Submonolayer films on the surface of metals

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1. INTRODUCTION

Under ordinary conditions the surfaces of any solid materials and liquids are covered with films of atoms or molecules adsorbed from the surrounding atmosphere or which have arrived at the surface in the course of diffusion. Study of the properties of adsorbed films has traditionally been one of the fields of physical chemistry. The development of such branches of technology as emission electronics, vacuum technology, catalysis, direct energy conversion, and so forth have led to accumulation of extensive information on the properties of films on the surfaces of solids (primarily metals), films whose thicknesses do not exceed that of a monatomic or monomolecular layer, i.e., submonolayer films. This is due to the fact that, as experiments have shown, it is in the course of filling of the first monolayer that the principal change occurs in the properties of the surface under the influence of the adsorbed film. The information which has been obtained has been mainly of an empirical nature. Measurements of the same quantities by different workers have frequently led to different results. Theoretical studies have been extremely few. However, it must be emphasized that in the study of adsorption phenomena, as in surface physics generally, significant progress has been made in the last 10 to 15 years. It is due to the fact that it has finally become possible to study processes on a surface under well controlled experimental conditions. Thus, ultrahigh vacuum technique has permitted us to control the composition and concentration of submonolayer films adsorbed on carefully cleaned surfaces. Advances in the technology of crystal growth have given us the possibility to work with large regions of the faces of single crystals and in this way to measure all quantities for each face individually, rather than working with quantities averaged over the surface of a polycrystalline sample. After the possibility of working with clear surfaces appeared, in a relatively short time many precise and very informative techniques were developed. A number of theoretical studies on this subject also appeared quickly. Nevertheless, it appears to us that many physicists who have not

worked in the field of surface physics do not suspect what extensive information can be given by contemporary experiments on the electronic state of adsorbed particles on metal surfaces, on their interaction with each other and with the substrate, on the atomic structure of the films, and on the effect of the films on the work function and other properties of the surface. The purpose of the present review is to acquaint readers with some principal results achieved in this field. In presenting this extensive and extremely diverse experimental material, we have attempted to distinguish the most characteristic features, which are present in many adsorption systems, and as far as possible to provide corresponding theoretical ideas.

2. THE ELECTRONIC STATE OF ADSORBED ATOMS

A. Theoretical ideas

The state of a single adsorbed atom (adatom) on the surface of a metal depends on the nature of the adsorption bond.

In physical adsorption the binding is accomplished by polarization forces. For adatoms with low polarizability these are mainly van der Waals forces; if the polarizability is appreciable the electron shells of the atom are somewhat deformed as the result of interaction with the substrate, and an induced dipole moment arises perpendicular to the surface. In this case the interaction forces of the adatom with the surface are mainly of a dipole–dipole nature. This type of adsorption is characteristic of noble gases on the surface of metals and also of graphite.

Most elements form a chemical bond in adsorption on metals. The electronic structure of chemisorbed atoms on a metal surface was first described qualitatively by Gurney.[1] A discrete level of an isolated atom as the result of interaction with the metal is spread out into a quasilevel with a density of states $\rho(\varepsilon)$ and is displaced relative to the initial location (Fig. 1). At $T = 0$ electrons fill all levels lying below the Fermi
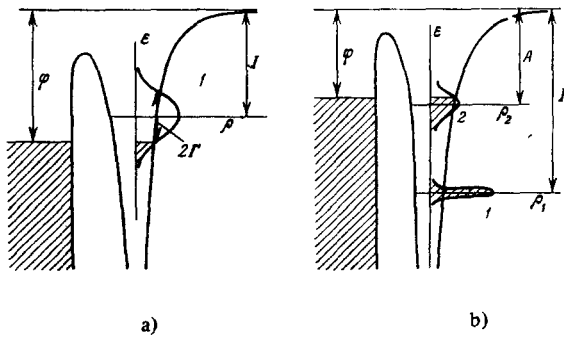
FIG. 1. Density of states $\rho(\varepsilon)$ in quasilevels of adsorbed atoms. 1) The case $I < \varphi$, adatom positively charged; b) the case $A > \varphi$, adatom negatively charged. 1—valence electron level, 2—electron affinity level, φ—work function, 2Γ—quasi-level half-width.

level, which is practically unchanged on addition of the adatom. Thus, the quasilevel can turn out to be filled only partially, and the adatom is characterized by a fractional charge γe which is determined by the relative location of the Fermi level and the center of the quasilevel, and also by the width of the quasilevel. The adatom is positively charged if its quasilevel is partially free, and negatively charged if the level of the negative ion is partly filled. The charged adatom in combination with the electron cloud screening it, which is concentrated in the region near the metal surface, forms a dipole perpendicular to the surface.

It is clear from the above that the nature of chemisorption binding can be conveniently classified on the basis of the relation between the ionization potential I of the atom, its electron affinity A, and the work function φ of the metal (see Fig. 1). For $I < \varphi$ or $A > \varphi$ the bond is primarily ionic in nature and the adatom is charged positively or negatively. On the other hand, for $A < \varphi < I$ the bond has mainly a covalent nature (or a metallic nature if the binding is accomplished by delocalized electrons). Of course, these criteria must be considered as approximate, since the levels in the adatom can be substantially displaced with respect to their locations in the free atom.

A number of reviews[2-6] have been published in recent years on the theory of chemisorption on metals. As in the theory of molecules, two principal quantum-mechanical approximations are developed in the theory of chemisorption: the molecular-orbital–self-consistent-field method (MO–SCF) and the valence-bond method (the Heitler-London approximation).

Up to the present time the MO approximation has been primarily used in discussion of adsorption, since it is more natural in that approach to take into account an extremely important factor—delocalization of the electrons in the metal. In the framework of this approach[7-13] the model Hamiltonian of Anderson[14] is generally used; this Hamiltonian was proposed for description of the electronic states of impurity atoms in alloys. This Hamiltonian has the form

$$\mathcal{H} = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_\sigma \tilde{E} n_{\alpha\sigma} + \sum_{k,\sigma} (V_{k\alpha} a^+_{k\sigma} a_{\alpha\sigma} + \text{H.c.}) + U n_{\alpha\sigma} n_{\alpha,-\sigma}; \quad (1)$$

here the index k numbers the energy states in the metal, α—those in the adatoms, and σ—the spin states; ε_k is the band energy of an electron in the metal; $\tilde{E}$ is the energy of an electron located in the adatom relative to the Fermi level (i.e., $\tilde{E} = \varphi - I$ in adsorption of electropositive elements and $\tilde{E} = \varphi - A$ in adsorption of electronegative elements); $V_{k\alpha}$ is the matrix element of the transition of an electron from the adatom to the metal; U is the Coulomb energy of interaction of the electrons in the adatom; $a^+_{\alpha\sigma}$, $a^+_{k\sigma}$ are the creation operators and $a_{\alpha\sigma}$, $a_{k\sigma}$ are the annihilation operators for electrons in atomic and metallic states, respectively; $n_{\alpha\sigma} = a^+_{\alpha\sigma} a_{\alpha\sigma}$, $n_{k\sigma} = a^+_{k\sigma} a_{k\sigma}$ are the electron filling number operators.

As is clear from Eq. (1), in the Anderson model the Coulomb interaction of the electrons is taken into account only inside the adatom.

If we use the Hartree-Fock (HF) approximation and neglect the overlap of the wave functions of the electrons of the adatom and the metal, the Hamiltonian (1) is easily diagonalized. As a result we can find the density of states in the adatom

$$\rho_{\alpha\sigma}(\varepsilon) = \frac{1}{\pi} \frac{\Gamma(\varepsilon)}{(\varepsilon - E_{\alpha\sigma} - \Lambda)^2 + \Gamma^2}, \quad (2)$$

where

$$\Gamma = \pi \sum_k \delta(\varepsilon - \varepsilon_k) |V_{k\alpha}|^2, \quad (3)$$

$$\Lambda = \sum_k{}' \frac{|V_{k\alpha}|^2}{\varepsilon - \varepsilon_k}, \quad (4)$$

$$E_{\alpha\sigma} = \tilde{E} + U \langle n_{\alpha,-\sigma} \rangle. \quad (5)$$

$$\langle n_{\alpha\sigma} \rangle = \int_{-\infty}^{\infty} \rho_{\alpha\sigma}(\varepsilon) n_F(\varepsilon) d\varepsilon, \quad (6)$$

and $n_F(\varepsilon)$ is the Fermi function.

For calculation of the quantities $E_{\alpha\sigma}$, Γ, and Λ, it is necessary to use specific models of the metal and adatom. The functions Γ and Λ which determine the width and displacement of the adatom level depend in a complicated way on the value of the matrix elements $V_{k\alpha}$ and the initial location of the atomic level relative to the conduction band of the metal.[3,13] In the case in which the energy $E_{\alpha\sigma}$ falls within the conduction band of the metal, the quasilevel is extremely broad and the adatom interacts with the metal as a whole. On the basis of the known density of states $\rho_{\alpha\sigma}(\varepsilon)$ it is possible to find the magnitude of the fractional charge of the adatom $\gamma = 1 - \langle n_{\alpha\sigma} \rangle$.

Also possible is the situation in which the displaced level of the adatom turns out to be outside the conduction band of the metal. For example, if $|V_{k\alpha}|$ is large in comparison with the width of the band, it is broken up into two rather narrow levels, one of which is located above the bottom of the conduction band of the metal, and the other—above the top of the band. Ultimately a localized bond is formed, i.e., the situation reduces essentially to formation of a "surface molecule" in which the lower level corresponds to the bonding orbital, and the upper level to the antibonding orbital.[15,16] The criterion of applicability of the concept of surface mole-

cule is the requirement that the width of the levels corresponding to the group orbitals of such a molecule be sufficiently small in comparison with $|V_{k\alpha}|$, i.e., that the interaction with the "residual" metal be relatively weak. A surface molecule differs from a free particle, in particular, in that in it all levels below the Fermi level E_F are occupied, and those above are free; in addition, its total charge can correspond to a nonintegral number of electrons. The binding energy in it has been calculated both in the HF approximation[15,16] and in the Heitler-London approximation. [17] The model of a surface molecule has been used to describe adsorption on a number of metals of hydrogen atoms[13] and carbon dioxide molecules[15] and also of sodium on nickel[16] and of the transition elements of the 5d period on tungsten. [18] Bennett et al. [19] have discussed in a similar way, but with use of the semiempirical method of Hückel, the adsorption of H, C, N, F, and O on graphite, the substrate being modeled by a group of 16 or 32 carbon atoms located in accordance with the surface structure.

A deficiency of the Anderson model is its neglect of the Coulomb interaction between electrons everywhere except the adatom itself. This limits the possibility of its use in calculation of surface molecules, in which the Coulomb interaction of the electrons in the rather narrow quasilevels of the substrate atoms can be extremely important. In this case more reliable results are obtained with use of Hubbard's Hamiltonian (see Refs. 18, 20-23).

Coulomb forces play an extremely important role also in absorption of atoms with low ionization potentials, for example, alkali and alkaline earth atoms. As we have noted, such adatoms are partially ionized and interact with the electron cloud screening them—with their electrical image in the metal. In these cases the image-force potential is in one way or another specially included in the Hamiltonian. [7,9,10,24,25]

Inclusion of the electron correlation energy, which is ignored in the HF approximation, is a serious problem in the theory of chemisorption. While each electron, from the point of view of the one-electron approximation, tends toward delocalization, the Coulomb interaction U facilitates localization of the electrons at the maximum separation between them. The criterion of applicability of the HF model is the requirement $U \lesssim \Gamma$, where 2Γ is the width of the virtual level (or in the case of formation of a local bond—the energy gap between the bonding and antibonding orbitals). For small U, Eqs. (3)-(6) have identical solutions corresponding to $\langle n_{\alpha\sigma} \rangle = \langle n_{\alpha, -\sigma} \rangle$, i.e., absence of a magnetic moment in the adatom. On the other hand, for $U \gtrsim \Gamma$ there are two "magnetic" solutions with $\langle n_{\alpha\sigma} \rangle \neq \langle n_{\alpha, -\sigma} \rangle$, which in the absence of an external magnetic field are degenerate in energy. However, in this case the HF model already is of no use. Various means of taking into account electron-correlation effects in calculation of the adsorption energy and the electronic structure of adatoms have been discussed in Refs. 9, 21, 22, 26, and 27.

For $U > \Gamma$, in general, it is more desirable to use not the molecular-orbital approximation, but the Heitler-London approximation (the valence-bond method). In the framework of this method Schrieffer and Gomer[17] introduced into adsorption theory the concept of an induced covalent bond formed between the adatom and the metal. For $I > \varphi$ transfer of an electron from the adatom to the metal is disadvantageous, and bonding can be accomplished only as the result of exchange. This turns out to be possible as a result of the fact that the adatom induces in the metal a spin density with which the electron of the adatom can interact, i.e., antiferromagnetic pairing of the spins occurs. The energy of such a bond can be calculated in several limiting cases with use of perturbation theory in the exchange interaction. By this means a quite reasonable energy value of several electron volts has been obtained for hydrogen on a model metal. [28]

In concluding this section let us mention an additional chemisorption model which is based on the theory of an inhomogeneous electron gas[29,30] and is developed by Lang and others. [31-33] In this theory the ground-state energy of an inhomogeneous multielectron system is represented by a functional which depends on the density of the electron gas (and generally also on its gradient) and includes terms describing the kinetic and exchange-correlation energy and the reaction of the system in an external electric field. The positive charge of the ionic cores in the metal is assumed to be uniformly distributed over space (the "jellium" model). On the (plane) metallic surface is distributed an adatom with nuclear charge Ze, and then from the condition of minimum energy the equilibrium distribution of the electron gas is calculated. This gives the possibility of determining the energy and dipole moment of the bond, the distance of the adatom from the surface and the frequency of its vibrations, and the location of the quasilevel of the adatom. Unfortunately, the model discussed does not take into account the details of the electronic and atomic structure of the substrate, and the only characteristic of the metal considered is the density of the electron gas. However, the problem can be solved rather accurately in this formulation, so that the final results of the calculations of these quantities for hydrogen, oxygen, and lithium on tungsten agree within 20-20% with the experimental data. [32,33]

The conclusions of the theory of the electronic state of adatoms of various types and of the adsorption bond can be summarized as follows.

1. In chemisorption of gases on metals, where $I > \varphi$, the main contribution to the bond is from the covalent component, and as a rule the charge of the adatoms is negative and small ($\sim 0.1 e$). The quasilevels are rather narrow (~ 0.5 eV) and the surface-molecule model can serve as a good approximation. [13,15,16,27] This applies to a significant degree also to adatoms of the transition elements such as Hf, Ta, Re, and Os on refractory metals. [16,21,34] In this case the theory is capable of correctly predicting the ratio of the heats of adsorption for different systems. However, as a consequence of the major simplifying assumptions (in particular, insufficiently correct allowance for the electronic struc-

TABLE I. Spectroscopic methods of investigation of electronic properties of surfaces.

Name of method	Means of probing surface property	What is analyzed	References
Field emission spectroscopy	Tunneling electrons	Emitted electrons	8, 36, 37
Photoemission spectroscopy	Ultraviolet light	Photoelectrons	38−40
Ion neutralization spectroscopy	Slow inert-gas ions	Auger electrons	41−43
Auger electron spectroscopy	Slow electrons	''	44−50
Plasma spectroscopy	''	Inelastically scattered electrons	51, 52
Ionization spectroscopy	''	''	53, 54
Spectroscopy of the threshold potential for appearance of x rays	''	X-ray photons	54, 55
X-ray photoelectron spectroscopy (ESCA)	X-ray photons	Photoelectrons	54, 56−58
Optical reflection spectroscopy	Light	Reflected light	59−62

ture of the substrates) the calculated absolute values of the heats of adsorption may differ from those observed experimentally by 1.5−2 times.

2. In adsorption of alkali elements on refractory metals ($I \lesssim \varphi$) the width of the quasilevels reaches 1−2 eV, and their displacement upward along the energy scale is about 1 eV, so that the degree of ionization of the adatoms must be close to unity. [9,10,25,26] Here up to 80% of the binding energy is provided by the ionic component, [9] and the dipole moment of the bond amounts to 5−10 debyes[24] (1 debye = 10^{-18} cgs esu = 3.33×10^{-30} coulomb-meter). In the alkaline earth adatoms—barium and strontium ($I \approx \varphi$)—the positive charge according to Ref. 26 is $(0.3-0.5)e$, and the contributions of the ionic and "metallic" components to the binding energy are comparable. The theory predicts[8] that the width and displacement of the virtual level in this case should amount to about 1 eV.

B. Experimental data

Up to the present time there have been developed a significant number of experimental methods which together provide rather complete information on the state of both individual adsorbed particles and of the films as a whole. The most extensively used spectroscopic methods, which are based on analysis of the energy distributions of various particles which have interacted with the surface, are listed in Table I. We have also given in the table references to reviews (if they exist) or original articles. A rather complete review[35] devoted to electron spectroscopy of surfaces has been published recently. We shall dwell here only on three methods, which have turned out to be most effective in study of the energy structure of adsorbed atoms.

1) *In the method of field emission spectroscopy (FES)* a comparison is made of the energy distributions of electrons emitted in field emission from a clean metallic point and from this same point covered by an adsorbed

film (Fig. 2a). The points are placed in an electron projection tube whose luminescent screen has a probe aperture. By observing the field-emission image, one can direct onto the aperture (by means of a deflecting system of some type) the current from any part of the tip of the point. Since the field-emission image is greatly magnified, this portion can in principle be made so small that it contains only one adsorbed atom. The FES method was first used in Refs. 63 and 64, and tunneling of electrons through adatoms was discussed theoretically in Refs. 8 and 65. Electrons with energies corresponding to allowed states in the film have an exaggerated probability of tunneling through the adsorbed film.

Thus, in the FES method electrons of the substrate itself are used for illumination of the energy spectra of the adatoms. The method has high sensitivity to
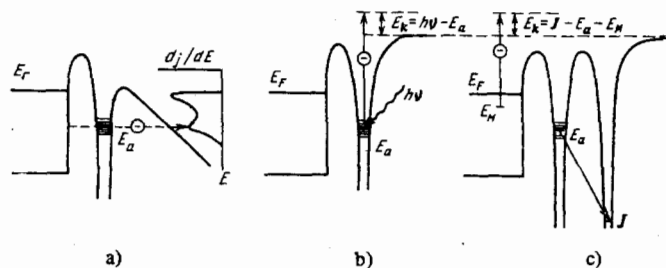
FIG. 2. Methods of investigation of the energy spectra of adsorbed particles. a) Field emission spectroscopy. Tunneling electrons probe the distribution of density of states in the quasilevel of the adatom E_a. At the right is the energy distribution of the field emission electrons. b) Photoemission spectroscopy. $h\nu$ is the photon energy and E_k is the kinetic energy of the photoelectron. c) Ion-neutralization spectroscopy. The energy released in transition of an electron from the adatom level E_a to the level of an inert gas ion J is expended in emission of an electron from the level E_M. E_F is the Fermi level. The energies are measured from the vacuum level.

changes in the conditions on the surface, but permits investigation of only a limited range of energies 1–2 eV below the Fermi level in the metal, since the probability of electron tunneling at lower energies is too small.

2) *The method of photoelectron spectroscopy (PES)* is based on analysis of the energy distribution of photoelectrons emitted in bombardment of samples by ultraviolet light and permits probing of electronic states over a wide range of energies (see Fig. 2b). The sensitivity of photoemission to the state of the surface and the near-surface region is due to the fact that in solids the mean-free paths of "hot" electrons with respect to inelastic collisions are extremely small (5–20 Å for electron energies in the range 10–1000 eV[66]). In these experiments one records the energy distribution of photoelectrons first from the clean substrate, and then from the substrate covered by a film. Subtraction of the spectra obtained permits one to find the peaks in the distribution due to emission of electrons from the levels of the adsorbed particles. The PES method can provide information also on the geometry of the adsorption bonds.[67–69] Its resolution is ≈ 0.2 eV (in comparison with 0.02 eV in the FES method).

3) *Ion-neutralization spectroscopy (INS)* permits information to be obtained on the energy structure of adsorbed particles by analysis of the energies of Auger electrons emitted in surface neutralization of inert-gas ions[41–43] (Fig. 2c). This method provides the possibility of more selective recording of the spectrum of just the adsorbed particles (or "surface molecules"), while use of the PES method probes a somewhat more extended region in the near-surface layer.[70] At the same time INS is substantially more complicated, both experimentally and from the point of view of deciphering the initial data.

Let us now discuss some of the most characteristic results.

The electron energy spectra of adatoms of the alkaline earth elements Ba, Sr, Ca, and also Zr on W, investigated by the FES method,[8,36,71] are qualitatively similar. For Ba, for example, the half-width of the virtual level is 0.75 eV, and the center of the level is displaced upward relative to the level of the free atom by about 1 eV (Fig. 3). Here the level of the Ba adatom must be filled to less than one half, i.e., the adatom must have a significant charge, which is consistent with other data.

The virtual levels of adatoms of the alkali elements are still wider, and therefore the FES method is inadequate to determine their shape and location.[36]

The energy structure of the atoms and molecules of adsorbed gases has been investigated most completely by means of the PES and INS methods. The photoelectron spectra of oxygen,[38,58,69,70,73] hydrogen,[38,68,73–76] and nitrogen,[38,73] on tungsten, of carbon dioxide on the transition metals,[38,58,73] and so forth contain peaks with a width 1–3 eV at energies 5–10 eV below the Fermi level of the substrate, which are associated more or less uniquely with the levels of the free particles. The effect of adsorption of gases on clean (100) and (110)
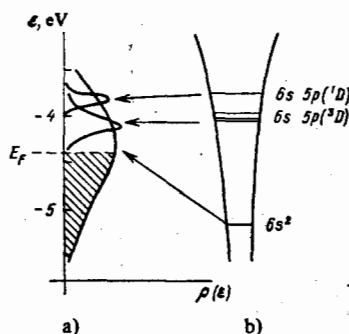

FIG. 3. Energy levels in a free atom of barium (b) and density of states in the corresponding quasilevels of a barium atom adsorbed on the (111) face of tungsten (a) (field emission spectroscopy).[36]

faces of tungsten has been studied.[37,74–78] For the oxygen-tungsten system a distinct correlation has been demonstrated between the changes in the energy spectrum of the adatoms and the rearrangement of the structure of the film.[38,58] The transition from the d levels of copper and palladium on increase of the film thickness to the d-band of the massive metal in deposition on silver has been followed.[72]

We believe that the examples presented above are quite sufficient to show how extensive and informative is the experimental information regarding the electron energy spectra of adsorbed particles accumulated in recent years by spectroscopic methods. It is therefore not surprising that in theoretical studies of recent years there has been a leaning toward calculation of specific systems. In fact, while ten years ago authors wishing to carry their calculations through to the numerical stage had at some stage to use crude models (see for example Bennett and Falicov[10]), the possibility has now appeared of taking part of the information from some experiments and on that basis predicting the results of other experiments. The time has arrived to construct more realistic models for numerical calculations, checking their applicability in an extensive set of experimental data.

In addition to study of such detailed properties of adsorbed films as the adatom energy spectrum described above, measurements of the broader characteristics of adsorption systems continue in full swing. Important information on the nature of the bonding of adatoms to the substrate can be obtained by recording the change in the work function of a particular face of a single crystal on absorption on it of a known amount of a given material. Actually, in the case $I \lesssim \varphi$ (see Sec. 2A of Chap. 2) the adatoms are positively charged, the magnitude of the charge can reach a value close to the electronic charge, and the distance between the centers of gravity of the charge and the effective surface of the metal, where the field of the charge begins to be screened, is of the order of atomic dimensions. We recall that the work function of a clean metal is due in a significant degree to displacement of the electron fluid outward relative to the surface layer of ions by an amount of the same order as the arm of the dipole formed by the charged adatom and

its image. It is not surprising that on adsorption of a complete monolayer of positively charged atoms the work function can decrease by an amount of its own order. A classical example which has found important practical applications is the system Cs–W. The W(110) work function is 5.35 eV, and the work function of this same phase covered by a monolayer of Cs is (at the minimum) 1.5 eV. In the case $A \gtrsim \varphi$ adsorption leads to a corresponding increase in the work function. Semi-quantitative information on the dipole moment of the bond is usually extracted from measurements of the dependence of the work function on the degree of coverage, associating the change in work function $\Delta\varphi$ with the drop in potential in the double electric (dipole) layer formed by the charged adatoms and the surface charges which screen them,

$$\Delta\varphi = 4\pi n p, \tag{7}$$

where p is the dipole moment of the bond and n is the surface concentration of adatoms. [79] The quantity $(1/4\pi)d\Delta\varphi/dn$ as $n \to 0$ determines the so-called initial dipole moment p_0 characterizing the adsorption of a single atom. In the region of not too high coverages, where the shells of neighboring atoms do not overlap (in this case it is meaningful to speak of the dipole moment or charge of an individual atom), the change in the dipole moment with increase of the coverage is due mainly to the decrease of the charge of the adatoms. Consequently, it is possible to extract quantitative information on the dependence of the charge of the adatoms on the degree of coverage from measurements of the work function.

Up to the present time, concentration dependences of the work function have been measured in a large number of adsorption systems.

The most completely studied systems have been those consisting of an alkali or alkaline earth atom on a transition metal: cesium, [80–84] potassium, [85,86] sodium, [87–90] lithium, [91] barium, [92–94] and strontium [95,98] on tungsten; cesium, potassium, and sodium on nickel [97]; barium on molybdenum [92] and rhenium. [98] For the systems enumerated the initial dipole moment is $P_0 \approx 10$ debyes, which corresponds to a charge $\approx e$. These data are consistent with the results of investigation of the drift of adatoms in a nonuniform electric field. [99–102]

Thus, adatoms of alkaline and alkaline earth elements on refractory metals have a significant positive charge.

It is interesting to note that even individual atoms deposited on the surface of a crystal of identical chemical nature (for example, tungsten on tungsten), have an appreciable positive charge, which is due to the tendency to smoothing of the contours of the electron cloud on the surface. [103,104]

Data on the dipole moments of adsorbed atoms and molecules of such gases as O_2, N_2, CO, and the halogens indicate that these particles usually have a small negative charge ($\sim 0.1\, e$), which corresponds to the case $A \gtrsim \varphi$; see Sec. A of Chap. 2. [105] We note that data obtained by spectroscopic methods confirm the results presented above.

3. INTERACTION OF ADSORBED PARTICLES. DEPENDENCE OF HEAT OF ADSORPTION AND WORK FUNCTION ON CONCENTRATION OF ADATOMS

A. Nature of the interaction. The electronic state of interacting adatoms

So far we have been talking about electronic states of isolated atoms. Let us now consider how the state of adatoms changes as the degree of coverage of the surface increases. The interaction between the adatoms depends on the nature of their bonding to the substrate.

In the case of physical adsorption the interaction forces between adatoms are made up of van der Waals and dipole–dipole forces, dipole–dipole repulsion dominating at large distances. If the bond is preferentially ionic, then at almost all distances dipole–dipole repulsion is dominant. For larger interatomic distances the potential of this interaction has the form

$$U_{aa}^{\alpha\beta}(r) = \frac{2e^2d^2}{r^3}(1-\langle n_{\alpha\sigma}\rangle)(-1\langle n_{\beta\sigma}\rangle) \tag{8}$$

for an electropositive film and

$$U_{aa}^{\alpha\beta}(r) = \frac{2e^2d^2}{|r^3}\langle n_{\alpha\sigma}\rangle\langle n_{\beta\sigma}\rangle \tag{8'}$$

for an electronegative film; here d is the distance from the center of gravity of the charge in the adatom to the plane which imitates the surface of the metal, and r is the distance between atoms α and β (it is assumed that $r \gg d$); $\langle n_{\alpha\sigma}\rangle$ and $\langle n_{\beta\sigma}\rangle$ are the average populations of the corresponding levels by electrons. The coefficient 2 in the expressions above (in place of the coefficient 4 which would be used in describing the interaction of free dipoles with a length $2d$) is due to the fact that interaction of the adatoms occurs only through the vacuum half-space. On approach of the adatoms, their charge decreases (see below) and then the direct exchange interaction becomes important.

In addition to the Coulomb interaction through the vacuum half-space, it is predicted that there will be long-range exchange interaction of the adatoms through the electron gas of the substrate (the so-called indirect interaction). [11,106] It is due to the existence of slowly damped oscillations of the electron density around the impurity atom, arising as the result of interference of electron waves scattered by it. [107] According to Grimley and Walker [106] for interatomic distances large in comparison with the lattice constant the energy of this interaction has the form

$$U_{aa}^{ind}(r) = \frac{C}{r^3}\cos(2k_F r), \tag{9}$$

where k_F is the momentum of an electron at the Fermi surface. In the case when the dipole moment of the bond is small ($\lesssim 1$ debye), the energy of the indirect action may be higher than the energy of dipole repulsion. In contrast to Ref. 106, Gabovich and Pashitskiĭ [108] concluded that in view of the cylindrical symmetry of the conditions in the problem the Friedel oscillations of the electron density at the surface and the energy U_{aa}^{ind} should die out more slowly—according to a $r^{-5/2}$ law

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(for a spherical Fermi surface). If the Fermi surface is cylindrical and the crystal face is perpendicular to the axis of the cylinder, then $U_{aa}^{ind} \sim r^{-2}$. Finally, if there are large plane portions of the Fermi surface, $U_{aa}^{ind} \sim r^{-1}$ in the directions perpendicular to these portions and falls exponentially in directions parallel to the plane portions.

We have been speaking above about the asymptotic behavior of U_{aa}^{ind} at large r. Einstein and Schrieffer[109] used the strong-coupling approximation to study the indirect interaction through the electrons of the substrate in the adjacent region and found that here U_{aa}^{ind} decreases exponentially with distance.

The indirect interaction between adatoms can occur also through the phonon field of the substrate, like the deformation interaction of impurity atoms in crystals (see Khachaturyan's book, [110] Chap. 7). However, the potential of this interaction is small and in most cases need not be taken into account. [111]

As the result of the superposition of all of the enumerated types of forces, the interaction of adatoms with each other, generally speaking, has a very complex nature and depends strongly both on the chemical nature of the adsorbate and substrate, and on the atomic structure of the surface. A wealth of information on the interaction of particles on the surface has been obtained in investigation of the structure of films by diffraction methods. We will discuss this in Chap. 4. However, this information is indirect in nature, since the same structures can be produced in different types of interactions. Important information on interactions on the surface is obtained by studying the combined adsorption of different materials. [121] In recent years there has been a substantial development of the methods of ion microscopy, which have permitted a start in studying the interaction of individual adatoms. For example, the method of field ion microscopy permits observation with atomic resolution (2.5–3 Å) of processes on the surface of metallic points having a perfect atomic structure. [112]

Up to the present time studies have been made of the interaction of atoms of Ta, W, Re, Zr, Pt, and Mo on the (110) and (112) faces of W, and also of the surface diffusion of isolated atoms, their dimers, and larger clusters. [113–120] It has turned out that even on close-packed faces the interaction of these atoms is isotropic and nonbinary.

Nevertheless, we can point out systems in which the interaction is of a rather simple nature. These are mainly systems in which the adatoms have a substantial charge (alkali and alkaline earth metals on refractory metals) or dipole moment (noble gases on metals). In most cases the principal role (at least for small coverages) in these systems is played by the dipole–dipole interaction. In addition, we can cite the adsorption of molecules of various gases (Xe, N_2, He) on graphite. The small dipole moment of the adsorbed particles leads in this case to a dominant role of the van der Waals' interaction.

The electronic state of individual adsorbed atoms

changes as the result of the interaction of the adatoms with each other, as we have already mentioned in Sec. B of Chap. 2. Experiments carried out by means of PES have revealed directly the substantial shift and change of shape of the quasilevels on change of the degree of coverage of the faces of W single crystals by molecules of H_2, O_2, and CO. [38, 73, 76] The quasilevel of each atom undergoes a Stark shift in the electric field produced by its neighbors. For this reason the filling of the quasilevels, and consequently also the charge of the adatoms, change with change of the density of the film. It is easy to see that, both for $I \lesssim \varphi$ (positively charged adatom) and for $A > \varphi$ (negatively charged adatom), the charge falls off in absolute value with increase of coverage. In classical language we can say that there is a depolarization of the dipoles formed by the charged adatoms and their images in the metal, under the influence of the field of the surrounding adatoms. [122]

Under certain conditions the depolarization can be so great that two-dimensional condensation of the adsorbate becomes possible (see Sec. A of Chap. 4).

As yet a small number of studies have been devoted to the microscopic theory of the electronic state of interacting adatoms. For the most part these studies treat the adsorption of alkali metals on refractory metals; this is due both to the relative simplicity of these systems and to their practical importance in emission electronics.

Several workers[10, 123–126] have used Anderson's model for self-consistent calculations of the charge of the adatom, taking into account its interaction with neighbors. The Hamiltonian (1) with addition of a dipole–dipole interaction potential $U_{aa}^{\alpha\beta}$ (8) is diagonalized in the HF approximation. For the density of states in one adatom (on the assumption that the states of all atoms are identical) we retain Eq. (2), where we now have

$$E_{a\sigma} = \tilde{E} + U_a \langle n_{\alpha, -\sigma} \rangle - \sum_{\alpha \neq \beta} U_{aa}^{\alpha\beta} (1 - \langle n_{a\sigma} \rangle). \qquad (10)$$

The expression (6) for $\langle n_{\alpha\sigma} \rangle$, when Eqs. (2)–(4) and (10) are taken into account, permits us to obtain a closed equation for $\langle n_{\alpha\sigma} \rangle$ and to find the dependence of the adatom charge on the degree of coverage. A discussion of this type is given in Refs. 10 and 123 for films of K, Rb, and Cs on W. It should be noted, however, that the distance from the adatom to the surface is introduced into the calculations as an external parameter and that the treatment in terms of Anderson's model is limited to low degrees of coverage where it is possible to neglect the contribution of the direct and indirect exchange interaction.

A similar procedure has been used in Refs. 126 and 127, where it is shown that, in addition to the homogeneous solution, where all adatoms in the film have identical charge, the case is possible in which adatoms having different charges alternate on the surface in a definite order. This type of superlattice of the electronic structure turns out to be energetically more favorable than the uniform charge distribution for the condition

(for a film with a square unit cell on the surface of a crystal with the same symmetry) $e^2 d^2/a^3 > 0.6\,\Gamma$, where a is the lattice constant in the film. This condition is obtained on the assumption that the quasilevel has a Lorentz shape and that Γ does not depend on E. Some of us[126] have introduced an even more general criterion for the existence of electron superlattices. The question of the possibility of observing the electronic phase transition predicted in Ref. 126 is discussed in detail in Bol'shov's thesis.[127] Another variant of the microscopic theory of the electronic state of absorbed films is being developed by Lang.[31] In his work the ionic lattices of the film and substrate are replaced by a uniform distribution of positive charge, and the electron distribution is found by numerical solution of the Schrödinger equation with allowance for correlation and exchange effects. The results obtained on the basis of this model will be discussed when we consider the question of the effect of films on the work function (Sec. C) of Chap. 3).

It is evident that further work on the microscopic de-description of the electronic state of adatoms as a function of their concentration on the surface will be of great interest.

The difficulties in constructing a rigorous theory and the practical requirement of predicting the properties of metal-film systems has resulted in the appearance of semiphenomenological theories which describe the interaction of adatoms.[128-132] For example, in Refs. 128-130 the concept of electronegativity has been used for this purpose. The contribution to the binding energy of the covalent and ionic components is calculated on the basis of semiempirical relations, data on the sublimation energies of the adsorbate and substrate being utilized, as well as data on the difference in the electronegativities. It is further assumed that the electronegativity of the substrate can be perturbed under the influence of the electric field of the adatom-dipoles. The covalent interaction of the adatoms on their approach to small distances is also taken into account. The dependences obtained for the charge of the adatoms, the heat
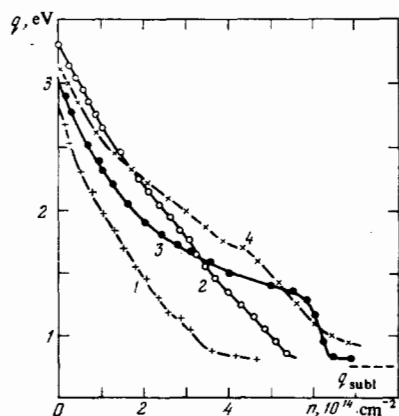

FIG. 4. Concentration dependences of heat of adsorption of cesium on the faces of a tungsten crystal: 1—(100), 2—(110), 3—(111), 4—(112); q_{subl} is the heat of sublimation of cesium.[81,94,96]
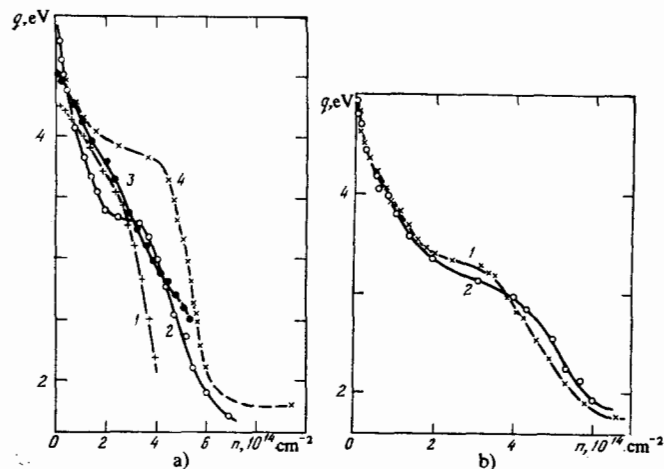

FIG. 5. Concentration dependences of the heat of adsorption of barium: a) on the faces of a tungsten crystal (1—(100), 2—(110), 3—(111), 4—(112)); b) on the (110) faces of crystals of tungsten (1) and molybdenum (2).[92,94]

of adsorption, and the work function on the degree of coverage contain a number of free parameters. It is obvious, however, that with this approach is not possible to learn the physical nature of the phenomena occurring.

B. Dependence of the heat of adsorption on the concentration of adsorbed particles

The heat of adsorption q is affected by the structure of the substrate, particularly by the degree of its uniformity, and by the interaction of the particles. Only recently have we begun to study adsorption on monocrystalline substrates, to avoid the effect of nonuniformities of the surface. The systems which have been investigated are: alkali metals on the faces of tungsten,[84,65,88,91,94,133] and nickel,[97] Ba and Sr on the faces of tungsten and molybdenum,[92-94,96,102] Cu, Au, and Ag on tungsten,[134-136] and carbon dioxide on a number of metallic single crystals.[138,139] We have shown for illustration in Fig. 4 the concentration dependence of the heat of absorption of Cs on the principal faces of a tungsten crystal. The repulsion of the positively charged adatoms leads to a rapid decrease in the heat of absorption with increase of the degree of coverage. The observed change in the heat of adsorption in the low-coverage region can be explained in terms of the classical dipole model.[137] As the second monolayer is filled, the heat of adsorption is already not very different from the heat of sublimation of massive cesium. Other systems of this type also behave in this manner.

The concentration dependence of the heat of adsorption is greatly affected by the atomic structure of the substrate. For example, the heat of adsorption of barium on different faces of a tungsten crystal differs appreciably more than on faces of tungsten and molybdenum of the same type (Fig. 5).

When a first-order phase transition occurs in a film, the heat of adsorption does not depend on the degree of coverage. It is known that a phase transition of the con-
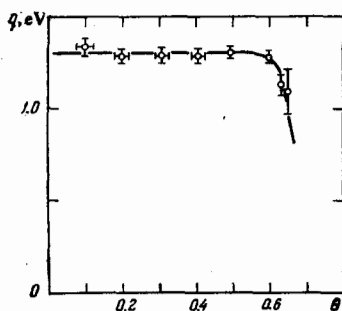
FIG. 6. Dependence of the heat of adsorption of CO molecules on the (100) face of nickel, on the degree of coverage.[136]

FIG. 7. Dependence of work function of the faces of a tungsten crystal on the surface concentration of cesium adatoms: 1—(100, 2—(110), 3—(111), 4—(112). $T = 77\,°K$. Contact potential difference method.[18,84,94]

densation type can occur when the adsorbed particles are attracted. An example of a dependence of the heat of adsorption on the degree of coverage in this case is given by Fig. 6, which is taken from the work of J. C. Tracy[136] and is for adsorption of CO on the (100) face in Ni. The decrease of the heat of adsorption for a high degree of coverage is explained by packing of the film, in which the repulsive interaction appears.

As will be discussed in more detail in the next section, condensation is possible also with a purely repulsive interaction. In this case there appears in the dependence of the heat of adsorption on the degree of coverage the same characteristic plateau, although the measurements of the heat of adsorption are carried out at increased temperatures, where the phase transition is not observed.

Up to the present time no satisfactory explanation has been obtained of the measured thermal desorption of films of copper, gold, and silver from tungsten.[134-136]

At the present time there are no systematic quantum-mechanical calculations of the dependence of the heat of adsorption on the degree of coverage. The accuracy of the predictions of the semiempirical theory based on use of the concept of electronegativity[128-130] are unsatisfactory from the practical point of view.[91]

C. Change of work function with adsorption

As was noted in Sec. B of Chap. 2, changes in the work function on adsorption have been most completely studied up to the present time for alkali and alkaline earth metals on refractory metals. These changes are usually characterized by curves with rather deep minima (Fig. 7). Recent studies in which the work function and structure of these films were investigated in parallel have shown reliably that the minimum of the work function is achieved with a submonolayer coverage, and with formation of a dense monolayer the changes in the work function are for the most part completed (see for example Refs. 88, 91–93, 97, and 140).[1]
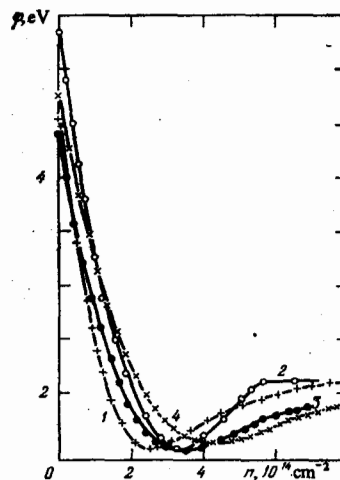
For a close-packed monolayer coverage the work function usually is within a tenth of an electron volt of that for the massive absorbate, as which we take the limiting value obtained on extensive evaporation of the adsorbate.[2]

In the simplest model[122] the change of work function of a surface covered by a uniform film is due to the jump in the potential in the electrical double layer formed by the charged adatoms and the electrons which screen them, which are concentrated in the near-surface region of the substrate. This model is applicable for those degrees of coverage in which the direct exchange interaction of adatoms is negligible. It is clear that when the film "metallizes" and screens the substrate, the dipole moment found from Eq. (7) loses its physical meaning. It is evident that the work function would change even in that case if the adatoms had no charge.[79] Thus, work-function measurements do not permit us to separate reliably the contribution of the dipole layer.

In order to obtain independent information on the strength of the dipole layer, the drift of adatoms over the surface of a metallic point in a nonuniform electric field has been studied near the tip.[101,102]

By this method the dipole moments of the adatoms of a number of alkaline and alkaline earth elements on the faces of a tungsten crystal have been determined in the range of coverage from $\Theta = 0.05–0.1$ to $\Theta = 0.7–0.8$. The measurements showed that in this coverage region the main contribution to the change in work function is from the dipole layer. In particular, as proposed by Langmuir,[141] the minimum of the work function corresponds to the coverage at which the strength of the electric dipole layer is greatest. The very existence of a minimum is due to the decrease of the adatom charge

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[1] We have in mind a so-called physical monolayer, i.e., the least coverage for which the adatoms densely populate the surface, leaving no appreciable gaps. In principle the adatoms in a physical monolayer need not be located in a single plane.

[2] Thick films deposited on substrates with different atomic structure often have somewhat differing values of work function, as the result of a difference in the structure and (or) crystallographic orientation of the growing films.

on increase of their density as the result of interaction of adatoms with each other.

Of the studies devoted to the microscopic theory of the work function, we shall discuss only two which characterize the level achieved in this subject.

Muskat and Newns[124,125] used Anderson's model Hamiltonian to calculate the change in the dipole moment of the bond and of the work function with change of the concentration of cesium adatoms on tungsten and rhenium. In their calculation the distance from the atom to the plane of the substrate was left as an adjustable parameter. Since the direct exchange interaction of adatoms is ignored, this approach is useful up to the beginning of metallization of the film.

On the other hand, for a sufficiently high density of the film, there is justification for the theory of Lang,[31] who generalized the "jellium" model used previously in calculation of the work function of clean metals[142] (see also the review by G. N. Shuppe[143]). Calculations of the potential barrier arising at the metal-adsorbate-vacuum interface, in agreement with experiment, gave a nonmonotonic dependence of $\varphi(\Theta)$. In Lang's calculations the thickness of the positive charged layer corresponding to adsorbate ions also is a free parameter.

At some degree of coverage the film metallizes. For example, a layer of cesium on tungsten at $\Theta = 0.8$ already has the properties of metallic cesium.[144]

It has been found experimentally[145,146] that at $\Theta = 0.5$[3] a peak is formed in the energy spectrum of electrons scattered at the surface, which corresponds to excitation of plasmons in the film. In Refs. 145 and 147 the analogy of film metallization with the well-known Mott dielectric-metal transition is pointed out. In the region of film metallization the Lang model is apparently close to reality.

According to Lang's calculations, the work function for a monolayer covering differs from the work function of a massive alkali metal by 0.05–0.1 eV, which is in agreement with experiment.

However, a quantitative calculation of the functions $\varphi(\Theta)$ for specific situations is not available at the present time. In order to carry out such calculations it is necessary to take into account the features of the atomic and electronic structure of the substrate. A number of experiments indicate the need of taking into account these factors. For example, the chemical nature of the substrate, when the atomic structure and work function of the clean surfaces are very similar, greatly affects the work function of the adsorption systems.[148]

In the general case the dependence $\varphi(\Theta)$ turns out to be complicated and difficult to interpret. This is characteristic of films of the noble metals,[134,135] the rare earth metals,[149] and the transition metals,[150,151] and also of films of gases, for example, oxygen on the (110) face of tungsten.[152]

In concluding this section let us mention the question of the relation of the work function to the structure of the films. On the one hand, it has been shown that the work function is affected not by long-range order, but by short-range order in the film.[81,88,95] On the other hand, it has been shown for a large number of systems that structural transformations which take place in the films (see Sec. B of Chap. 4) are correlated with features in the concentration dependence of the work function.[81,88,89,92,95,153,154] For many systems the minimum of the work function is reached for a filling by adatoms of the maximum number of identical centers on the substrate, as was predicted earlier by Shrednik[155] on the basis of crystal geometry considerations.

4. ATOMIC STRUCTURE OF SUBMONOLAYER FILMS AND PHASE TRANSITIONS IN THEM

A. Main types of structures and regularities of transitions between them

The beginning of studies of phase transition in monolayers was marked by the study of films adsorbed on liquid surfaces.[156,157] It is known that, depending on the substrate temperature and the average density of the film, these layers exist in two aggregate states—a two-dimensional liquid and a two-dimensional gas. The transition between them is a first-order phase transition. The crystalline phase of monolayers absorbed on a liquid does not exist. This is due to the fact that in a two-dimensional film absorbed on an ideally smooth substrate (or, as in the present case, on a disordered substrate), fluctuations of long-range order diverge logarithmically.[158-161] In other words, if we choose some atom as the origin, the mean square deviation of the coordinate of a distant neighbor of this atom relative to its value in an ordered (at $T = 0$) two-dimensional lattice increases logarithmically with the distance.

Thus, at $T > 0$ and a sufficiently large interatomic distance the correlation in the relative location of the adatoms is completely lost, i.e., in such a film there is only short-range order.[4] Monolayers adsorbed on a crystalline substrate are in a completely different situation.

The periodic field near the crystal surface, which is formed by volume forces, suppresses the fluctuations in particle location in the film so strongly that it becomes possible for two-dimensional crystalline phases to exist. Jancovici[162] has shown that in a two-dimensional harmonic model which usually demonstrates the absence of long-range order in a monolayer on a smooth substrate, as the temperature is reduced a unique transformation occurs to a state with infinite susceptibility with respect to the external periodic field. In this state it is sufficient to turn on an arbitrarily small periodic field, since long-range order arises in a film described by this model. Actually the phonon spectrum of

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[3] The article of MacRae et al.[145] gives coverages which by error are three times too large (see Ref. 82).

[4] However, since a logarithmic divergence is weak, the region of short-range order can be rather extensive and can include the entire surface region studied with dimensions of the order of the coherence width of the electrons in diffraction experiments.

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a film adsorbed on a real surface with a periodic relief of finite depth differs substantially from the phonon spectrum of a film on the surface of a liquid. For adsorption on a smooth substrate (or in the complete absence of structural consistency between the film and the substrate) the spectrum of vibrations of the film begins with a frequency $\omega = 0$. [161,163,164] The abundance of "soft" modes of vibrations with low excitation energy also is a primary cause of instability of such a two-dimensional crystal for $T > 0$. On the other hand, for location of the adatoms in potential wells on a crystalline substrate the spectrum of frequencies of the film begins with $\omega_i > 0$, where ω_i is the frequency of vibrations of a solitary atom in the potential well. [161,165] For just this reason long-range order is possible in such films at $T > 0$.

Extensive experimental data indicate the existence of a large number of ordered two-dimensional structures in monolayers adsorbed on faces of single crystals, the phase diagrams often being extremely complicated (see below). The reason for this diversity is that the complicated periodic field of the substrate $U_{an}(r)$ is imposed on the interaction $U_{aa}(r)$ of the adatoms with each other.

$U_{an}(r)$ describes the potential relief for an isolated adatom. The characteristic depth of this relief is the activation energy for surface diffusion of isolated adatoms q_M, which usually amounts to ~ 0.1–1 eV.[5] It should be emphasized that the potential relief "felt" on the surface by the adatom depends both on the nature of the adatom itself and on the nature of the substrate, i.e., it characterizes the system as a whole.

For sufficiently low T, when the principal role in the free energy is played by the energy term rather than the entropy term, the nature of the film structure formed is determined by the ratio of the quantities $U_{an}(r)$ and $U_{aa}(r)$. In regard to the correspondence of the film and substrate lattices, we can speak of the following basic types of two-dimensional structures observed experimentally. [166]

1) Matched structures are characterized by a ratio of the periods of the film and substrate expressed by an integer (simple matched structures) or a rational fraction (vernier structures). In the first case all adatoms occupy equivalent adsorption centers on the surface; in the second case only a fraction of the adatoms turn out to be in identical locations (for example, every second or third adatom).

2) Unmatched (incoherent) structures are characterized by an irrational ratio of the periods of the film and substrate. In correspondence with the statements above in this case only a more or less extended short-range can be established in the film.

It is clear that a potential relief on the substrate sufficiently deep in comparison with U_{aa} will facilitate formation of structures matched with the substrate. On

the other hand, if the interaction between the adatoms is large, the potential relief of the substrate cannot localize the adatoms in its own potential wells and an unmatched structure is formed.

Let us now consider the main regularities of the changes in film structure with increase of the degree of coverage of the surface by the adsorbate.

The simplest phase diagram is obtained in the case in which short-range attractive forces—for example, exchange forces—act between the adatoms. Here, after a critical concentration (which depends on T) of the two-dimensional gas is reached, with increase of the coverage the growth of condensate islands begins, i.e., a phase transition of the first type is observed. These islands are two-dimensional if the binding energy of the adatoms with the substrate is higher than the binding energy between adatoms, [134,135] or three-dimensional in the opposite case. [217] Usually in adsorption on metals two-dimensional islands grow in the first stage, until the entire surface is covered with a continuous monolayer.

Let us discuss in more detail the effect of a long-range repulsive interaction of adatoms on the structure of films.

If the quasilevel of the electron in the adatom is sufficiently narrow and is located some distance from the Fermi level, its shift on change of the coverage will not lead to a substantial change of the charge of the adatom (as long as the quasilevel does not approach the Fermi level). In this case we can assume that the interaction of the adatoms is due to dipole–dipole repulsion and is binary. On a smooth substrate at $T = 0$ such a film obviously would have hexagonal symmetry whose period would decrease smoothly with packing of the film. However, on the surface of a crystal, as we have already noted, the depth of the potential relief is $(10^{-1}$–$1)$ eV, and as a result even at room temperature the adatoms will be located preferentially in minima of the potential relief in equivalent adsorption centers (at least for small coverages). The structure of this lattice is determined by the symmetry of the corresponding crystal face. The ground state and thermodynamics of such a film can be described by the model of a lattice gas with binary interaction, which corresponds to the Ising Hamiltonian

$$\mathcal{H} = -q_0 \sum_{\alpha} n_{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} U_{aa}^{\alpha\beta} n_{\alpha} n_{\beta}; \qquad (11)$$

here q_0 is the energy of adsorption of an isolated atom; $n_{\alpha} = 1$ if site α is occupied and $n_{\alpha} = 0$ if the site is empty; $U_{aa}^{\alpha\beta}$ is determined by Eq. (8) or (8'); $\langle n_{\alpha} \rangle = \Theta$ is the degree of coverage of the surface (in a dense monolayer $\Theta = 1$). The qualitative features of structural transitions in a lattice gas with a repulsive interaction can be revealed in the example of a one-dimensional model. [187] It is evident that the ground state of a free string of particles repelling each other corresponds to their ordered location with a period which decreases with increasing concentration. Let us place this string in a periodic external field of infinitely large amplitude with

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[5] The measured value of q_M usually characterizes the depth of the relief for those directions on the surface for which this depth is minimal.

unit period. If the interaction of the particles with each other is finite

$$\left(\sum_{\alpha \neq \beta} U_{\alpha \alpha}^{\alpha \beta} < \infty \right) ,$$

they all will turn out to be on the bottom of some kind of well. For concentrations $\Theta = 1/m$, where m is an integer, the energy of the string, measured from the bottom of the wells, does not change; for all other concentrations it increases, since some particles must be shifted, and the initial state had the minimum energy. The question of the structure for intermediate concentrations arises. For the case

$$\frac{1}{m+1} < \Theta < \frac{1}{m}$$

it would be possible to distribute the particles in large lumps of structures with periods m and $m+1$, choosing their length such that the average concentration is equal to Θ. However, such a distribution turns out to be energetically less advantageous than for maximal mixing of these cells. Thus, for $\Theta = 1/[m+(1/2)]$ this corresponds to alternation of cells of the types $1/m$ and $1/(m+1)$, i.e., to a structure with two atoms in a cell $2m+1$. The energy of an arbitrary periodic structure with period l and with s particles in the unit cell interacting according to a law $U_{\alpha \alpha}^{\alpha \beta} \sim r^{-k}$ can be represented in the form[167]

$$E \sim \frac{1}{2} l^{-k} \sum_{i,j=1}^{s} \left[\zeta\left(k, \frac{|x_i - x_j|}{l}\right) + \zeta\left(k, 1 - \frac{|x_i - x_j|}{l}\right) \right], \qquad (12)$$

where $\zeta(k, v)$ is the generalized Riemann zeta function ($\zeta(k, 0) = 0$), $0 \leqslant x_i \leqslant 1$ are the integral coordinates of the particles, measured from the origin of the unit cell. Analysis of Eq. (12) shows that the energy of the string is a continuous function of Θ with breaks at each rational point.[6] This means that for an increase of the average concentration the transition from the structure $1/(m+1)$ to the structure $1/m$ would occur at $T = 0$ through an infinite number of successive phase transitions. In these structural transitions structures with arbitrarily large periods take part, and for a small change of energy a large rearrangement of the structure occurs.[7] Phases with concentration near $\Theta = 1/m$, for example, for $\Theta = s/(sm+1)$, where $s > 1$, can be considered as consisting of antiphase domains. This means that after s cells of phase $1/m$ a break in the phase occurs, and the next s cells are shifted by one period of the external field. An additional energy ($\sim 1/m^{k+1}$) is associated with the boundary between domains; in addition, these defects themselves repel each other. Therefore at $T = 0$ even very infrequent defects are ordered, which corresponds to formation of periodic structures with a large period.

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[6] The dependence of the surface energy of a two-dimensional crystal on the orientation of the face is similar.[168]

[7] Gradmann[169] has shown that the energy of such structures increases on rearrangement of any atom. However, any periodic structure has this property, and therefore the question of the choice of a periodic structure with minimal energy has not been solved in Ref. 169.

In the two-dimensional case at $T = 0$ the transition pattern is similar to that discussed above with the distinction that it is necessary to take into account the symmetry of the potential relief and the energy of the "corners" in mixing of the gas (in addition to the "surface" energy). The simplest structures could be revealed by considering the interaction of only a limited number of closest neighbors, and the realization of specific structures depends on the ratio between the interaction energies of the various neighbors. In a recently published article[170] Klaburagi and Kanamori have studied the ground state (11) for two-dimensional lattices of various symmetries with inclusion of the interaction of several neighbors (see also Ref. 127).

Let us now consider the situation at $T > 0$. In a truly one-dimensional case the fluctuations destroy the order, although traces of the existence of an ordered structure can be observed in the corresponding maxima of the correlation function. In a two-dimensional lattice system at low temperatures a finite number of structures with not very large periods survive. The point is that long-range order is maintained by the interaction at distances of the order of the period, and at temperatures greater than the energy of this interaction, disordering sets in (first of all, naturally, of structures with a large period). However, if the temperature is less than the energy of short-range interactions, the order cannot disappear at all. For example, for $\Theta \approx 1/m$ the superstructure formed by the boundaries of antiphase domains is destroyed at some temperature, although inside the domains there remains an order maintained by the short-range interaction. Unfortunately, accurate results have been obtained only for the case of interaction of nearest neighbors in certain plane lattices.[171] With increasing concentration of adatoms at sufficiently low temperatures a systematic change of the structures occurs by means of phase transitions, whose nature is associated with the symmetry of the alternating phases. In a first-order phase transition, where the phases are separated in space, their symmetry can be arbitrary, but for a type II transition definite limitations are imposed on the change of symmetry at the critical point (Ref. 160, § 139). In particular, for $T > 0$ a transition from one ordered phase to another can in principle occur through an intermediate disordered phase. Finally, for a constant concentration with increase of the temperature, a film can undergo a polymorphic transition, i.e., it can transform from one ordered phase to another and then transfer to the disordered state (see below). The theory of these transformations is in its early stages. Many questions are not even qualitatively clear.

Similar phenomena have been considered in the theory of ordered substitutional and interstitial alloys, for example, in solutions of hydrogen in metals.[110] The approaches developed there are based on the method of self-consistent fields, which evidently is not completely suitable for analysis of structural transitions in the case considered, if only because in the interesting low temperature region, strictly speaking, there is no region far from the phase transition point. Transitions follow each other at closely spaced adatom concentrations.

We have described above structural transformations in a monolayer of repulsive particles with a binary interaction. It is important that in such a system at a sufficiently low temperature the uniformity of the film is preserved at all coverages. For a smooth substrate this statement is obvious, and for a periodic potential relief the uniformity is apparently achieved as the result of structures with large periods. (We note that the latter circumstance is not described by the self-consistent field theory.)

In spite of numerous investigations of the structure of charged films by diffraction methods and even observation of diffraction patterns from two different structures simultaneously (see for example Ref. 88), the condensation of films has been discussed in the literature only in connection with classical adsorption experiments, [156] in which attractive forces act between adsorbed molecules. It was assumed that charged films must be compressed with increase of coverage, remaining uniform. However, as one of the authors[172] has shown, taking into account mutual depolarization (i.e., the nonbinary nature of the interaction) of the adatoms leads to the possibility of condensation of films with a rather large polarizability of the particles. The phenomenon is due to the fact that for a sufficiently high density of the film an increase of the coverage and the increase associated with it of the electric field produced by the adatoms is felt in the decrease of the dipole moment of the particles more substantially than in their repulsion. Break-up of a film into rarefied and dense phases leads to a greater gain in energy as the result of the rarefied phase than the loss due to the denser phase.

The theory of such a transition has been developed both in the model of classical dipoles with linear polarizability[172] and in the more realistic model in which the electronic states are described by Anderson's Hamiltonian with inclusion of the electrostatic interaction of the adatoms. [126] The boundary of the two-phase region in the phase diagram is determined by the question

$$T = -\Theta(1-\Theta)\frac{\partial^2 E}{\partial \Theta^2}, \tag{13}$$

where E is the internal energy of the film per lattice site and Θ is the degree of coverage. Since the differential heat absorption $q \sim -\partial E/\partial\Theta$, then it follows from Eq. (13) that condensation is possible in that region of coverage where $\partial q/\partial\Theta > 0$. In terms of the models studied, the condition of existence of condensation is a large polarizability of the adatoms, which corresponds to the requirement that the quasilevel of the adatoms be not too wide and be located near the Fermi level. Criteria have been obtained[126,127,172] for the existence of two-dimensional condensation in films on faces with quadratic symmetry, and in addition it has been shown that taking into account the potential relief of the substrate can substantially complicate the phase diagrams of such films, leading to the existence of several two-phase regions.

B. Experimental data

Up to the present time the most extensive information on the atomic structure of adsorbed films has been ob-

tained by means of low energy electron diffraction (LEED) and field ion microscopy (FIM). We shall not describe in detail these methods, which have been the subject of special reviews and monographs (for LEED see Refs. 166 and 173–175; for FIM see Refs. 112 and 176). We shall confine ourselves to certain remarks. In the LEED method electrons with energy 10–100 eV are used (De Broglie wavelength ~ 1–4 Å). The diffraction patterns obtained with them are formed in the several layers of atoms closest to the surface. The coherence width of the electrons in contemporary low-voltage electron diffraction patterns is usually ~ 10^2 Å (just this region of surface is covered by the electron in diffraction). For this reason the LEED method has comparatively low sensitivity to imperfections of the surface structure. At this stage, when the main efforts are directed toward study of how the type of two-dimensional lattice formed depends on the crystal symmetry of the surface and the nature of the absorption bond, this can be considered more an advantage than a deficiency. In most studies up to this time information on the structure of the films has been obtained by analysis of the geometry of the electron diffraction patterns with qualitative use of the ratio of intensities of the various reflections. Strictly speaking, such an analysis permits determination only of the symmetry of the surface lattice, and therefore for construction of a probable model of the film it is necessary to draw on additional data— on the nature of the bond, the potential relief of the surface, the concentration of adatoms, and so forth. In recent years as a result of advances in the development of the dynamic theory of LEED the possibility has appeared of carrying out a more correct deciphering of diffraction patterns on the basis of a quantitative analysis of the intensities of the reflections. For many systems complete data on the structure have already been obtained, i.e., data on the composition of the surface unit cell and the relative location of the atoms in it (see the review of these studies in Refs. 177 and 178).

The advantage of the FIM method is that it gives more direct information about the processes on the surface than does the diffraction method. In addition, its use turns out to be extremely informative in the region of very small degrees of coverage, which is poorly served by the LEED method. However, the range of materials which can be studied in FIM is limited by the need of maintaining without destruction electric fields of ~ (2–5) $\times 10^8$ V/cm.

Recently there has been intensive development of a method based on study of the elastic scattering of ions by a surface. [177–182] This method permits investigation first of all of short-range order in the location of the atoms on the surface. Note that the scattering of conduction electrons at the surface of metallic crystals also turns out to be sensitive to its structural state. [183,184]

In regard to the structure of clean metal surfaces, the existing data indicate that the surface layer of most metallic crystals retains in the surface plane the translational symmetry present in the bulk. Only a small number of exceptions are known (certain faces of the crystals of gold, palladium, iridium, and platinum[185]).

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In this sense metals differ substantially from semiconductors, for which formation on the surface of a specific structure ("reconstruction" of the surface) is observed very frequently. [186]

The interplanar distance measured along the normal to the surface may differ in the near-surface region of metallic crystals by about 10% from its value in the interior (see for example Ref. 187 and references cited there). The mean square amplitude of thermal vibrations of the surface atoms (along the normal to the surface) is 1.5-2 times larger than in the interior. [185,188]

As has been stated above, the main factors which determine the type of atomic structure of a submonolayer film are the nature of the adsorption bond and the atomic structure of the substrate. Let us consider from this point of view the film structures most characteristic for systems of different classes. Here we shall use the means of designation of surface structures most frequently used at the present time, proposed by E. A. Wood. [189] A designation $(N \times M)$ corresponds to a lattice whose period in one direction is N times greater than the substrate period, and in the other direction— M times greater. The index p in front of the parentheses (sometimes omitted) denotes that the unit cell is primitive, and the index c—that the cell is centered. The existence of azimuthal rotation of the film lattice relative to the substrate is noted after the parentheses by the letter R with indication of the rotation angle in degrees.

Before presenting the experimental results on structural transformations in adsorption systems of different types, let us make the following remark. The structure of films, like the adatom electronic state, heat of adsorption, and film work function described above, is determined by the nature of the interaction of the adatoms with the substrate and with each other. As we have already stated, these interactions in adsorbed films are rather complicated. It is not surprising that phase diagrams in the systems considered can have a very complex form. [95] Two-dimensional crystallography turns out to be richer than three-dimensional. For example, in massive Li, only two crystalline modifications are known, but Li on just one surface, the (112) face of tungsten, forms at 77 °K eight different ordered structures. [133] However, in analysis of the diverse experimental material we can distinguish two simple situations: 1) In the presence of attraction (long-range van der Waals or short-range exchange forces) condensation occurs into two-dimensional islets; 2) in the presence of repulsion (due to polarization of the adatom or strong polarity of the bond) the film is more or less uniformly compressed on increase of the coverage, passing through a succession of ordered structures. A first-order phase transition, due to depolarization, [172] is also possible.

In adsorption of metals of inert gas atoms, in most cases the principal role is played by dipole–dipole interaction of the adatoms due to their strong polarization at the surface. [190] As a consequence of isotropic long-range repulsion $(U_{aa} \sim r^{-3})$ for small degrees of

coverage complicated films are formed with large interatomic distance and a lattice matched to the substrate. Of this type, for example, are the structures Ir(001)-(5×3) Xe, [191] Ir(001)-(5×3) Kr. [192] As $\Theta \to 1$ the match with the substrate is generally lost as the result of increase of the interaction between adatoms, and a hexagonal monolayer is formed (an exception is in cases of pseudomorphism when the lattice periods of the adsorbate and substrate are close together). On other substrates, for example, on graphite, the polarization of the adatoms is small and the film is formed mainly with participation of van der Waals forces, which are attractive and isotropic $(U_{aa} \sim r^{-6})$. In this case after reaching some critical concentration of the two-dimensional gas in the film, a first-order phase transition begins—growth of the two-dimensional islets occurs, with a structure matched or not matched with the substrate, depending on the ratio of U_{aa} and U_{an}. For example, it has been established by the LEED method that xenon on the basal face of graphite is condensed into islets having a structure $(\sqrt{3} \times \sqrt{3})R$ 30°. [193,194] Similar transitions in films of nitrogen on the basal face of graphite have been observed by means of neutron diffraction. [195]

Interesting results have been obtained in study of submonolayer films of helium on the (0001) face of graphite. [161,165,196] On the basis of data on the temperature dependence of the heat capacity of these films, a phase diagram has been constructed in which there are regions of a two-dimensional phase, of ordered phases matched with the substrate $(\Theta = 0.2-0.3)$, liquids, and finally at $\Theta \to 1$ a "solid" two-dimensional film not matched with the substrate. The heat capacity of the unmatched films varies at low T in proportional to T^2, as predicted by the Debye theory for a two-dimensional crystal.

In adsorption of nonmetals the main role is played by the covalent component of the bond. Systems of the type under discussion are characterized by formation of a series of structures matched with the substrate. Surfaces are extremely specific and depend on the number and directionality of the orbitals of the substrate and adsorbate. [197–204] For illustration we have shown in Fig. 8 the structures formed by oxygen on the (110) face of W.

To explain the geometry of such two-dimensional lattices, Tamm and Schmidt[198] drew on quantum-mechanical representations of the structure of the orbitals of
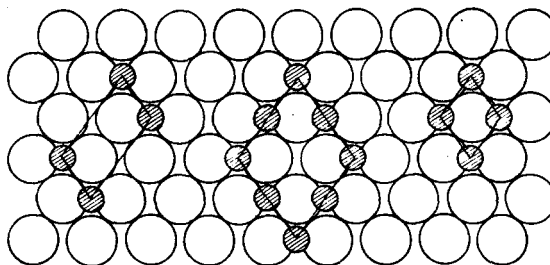

FIG. 8. Geometry of two-dimensional lattices formed on adsorption of oxygen on the (110) face of tungsten. [197]

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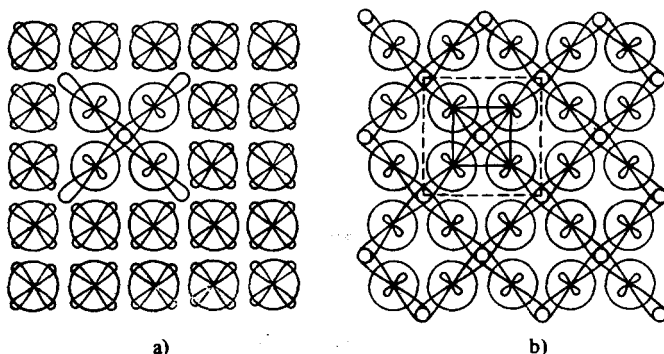
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a)   b)

FIG. 9. Formation of the structure $c(2 \times 2)$ of hydrogen atoms on the (100) face of tungsten according to Tamm and Schmidt.[198] a) Free surface atoms of tungsten (large circles) each have four symmetrically located $5d$ orbitals. On adsorption of a hydrogen atom (small circle) a hybridization of the $5d$ and $6s$ orbitals occurs and separated adsorption centers appear. b) A completely formed $c(2 \times 2)$ structure. The solid line shows the unit cell of tungsten (1×1), and the dashed line the unit cell $c(2 \times 2)$.

the substrate. For example, an adatom of hydrogen produces on the W(100) face a rearrangement of the orbitals such that among the initially equivalent adsorption centers there appear some which are energetically more advantageous, corresponding to a lattice $c(2 \times 2)$ (see Fig. 9). The hydrogen atoms are distributed over the sites of this lattice and interact through hybrid $5d6s$ orbitals of tungsten. Islets of the phase $c(2 \times 2)$ expand with addition of adsorbate, and only after coverage by this phase of the entire surface are locations with lower binding energy filled. The phase diagram of this system is described in terms of the model of a lattice gas on a substrate with two types of adsorption centers and attraction between adatoms, which has been considered by one of the authors.[172]

Einstein and Schrieffer[109] have discussed in more detail the interaction of adatoms through the substrate. They found that for a definite relation of the adsorbate and substrate parameters the interaction of nearest neighbors on the face of a cubic single crystal can be repulsive, and that of second, third, and fourth neighbors attractive, which explains the formation of the structures $c(2 \times 2)$, $p(2 \times 2)$, and $c(4 \times 2)$, which are frequently observed in experiments with nonmetals.[185,199]

In a number of cases the adatoms of nonmetals have an appreciable negative charge, for example, iodine on tungsten,[205] and sulfur and oxygen on various metals.[206-210] The lattices which arise for not too large coverages are typical for adatoms with dipole–dipole repulsion (see Sec. A of Chap. 4).

It should be noted that in discussion of adsorbed films with covalent binding the assumption is rather frequently made that the substrate atoms are substantially shifted from their previous positions and mixed with the adsorbate atoms, forming specific surface compounds. Such adsorption has been called reconstruction.[186,211] However, there is not enough reliable information on reconstruction adsorption on metals, and the conclu-

sions of different authors frequently are inconsistent (see for example Refs. 154, 182, 212). Apparently the clarification of this question is an event of the near future.

Phase transitions in films with covalent binding are accompanied by substantial changes in the properties of the system—heat of adsorption, work function, and so forth.[138,154] For example, Zandberg et al.[213,214] by simultaneous investigation of surface ionization and thermionic emission observed two-dimensional condensation in films of carbon on Ir(111). It turns out that in the two-dimensional-gas state carbon increases the work function of iridium from 5.8 to 6.0 eV, and in the two-dimensional-crystal state (which probably has the structure of graphite) it reduces the work function to 4.8 eV. At the same time the catalytic activity of the surface also changes greatly.

On adsorption of metal atoms, the bonding with the substrate, as we have already noted, is provided by several main components—ionic, metallic (delocalized electrons), and covalent (localized electrons). If the bond polarity is high, then the most important factor affecting the film structure is dipole–dipole repulsion of the adatoms. This is especially characteristic for adatoms of the alkali and alkaline earth elements on various metals.[81,88,92,95,97] In this case at small Θ lattices with large periods are formed, and the adatoms occupy identical adsorption centers on the substrate (Fig. 10). To observe these structures in an ordered state, the substrate must be cooled to rather low temperatures.[88,95]

Analysis of the observed structures permits the conclusion that on close-packed faces the interaction of adatoms at small coverages is close to isotropic, although some contribution can be made also by an isotropic interaction of adatoms through the substrate.[170]

As the degree of coverage of an adsorbate with a highly polar bond is increased, denser and denser lattices are formed, matched with the substrate, then

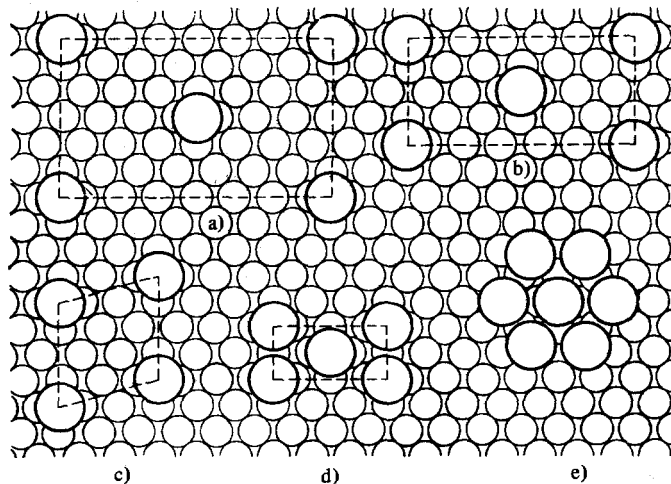

c)   d)   e)

FIG. 10. Two-dimensional lattices of strontium atoms on the (110) face of tungsten: a) $c(7 \times 3)$, b) $c(6 \times 2)$, c) $c(5 \times 2)$, d) $c(3 \times 1)$, e) hexagonal with smoothly changing period.[95]
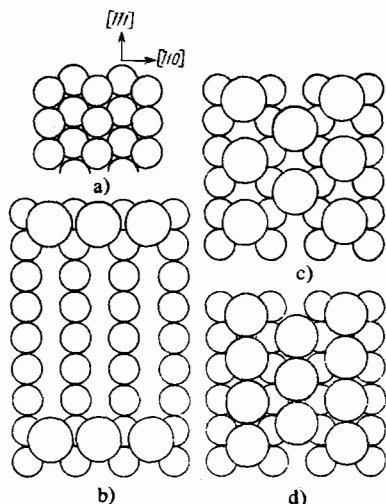
FIG. 11. Two-dimensional lattices of strontium atoms on the (112) face of tungsten. a) Clean (112) face, b) (1×7) structure, c) c(2×2) structure, d) one-dimensional unmatched structure of the first layer. [96]

vernier lattices, and finally in the general case unmatched lattices (on smooth faces—of hexagonal symmetry) with a smoothly decreasing period (Figs. 10 and 11). The formation of unmatched structures is energetically advantageous: Actually, at this stage the heat of adsorption in the first layer is significantly greater than in the second layer. Packing of the first monolayer is continued until the heat of adsorption, which decreases as the result of the repulsive interaction of the adatoms, approaches the heat of adsorption in the second layer.[6] The shortest interatomic distance in a dense monolayer is frequently 10–15% less than in the massive adsorbate.[81,97] Usually the region of existence of unmatched structures is wider, the greater the dipole moment of the adatoms. For example, for cesium films on W(110) this region, measured at $T = 77°K$, extends from $\Theta = 0.46$ to $\Theta = 1$.[81]

Transitions between matched structures in films with repulsion occur in accordance with the ideas developed in Sec. A of Chap. 4. The film is gradually packed with increase of Θ, remaining macroscopically uniform, and in the electron diffraction patterns the reflections of the first structure are smeared (the intermediate structures are fused), or are broken up and shifted (intermediate structures with large periods), until they turn out to be at the sites of the reciprocal lattice of a new structure.[200] As we have noted above, with a strong repulsion of the adatoms, unmatched lattices can be formed whose period smoothly decreases with increasing degree of coverage.

With careful measurements of the work function at

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[6]Eventually this close-packed monolayer turns out to be stressed—compressed in the surface plane. This is manifested, in particular, in the nature of the surface diffusion from multilayer coverages. Here on the leading edge of the diffusion distribution there is formed not a dense monolayer, but the more rarefied phase.[92]

low temperatures, breaks have recently been observed in the dependence of the work function on the degree of coverage, which are correlated with structural transitions in the film.

It may be worth mentioning specially the extremely unusual interaction of adatoms on faces with a sharply anisotropic atomic relief, such as the (112) face of a body-centered-cubic lattice and the (110) face of a face-centered-cubic lattice. These faces are constructed of parallel close-packed rows of atoms separated by furrows of atomic depth. On such surfaces, atoms of metals and nonmetals form structures with a clearly expressed one-dimensional nature. As an example we mention Na on Ni (110).[97] In the coverage region $1/6 < \Theta 1/4$, the Na atoms fill every second trough on the surface, and inside a trough with increasing degree of coverage an ordered alternation occurs of cells of the phase $\Theta = 1/3$ and the phase $\Theta = 1/2$. No less astonishing is the behavior of oxygen on the same face.[197] Here already in the region $1/2 < \Theta < 2/3$ the rows of oxygen atoms themselves, located identically in troughs, are distributed over the surface in a certain sequence, so that the lattice of the film consists of a mixture of cells of structures corresponding to $\Theta = 1/2$ and $\Theta = 2/3$. We note that the one-dimensional model discussed in Sec. A of Chap. 4 is directly applicable to both of these systems. The point is that even a weak lateral interaction can preserve one-dimensional order at finite temperatures. In addition, on surfaces with a furrowed atomic structure the interaction of the adatoms is sharply anisotropic in nature,[89,96,97,133] and therefore in addition to the general regularities due to repulsion between the adatoms in one direction, specific features are observed in each system of this type (see for example Fig. 11).

In recent years in films with a highly polar bonding (for example, alkali and alkaline earth elements on refractory metals), a large number of first-order phase transitions have been observed.[88,92,93,95,96,133,215–217] In the phase-transition process the coverage becomes spotlike, and in the electron diffraction pattern reflections from the two phases co-exist, and with increase of the average degree of coverage the reflections from the rarefied phase become weaker and those from the denser phase become stronger. A nonuniformity in the work function over the surface is also observed, and the experimentally measured average work function depends linearly on the average coverage. In the intervals of homogeneity of the film the heat of adsorption decreases substantially with increase of coverage (Fig. 12), which indicates a repulsive interaction between adatoms. Regions of first-order phase transition correspond to the plateau portions on the curve of heat of adsorption versus degree of coverage. The available experimental facts are in agreement with the theory of a depolarization phase transition in a film of repulsive particles,[172] which was described in Sec. A of Chap. 4.

We have been discussing above the changes in structure of films of different nature with change in the degree of coverage and for $T = $ const. If we now raise the temperature with a constant degree of coverage, poly-

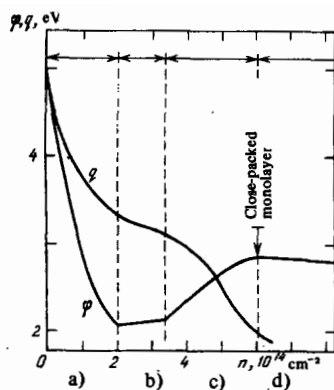FIG. 12. Correlation of work function, heat of adsorption, and structural transformations in a film of barium on the (110) face of molybdenum. [92] φ is the work function, q is the heat of adsorption, and n is the surface concentration of barium adatoms. The arrows indicate the regions of existence of the structures: a) single-phase region terminated by the (2×3) structure, b) region of coexistence of two structures (2×3) and (2×2), c) single-phase region (hexagonal structure with smoothly decreasing period), d) filling of second monolayer.

morphic transitions and (or) order-disorder transitions are observed.

These transitions are studied by means of LEED, [88,92,96,218,219] FEM, [220,221] surface ionization. [214] nuclear magnetic resonance, [222] and also by investigation of the temperature dependence of the heat capacity of the adsorbed films. [161,196] These investigations permit information to be obtained on the interaction of the adsorbed particles.

For example, the regularities of disordering of films of sodium on the (110) face of tungsten are consistent with the idea that the interaction between sodium atoms at small coverages is a dipole-dipole repulsion. [88,223] Data have also been obtained on the interaction of hydrogen atoms[218,224] and oxygen atoms[201,219] on the crystal faces of tungsten.

The disordering of submonolayer films of helium on graphite matched in structure with the substrate can be described on the basis of the two-dimensional Ising model. [161,196] For coverages close to a dense monolayer, films of helium are incoherent with the substrate and fuse gradually in a certain temperature range (but not sharply, as in the three-dimensional case). J. G. Dash and his colleagues[161,165,196] explain this by the fact that in unmatched films, as theoretically predicted, [158,160] there is no long-range order, but only a more or less extended short-range order.

Even this short list of the results obtained in recent years shows that the study of phase transitions in adsorbed films is now one of the most interesting directions in surface physics.

In connection with the discussion of two-dimensional phase transitions, let us briefly discuss the question of the dynamics of establishment of an equilibrium state of films. Equilibrium is achieved as the result of migration of adatoms, characterized by an activation en-

ergy q_M. As model calculations show, [200,224] equilibrium of a film is essentially established when each atom completes about 10 migration jumps on the surface. If we know the value of q_M, we can estimate the temperature T_M at which this number of jumps will be completed in a given time interval. On the other hand, ordering of film is in principle possible only for $T < T_C$, where $T_C \approx \mathscr{E}_0$ is the critical temperature of the order-disorder transition ($\mathscr{E}_0$ is the interaction energy of nearest neighbors in the film). It is evident that on faces with a deep potential relief (large q_M) a situation is possible in which $T_C < T_M$, so that a very long time may be required to reach an equilibrium ordered state in this case.

5. CONCLUSION

The physics of adsorption is experiencing a period of violent development at the present time. For example, the annual number of publications devoted to study of the structure of adsorbed films by the LEED method alone has increased from several articles in the fifties to 200-250 articles at the present time.

There has also been a substantial increase in the number of theoretical articles devoted to phenomena on surfaces. A number of important results have been obtained which relate to the theory of interaction of adatoms with the substrate and with each other, phase transitions in films, the dynamical theory of low energy electron diffraction, and so forth. Nevertheless, the extensive information accumulated during the last 10-15 years is only now beginning to find reliable explanations. Many phenomena are not understood even qualitatively. The situation regarding films of alkali and alkaline earth elements on refractory metals is now somewhat more understandable (here we can also include films of noble gasses on metals). In these systems a substantial role is played by electrostatic repulsion between adatoms, which leads to regularities common to different specific systems, although many features are observed in them which are specific for each adsorption system. The last remark applies to an even greater degree of films of nonmetals. However, in our opinion we can expect in the near future achievement of a higher level of understanding of the processes occurring on the surfaces of solids. On the one hand, experimental investigations should be stimulated by the advances which these studies can provide in such regions of technology as emission electronics, microelectronics, catalysis, vacuum technique, crystal growth, protection of metals from corrosion, and many other fields. On the other hand, in spite of the complexity and diversity of the interactions which are important for description of the phenomena occurring in adsorbed films, theoreticians should extract a wealth of diverse and detailed information enabling them to check models not only on the basis of the final result but also with regard to the intermediate dependences of the quantities used in the calculation on experimentally measurable parameters. The theory of adsorption has still to travel the path traveled, for example, by solid-state theory.

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