing on the experimental data of Moss and Blott (1969) we computed dipole moment for copper adsorbed on the $W$ (110) face as a function of time of deposition using the Helmholtz formula. The curve (Fig. 2) has a visible discontinuity at $\theta_m$. According to our opinion the Helmholtz formula has no physical meaning for coverages higher than $\theta_m$ and we will not draw any significant conclusion from this fact. We would only show that the dependence of the dipole moment on the coverage
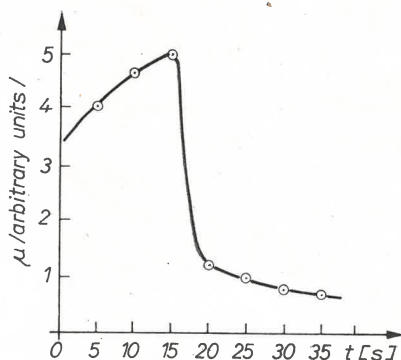


Fig. 2. Dipole moment (in arbitraty units) *versus* time of deposition for copper adsorbed on $W$ (110) face computed on the base of experimental results of Moss and Blott (1969)

obtained using the Helmholtz equation does not support sufficiently the view that there is no transition at $\theta_m$.

On Fig. 1 we plotted after Schmidt and Gomer (1965) the temperature required for equilibration of small potassium doses over the field-emission tip in 60 sec as the function of potassium coverage (dashed curve). The dependence of the activation energy of surface diffusion on coverage has the same shape (see Fig. 17 in work of Schmidt and Gomer 1965). Again two regions of coverage divided by the characteristic coverage $\theta_m$ can be distinguished. At coverage lower than $\theta_m$ the activation energy increases steeply with increasing coverage and decreases slightly in the high coverage range. Most probably the mechamism of surface diffusion is different on both sides of $\theta_m$. This may be due to the different electron structure of the adlayer in these ranges of coverage. The abrupt drop of activation energy occuring at $\theta_m$ provides evidence that the change of adlayer properties takes place at this coverage and is sharp.

A very interesting phenomenon was found by Fedorus and Naumovets (1970). The hexagonal array of cesium atoms adsorbed on the $W$ (110) face changes its orientation relative to the substrate very abruptly when the work function passes through its minimum. This can be cuased by a sharp change in the interaction of atoms within the adlayer.

As further evidence that at $\theta_m$ a sharp transition takes place we can consider the ap-

pearance of plasma losses only for coverages higher than $\theta_m$. According to the Gadzuk (1970) theory of plasmon modes in metal-thin film-vacuum sandwiches the energy of plasmons in very thin films should be proportional to the square root of electron density. The experimentally observed loss peak appears at 1.5 eV and does not change at the coverage range $\theta_m < \theta < 1$. The absence of plasma losses for coverages lower than $\theta_m$ can be connected with the non-metallic character of the adsorbed layer in this coverage range. At $\theta_m$ the transition to the metallic state occurs and electron plasma appears abruptly. with the density only slightly lower than that of the corresponding monolayer. The excited plasmons have constant energy. The observed loss peak could be interpreted as connected with band-to-band transitions as well. The latter interpretation supports also the view that a metallic state appears at $\theta_m$.

## 4. Conclusions

Experimental results recently obtained showed that alkali metal atoms adsorbed on a low indices crystal face of a metallic substrate form a two-dimensional crystal. The regular arrangement of adatoms at very low coverages indicates that the interaction between adatoms is not negligible at this coverages. The structure of the adsorbed layer may be incoherent. When the degree of coverage increases the lattice constant of 2D crystal formed by adatoms decreases continuously. According to the hypothesis put forward by Mott, the sharp transition from the non-metallic to the metallic state is expected to occur in a regular array of one valence electron atoms when the distance between atoms decreases. The situation in the adsorbed layer of alkali atoms is very similar to that considered by Mott.

Experimental results concerning the alkali metal adsorption on single crystal faces showed also that a characteristic degree of coverage $\theta_m$ i.e. a characteristic lattice constant of 2D crystal exists at which the properties of the adlayer change considerably. The work function decreases steeply for coverage lower than $\theta_m$, passes through a distinct minimum and increases for coverages higher than $\theta_m$. The surface diffusion activation energy increases steeply in the low coverage range, drops abruptly at $\theta_m$ and decreases slightly at higher coverages. An abrupt change of orientation of the adsorbed 2D crystal relative to the substrate surface was observed at $\theta_m$. No losses were observed in scattered electrons for coverage lower than $\theta_m$. A loss peak of constant energy was found in the coverage region $\theta > \theta_m$. We consider all these facts as evidence that a sharp change in the electron structure of the adlayer occurs at $\theta_m$. It is commonly believed that the adlayer for $\theta > \theta_m$ is metallic. Observation of plasma losses in this coverage region supports this opinion strongly. The absence of energy losses for coverage lower than $\theta_m$ indicates that the adlayer in this coverage range is rather non-metallic. This gives reasons to consider the phenomenon occuring at $\theta_m$ as the transition from the non-metallic to the metallic state predicted by Mott.

Mott (1958, 1961) estimated roughly the mean distance between atoms when the transition is expected to occur. It should be about four times the mean radius of atom. For cesium adsorbed on the $W$ (110) face the nearest neighbour adatom distance at $\theta_m$ is 6 Å (Fedorus and Naumovets 1970) compared with cesium atomic radius 2.62 Å.

However Mott's estimation should not be taken too seriously, on the other hand the situation in the adlayer is different from that considered by Mott. There still exists the interaction with the substrate and some charge transfer from the adlayer to the substrate. This is most probably responsible for the fact that adatoms in monolayer are packed closer than in bulk metal. For example for cesium monolayer (hexagonal) formed on the $W$ (110) face the atomic radius is only 2.35 Å (Fedorus and Naumovets 1970). It can be assumed that because of charge transfer the electron density at $\theta_m$ is so low that transition to non-metallic state occurs.

Mott (1968) predicted that it may be very difficult to observe the Mott transition in a crystalline lattice because of its instability associated with the transition. It seems that observation of the Mott transition is possible in adsorbed layers due to binding forces between adatoms and substrate which are strong enough to keep adatoms in position. In this respect the situation in the adsorbed layer is to some extend similar to that in doped semiconductors. The abrupt change of orientation of adsorbed $2D$ crystal observed by Fedorus and Naumovets (1970) at $\theta_m$ may be caused by the instability of the adatoms lattice connected with the Mott transition. It seems also that the Mott transition in the adsorbed layer of an alkali metal is conceivable when adsorbed atoms are distributed at random.

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