Interaction between particles adsorbed on metal surfaces

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Theoretical and experimental studies of the interaction between atoms and molecules chemisorbed on the surface of a metal are described. The basic interaction mechanisms are studied theoretically: 1) direct—owing to the direct exchange of electrons between adatoms; 2) indirect—owing to the exchange of electrons through the conduction band of the metal substrate; and, 3) electrostatic—owing to the exchange of photons and surface plasmons between charged adatoms. Experimental studies performed with a field-ion microscope and by the LEED technique are described in detail. The two-dimensional adatom structures observed on the channeled faces of transition metals enable studying the interaction at record large distances (up to 25 Å). The following are studied briefly: the interaction of adatoms on a semiconductor surface, interaction-induced restructuring in an adsorbed atomic film, reconstruction of clean metal and semiconductor surfaces, and other manifestations of interaction in adsorption systems.

1. INTRODUCTION

When foreign atoms or molecules are adsorbed on the surface of a solid the main change in most properties of the surface is brought about by the deposition of an extremely thin (thickness of one atom or molecule) layer. This is why there is such great interest in studying the properties of submonolayer (less closely packed than a monolayer) coatings.[1]

The interaction between adsorbed particles plays an important role in all surface phenomena. It significantly affects virtually all properties of the adsorbed layer—its structure and thermal stability, the vibrational spectra of the adatoms, migration of particles along the surface, reactions on the surface, etc. It also affects the characteristics of the changes induced by the adsorbed layer in different properties of the surface (the work function, catalytic activity, etc.).

From the physical viewpoint an adsorbed film is a system with reduced dimensionality at the boundary between two media—the vacuum and a solid body. The interaction between adsorbed atoms is realized simultaneously through both media and for this reason it differs significantly from both the interaction between free atoms and the interaction between impurity atoms in the bulk of the crystal. In this review we shall describe the basic mechanisms of the interaction between adatoms, the laws governing these interactions in different systems, and the effect of the interaction on the properties of adsorption systems. Unlike Einstein's review[2] published in 1978, in this work the role of the electronic structure of the substrate in the interaction of adatoms is studied in detail and the extensive experimental data, obtained in the last few years, are analyzed based on existing theoretical models.

We note that although we shall be discussing primarily adsorbed atoms, everything we say is equally applicable to molecules adsorbed on the surface of a crystal. Only chemisorption systems will be studied; the interaction of physically adsorbed atoms and molecules is described in the review of Ref. 2.

2. THEORETICAL CONCEPTS CONCERNING MECHANISMS OF INTERACTION BETWEEN ADSORBED ATOMS

It is convenient to study different mechanisms of interaction of adatoms by classifying them according to the nature of the virtual quasiparticles exchanged by them. Thus the interaction owing to the direct exchange of electrons between adatoms, according to the terminology adopted in the theory of chemisorption, is said to be *direct* while the interaction owing to the exchange of electrons through the conduction band of the substrate is said to be *indirect*.[1] *Electrostatic* interaction between charged adatoms arises owing to the exchange of photons and surface plasmons, *elastic* interaction arises owing to the exchange of phonons, etc. It is obvious, however, that this classification of the mechanisms is accurate only to the extent that the substrate can be accurately studied as a system consisting of noninteracting quasiparticles. The terminology adopted is also arbitrary, since strictly speaking any interaction of adatoms is indirect, because the substrate participates in it.

It is natural that analogous mechanisms were previously studied in the investigations of the interaction of impurities in the bulk of solids. Ruderman and Kittel[3] first showed that "indirect exchange coupling" between the conduction electrons of a metal, whose energy depends on the distance between impurities according to the law

$$E\,(R) \sim R^{-3} \cos\,(2k_F R). \tag{1}$$

plays an important role in the interaction of impurities. The long-range oscillating character of this interaction is attributable to the sharp cutoff of the distribution of conduction electrons in the metal at the Fermi energy $\varepsilon = \varepsilon_F$, so that the interference of electron waves with the Fermi momentum $k = k_F$ scattered by the impurities leads to the well-known Friedel oscillations of the electron density.[4,5] Friedel oscillations should obviously depend strongly on the form of the Fermi surface (FS) of the metal. Indeed it has been shown[6] that if the FS contains cylindrical sections, then in the direction perpendicular to the axis of the cylinder

$$E\,(R) \sim R^{-2} \sin\,(2k_F R), \tag{2}$$

and if the FS contains flat sections then in the direction perpendicular to them[7]

$$E\,(R) \sim R^{-1} \cos\,(2k_F R). \tag{3}$$

Analogous Friedel oscillations also occur for the interaction between adsorbed atoms on the surface of a metal, and

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for a number of reasons they are stronger here. The oscillatory character of the interaction of adatoms was first noted by Grimley.[8-10] Gabovich and Pashitskiĭ[11] as well as Lau and Kohn[12] called attention to the fact that if the FS of the substrate contains cylindrical or flat sections perpendicular to the surface, then in accordance with (2) and (3) the interaction of the adatoms must be long-ranged. It should be noted immediately that if the interaction is attributable to the exchange of quasiparticles of the metallic substrate, then it will always have a Friedel oscillating component whose amplitude decreases as some power of R as $R \to \infty$, and the exponent is determined solely by the electronic structure of the substrate.

We shall begin our study of different interaction mechanisms with the most interesting one—indirect interaction of adatoms. First, however, we shall give a brief presentation of the necessary information from the theory of chemisorption.

2.1. Basic information from the theory of chemisorption

In 1935 Gurney[13] proposed that when an atom is chemisorbed a so-called virtual electonic level is formed. Namely, as the atom approaches the surface of the metal at some short (on an atomic scale) distance a the electronic level of the free atom is shifted due to the action of the field of the metal near the surface. If in the process the level lies opposite the conduction band of the metal, then electrons can tunnel from the conduction band into that level of the adatom and vice versa, as a result of which the discrete electronic level is transformed into a virtual level with a finite half-width Δ. This process is described theoretically by the Hamiltonian

$$H = H_A + H_S + H_{\rm mix}. \tag{4}$$

In what follows we shall employ the technique of advanced Green's functions.

If only one valence orbital $|A\rangle$ of the adatom participates, then the Hamiltonian of the adatom $H_A = \varepsilon_A c_A^* c_A$ (c and c^* are second-quantization operators) and the Green's function of the free atom is $G_A(\varepsilon) = (\varepsilon - \varepsilon_A - i0)^{-1}$.

The Hamiltonian H_S in (4) corresponds to a metal substrate (semiinfinite crystal). In the theory of chemisorption, as in the description of impurities in the bulk of a crystal, it is convenient to employ a "point" basis $\{|i\rangle\}$ ($|i\rangle$ is the electronic wave function localized on a surface atom of the substrate with the coordinates $\mathbf{R}_j$). In this basis the Green's function of the substrate is given by the expression

$$G_S(\mathbf{R}_i - \mathbf{R}_j;\ \varepsilon) = \langle i \mid (\varepsilon - H_S - i0)^{-1} \mid j\rangle. \tag{5}$$

The method for calculating the function G_S for substrates with different electronic structure will be described in Sec. 2.3. It will be shown there that for $R \geqslant a_0$ (a_0 is the lattice constant of the substrate)

$$G_S(R;\ \varepsilon) \approx R^{-\nu} g_\nu(\varepsilon) \exp(-ik(\varepsilon) R), \tag{6}$$

where $k(\varepsilon)$ is the wave vector in the direction of the vector $\mathbf{R}$ for a substrate electron with energy ε, ν is a nonnegative integer determined by the structure of the FS of the substrate, and $g_\nu(\varepsilon)$ is a smooth function.

The operator $H_{\rm mix}$ describes the coupling of the adatom with the substrate. If the adatom binds only with one surface atom of the substrate $|i\rangle$, then

$$H_{\rm mix} = V c_A^* c_i + \text{h c}, \tag{7}$$

where $V = \langle A | H | i\rangle$ is the overlap integral of the wave functions. The generalization to the case when the adatom binds with several surface atoms of the substrate does not present any difficulties and reduces to renormalization of the parameters ε_A and V.[14,15]

The foregoing model of chemisorption is called the "Anderson-Newns model."[16,17] To calculate the Green's function $\tilde{G} = (\varepsilon - H - i0)^{-1}$ of the system it is convenient to employ Dyson's equation

$$\tilde{G} = G + G H_{\rm mix} \tilde{G}. \tag{8}$$

The advantage of this approach is that different terms in the operator $H_{\rm mix}$ can be taken into account systematically. The equation (8) is a matrix equation; for the adsorption of one atom the matrices are 2×2 (the basis is $|A\rangle$ and $|i\rangle$). Since the matrix G is known and $\langle A|G|i\rangle = 0$, the Green's function of the adatom can be easily obtained from (8):

$$\tilde{G}_A(\varepsilon) \equiv \langle A|\tilde{G}(\varepsilon)|A\rangle = (\varepsilon - \varepsilon_A - V^2 G_S(0;\ \varepsilon))^{-1}. \tag{9}$$

Thus the shift of the electronic level of the adatom accompanying chemisorption equals $\Lambda \equiv \Lambda(\varepsilon_A) = \operatorname{Re} V^2 G_S(0;\varepsilon_A)$, and its half-width equals $\Delta \equiv \Delta(\varepsilon_A) = \operatorname{Im} V^2 G_S(0;\varepsilon_A)$. We note that for chemisorption usually $\Lambda \sim \Delta \sim 1$ eV.[15]

The adsorption of an atom changes the density of the electron states of the system $\rho(\varepsilon) = \pi^{-1} \operatorname{Im} \tilde{G}(\varepsilon)$, which "feels" the second adatom. This is what leads to the indirect interaction between adatoms, first studied by Koutecky.[18] When two identical atoms A and B are adsorbed at the locations $|i\rangle$ and $|j\rangle$ separated by the distance $R = |\mathbf{R}_i - \mathbf{R}_j|$ Dyson's equation (8) is 4×4 (the basis is $|A\rangle$, $|B\rangle$, $|i\rangle$ and $|j\rangle$) and can also be easily solved.[2]

The interaction energy of the adatoms is defined as

$$E_{\rm int}(R) = \langle H(R)\rangle - \langle H(R = \infty)\rangle.$$

The representation of $E_{\rm int}(R)$ in terms of the Green's function $\tilde{G}$ is described in detail in the reviews of Refs. 2 and 19–23 as well as in Refs. 14 and 24–26. We shall therefore present immediately the expression for the indirect-interaction energy, obtained using the temperature technique of Green's functions[27]:

$$E_{\rm ind}(R) = -\frac{2}{\pi} \int_{-\infty}^{+\infty} d\varepsilon f_F(\varepsilon) \operatorname{Im} \ln (1 - V^4 \tilde{G}_A^2(\varepsilon) G_S^2(R;\ \varepsilon)),$$

$$f_F(\varepsilon) = \{\exp[(\varepsilon - \varepsilon_F)(k_B T)^{-1}] + 1\}^{-1}. \tag{10}$$

The factor of two here arises owing to summation over the electron spins. If $V^2 \tilde{G}_A G_S \ll 1$, which always holds, at least in the limit $R \to \infty$, the expression (10) simplifies:

$$E_{\rm ind}(R) \approx \frac{2V^4}{\pi} \operatorname{Im} \int_{-\infty}^{+\infty} d\varepsilon f_F(\varepsilon) \tilde{G}_A^2(\varepsilon) G_S^2(R;\ \varepsilon). \tag{11}$$

Using the expression (6) for the Green's function of the substrate and integrating (11) by parts we obtain in the limit

$$E_{\rm ind}(R) \approx -\frac{2V^4}{\pi R^{2\nu+1}} \operatorname{Re} \int_{-\infty}^{+\infty} d\varepsilon f_F'(\varepsilon) \frac{\varepsilon\alpha(\varepsilon)}{k(\varepsilon)} \tilde{G}_A^2(\varepsilon) g_\nu^2(\varepsilon) \times \exp(-2ik(\varepsilon) R), \tag{ii}$$

where $\alpha^{-1}(\varepsilon) = (2\varepsilon/k(\varepsilon)) dk(\varepsilon)/d\varepsilon$ (for the quadratic dispersion law for the substrate electrons $\alpha(\varepsilon) \equiv 1$). The function $f'_F(\varepsilon)$ cuts out on integration a narrow region of width $k_B T$ near the Fermi energy. Using the expansion $k(\varepsilon) \approx k_F[1 + (\varepsilon - \varepsilon_F)(2\varepsilon_F \alpha_F)^{-1}]$, where $\alpha_F = \alpha(\varepsilon_F)$, and removing the smoothly varying functions from the integrand we obtain the following expression for the indirect-interaction energy:

$$E_{\text{ind}}(R) \approx \frac{2V^4}{\pi R^{2\nu+1}} \frac{\varepsilon_F \alpha_F}{k_F} f\left(\frac{R}{R_T}\right) \times \operatorname{Re}[\tilde{G}_A^2(\varepsilon_F)\, g_\nu^2(\varepsilon_F) \exp(-i2k_F R)], \qquad (12)$$

where

$$f(x) = \frac{x}{\operatorname{sh} x}, \quad R_T = k_F^{-1} \frac{\alpha_F \varepsilon_F}{\pi k_B T}. \qquad (13)$$

Naturally for a substrate temperature $T > 0$ at very large distances $R \gg R_T$ the interaction decays exponentially as a function of the distance R:

$$E_{\text{ind}}(R) \sim R^{-2\nu} \cos(2k_F R + \varphi) \exp\left(-\frac{R}{R_T}\right). \qquad (14)$$

The quantity $R_T \sim a_0(\varepsilon_F / k_B T)$ for the typical parameters $\varepsilon_F \approx 5$ eV and $T \approx 300$ K constitutes hundreds of lattice constants, so that in what follows we shall neglect the temperature dependence of $E_{\text{ind}}(R)$. We note, however, that in real crytals R_T is also determined by the mean free path of conduction electrons, owing to their scattering by impurities, by phonons of the crystal lattice, etc.

Since at large distances the interaction is transferred by electrons with energies close to the Fermi energy ε_F the period of the oscillations of $E_{\text{ind}}(R)$ and the rate of decay of the interaction amplitude are determined solely by the structure of the FS of the substrate in the given direction. Indeed, from (12) at $T = 0$ we obtain $f(R/R_T) = 1$ and

$$E_{\text{ind}}(R) \sim R^{-(2\nu+1)} \cos(2k_F R + \varphi). \qquad (15)$$

The range of the indirect interaction is longest in the cases of flat ($\nu = 0$) and cylindrical ($\nu \frac{1}{2}$) Fermi surfaces, when the interaction is transferred by large groups of electrons. A detailed analysis of the asymptotic behavior for substrates with different electronic structure will be given in Sec. 2.3. First, however, we shall study the behavior of $E_{\text{ind}}(R)$ in the near zone.

2.2. Indirect interaction of adatoms: the near zone

If at large distances $R \gg R_A$ the interaction is transferred only by electrons with energies $\varepsilon \approx \varepsilon_F$, then in the near zone $R < R_A$ all electrons in the conduction band of the substrate participate in the interaction; in the process different parts of the FS make different contributions to the interaction energy. For example, for the system H/W (110) the electronic "jack" of the FS of tungsten leads to attraction of hydrogen adatoms in the [111] direction and repulsion in the [110] and [100] directions, while the contribution of the hole "pockets" is completely opposite.[28]

Numerical calculations have shown that the near zone is large compared with a_0. For example, in the case of adsorption of hydrogen atoms on the surface of aluminum in the "gellium" model $R_A \approx 5$ Å,[29] while for adsorption on the (100) face of a simple cubic lattice R_A equals several lattice constants.[30] The qualitative behavior of the indirect interaction in the near zone can be studied with the help of the expressions (6) and (11). Going over to integration over the variable k, substituting $d\varepsilon = \left(\frac{2\varepsilon(k)\alpha(k)}{k}\right)dk$, and $\alpha(k) = \left(\frac{k}{2\varepsilon(k)}\right)\frac{d\varepsilon(k)}{dk}$, and removing the smoothly varying function from the integral, we obtain the following expression for the interaction energy:

$$E_{\text{ind}}(R) \approx \frac{2V^4}{\pi R^{2\nu}} \frac{2\varepsilon_F \alpha_F}{k_F} \operatorname{Im}\left\{g_\nu^2(\varepsilon_F) \exp(-i2k_F R) \int^{k_F} dk\, \tilde{G}_A^2(\varepsilon(k)) \exp[-i2(k - k_F)R]\right\}.$$

Regarding the variable k as complex and shifting the integration contour into the lower half-plane, using the expression (9) for $\tilde{G}_A(\varepsilon)$ and the expansion $\varepsilon(k) \approx \varepsilon_F[1 + (k - k_F)\alpha_F(2k_F)^{-1}]$ we obtain

$$E_{\text{ind}}(R) \approx -\frac{2V^4}{\pi R^{2\nu}} \frac{16 k_F R}{\varepsilon_F \alpha_F} \operatorname{Re}\{g_\nu^2(\varepsilon_F) \times [\exp(-SR)\operatorname{Ei}(SR) - (SR)^{-1}] \exp(-i2k_F R)\}, \qquad (16)$$

where Ei is the integral exponential function,

$$S = i\frac{4k_F}{\alpha_F}(\tilde{\varepsilon}_A - \varepsilon_F + i\Delta_F)\varepsilon_F^{-1}, \quad \tilde{\varepsilon}_A = \varepsilon_A + \Lambda(\varepsilon_F), \quad \Delta_F = \Delta(\varepsilon_F). \qquad (17)$$

In the far zone $R \gg R_A$ the asymptotic expression (15) follows from (16), and in the near zone $R \lesssim R_A$ we obtain approximately (compare with the results of Refs. 31 and 32)

$$E_{\text{ind}}(R) \approx -\frac{8V^4}{\pi R^{2\nu}} \operatorname{Im}[\tilde{G}_A(\varepsilon_F)\, g_\nu^2(\varepsilon_F) \exp(-i2k_F R)]. \qquad (18)$$

We note that in the near zone the period of the oscillations is also determined by the Fermi momentum k_F and does not depend on the parameters of the adatom.[31]

The size of the near zone is determined by the parameters of the adatom:

$$R_A = |S^{-1}| = (4k_F)^{-1}\alpha_F \varepsilon_F[(\tilde{\varepsilon}_A - \varepsilon_F)^2 + \Delta_F^2]^{-1/2}. \qquad (19)$$

For parameters that are typical for chemisorption systems $|\tilde{\varepsilon}_A - \varepsilon_F| \approx \Delta_F \approx 0.5$ eV, $\varepsilon_F \approx 5$ eV, $k_F \approx a_0^{-1}$ we obtain $R_A \approx 2a_0$, which agrees with the numerical results presented above. If, however, the adatom strongly perturbs the electronic spectrum of the substrate, i.e., if the adatom has a narrow virtual level near the Fermi level ($|\varepsilon_A - \varepsilon_F| \lesssim \Delta \ll \varepsilon_F$), then the near zone is significantly larger ($R_A \gg a_0$). We emphasize that in this case the amplitude of the indirect interaction is also large,[26,33] and it decays as a function of R in the near zone more slowly than in the far zone.[31,32]

It is difficult to calculate the energy E_{ind} in the near zone accurately, since the electronic structure of the substrate must be taken into account exactly. Calculations performed in a number of papers (Refs. 2, 14, 24, 28, 31, and 34) have shown that in the case of the adsorption of alkali atoms $E_{\text{ind}} \sim 0.1$ eV in the near zone. More accurate values of the interaction energy for different chemisorption systems can be obtained by analyzing the experimental data (see Sec. 3).

2.3. Indirect interaction of adatoms: the asymptotic zone

Since the behavior of the indirect-interaction energy in the far zone $R \gg R_A$ is completely determined by the shape of the FS of the substrate the study of the asymptotic behavior of the function $E_{\rm ind}(R)$ reduces to calculating the Green's function $G_S(R;\varepsilon)$. For this it is convenient to employ the strong-coupling approximation, which enables modeling substrates with different electronic structure.[31]

2.3.1. Flat FS

The simplest model of a metal with a flat FS is a one-dimensional linear chain of atoms with the dispersion law for electrons $\varepsilon(k) = \varepsilon_c - 2\gamma\cos(a_0 k)$, where γ is the overlap integral of the orbitals of neighboring atoms, ε_c is the center of the conduction band, and $W = 4\gamma$ is the width of the conduction band. We choose a system of units in which $\varepsilon_c = 0$, $\gamma = 1/2$ and $a_0 = 1$. Then the Green's function of the substrate in the "point" basis ($R = ma_0$) equals

$$G_S(m;\ \varepsilon) = (2\pi)^{-1}\int_{-\pi}^{+\pi} dk \exp(imk)\,(\varepsilon - \varepsilon(k) - i0)^{-1}$$

$$= i(-i)^m (1-\varepsilon^2)^{-1/2}\,[\varepsilon + i(1-\varepsilon^2)^{1/2}]^{|m|}$$

$$= \frac{i}{\sin x_0}\exp(-i|m|x_0), \tag{20}$$

where $\cos x_0 = -\varepsilon$, $0 < x_0 < \pi$. Thus for the interaction of adatoms along closely packed chains of atoms of the substrate (i.e., perpendicularly to the flat sections of the FS) $E_{\rm ind}(R) \sim R^{-1}(\nu = 0)$. The situation described corresponds, for example, to the interaction of adatoms on the (112) face of tungsten in the [111] direction.

2.3.2. Cylindrical FS; the axis of the cyclinder is perpendicular to the surface of the crystal

A metal with a cylindrical FS can be modeled by a simple square lattice. For the coordinate system shown in Fig. 1 the expression for the dispersion of the electrons assumes the form $\varepsilon(\mathbf{k}) = -2\cos(k_y)\cos(k_x/2)$, $-\pi < k_x,\ k_y < +\pi$, so that the Green's function in the "point" basis in the [11] direction is determined by the integral ($R = \sqrt{2}ma_0$)

$$G_S(m;\ \varepsilon) = i(2\pi)^{-1}\int_{-\pi}^{+\pi} dk_x \exp(imk_x)\left(4\cos^2\frac{k_x}{2} - \varepsilon^2\right)^{-1/2}. \tag{21}$$

A method for calculating integrals of the type (21) is described in detail in Ref. 35. It reduces to transforming into the complex plane, finding the branch points of the integrand, and shifting the integration contour into the upper half-plane. As a result, for $m \gtrsim 1$ we obtain

$$G_S(m;\ \varepsilon) \approx (-4m_v \sin 2x_0)^{-1/2}$$

$$\exp\left(-i2mx_0 + \frac{im}{m_v}\right) H_0^{(2)}\left(\frac{m}{m_v}\right) \tag{22}$$

$$\approx (-4m_v \sin 2x_0)^{-1/2}\exp(-i2mx_0)\left[1 - i\,\frac{2C}{\pi} - i\,\frac{2}{\pi}\ln\frac{m}{2m_v}\right],$$

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$$m \ll m_v, \tag{22a}$$

$$\approx (-2\pi m \sin 2x_0)^{-1/2}\exp\left(-i2mx_0 + i\frac{\pi}{4}\right)\left(1 + i\,\frac{m_v}{8m}\right),$$

$$m \gg m_v, \tag{22b}$$

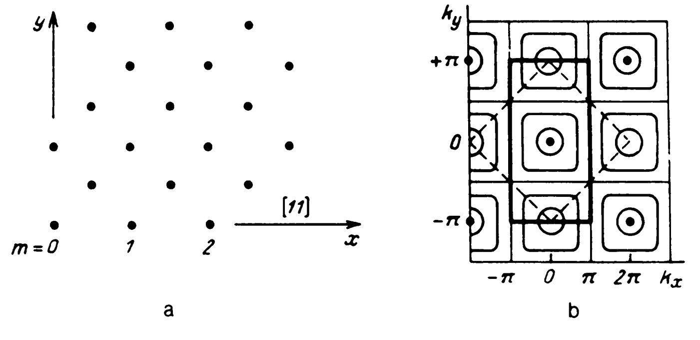
where $\cos x_0 = -\varepsilon/2$, $H_0^{(2)}$ is Hankel's function, $C = 0.577\ldots$ is the Euler–Mascheroni constant,

$$m_v(\varepsilon) = \frac{1}{2}\left[\frac{(4-\varepsilon^2)^{1/2}}{\varepsilon} - \frac{\varepsilon}{(4-\varepsilon^2)^{1/2}}\right], \tag{23}$$

and for definiteness here and below it is also assumed that $x_0 > \pi/2$, $\varepsilon > 0$, $m > 0$, $m_v > 0$. One can see from (22b) that $E_{\rm ind}(R) \sim R^{-2}(\nu\tfrac{1}{2})$ as $R \to \infty$. This situation corresponds, for example, to the interaction of adatoms on the (0001) surface of rhenium.

2.3.3. Flat sections of the FS

The [11] direction in a simple square lattice was not chosen randomly, because it permits demonstrating the transition from a flat to a cylindrical FS. The presence of flat sections on the FS is, of course, exotic. The Fermi surface of a metal usually can have only flattened sections, characterized by a large radius of curvature. We shall show that in this case at short distances $R \ll R^*$ the interaction is of the same character as for a flat FS. Indeed (see Fig. 1b), as $\varepsilon \to 0$ the isoenergetic surface (more precisely, line) for a square lattice becomes flat (straight). It is obvious from the expressions (22) that the asymptotic formula $E_{\rm ind}(R) \sim R^{-2}$ holds only at large distances $R \gg R^* = m_v(\varepsilon_F)a_0$; in the near zone $R \ll R^*$ the preasymptotic formula $E_{\rm ind}(R) \sim R^{-1}$ holds. The quantity R^*, separating the far and near zones, is proportional to the radius of curvature of the flat section of the FS in this direction. We note that as $\varepsilon_F \to 0$, when the FS becomes flat, it follows from (23) that $R^* \to \infty$, i.e., the preasymptotic formula holds in the entire space.



a

b

FIG. 1. Simple square lattice (a) and the corresponding reciprocal lattice (b). The lattice sites (points), the lines of constant electron energy (thin solid lines), the choice of coordinate axes, and the Brillouin zones (thick line) are shown.

2.3.4. Open sections of the FS

In some metals, for example, in rhenium in the [0001] direction, the FS intersects the boundary of the Brillouin zone, i.e., it has open sections. This case can be easily modeled by a rectangular lattice with unequal overlap integrals $\gamma_1 \neq \gamma_2$. Then in the direction of the open sections we obtain $G_S(R) \sim \exp(-\alpha R)$, so that the indirect interaction decays exponentially (see also Ref. 11).

2.3.5. Cylindrical FS; the axis of the cylinder is parallel to the surface

The asymptotic behaviors studied above are completely analogous to the "volume" behavior. It is convenient to study the "surface" case by the method of Calkstein and Soven.[15,36,37] First, the Green's function of an infinite crystal is calculated in a mixed basis $|n,k_{\parallel}\rangle$, where $n = 0, \pm 1, \pm 2, \ldots$ enumerates the atomic planes, parallel to the future surface, while $k_{\parallel}$ is the two-dimensional wave vector along them. Then the infinite crystal is "cut" between the atomic planes $n = 0$ and $n = -1$ into two halves; the perturbations due to the "cut" can be easily taken into account with the help of Dyson's equation. Thus if the Green's function of an infinite square lattice is determined by the integral (21), then after the "cut" along the Ox axis the "surface" Green's function equals

$$G_S(m;\ \varepsilon) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} dk_x e^{imk_x} \frac{\varepsilon + i\,[4\cos^2(k_x/2) - \varepsilon^2]^{1/2}}{2\cos^2(k_x/2)} \tag{24}$$

$$\approx \left(-\frac{\pi}{\sin 2x_0}\right)^{-1/2} (2m)^{-3/2} \frac{4}{\varepsilon^2} \exp\left(-i2mx_0 - i\frac{\pi}{4}\right) \tag{24'}$$

for $m \gg m_s = (4 - \varepsilon^2)^{1/2}/\varepsilon$. Thus for the interaction of adatoms in a direction perpendicular to the axis of a cylindrical FS, when the axis is parallel to the surface, $E_{\rm ind}(R) \sim R^{-4}$.[31] This case corresponds, for example, to the interaction of adatoms on the (10$\bar{1}$0) face of rhenium in the [$\bar{1}$2$\bar{1}$0] direction.

2.3.6. Spherical FS

If the FS of the substrate does not have the features mentioned above (flat, cyclindrical, or open sections), then $E_{\rm ind}(R) \sim R^{-5} (\nu = 2)$. This was shown in Refs. 2 and 30 for the (100) face of a simple cubic lattice. An analogous result ($\nu = 2$) is obtained in the [100] and [110] directions for the (110) face of a crystal with a bcc lattice.[31] The correct asymptotic behavior $E(R) \sim R^{-5}$ for the interaction energy of adatoms was first found by Flores *et al.*[38]; this result was later confirmed in Refs. 12, 29, 39, and 40 in the "gellium" model and in Refs. 2, 12, 30, and 31 in the tight-binding approximation. We emphasize[12,31] that the difference between the volume $E(R) \sim R^{-3}$ and surface $E(R) \sim R^{-5}$ asymptotic behaviors is attributable to the smoother behavior of the density of electron states at the surface as compared with the volume (compare the expressions (21) and (24), and see Fig. 2 also) and is not linked with the geometric factors of the "critical direction" type, as assumed in Refs. 8–10 and 30. In this case the amplitude of the Friedel oscillations decays as R^{-3} into the bulk of the metal.[29,38–40] More accurately, if two impurity atoms lie in the bulk of the metal at a distance d from the surface, then at large distances $R \gg d$ their interaction is also of a "surface" character $E(R) \sim R^{-5}$, though at small distances $R \lesssim d$ the "volume" Ruderman-Kittel law (1) holds.[29]

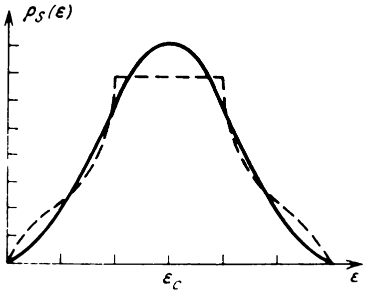


FIG 2 The local density of electron states $\rho_s(\varepsilon)$ on the surface (solid line) and in the volume (broken line) for the (100) face of a simple cubic lattice

2.3.7. Role of surface electron states

As a rule, the surface of a crystal contains electronic surface states (ESS).[21] In a two-band model of a crystal they arise in the gap owing to the mixing of the bands (Shockley ESS) caused by the cutoff of the lattice.[41,42] In the one-band model ESS appear if the perturbation U acting on the surface owing to the finiteness of the surface potential barrier and relaxation of the surface layer of atoms (Tamm ESS) is taken into account.[16] We shall study their role in the interaction of adatoms with the help of the simple square lattice, cut along the Ox axis, studied above. If the surface perturbation U is taken into account in Dyson's equation (for definiteness let $U > 0$), then the surface Green's function will be determined by the formula

$$G_S(m;\ \varepsilon) = \pi^{-1} \int_{-\pi}^{+\pi} dk_x \times \exp(imk_x)\left[\varepsilon - 2U - i\left(4\cos^2\frac{k_x}{2} - \varepsilon^2\right)^{1/2}\right]^{-1} \tag{25}$$

instead of the expression (24). The expression in the integrand in (25) has, aside from branch points, poles at $\varepsilon_L(k_x) = U + U^{-1}\cos^2(k_x/2)$. If $U \leqslant 1$ (we recall that in the system of units chosen $W = 4$), then there exists a band of ESS, occupying the region $U < \varepsilon < 2U$ and lying within the conduction band of the substrate. If ε falls in the region of ESS, then the additional bands make the contribution

$$G_L(m;\ \varepsilon) = 2i\,(2U - \varepsilon)\,(-\sin 2x_L)^{-1} \exp(-i2mx_L), \tag{26}$$

where $\cos^2 x_L = (\varepsilon - U)\,U$, to the Green's function. Thus if the Fermi level crosses the ESS band, then the asymptotic behavior of the indirect interaction of the adatoms will be determined by the ESS: $E_{\rm ind}(R) \sim R^{-1} (\nu = 0)$.

The situation is analogous for a three-dimensional semiinfinite crystal also—if the conduction band contains ESS (and their existence is predicted by accurate calculations[43–45]) and if the Fermi level crosses the ESS band, then the amplitude of the oscillations of $E_{\rm ind}(R)$ will decay more rapidly than R^{-2}, and the period of the oscillations will be determined by the Fermi momentum corresponding to the ESS.

2.4. Electrostatic interaction of adatoms

Since only the part of the virtual level of the adatom lying below the Fermi level ε_F is filled with electrons the adatom has a nonzero charge

$$Q = Z - \sum_{A} \langle n_A \rangle, \quad \langle n_A \rangle = \pi^{-1} \int_{-\infty}^{\varepsilon_F} \mathrm{d}\varepsilon \, \mathrm{Im}\, \tilde{G}_A(\varepsilon), \tag{27}$$

where Z is the charge of the ionic core; the summation is performed over the quantum numbers of the valence orbitals of the adatom, in particular, over the spin. The Coulomb interaction between the electrons leads to screening of the charge of the adatom, so that the charged adatom together with the electron cloud screening it in the metal form a dipole. The dipole-dipole repulsion of adatoms, which has been known since Langmuir's day,[46] is the main component of the electrostatic interaction.

The interaction of a localized charge with the electrons of the metal theoretically reduces to the interaction with fluctuations of the electron density, which can be described by a boson field.[47,48] In the case when the charge lying above a semiinfinite crystal is screened these bosons are surface plasmons.[49–51] For this reason, to take into account the screening effects accompanying chemisorption the terms describing the interaction of the surface plasmons with the ionic core and the valence electrons of the adatom must be added to the Hamiltonian (7).[52–56] This interaction leads to renormalization of the parameters ε_A and Δ and is responsible for the "ionic" contribution to the chemisorption energy, determined by the ratio of the frequency of the fluctuations of the charge of the adatom ω_f and the frequency of the surface plasmons ω_S.[55,56] The charge of the adatom Q excites the plasma subsystem of the substrate, which "feels" the second adatom. An electrostatic interaction between the adatoms arises as a result. Since the charges of the adatoms fluctuate independently, the contribution of screening effects to the interaction energy of the adatoms reduces to the interaction of static electric charges Q lying at a distance a (a is determined by the radius of the adatom) from the surface of the crystal.[54,57]

In the linear-response approximation the external charges with density $\rho_0(\mathbf{r},t)$ create near the surface of a solid an electric-field potential

$$\varphi(\mathbf{r}, t) = \int \mathrm{d}\mathbf{r}' \int_0^{\infty} \mathrm{d}\tau D(\mathbf{r}, \mathbf{r}; \tau)\, \rho_0(\mathbf{r}', t-\tau), \tag{28}$$

where D is the delayed Green's function of the longitudinal Coulomb field.[27] In the case when the surface of the solid, occupying the half-space $x<0$, is flat (i.e., neglecting the potential relief of the substrate), it is convenient to perform a Fourier transformation

$$D(x, x'; \mathbf{q}; \omega) = \int \mathrm{d}t \int \mathrm{d}\mathbf{R} \exp(i\omega t - i\mathbf{q}\mathbf{R})\, D(\mathbf{r}, \mathbf{r}'; t).$$

Then an integrodifferential equation for the Green's function follows from Poisson's equation for the potential $\varphi(\mathbf{r},t)$:

$$\left(\frac{\partial^2}{\partial x^2} - q^2\right) D(x, x'; \mathbf{q}; \omega) - 4\pi \int \mathrm{d}x'' \Pi(x, x''; \mathbf{q}; \omega) D(x'', x'; \mathbf{q}; \omega) = -4\pi\delta(x-x'), \tag{29}$$

where

$$\Pi(\mathbf{r}, \mathbf{r}'; \omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} \mathrm{d}\omega' G_\sigma(\mathbf{r}, \mathbf{r}'; \omega')\, G_\sigma(\mathbf{r}', \mathbf{r}; \omega'-\omega) \tag{30}$$

is the polarization operator of the system, while G_σ is the casual Green's function of electrons with spin σ in the solid.

On the basis of the "gellium" model with a sharp boundary the expression

$$\Pi(x, x') \equiv \Pi(x, x'; \mathbf{q}; \omega) = \theta(x \cdot x')\, [\Pi_\infty(|x + x'|) + \Pi_\infty(|x - x'|)], \tag{31}$$

is often employed for the polarization operator of the crystal-vacuum system (see the review of Ref. 58). Here $\theta(x)$ is the Heaviside step function and Π_∞ is the polarization operator of an infinite medium, which for a uniform crystal is given by

$$\Pi_\infty(x) \equiv \Pi_\infty(x; \mathbf{q}; \omega) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}k_x}{2\pi} e^{ik_x x} \frac{k_x^2 + q^2}{2\pi} (\epsilon_l(k_x, \mathbf{q}; \omega) - 1); \tag{32}$$

where $\epsilon_l(\mathbf{k};\omega)$ is the longitudinal permittivity of the medium (for a vacuum $\epsilon_l = 1$ and $\Pi_l = 0$). The approximation (31) corresponds to mirror reflection of electrons in the metal from the surface of the metal[59,60] and describes well both the spectrum of surface plasmons[61–63] and the penetration of the electromagnetic field into the metal.[64,65]

The equation (29) we first solved by Romanov[61–63] on the basis of the "mirror" approximation (31); in the region $x, x' \geqslant 0$ it has the form

$$D(x, x'; \mathbf{q}; \omega) = 2\pi q^{-1} \{\exp(-q\,|x - x'|) - g(\mathbf{q}; \omega) \exp[-q(x + x')]\}, \tag{33}$$

where the response function of a simiinfinite medium

$$g(\mathbf{q}; \omega) = \frac{\epsilon_S(\mathbf{q}; \omega) - 1}{\epsilon_S(\mathbf{q}; \omega) + 1}, \quad \epsilon_S^{-1}(\mathbf{q}; \omega) = \frac{q}{\pi} \int_{-\infty}^{+\infty} \mathrm{d}k_x [(k_x^2 + q^2)\, \epsilon_l(k_x, \mathbf{q}; \omega)]^{-1} \tag{34}$$

completely describes the surface properties of the medium, while the poles of the function $g(\mathbf{q}; \omega)$ determine the spectrum of the surface collective excitations.

The Green's function $D(\mathbf{r}_1, \mathbf{r}_2; \omega)$ determines the electrostatic interaction energy of two charges Q_1 and Q_2 located at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ near the surface of the solid:

$$E(\mathbf{r}_1, \mathbf{r}_2) = Q_1 Q_2 D(\mathbf{r}_1, \mathbf{r}_2; \omega = 0). \tag{35}$$

In particular, assuming in the Fermi-Thomas approximation that

$$\epsilon_l(k) = 1 + \frac{\varkappa^2}{k^2}, \quad \epsilon_S(q) = \frac{(q^2 + \varkappa^2)^{1/2}}{q}, \tag{36}$$

where $\varkappa^{-1}$ is the screening length in the volume of the metal ($\varkappa^{-1} \lesssim 1$ Å), from (33)–(35) we obtain the electrostatic interaction energy of two adatoms separated by a distance R:

$$E_{\text{el stat}}(R) = Q^2 \left\{ R^{-1} - \int_0^\infty \mathrm{d}q J_0(qR) \right.$$

$$\left. \times \exp(-2qa)\, \varkappa^{-2} [(q^2+\varkappa^2)^{1/2} - q]^2 \right\} \qquad (37)$$

$$\approx Q^2 [R^{-1} - (R^2 + 4a^2)^{-1/2}], \qquad a \gg \varkappa^{-1}, \quad (37a)$$

$$= 2Q^2 \varkappa^{-2} R^{-3} [1 - (1+\varkappa R) \exp(-\varkappa R)], \ a = 0. \qquad (37b)$$

It follows from here that Coulomb repulsion $E_{\text{el stat}}(R) \sim R^{-1}$ operates between the adatoms at small distances $R \lesssim (a + \varkappa^{-1})$ and dipole-dipole repulsion operates at large distances $R > (a + \varkappa^{-1})$:

$$E_{\text{dip-dip}}(R) = 2p^2 R^{-3}, \qquad (38)$$

where

$$p = Q\,(a + \varkappa^{-1}) \qquad (39)$$

is the dipole moment of an adatom. The formula (38) was first presented in Refs. 1, 66, and 67. We note that for a nonzero number density N_A of adatoms the change in the work function of the substrate is given by Helmholtz's formula:

$$\Delta\Phi = -4\pi p N_A. \qquad (40)$$

The typical values of the electrostatic interaction energy at distances of several lattice constants for chemisorption of alkali and alkaline-earth atoms on the surface of a transition metal are 0.05–0.5 eV. Detailed data on the magnitudes of the dipole moments for different chemisorption systems will be presented in Sec. 3.

If a more accurate expression,[68] taking into account the Kohn anomaly at $k = 2k_F$, is employed in the formula (34) for the volume permittivity $\epsilon_l(k)$, then aside from the dipole-dipole pedestal (38) the electrostatic interaction energy will also have an oscillating Friedel component E_{Friedel}. Since the Fourier components of the potential decay as a function of the distance a as $\exp(-2ka)$ (see (33)) while momenta with $k = 2k_F$ are responsible for the Friedel oscillations, then the small factor $\exp(-4k_F a)$ will appear in the amplitude of the Friedel component.[69] For the cases when the FS of the substrate has flat or cylindrical sections oriented perpendicular to the surface the amplitude of the oscillations decays with the distance R as R^{-1} or R^{-2}, respectively.[11,70,71] We note, however, that in the case of a spherical FS the described "mirror" approximation leads to an incorrect asymptotic behavior $E_{\text{Friedel}} \sim R^{-3}$.[71,72] This is attributable to the fact that the polarization operator $\Pi(x,x')$ given by the expression (31) does not vanish at the surface $x = x' = 0$, as should happen according to its definition (30).

2.5. Direct interaction of adatoms

When the adatoms A and B lie so close to one another on a substrate that their orbitals Φ_A and Φ_B start to overlap the direct mechansim of interaction comes into play. It is fundamentally identical to the interaction leading to the formation of a chemical bond in molecules. We recall that an isolated molecule (for example, of the H_2 type) has binding $\Phi_+ \sim \Phi_A + \Phi_B$ and antibinding $\Phi_- \sim \Phi_A - \Phi_B$ orbitals. The gain in the energy, proportional to the overlap integral $T(R) = \langle \Phi_A | H | \Phi_B \rangle$, is attributable to the fact that only the orbital with the lower energy Φ_+ is filled with electrons. The direct interaction leads to attraction decaying exponentially with the distance R:$E(R) \sim T(R) \sim \exp(-\alpha R)$, where α^{-1} is of the order of the size of the adatom. It is obvious that the direct interaction will be significant only for close to monolayer coatings, when the electronic shells of the adatoms start to overlap. To take into account the direct interaction in the model employed above the term $T(R) c_A^* c_B$ + h.c. must be added to the Hamiltonian (7). As the molecule approaches the surface the discrete levels of the isolated molecule transform into virtual levels, which are filled with electrons only up to the Fermi level ε_F (Fig. 3). As a result of this, first of all, the antibinding orbital is partially filled and the binding orbital is emptied and, second, a charge $Q \neq 0$ appears on the constituent atoms of the molecule causing them to repel one another. For this reason the binding energy of the atoms in the molecule decreases on adsorption, and all the more strongly the larger Δ and Q,[26,33,73] i.e., the stronger the ionic or covalent bond of the molecule with the substrate. For adsorption of H_2 molecules this question was studied in Ref. 74 with the help of Anderson's model and in Ref. 75 on the basis of the "gellium" model. We note, however, that as in the case of the calculation of the energies of chemical bonds in isolated molecules correlation effects must be taken into account to obtain quantitative results.[76]

Other mechanisms of interaction of adatoms (elastic, van-der-Waals) lead to energies that, as a rule, are more than an order of magnitude lower than those studied above. For this reason they can be significant only for physically adsorbed films; these interactions are studied in the review by Einstein.[2] We note only that the elastic interaction leads to repulsion, decaying with distance as R^{-3}.[77-79]

2.6. Interaction of atoms adsorbed on the surface of a semiconductor

The mechanisms of interaction between atoms adsorbed on the surface of a semiconductor are fundamentally identical to those studied above. In the case of chemisorption on semiconductors the covalent component of the adsorption energy is, as a rule, large; for this reason the energy of indirect interaction of adatoms through the valence orbitals of the substrate atoms should also be large. Since the electrochemical potential of the semiconductor lies in the gap, the energy $E_{\text{ind}}(R)$ decays rapidly (exponentially) with the distance R between the adatoms. If, however, the surface of the semiconductor contains an ESS band that crosses the electrochemical potential, then the indirect interaction should have a long-ranged oscillatory character ($E_{\text{ind}}(R) \sim R^{-\mu}$; $\mu < 2$).[35] We note that the indirect interaction via the ESS band can explain, in particular, the existence of a 7×7 structure on the reconstructed (111) fact of silicon (see Sec. 4).

If the adatoms have a nonzero charge Q, then an electrostatic interaction will exist between them. The feature that distinguishes a semiconductor from a metal is the low density of conduction electrons n, which leads to a large screening radius $\varkappa^{-1}$ ($\varkappa = (4\pi n e^2/\epsilon_0 k_B T)^{1/2}$ for a nondegenerate and $\varkappa = (6\pi n e^2/\epsilon_0 \varepsilon_F{}^{1/2}$ for a degenerate electron

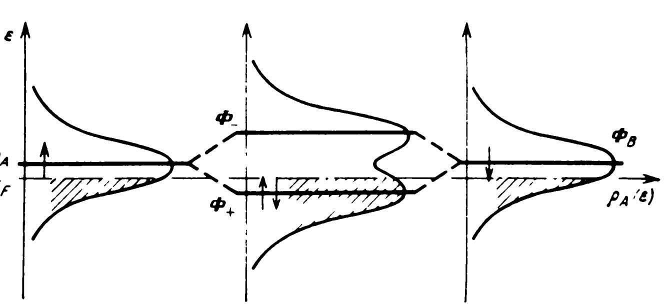


FIG. 3 Formation of the electronic spectrum in the case of direct interaction of the adatoms

gas) and also a static permittivity $\epsilon_0 = \epsilon\,(k \sim \varkappa_0) > 1$ ($\varkappa_0^{-1}$ is the radius of the inner shell of the substrate atom). Using for the volume permittivity the expression

$$\epsilon\,(k) = \epsilon_0\left(1 + \frac{\varkappa^2}{k^2}\right), \qquad (41)$$

it can be shown that the dipole-dipole repulsion

$$E_{\mathrm{dip\text{-}dip}}\,(R) = 2p^2R^{-3}, \quad p = Q\left(a + \frac{1}{\varkappa\epsilon_0}\right) \qquad (42)$$

operates only at large distances between the atoms $R \gg (\varkappa\epsilon_0)^{-1} \gg a$, while in the near zone $R \ll (\varkappa\epsilon_0)^{-1}$ whose size for $n < 10^{19}\,\mathrm{cm}^{-3}$ is greater than ten angstroms, the adatoms are repelled according to the Coulomb law[80]

$$E_{\mathrm{el.stat}}\,(R) \approx \frac{2Q^2}{R\,(\epsilon_0+1)}. \qquad (43)$$

2.7. Interaction of atoms in an adsorbed film

2.7.1. Unpaired nature of the interaction

It is obvious that the interaction of adatoms is not additive, especially since the substrate always participates in the interaction. For example, when three atoms are adsorbed their interaction energy E_{ijk} does not equal the sum of the pair interactions: $E_{ijk} - (E_{ij} + E_{jk} + E_{ki}) = \Delta E_{ijk} \neq 0$. Calculations performed in the tight-binding approximation have shown[28,81-83] that for the indirect interaction mechanism the degree to which the "triple" (trio) interaction departs from pairwise interaction can be both greater and less than zero, while for atoms occupying neighboring adsorption centers its amplitude can reach that of the pair interaction. It is obvious that the value of ΔE_{ijk} depends significantly on the electronic structure of the substrate. The triple interaction must be taken into account in order to explain, for example, the formation of a (2×2) structure with the coverage $\theta = 0.75$ in the adsorption systems H and O/W (110).[84] At the same time higher order interactions ("quadruple," etc.) can be neglected.[2,82]

It is even more important to take triple interactions into account in order to calculate the density of electron states of an adsorption system.[81] We note that the Green's function for an ordered lattice of adatoms with coverage $\theta = N_{\mathrm{A}}/N_{\mathrm{S}}$ (N_{A} is the concentration of adatoms and N_{S} is the concentration of surface adsorption centers) is determined by the expression[85]

$$\widetilde{G}_{\mathrm{A}}\,(\varepsilon) = N_{\mathrm{A}}^{-1} \sum_{\varkappa} \left(\varepsilon - \varepsilon_{\mathrm{A}} - \theta \sum_{\mathbf{q}} V^2 G_{\mathrm{S}}^{-1}(\varkappa + \mathbf{q};\ \varepsilon)\right)^{-1}, \qquad (44)$$

where the summation over $\varkappa$ extends over the two-dimensional Brillouin zone of the lattice of adatoms and $\mathbf{q}$ is the reciprocal lattice vector of the adatoms; the vector $\varkappa + \mathbf{q}$ must fall within the two-dimensional Brillouin zone of the pure substrate. The Green's function for a disordered adsorbed film was found in the T-matrix approximation (a variant of the mean-field approximation) in Refs. 86–88. Application of the results obtained for modeling the system H/Pt (111) showed[87,88] that in this system the indirect mechanism is the main mechanism of interaction, and for coverages $\theta > 0.5$ the unpaired nature of the interaction plays an important role.

We note that the unpaired nature of the interaction also arises owing to the mutual depolarization of the adatoms studied below.

2.7.2. Depolarization

Thus far we have assumed that the parameters of an adatom ε_{A} and V, characterizing its capability to bind with the substrate, are constants. It is obvious, however, that all interaction mechanisms studied above will bring about a change in these parameters. For example, the level ε_{A} is shifted in an electrostatic field of a second adatom ($|\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{F}}|$ decreases by the amount $2p^2R^{-3}$), so that the electrostatic interaction leads to a mutual change in the charges of the adatoms. This phenomenon, called "depolarization," causes the dependence $\Delta\Phi(N_{\mathrm{A}}) = -4\pi p N_{\mathrm{A}}$ to deviate from a linear dependence. It has been well known since Langmuir's time.[46] Depolarization effects were studied within the framework of Anderson's model in Refs. 54 and 89–91. If the adatom has a narrow virtual level, lying near the Fermi level, then depolarization may be so strong that as the adatoms approach their electrostatic repulsion energy will decrease. In addition, as shown by Bol'shov,[92] a first-order phase transition should occur in adsorption films with repulsion as the concentration of adatoms is increased.

The direct and indirect mechanisms of interaction also lead to the depolarization effect.[93,94] Depolarization appears in this case owing to the interaction-induced splitting of the electronic levels of the adatoms (see Fig. 3). The splitting of a virtual level is equivalent to an effective broadening of this level, which leads to the same result as a shift in the level toward the Fermi level. The combined action of different mechanisms of interaction can lead to more than one first-order phase transition as the concentration of adatoms increases; this is in fact observed experimentally for many systems.

2.7.3. Superposition of interactions

In studying real adsorption systems mechanisms of interaction must usually be taken into account, and their combined action does not reduce to a simple summation of the energies. First of all, some mechanisms alter the parameters determining the interaction energy for the others; second, interference terms appear in the calculation. For example, taking into account simultaneously the direct and indirect interactions[24,26,31,33] leads as $R \to \infty$ to an additional contribution to the interaction energy

$$E_{\rm direct+ind} \sim T(R)\, R^{-2\nu} \sin(2k_F R + \varphi). \qquad (45)$$

Finally only a self-consistent calculation offers any hope of obtaining quantitative results. The question of self-consistency is especially important in studying indirect interaction through the ESS band of the crystal with finite coverage of the substrate by adatoms. In this case the adsorbed film shifts the ESS band owing both to flow of electrons from the adatoms into the substrate and the action of the electrostatic field of the charged film. The shift in the ESS band, in its turn, changes the two-dimensional Fermi momentum k_F, which determines the period of the oscillations of the indirect interaction. For this reason, the total interaction energy of two adatoms $E_{\rm int}$ can be calculated comparatively accurately only for adsorption on substrates with a simple electronic structure—such as alkali metals or aluminum. Such substrates, however, are not interesting from both the practical and theoretical viewpoints; moreover, there are few experimental data for them. Substrates with a complicated electronic structure, for example, transition metals, are incomparably more interesting. Although it is impossible to make an accurate calculation of $E_{\rm int}$ in this case, the foregoing theory gives a number of qualitative results, enabling prediction of the behavior and order of magnitude of different contributions to $E_{\rm int}$.

As shown above the main mechanisms of interaction of adsorbed atoms are indirect, electrostatic, and direct; the first two are determining, at least for sparse structures ($\theta < 0.5$). The direct interaction, equal in order of magnitude to $E_{\rm direct} \sim T(R)$, must be taken into account only for high coverages ($\theta > 0.5$), when the electronic shells of the adatoms start to overlap.

The electrostatic interaction energy

$$E_{\rm el.stat} \simeq 2p^2R^{-3} + E_{\rm Friedel},\ E_{\rm Friedel} \sim Q^2 \exp(-4k_F a)\, R^{-\mu} \cos(2k_F R + \varphi)$$

is determined by the magnitude of the dipole moment of the adatoms $p = Q(a + \varkappa^{-1})$, which can be determined independently based on (40) from the experimentally measured change in the work function $\Delta\Phi$.

The indirect interaction between adatoms is anisotropic and oscillates with the period π/k_F; the amplitude of the oscillations

$$E_{\rm ind} \sim V^4 \rho_A(\varepsilon_F)\, R^{-\mu}$$

is determined by the magnitude of the overlap integral, proportional to the covalent component of the adsorption energy, between the orbitals of the adatom and the nearest atoms of the substrate and by the electronic density of states of the virtual level of the atom $\rho_A(\varepsilon_F) = (\Delta_F/\pi)[(\tilde{\varepsilon}_A - \varepsilon_F)^2 + \Delta_F^2]^{-1}$. The electronic structure of the substrate is determining in the dependence $E_{\rm ind}(R)$, so that when the indirect interaction predominates different adatoms on the same substrate must form identical (or close) structures. When ESS are present or the Fermi surface of the substrate contains flat sections the indirect interaction is long-ranged ($\mu \leqslant 2$). Moreover, in the near zone, whose size is determined by the quantity $R_A \sim \rho_A(\varepsilon_F)$, the amplitude of the oscillations of $E_{\rm ind}(R)$ drops off with R more slowly than in the far zone.

It is obvious from what was said above that when atoms of alkali metals, having a large positive dipole moment $p \gtrsim 1$ a.u. $(\varepsilon_A - \varepsilon_F \approx \Delta)^{1}$, are adsorbed the electrostatic mechanism is the main mechanism of interaction of the adatoms, while for adsorption of gases (H,O), when the dipole moment is small, the indirect mechanism predominates. We shall now compare the contribution of different mechanisms of interaction for the adsorption of atoms of alkali and alkaline-earth metals. For alkali-metal atoms ($Z = 1$) the charge $Q \simeq 1$ is reached with $\varepsilon_A - \varepsilon_F \gg \Delta$, while for alkaline-earth metal atoms ($Z = 2$) the charge $Q = 1$ is reached with $\varepsilon_A = \varepsilon_F$. For this reason, for the same magnitude of the dipole-dipole repulsion energy the value of $E_{\rm ind}$ for alkaline-earth atoms should be higher than for alkali atoms. It is obvious that the indirect mechanism should play an even larger role in the interaction of adsorbed atoms of rare-earth and transition metals.

In the next section we shall analyze the available experimental data based on these results.

3. EXPERIMENTAL STUDIES OF THE INTERACTION OF ADSORBED ATOMS

The interaction between adatoms affects many properties of adsorbed layers, and the study of each of these properties can in principle yield information about the interaction. Studies of the correlation between the mutual arrangement of adatoms migrating along the surface (the experiments are performed in a field-ion microscope) and the structure of the adsorbed layer (with the help of LEED) yield information about the dependence of the interaction energy of adatoms on their mutual arrangement on the surface. Studies of the concentration dependence of the heat of adsorption[95] or the form of the diffusion-spreading front[96] yield information about the character of the interatomic interaction (predominance of attractive or repulsive forces), while the shift and splitting of lines in the phonon or electronic spectrum of the adsorbed layer indicate only the existence of an interaction. We shall examine information about the interaction between adatoms obtained only with the help of the most informative methods—field-ion microscopy and LEED.

Experiments on adsorption on two closely packed faces of a bcc crystal—(110) and (112)—will be described in greatest detail. These faces are qualitatively different: the potential relief of the (110) face is smooth on an atomic scale while that of the (112) face is channeled (the activation energy of diffusion of an adatom along a channel in the [111] direction is significantly lower than across the channels). The strong anisotropy of the interaction of adatoms on channeled faces makes them, as will be shown below, a unique object for experimental study of the long-range character of the interaction.

3.1. Investigations with the help of a field-ion microscope

The main advantage of a field-ion microscope is that it permits observing the behavior of separate adatoms, though the strong working fields limit the range of possible adsorbates to atoms of refractory metals. The migration of these adatoms is most conveniently studied on closely packed faces, in particular, on the tungsten point—on the (110) and (112) faces. The surface of the tip of the point contains relatively large sections of closely packed faces with a perfect atomic structure. Atoms of refractory metals migrate along them with an appreciable rate at quite low temperatures, at which displacement of the surface atoms of the substrate is not yet observed. In addition, potential barriers that reflect the migrating adatoms exist on the boundaries of the closely–packed faces,[97] so that at sufficiently low temperatures the adatoms remain on these faces for a long time. In addition, on the smooth faces each adatom migrates along the entire surface, while on the channeled faces each adatom migrates only along the atomic channel in which it was initially adsorbed.

The experiment is performed as follows. One or several atoms settle on the surface of a selected face on the tip of a point cleaned by means of field desorption. Then cycles in which the point is heated for a definite time up to some temperature without an applied field and cooled to the working temperature of the field-ion microscope (at which the mobility of the adatoms is suppressed) followed by application of the working voltage and photographing of the field-ion image are repeated several times. Statistical analysis of the obtained collection of adatom positions, realized as a result of random walks, gives information about the migration characteristics of adatoms and about the interaction between them. The accuracy of this information is determined by the maximum possible number of observations, which depends strongly on the vacuum conditions in the experimental apparatus, since adsorption of even one molecule of the residual gas on the face studied can strongly affect the behavior of the adatoms under study. It is usually possible to perform up to 1000 observations.[98] This is sufficient for determining quite accurately the migrational characteristics of a separate adatom or the parameters of the interaction between adatoms at small ($\lesssim 10$ Å) distances. This number of observations is not sufficiently large to obtain reliable information about the interaction between adatoms at large distances taking into account the possible anisotropy of the interaction.[99]

For most adatom pairs (consisting of identical or different atoms) studied a deep minimum of the interaction energy is observed when the adatoms occupy neighboring adsorption centers in the same channel on the (112) face of W[100] or neighboring adsorption channels on the (110) face of W. The binding energy of the adatoms in this case reaches several tenths of an electron volt; several types of adatoms were studied on the W (110) face, and it was found that this energy depends on the type of adatom—the stronger the bond between the adatoms and the substrate the weaker is the interatomic bond in the pair (Fig. 4[101,102]). For rhenium adatoms repulsion is observed instead of attraction; this apparently can be explained by the fact that the dipole-dipole repulsion of the adatoms predominates. For two silicon adatoms the deepest minimum of the interaction energy (~ 0.05 eV) on the W (110) face is observed when the atoms occupy centers separated by a distance of 4.47 Å along the [110] direction.[99] In this case the silicon adatoms apparently interact through unsaturated[103] d-orbitals of the substrate with e_g symmetry.

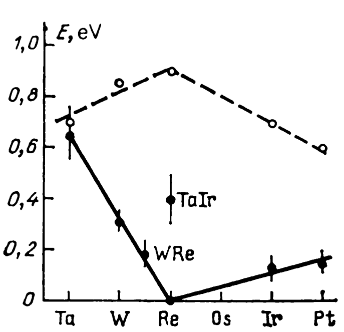


FIG 4 Change in the interaction energy of adatoms occupying neighboring adsorption centers on the (110) face of W in the series of $5d$-transition metals [102] WRe and TaIr denote, respectively, the tungsten-rhenium and tantalum-iridium interaction energy. The broken line shows the change in the activation energy of surface diffusion of single adatoms,[113] reflecting the change in the binding energy of adatoms with the substrate.

In polyatomic clusters on the W (110) face adatoms of refractory metals usually occupy neighboring adsorption centers and form two-dimensional islands.[102] Rhenium adatoms behave in the same manner, i.e., in polyatomic clusters the interaction of rhenium adatoms on neighboring adsorption centers differs from the interaction of adatoms in a pair. Platinum and iridium adatoms in polyatomic clusters form linear chains, oriented along the [111] direction on the surface. If the number of iridium adatoms exceeds the number that can fit into one chain, then the adatoms form several linear chains, spaced by quite large (> 10 Å) identical distances.[102] The ordering of the mutual arrangement of these chains is apparently determined by the long-range interaction of the iridium adatoms. Analogous effects are observed in chain structures of adatoms on the W (112) face and will be studied in detail below in Sec. 3.3. Silicon adatoms form on the W (110) face an ordered (2×1) structure in which the interatomic distance in the [100] direction equals 4.47 Å and corresponds to the deepest minimum of the interaction energy of two silicon adatoms, while in the [110] direction it equals 6.33 Å (the position of the second minimum of the interaction energy of two silicon adatoms),[99] i.e., in this case the structure of the adsorbed layer agrees well with the characteristics of the interaction of two silicon adatoms.

The study of the interaction between adatoms located in neighboring channels on the W (112) face gave interesting results. When such adatoms encounter one another they form a bound pair which migrates along the surface by means of alternate displacement of the adatoms by one lattice constant of the substrate along the channels. In the process the pair occupies three positions relative to the substrate atoms: the line connecting the adatoms is either perpendicular to the channels ("straight" pair) or it makes an angle of ± 58° with this direction ("oblique" pair, Fig. 5). In this simple situation the available observations are sufficient to obtain quite accurate information about the interatomic interaction in the pair. The results of four experiments were employed: 1) the study of the migration of solitary adatoms, giving information about the depth of the potential relief of the surface for one adatom; 2) the study of the migration of pairs, giving information about the change in the depth of the potential relief of the surface owing to the interaction of adatoms; 3) the study of the probability of observing "straight" and "oblique" pairs, enabling evaluation of the

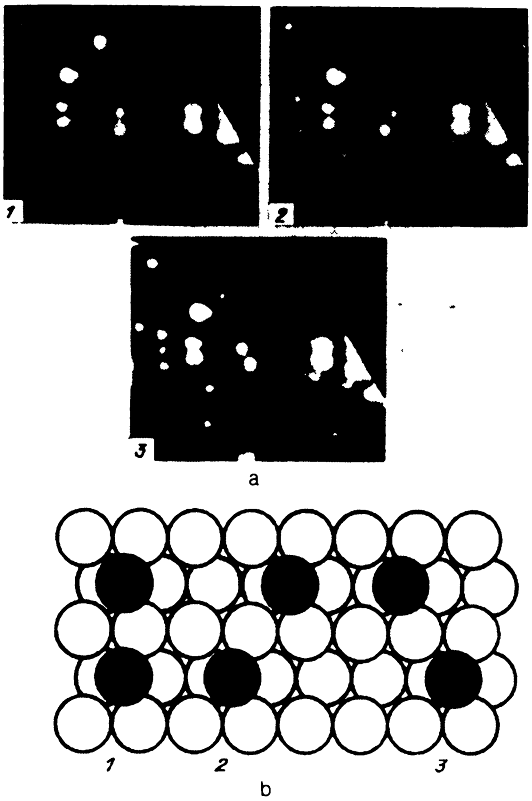


FIG. 5 Three orientations of a bound pair of adatoms in neighboring channels of the (112) face of W, relative to the atoms of the substrate. a) Field-ion images; b) models of the arrangement of adatoms on the substrate.

difference of their binding energies; and, 4) the study of the thermal decomposition of the pairs, giving information about the binding energy in an "oblique" pair. As a result the interaction energies in "straight" and "oblique" pairs as well as in the intermediate state, when one of the adatoms of a pair lies at the top of the potential barrier separating the "straight" and "oblique" pairs, were determined for tungsten[99] and rhenium[104,105] adatoms. In both cases the interaction energy of the adatoms depends nonmonotonically on the distance between them (Fig. 6). The interaction energy of tungsten and rhenium adatoms equal, in absolute magnitude, 0.1–0.3 eV. Only "straight" pairs are observed for iridium adatoms on the W (112) face.[105] No interaction was recorded, within the limits of accuracy of the experiments, between adatoms in neighboring channels of the W (112) face, shifted relative to one another by two or more lattice constants along the channels,[105] as well as between adatoms in neighboring channels of the W (321) face (the distance between the channels equaled 7.08 Å) or over one channel on the W (112) face.[106] It should also be noted that the formation of bound pairs of rhodium adatoms, located in neighboring channels, was also observed on the (110) face of rhodium, which has an fcc lattice.[107]

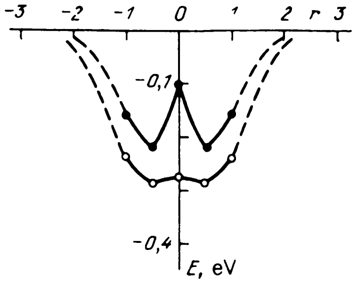


FIG 6. The interaction energy of two tungsten[99] (open circles) or rhenium[105] (dark circles) adatoms in neighboring channels on the (112) face of W as a function of their mutual displacement (in units of the lattice constant of the substrate) in the direction along the channels

The most reliable information about the interaction between adatoms at relatively large (of the order of 10 Å) distances on the W (110) face was obtained in Ref. 108, where the interaction between different adatoms was studied; in addition, the temperature of the substrate was chosen so that one adatom (W, Re) remained stationary while the other (Pd) migrated along the surface. Figure 7 shows the histogram obtained of the distances between W and Pd adatoms, showing that the interaction between the adatoms is of an oscillatory character. It should be noted, however, that the representation usually employed in practice for the data on the interaction between adatoms on the W (110) face in the form of the number of observed effects or the interaction energy as a function of the distance between the adatoms, ignoring the possible anisotropy of the interaction, is not entirely correct.

3.2. LEED studies. Smooth faces

For a fixed concentration of adatoms the structure of the adsorption film is determined by the characteristics of the interaction of the adatoms, the symmetry and depth of the potential relief of the substrate, and the temperature of the substrate. If the strongest interaction between the adatoms is the direct interaction, then dense two-dimensional (and three-dimensional in the case when the interaction en-

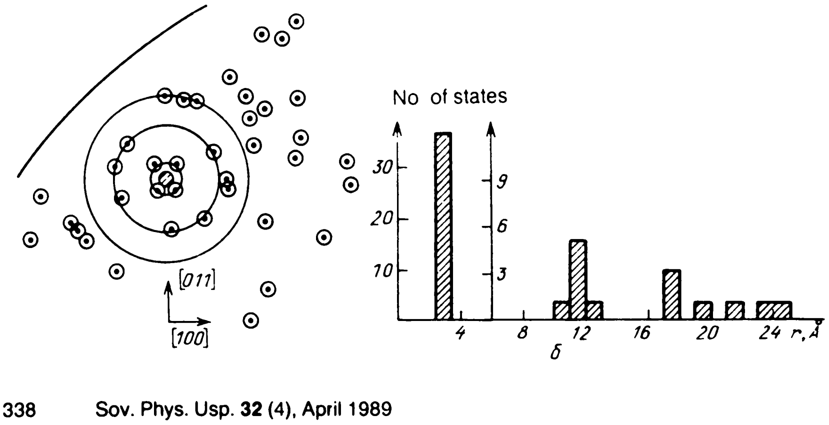


FIG. 7. Diffusion of palladium adatoms near a tungsten adatom on the W (110) face.[108] a) Distribution of locations at which a palladium adatom was observed during diffusion, b) histogram.

ergy between the adatoms themselves is greater than the interaction energy between the adatoms and the substrate) islands of adsorbate appear already with low coverage.[109-112] If the electrostatic and indirect interactions, decaying relatively slowly with distance, predominate in the interaction between adatoms, then as the coverage θ is increased a sequence of ordered, two-dimensional structures of adsorbed atoms is observed on the surface. The study of these structures (their symmetry and the characteristics of the thermal disordering) as well as the structure of the adsorbed film with intermediate coverage gives information about the interaction between adatoms. It is of special interest to prepare and study ordered structures with the lowest coverage possible, since this gives information about the interaction between adatoms at large distances; such is virtually inaccessiblely other experimental methods. The possibility of forming sparse structures depends strongly on the depth of the potential relief of the substrate, determining the mobility of the adatoms. Among all the energetically favorable structures only those in which the adatoms have adequate mobility for ordering at temperatures below the temperature of the order-disorder transition can be realized over real times. In addition, the substrate must be cooled to the lowest possible temperatures in order to realize experimentally the sparsest possible ordered structures in films exhibiting high mobility.

Examination of the migration of isolated adatoms in a field-ion microscope (see, for example, the review of Ref. 113) confirms the intuitive notion that closely packed faces have the shallowest potential relief: the (110) face of a bcc crystal, the (111) and (100) faces of an fcc crystal, as well as—in the direction along channels—the (112) face of a bcc crystal and the (110) face of an fcc crystal. In hcp crystals the "smoothest" faces should apparently be the (0001) and $(10\bar{1}0)$ faces (along channels). The depth of the potential relief should also depend on the character of the bond between an adatom and the substrate. Since a covalent bond is strongly localized the potential relief for adsorbates with such a bond should be deeper than for adsorbates with a predominately ionic bond. For metal adsorbates the depth of the potential relief of the substrates should apparently increase as the contribution of the covalent component to the adsorption bond increases, i.e., as one transfers from alkali to alkaline-earth and rare-earth adsorbates, while within the same group it should increase as the size of the adatoms decreases.

The adsorption bond between the closely-packed faces of refractory metals and alkali and alkaline-earth adatoms has the strongest polarizability, and correspondingly in these films the isotropic dipole-dipole repulsions of adatoms plays an important and often the main role. For low coverage ordered two-dimensional lattices of adatoms, in which the adatoms are situated at the maximum possible (for the given concentration and geometry of the arrangement of the potential wells on the surface) distances, are formed successively in these films.[114-123] A mathematical simulation (by the Monte Carlo method in the lattice-gas model) of an order-disorder transition in a sodium film on the W (110) face with relative coverage $\theta = 0.25$ was performed in Ref. 124, and it was shown that the ordered structure of the sodium film corresponds to the experimentally observed (2×2) structure,[114] while the dipole moment of the adatom, which must be introduced into the calculation in order that the computed and experimental temperature dependences of the intensity of the additional reflection should agree at this concentration to within 10% with the dipole moment of the sodium adatom, determined based on the formula (40) from the change in the work function of the surface.

The foregoing facts indicate that dipole-dipole repulsion is indeed the main type of interatomic interaction in films of alkali and alkaline-earth elements on the smooth faces of refractory metals with low coverage. However, a detailed comparison of the structure of films of the same adsorbates (Na, Sr, Ba) on the (110) faces of W and Mo, the atomic structure of whose surfaces is virtually identical, showed[122,123] that on these substrates with low coverage the adatoms form different sequences of ordered structures, i.e., a weak anisotropic interaction that depends on the nature of the substrate operates between the adatoms together with the dipole-dipole interaction, as a result of which certain quasihexagonal structures become preferable. It was proposed in Refs. 122 and 123 that this additional interaction of the adatoms is indirect.

The indirect interaction of adatoms on the smooth faces of refractory metals is more clearly manifested in films of rare-earth and actinide elements. Thus in lanthanum and thorium films on the (110) face of W[125,126] the growth of islands of commensurate structures, consisting of linear chains of adatoms oriented along the [110] direction, as in the case of the (2×1) silicon structure on the W (110) face studied above,[99] is observed already for low coverage. The mutual arrangement of the chains in these structures is quite complicated and changes with further packing of the films, but the chains themselves remain unchanged in virtually the entire region of submonolayer lanthanum and thorium coatings.

The adsorption bond between the surfaces of closely packed faces of refractory metals and hydrogen and oxygen adatoms is markedly covalent. Correspondingly the dipole-dipole interaction of the adatoms plays an insignificant role in such films, and the indirect interaction mechanism apparently plays the main role in the interatomic interaction. Because of the large depth of the potential relief of the substrates only several of the most dense structures of adsorbed films,[127-131] whose analysis indicates that the character of the interaction is strongly anisotropic,[132] is usually realized.

3.3 LEED studies. Channeled faces

3.3.1. Experimental results

Up to now the structure of adsorbed films has been studied in greatest detail for the channeled W (112), Mo (112), and Re (1010) faces. On all these faces the structure of the top atomic layer is virtually identical; the lattice constant a_1 in the direction across the channels equals 4.47 Å on tungsten, 4.45 Å on molybdenum, and 4.45 Å on rhenium, while the lattice constant a_2 in the direction along the channels equals 2.74 Å on tungsten, 2.73 Å on molybdenum, and 2.76 Å on rhenium. The existing information on the structure of submonolayer films of alkali, alkaline-earth, and rare-earth elements on these substrates is summarized in Fig. 8. The following structural features of the adsorbed films on channeled faces should be noted.

1. In many systems with low coverage the adatoms form linear chains, oriented perpendicular to the channels (Fig. 9).

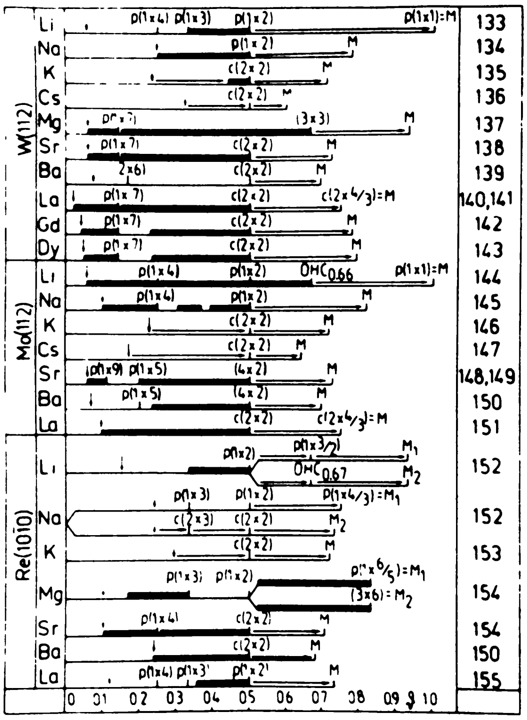


FIG. 8. Diagrams of structural transitions in films of electropositive elements on W (112), Mo (112), Re (1010) faces at 77 K (in Na and Cs films on the W (112) face at 300 K). The vertical arrows mark coatings for which additional reflections appear; the dark thick lines indicate regions of first-order phase transitions; the horizontal arrows mark regions of one-dimensional compression of adsorbed films. In the other regions of submonolayer coatings the films consist of statistical mixtures of cells. ONS denotes a one-dimensionally noncoherent structure; M denotes monolayer; θ is the relative coverage, equal to the ratio of the concentration of adatoms to the concentration of surface atoms of the substrate. The references are indicated on the right side of the figure.

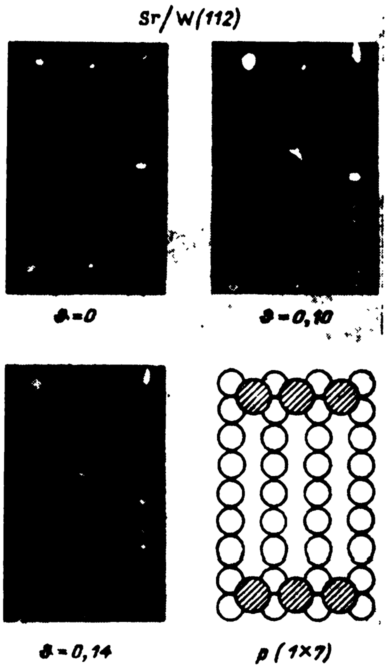


FIG. 9. Diffraction pictures of the system Sr/W (112) for different relative coverages θ and model of the p(1×7) lattice of strontium.[138]

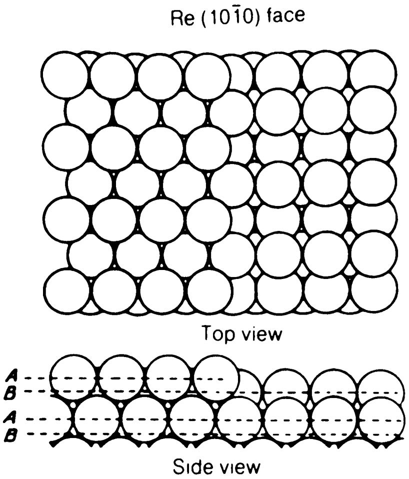


FIG. 10 Model of the structure of the surface of the (10$\bar{1}$0) face of rhenium

2. The sparsest structures consisting of linear chains of adatoms in most systems with low coverage grow in the form of islands on a background of even more sparse coatings. The reflections from these structures appear on diffraction pictures at concentrations much lower than stoichiometric and their brightness increases right up to the stoichiometric concentration (Fig. 9).

3. In regions with medium coatings first-order phase transitions are observed in many systems; in this case, islands with c(2×2) or p(1×2) structures with $\theta = 0.5$ grow most often.

4. In lithium, sodium, and magnesium films on the Re (10$\bar{1}$0) face two sequences of structural states are observed in some concentration ranges. This is apparently linked with the fact that the Re (10$\bar{1}$0) faces contain sections with different arrangement of atoms of a second layer relative to atoms of the first layer (Fig. 10) and these sections are separated by atomic steps. On these sections the atoms of the top layer have a different number of nearest neighbors and the depth of the atomic channels differs significantly (by a factor of two). The structure of the adsorbed films on these sections naturally can be different.

Detailed study of the structural features permits drawing definite conclusions regarding the interaction between atoms adsorbed on channeled faces.

3.3.2. Formation of linear chains of adatoms

In order for linear chains of adatoms to form under conditions of sparse coatings attractive forces must act between the adatoms in these chains. Since alkali, alkaline-earth, and rare-earth adsorbates are characterized by significant polarizability of the adsorption bond a quite strong dipole-dipole repulsion acts between the adatoms. In addition, the diameter of most adatoms (with the exception of Cs) is less than a_1, as a result of which the overlapping of the electronic shells of the adatoms, leading to the direct interaction, is small. Therefore the fact that chains form indicates that an indirect interaction stronger than the dipole-dipole repulsion is realized between the adatoms. From the fact that sodium adatoms form linear chains on one surface on the Re (10$\bar{1}$0) face and do not form on the other it may be concluded that the absolute energies of the dipole–dipole repulsion

TABLE I The starting heats of adsorption of an adatom q_0 and dipole moment p_0 as well as the presence of linear chains of adatoms with low coverage and the distance between them (in units of the lattice constant a_2), corresponding to minima of the interaction potential for electropositive adsorbates on channeled faces of W, Mo, and Re (1 debye = 10^{-18} CGSE = 0.394 a u)

Face	Adsorbate	q_0, eV	p_0, Debye	Presence of linear chains	N
W (112)	Li	2.8 [133]	1.7 [133]	Yes	2
	Na	2.55 [156]	1.9 [156]	Yes	2
	K	2.7 [135]	3.7 [135]	No	—
	Cs	3.15 [157]	4.0 [157]	No	—
	Mg	2.5 [137]	0.6 [137]	Yes	7
	Sr	3.6 [138]	3.7 [138]	Yes	7
	Ba	4.5 [139]	4.4 [139]	No	—
	La	5.7 [141]	2.5 [141]	Yes	7
	Gd	5.5 [142]	1.8 [142]	Yes	7
	Dy	4.7 [143]	1.6 [143]	Yes	7
Mo (112)	Li	2.65 [144]	1.4 [144]	Yes	4; 2
	Na	2.3 [145]	1.7 [145]	Yes	4; 2
	K	2.5 [146]	3.3 [146]	No	—
	Cs	2.8 [147]	3.6 [147]	No	—
	Sr	3.25 [149]	2.9 [149]	Yes	9; 5
	Ba	4.25 [150]	3.6 [150]	Yes	5
	La	5.85 [151]	1.8 [151]	No	—
Re $(10\bar{1}0)$	Li	2.95 [152]	1.7 [152]	Yes	2
	Na	2.65 [152]	1.8 [152]	Yes/No	—
	K	2.9 [153]	3.7 [153]	No	—
	Mg	2.7 [154]	1.5 [154]	Yes	3
	Sr	3.7 [154]	4.4 [154]	Yes	4
	Ba	4.8 [150]	5.1 [150]	No	—
	La	5.5 [155]	1.9 [155]	Yes	2

and indirect attraction of neighboring atoms in the chains in this system are close. This permits estimating the indirect-interaction energy of alkali adatoms:

$$E_{\rm ind}(a_1) \approx -2p_{\rm Na}^2 a_1^{-3} \approx -0.05 \text{ eV}.$$

The main reason that linear chains of adatoms do not form in some systems is that the dipole-dipole repulsion is too strong or, as for the system La/Mo (112), islands with a c(2×2) structure start to grow with low coverage.

Since W (112), Mo (112), and Re $(10\bar{1}0)$ faces have virtually identical surface geometry it may be assumed that the dipole-dipole interaction in the chains is the same on all three faces and the dipole moment of the adatom p is the same (see Table I). One can see from the table that linear chains of adatoms in films of alkaline-earth elements are formed with much larger starting dipole moments of the adatoms than in films of alkali elements. Thus potassium adatoms do not form linear chains on any of the substrates studied, while strontium adatoms form chains on all substrates, though the dipole moment of strontium on the Re $(10\bar{1}0)$ face (~4.4 debye) is significantly larger than the dipole moment of the potassium adatom on the Mo (112) face (~3.3 debye). From here it may be concluded that the indirect-interaction energy in the case of alkaline-earth adatoms is larger than in the case of alkali adatoms, and its magnitude can be estimated to be

$$E_{\rm ind}(a_1) \lesssim -2p_{\rm Sr}^2 a_1^{-3} \approx -0.3 \text{ eV}.$$

Aside from the indirect interaction the Friedel component of the electrostatic interaction $E_{\rm Friedel} \sim Q^2 \exp(-4k_{\rm F}a)$ (see Sec. 2.4) can lead to attraction between adatoms. Since the electronic shells of alkali ions with the same charge are close to the shells of inert gases while those of alkaline-earth ions with the same charge are close to the shells of alkali atoms the distance a between adatoms on the surface in the case of alkali adatoms can be less than in the case of alkaline-earth atoms. This is also indicated by the smaller width of the virtual levels of alkaline-earth adatoms as compared with alkali atoms. Therefore for the same dipole moment (as, for example, in the case of potassium and strontium on the W (112) face) alkali adatoms must have higher charges Q and smaller sizes a, i.e., the energy $E_{\rm Friedel}$ for alkali adatoms must be higher than for alkaline-earth adatoms. Since the opposite situation is observed experimentally it is obvious that the attraction between adatoms in chains is due precisely to the indirect mechanism of interaction of the adatoms.

The growth of islands of dense submonolayer coatings is more strongly manifested in films of alkaline- and rare-earth elements. This effect is also apparently due to the indirect interaction of adatoms.

3.3.3. Interaction between chains of adatoms

The growth of islands of the most sparse structures consisting of linear chains of adatoms indicates that it is energetically more favorable for chains to be arranged at the distance that is realized in a sparse structure, i.e., at this distance the interaction potential of the adatoms has a minimum. In some systems another minimum is observed experimentally in the interaction potential of the adatoms at shorter distances between the chains. Its existence is manifested in the fact that for coverages exceeding the stoichiometric coverage of a sparse structure one observes either the growth of islands with a more dense structure, consisting of linear chains of adatoms, or a transition from a sparse structure to a more dense structure (from the p(1 × 9) structure to the p(1 × 5) structure in strontium films on the Mo (112) face) by means of statistical mixing of the cells of these structures without formation of intermediate structures. The existence of two minima clearly indicates that the interaction energy of the chains oscillates as a function of the distance between them.

The positions of the minima of the interactions of chains of adatoms observed in different systems are given in Table I. One can see from the table that in films of alkaline and rare-earth elements the minima of the interaction potential of the chains of adatoms are observed at significantly larger distances between chains than in films of alkali elements. If this result is analyzed in the same way as is done for the formation of linear chains of adatoms, then it becomes obvious that the indirect mechanism of interaction also plays the main role in the interaction between linear chains of adatoms. The minima of the interaction potential of the chains are determined by the superposition of the indirect and electrostatic interaction mechanisms.

The data presented in Table I indicate that the position of the minima of the interaction potential of the chains for the same adsorbate shifts strongly from one substrate to another and at the same time remains virtually unchanged for different adsorbates on the same substrate. In the latter case the position of the minima differs by not more than one lattice constant of the substrate, and the largest distance is observed for adsorbates with a large dipole moment. Thus experiment confirms the theoretical conclusion that the electronic structure of the substrate plays the determining role in the indirect interaction of the adatoms.

We note that the Fermi surface of tungsten and molybdenum has flat sections in the [111] direction (along the channels). The presence of an adsorbed layer on the surface does not change the electronic structure of the volume states, but can, in principle, change substantially the energy (and correspondingly the form of the Fermi line) of the surface states owing both to a shift in the entire ESS band and a change in the symmetry of the surface (change in the surface Brillouin zone). If it is assumed that the contribution of ESS to the energy $E_{\rm ind}$ for the systems under study is large, the data presented in Table I can be interpreted either as indicating that in the case of quite sparse structures the effect of the adsorbed layer on the ESS is still relatively small or this effect is approximately the same for all adsorbates. A study of the interaction of separate adatoms, which for these adsorbates is impossible at the present time, or self-consistent calculations of adsorption systems by the method of Refs. 43–45 could resolve this question.

The formation of linear chains of adatoms in an oxygen film on the channeled (110) face of silver was observed in Ref. 221. However only repulsive forces act between these chains, and they increase monotonically as the distance between the chains decreases, so that as the oxygen concentration is increased the structures p(1 × 6), p(1 × 5), p(1 × 4), p(1 × 3), and p(1 × 2) are observed successively. This character of the interchain interaction in the system O/Ag (110) is probably attributable to the nearly spherical form of the Fermi surface of silver.

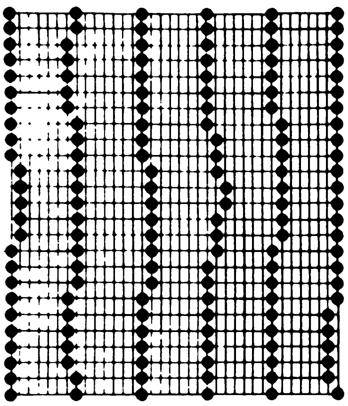


FIG 11 Schematic image of thermal excitations in a chain structure of an adsorbed layer.[158]

3.3.4. Thermal disordering of chain structures[158]

One of the most surprising properties of structures consisting of linear chains of adatoms is their high thermal stability. For any interaction mechanism the interaction energy of separate adatoms for the large distances between neighboring chains in such structures (up to nine lattice constants of the substrate) must be quite small. Nonetheless linear superstructures become disordered at temperatures of the order of 100 degrees. This feature of the behavior of linear superstructures is associated with the fact that in these structures there is a weak interaction between adatoms combined in strong linear chains. The thermal excitations in these structures are displaced lines of adatoms (Fig. 11). Under conditions of thermal excitation of these lines displacement of the first adatom from the chain is energetically most difficult—the energy required to break the chain $2\varepsilon_0$ ($\varepsilon_0 \sim E_{\rm int}(a_1)$) is expended on this process. Significantly less energy ε_1 ($\varepsilon_1 \sim E_{\rm int}({\rm Na}_2)$) is required to displace a neighboring or each subsequent adatom; this energy is associated with the change in the interaction of the displaced section of the line with neighboring chains per adatom in the line. The length of the displaced section increases until the total interaction energy of its constituent adatoms with adatoms from neighboring chains equals $k_{\rm B}T$, i.e., the average length of the displaced section $l \sim a_1 k_{\rm B} T/\varepsilon_1$. The average distance between the displaced sections $L \sim a_1 \exp(2\varepsilon_0/k_{\rm B}T)$ is quite large. The disordering of the films occurs at temperatures when $L \sim l_j$ from here we obtain the following condition for estimating the disordering temperature T_c

$$k_{\rm B}T_{\rm c} \sim \varepsilon_1 \exp\frac{2\varepsilon_0}{k_{\rm B}T_{\rm c}}.$$

A characteristic feature of this condition is that even for $\varepsilon_1 \ll \varepsilon_0$ the transition temperature T_c will be quite high.

In real adsorbed films two additional circumstances are added to this simple picture. First, the substrate has a potential relief in the direction along the channels and to displace an adatom in this direction it is also necessary to expend the migration energy. This fact is manifested experimentally in that there exists a temperature T_M below which ordering or disordering of the adsorbed film cannot occur over reasonable lengths of time. Second, the surface is not ideal—it contains atomic steps, impurity adatoms, etc. This restricts the length of the displaced section l—it cannot be longer than the average distance between nonuniformities on the surface l_N. These two restrictions together determine the minimum value of ε_1 for which ordering of the mutual arrangement of the chains is possible: $\varepsilon_{1\min} \sim a_1 k_B T_m / l_N$. This quantity is nonetheless significantly less than the values of the interatomic interaction energy observed by other methods, for example, with the help of a field-ion microscope.

Thus the specific nature of thermal excitations in structures consisting of linear chains of adatoms leads to a unique "intensification" of the weak interaction between adatoms in different chains. This fact makes chain structures unique objects for studying long-range interaction between adatoms.

4. EFFECT OF INTERATOMIC INTERACTION ON THE PROPERTIES OF ADSORPTION SYSTEMS

In the preceding section we studied the manifestation of different mechanisms of interaction between adatoms in the formation of ordered two-dimensional structures. In this section we shall briefly describe some examples demonstrating the effect of the interatomic interaction on other properties of clean surfaces and surfaces coated with adsorbed films.

4.1. Restructuring of an adsorbed layer

The theory predicts that in some systems changing the external conditions (for example, the applied field) can cause the adsorbed layer to be restructured with a change in symmetry. To determine the possibility of restructuring usually the phonon spectrum $\omega(q)$ is calculated for the nonrestructured structure of the interaction adatoms.[159,160] If for some two-dimensional wave vector q^* the condition $\omega(q^*) = 0$ is satisfied, then the force $F \sim \omega^2$ returning the system to a position of equilibrium vanishes and the system becomes unstable with respect to the wave vector q^*. As a result of this there should arise a new structure with the superperiod $a^* \approx 2\pi/q^*$ that in the general case is not commensurate with the period of the substrate, though it may be energetically more favorable than the commensurate structure. We note that aside from the gradual appearance, described above, of the instability, in some cases the instability can appear abruptly, if for some value q^* the frequency $\omega(q^*)$ becomes complex and $\mathrm{Re}\,\omega(q^*) > 0$.

The stability of structures decreases significantly for "soft" (easily "depolarizing") adatoms, i.e., adatoms having a narrow virtual electronic level ε_A near the Fermi surface ε_F. Then a small shift in ε_A, caused by the interaction between adatoms, displacement of the adatoms perpendicular to the surface, or an applied field, produces a large change in the occupation of the virtual level and, therefore, changes the interaction energy of the adatoms. For example, a lattice of "soft" dipoles becomes unstable, as their concentrations is increased, relative to displacements of the adatoms parallel to the surface,[161] though adatoms with permanent dipoles on a smooth substrate form a stable hexagonal lattice.[3]

If the adatoms are immobile (lattice-gas model), then a lattice of "soft" dipoles with sufficiently high polarizability becomes unstable relative to the formation of a c(2×2) structure (or more complicated structures) with a nonuniform charge distribution.[66] The energy of such a structure decreases owing to the decrease in the Coulomb repulsion of the dipoles proportional to the amplitude of charge alternation:

$$(Q + \Delta Q)(Q - \Delta Q) - Q^2 = -(\Delta Q)^2.$$

The stability of the structures also decreases if the possibility of displacement of adatoms perpendicular to the surface is taken into account; in this case charge alternation is accompanied by alternation of the distances between the adatom and the surface.[163,164] If the Coulomb repulsion of electrons on an adatom is taken into account, then restructuring can be accompanied by alternation of the local magnetic moments.[165,166] We note that the stability of structures was also studied taking into account the indirect[167,168] and direct[169] mechanisms of interaction as well as the role of band bending at the surface in the case of a semiconductor substrate.[170]

If the interaction between adatoms has a long-range Friedel component with a large amplitude, for example, when ESS crossing the Fermi level are present then $q^* = 2k_F$. It is important to note that in this case the spectrum of electronic states responsible for the appearance of Friedel oscillations should become "dielectrified" after restructuring, i.e., an energy gap separating the occupied and free electronic states should appear in it. Since the damping of Friedel oscillations with distance (14) increases as the temperature is raised, at some critical temperature T_c the restructuring of the adsorbed layer should vanish. This temperature-reversible phase transition is called a Peierls transition.

4.2. Reconstruction of the surface of a crystal

Since the surface atoms of a substrate do not differ in any fundamental way from chemisorbed foreign atoms the interaction between the atoms of the substrate in the surface layer differs from their interaction in the bulk. This is most strongly manifested in the reconstruction (i.e., restructuring with a lowering of the symmetry) of the surface layer of atoms. Many surfaces of metals and semiconductors are subject to reconstruction, which can be easily observed by the LEED method.

Among transition and noble metals surface reconstruction is most often observed for iridium, platinum, and gold. On the (100) face of these metals reconstruction encompasses the upper layer[171]—it acquires a nearly hexagonal structure, joining in a quite complicated manner with the lower-lying layers, and becomes slightly wavy (the displacement of the atoms from the plane ~0.4 Å).[172,173] The channeled (110) faces of iridium, platinum, and gold acquire a p(1×2) structure as a result of reconstruction.[174–178]

In bcc metals—tungsten, molybdenum, and chromium—the (100) face is reconstructed: reflections of a c(2×2) structure appear at temperatures below room temperature (the incommensurate structure c(2.2×2.2) arises on the Mo (100) face).[179–181] The model of reconstruction that agrees best with experiment is one in which the two sublattices of atoms of the top layer, having a c(2×2) structure, are displaced toward one another along one of the [11] directions until closely packed, zigzag-shaped chains of atoms are formed (Fig. 12).[182–186] Adsorption of small quantities of hydrogen intensifies reconstruction, but in the presence of a monolayer coating the adsorbed hydrogen restores the nonreconstructed structure of the top layer.

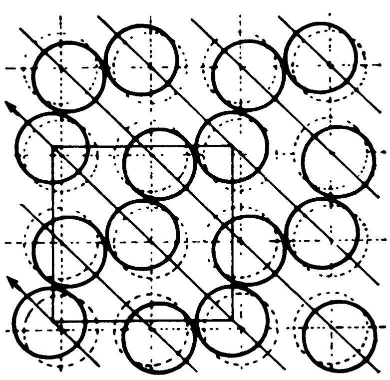


FIG. 12 Model of the reconstruction of the (100) face of W [179] The dashed line shows the positions of atoms in the top layer on the unreconstructed surface, the arrows mark the direction of displacement of atoms accompanying reconstruction

Accurate self-consistent calculations of the electronic structure of nonreconstructed (100) faces of tungsten[45] and molybdenum,[44] which agree well with the experimental study of the electronic structure of these faces with the help of UV photoelectron spectroscopy with angular resolution,[187,188] showed that these surfaces contain ESS with an electron density distribution of the d_{zx} and d_{zy} type, whose band the Fermi level crosses. As calculations[189,190] and experiment[191,192] show, on the reconstructed surfaces the bands of these ESS split and a gap forms near the Fermi level. In the process the energy of the electronic subsystem decreases. When a monolayer of hydrogen is adsorbed the ESS shift approximately by 1 eV downwards on the energy scale[193] and they turn out to be completely below the Fermi level. This can explain the fact that the monolayer coating of hydrogen restores the non-reconstructed structure of the top layer. One also does not observe reconstruction of the Ta (100) face,[194] on which the ESS bands do not cross the Fermi level.[195] These facts indicate that the reconstruction of the (100) faces of W and Mo occurs owing to the continuous interaction between the surface atoms through the ESS band. In addition, both experiment[222] and theory[223] show that the transition from a reconstructed to a non-reconstructed surface, occurring as the temperature is raised, is a phase transition of the order-disorder type (two-dimensional melting of the surface superstructure) and not a Peierls transition, as assumed previously.[196]

Reconstruction on the surfaces of semiconductors is encountered very often.[197] The most dramatic example is the reconstruction of the (7×7) (111) face of silicon. Since the Si(111) surface contains an ESS band, lying in the gap of the silicon crystal, it is natural to assume that reconstruction occurs by the Peierls mechanism, owing to indirect interaction of the Si atoms at the surface through the ESS band.[198] However, experiments performed with the help of high-resolution electron spectroscopy have not revealed an energy gap, which must exist in the case of Peierls reconstruction.[199,200] In the last few years tunneling microscopy has made it possible to determine the structure of the unit cell of the reconstructed face of Si: the (7×7) face contains 12 "humps" and one "well."[201] The nature of the "humps" has not been completely clarified (they could be adsorbed silicon atoms[201] or small pyramids consisting of four silicon atoms[202]); however, irrespective of the structure of the "humps" an indirect interaction through the ESS band should operate between them. Nakamura *et al.*[203] showed that the total interaction energy between the "humps" has a minimum precisely for the (7×7) structure, and in addition for an arrangement of the "humps" in a cell that is identical to the experimentally observed arrangement. In addition the temperature-induced transition $(7\times7)\rightarrow(1\times1)$ at $T_c\approx1150$ K can be explained by thermal disordering (two-dimensional melting) of the (7×7) structure. Moreover, as the period of the oscillations of the indirect interaction changes, which occurs when the occupation of the ESS band changes, the sequence of structures $(2\times2)\rightarrow(7\times7)\rightarrow(5\times5)$ gives a minimum of the interaction energy. The occupation of the ESS band can be changed by adsorbing on the surface electronegative atoms that give up their electrons to the substrate. Indeed, the sequence of structures $(2\times8)\rightarrow(7\times7)\rightarrow(5\times5)$ is observed experimentally for the system Sn–Ge (111) as the concentration of Sn adatoms is increased.

4.3. Thermal stability of adsorbed films

The ratio of different types of interactions of adatoms significantly affects the concentration dependences of the heat of adsorption. In systems in which the main type of interatomic interaction is dipole-dipole repulsion of adatoms the heat of adsorption drops sharply starting with the lowest coverage.[1] Indirect interaction of adatoms, which is most clearly manifested on channeled surfaces, compensates the dipole-dipole repulsion of the adatoms, as a result of which the coating-induced drop in the heat of adsorption decreases appreciably (Fig. 13).[139] This indicates that faces with a channeled atomic surface structure are promising as substrates in making highly efficient metal-film cathodes, in which the adsorbed film must have a high thermal stability with high coverage.

4.4. Work function of adsorption systems

The effect of the interaction of adatoms on the concentration dependences of the work function $\Phi(\theta)$ of adsorption systems is well known.[1,204] First of all, it consists of the

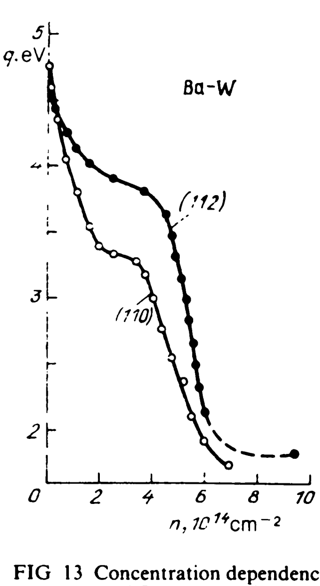


FIG 13 Concentration dependences of the heat of adsorption of barium on the (110)[117] and (112)[139] faces of [illegible]

deviation of the dependence $\Phi(\theta)$ from a linear dependence owing to depolarization effects (see Sec. 2). Second, for some coverage θ_c, close to a monolayer coating, the direct interaction between adatoms leads to "metallization" of the adsorbed film, i.e., to collectivization of the electrons of the adatoms.[205,206] For coatings with $\theta \geqslant \theta_c$ plasmon modes, characteristic for an adsorption film,[207–210] appear in the adsorption system and the work function starts to approach the value corresponding to part of a bulk sample of the adsorbate. It is interesting that in many systems the dependence $\Phi(\theta)$ has a minimum for $\theta \approx \theta_c$.[1,204]

4.5. Catalytic activity of the surface

A heterogeneous catalytic reaction can be conditionally divided into several stages: adsorption of the starting molecules, dissociation of these molecules into component parts, migration of separate atoms along the surface of the catalyzer prior to formation of new molecules, and desorption of the reaction products. It is obvious that the interaction between adsorbed particles plays the main role in at least three stages—dissociation, migration, and association. Therefore in the light of the foregoing discussion the catalytic activity of the surface should be determined by the surface density of electron states near the Fermi level and by local values of the electrostatic potential near adsorbed molecules.

The characteristics of the surface determining its catalytic activity can be controlled with the help of both doping of the bulk of the catalyzer and, even more efficiently, by doping of the surface. Surface doping with small quantities of alkali-metal atoms in order to increase the catalytic activity for certain reactions is called promotion and has been employed for a long time in commercial heterogeneous catalysis.[211] The action of the promotors is apparently due both to the shift of the ESS band owing to the flow of electrons from the adatoms into the substrate and the shift in the levels of the reagent molecules owing to the electrostatic potential of the positively charged alkali adatoms.[212,213]

We note that usually the main effect of the catalyzer consists of decreasing the dissociation energy (and, therefore, increasing the rate of dissociation) of the starting molecules (H_2, O_2, N_2, etc.) accompanying their adsorption on the surface of the catalyzer.[214] The mechanism of this effect was studied in detail in Sec. 2.

The mechanism of passivation ("poisoning") of a catalyzer accompanying adsorption of carbon has recently been studied in detail for the example of the dissociation of alkali-halide compounds on the surface of metals of the platinum group. It turned out that owing to the strong direct interaction between carbon adatoms these atoms collect in islands with a graphite-like structure.[112] The adsorbed film, bound with the substrate only by weak van-der-Walls forces,[215] prevents the reagents from reaching the surface of the catalyzer.

5. CONCLUSIONS

Thus the following interactions play the main role in the interaction between chemisorbed particles: 1) electrostatic interaction, whose main component is Coulomb or dipole-dipole repulsion of the particles; 2) direct interaction, which is significant only for nearly monolayer coatings; and, 3) indirect interaction, which has a long-range oscillatory character, determined by the electronic structure of the substrate.

For alkali adatoms characterized by highly polar bonds the electrostatic interaction plays the main role. The role of the indirect interaction increases from alkali to alkaline-earth, rare-earth, and transition adatoms, and for adsorption of atoms of simple gases it plays the main role. The role of the indirect interaction also increases as the surface changes from smooth to channeled or open on an atomic scale.

The interaction between adatoms differs from the interaction between impurity atoms in the volume of a solid because of the following: 1) the presence of surface quasiparticles (plasmons, ESS, etc.); 2) asymmetry of screening effects; and, 3) the difference in the spectral density of quasiparticles on the surface and in the volume. In addition, on the surface the activation energy of diffuse is lower, as a result of which the interaction is more easily manifested in the mutual arrangement of the adsorbed particles. Finally, the fact that it is easier to observe experimentally adatoms on the surface than impurity atoms in the volume of a solid is also important.

A number of questions associated with the interaction of adsorbed particles have not yet been adequately studied. These include the interaction of adatoms of different elements and the interaction of adsorbed particles with steps and other surface defects. There is no final answer to the question of whether or not surface electronic states play the main role in the indirect interaction of adsorbed particles and in surface reconstruction. We note that surface reconstruction is of great practical value, since the rate of surface diffusion on reconstructed and non-reconstructed surfaces can differ by several orders of magnitude.[216] It is also well known that after the surface of a Pd or Pt film adsorbed on niobium or tantalum is reconstructed the rate of absorption of hydrogen is sharply higher.[217,218]

On the other hand, surface reconstruction, dissolution of adsorbate in the substrate, and chemical reactions of the adsorbate with the substrate make the structure of adsorbed films much more complicated and make it difficult to separate effects associated with the interaction between adatoms. This is especially characteristic of semiconductor surfaces, as a result of which the interaction between adatoms on them has thus far not been studied in detail experimentally.

Finally, the question of the dynamic interaction between moving (oscillating) adatoms, when effects due to nonadiabaticity and delay in the response of the solid are manifested is important.[219,220]

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[1)] The terms "direct (indirect) exchange electronic" interaction are sometimes employed

[2)] The term "broken bonds" is sometimes employed for the surfaces of covalent semiconductors

[3)] A two-dimensional lattice of adatoms on a smooth substrate can have only quasi-long-range order[162]

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