Structural and electronic alterations in an adsorbed layer

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The effect is considered of the electron-phonon interaction on structural and electronic alterations of the ground state of a system of adsorbed atoms on the surface of a metal. It is shown that allowance for this interaction leads to a qualitative change of the character of the alteration, with doubling of the period of the two-dimensional lattice of the adsorbed atoms if the electron-phonon interaction is strong enough. These transitions are accompanied by both jumplike and smooth changes of the effective charge of the adsorbed atoms and of their equilibrium positions, and can occur also at arbitrarily small interaction between the adsorbed atoms. It is also shown that the structure with the doubled period can be unstable to formation of a long-wave superstructure that is not commensurate with the period of the adsorbed-atom lattice. The possibility of using the employed model to explain the experimentally observed alterations on clean surfaces of transition models is discussed.

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§1. INTRODUCTION

The structures of films adsorbed on metal surfaces differ greatly from one another. Both ordered and disordered phases are observed, as well as transitions between the different phases with changing temperature and with changing degree of coating. These transitions can be accompanied by alterations of the electronic states of adsorbed atoms (see Ref. 1 for a review). Phase transitions with changing temperature are observed also on clean metal surfaces. In particular, the method of diffraction of slow electrons has revealed a doubling of the period of the lattice surfaces on the (100) face of tungsten,[2,3] while on the electron diffraction patterns of the quartet of the (100) face of molybdenum there were observed closely lying points near the 1/2, 1/2 positions; this corresponds to a doubling of the period of the initial two-dimensional lattice with superposition of a superstructure having a large period.

Many theoretical studies were made of the structure and of the electronic states of adsorbed films on metal surfaces. It was demonstrated[4,5] that a homogeneous electronic state in which all the adsorbed atoms have the same charge can be altered into a state in which the charge changes from adsorbed atom to adsorbed atom as a result of their interaction with one another. The energy relations between the different films structure were considered also on the basis of the pair interaction of the adsorbed atoms with one another at a fixed electronic state (see Ref. 1 for a review of these studies). We make special mention of Ref. 5, where condensation of two-dimensional films was investigated, with allowance for the change of the electronic states of the adsorbed atoms (depolarization) with increasing density of the coating.

The purpose of the present paper was to investigate the phase transitions in an adsorbed layer, which lead to alteration of both the electronic state and of the structure of the surface layer. We shall consider transitions corresponding to small displacements of the equilibrium positions of the adsorbed atoms. The alteration is the result of simultaneous account of both the interaction of the adsorbed atoms with one another and of the electron-phonon interaction.

To clarify the role of the electron-phonon interaction, we consider in § 2 a simple model of one adsorbed atom on the surface of a metal. We show that the electron-phonon interaction makes possible transitions in which the equilibrium position of the adsorbed atom and its effective charge change jumpwise.

In § 3 we consider a two-dimensional lattice of adsorbed atoms that interact with one another. It is shown that the initial state may be unstable to doubling of the period of the two-dimensional lattice of the adsorbed atoms. The transitions to the new state can be of either first order (jumpwise) or of second order (smooth) with respect to the parameters (the temperature T is taken equal to zero).

In § 4 is investigated the stability of the phase with the doubled period. It is shown that instability to the formation of a long-wave superstructure appears in a certain region of the parameters and is accompanied by the appearance of a soft mode; the period of the superstructure need not necessarily commensurate with the period of the initial two-dimensional lattice of the adsorbed atoms. We note that this situation is reminiscent of the picture observed on a clean (100) face of Mo. The last section discusses therefore the possibility of using the model considered in the paper to describe clean surfaces of transition metals.

§ 2. STATE OF ISOLATED ADSORBED ATOM ON THE SURFACE OF A METAL

We examine the effects resulting from allowance for the dependence of the charge of the atoms on their displacements, using as an example a simple model with one atom on the surface of the metal. This example explains the qualitative features of the structural and electronic alterations in the adsorbed layer. In fact, assume that the level ε of some adsorbed atom in an equilibrium position lies higher than the Fermi level. Then the level is empty in the ground state. We now produce an excitation and transport one electron to this level.

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The change in the charge of the adsorbed atom changes the polarization of the metal and the force of interaction between the atom and the polarization it produces. This leads in turn to a shift of the equilibrium position of the atom, so that the level rises by an amount $\Delta\varepsilon$. If the level was initially close enough to the Fermi level ε_F, then the displacement $\Delta\varepsilon$ can move it to a position lower than ε_F and it should be filled in the ground state. Two equilibrium positions of the adsorbed atom are then possible, and correspond to its different charges, while the difference $\mathscr{E}_1 - \mathscr{E}_2$ between these states depends on the parameter ε. If ε is changed in one way or another, then at a certain value of this parameter, corresponding to $\mathscr{E}_1 - \mathscr{E}_2 = 0$, an alteration of the ground state, due to the jumplike change of the equilibrium position and of the charge of the adsorbed atom, will be observed.

For a quantitative description of the system in question we shall use Anderson's Hamiltonian,[8] which is extensively employed in investigations of the adsorbed state,[1,7] and include in it the dependence of the energy of the electron localized on the adsorbed-atom level on the small displacement of the adsorbed atom in a direction perpendicular to the metal surface, as well as the oscillation energy of the adsorbed atom. Assuming the repulsion energy $U_{\uparrow\downarrow}$ of two electrons with opposite spins, at the level of the adsorbed atom to be the largest energy quantity of the problem, we exclude from consideration states with two electrons on one level; this is equivalent to inclusion of operators with only one spin direction in the Hamiltonian, and exclusion of the term $U_{\uparrow\downarrow}\hat{n}_\uparrow\hat{n}_\downarrow$ from Anderson's Hamiltonian. This approach is obvious and has already been used in similar problems.

Taking the foregoing into account we express the Hamiltonian in the form

$$\hat{H} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}\hat{n}_{\mathbf{k}} + (\varepsilon(q_0) + \gamma(q - q_0))(\hat{n} - n_0) + g\sum_{\mathbf{k}}(c_{\mathbf{k}}^{+}a + a^{+}c_{\mathbf{k}}) + (M\omega_0^2/2)(q - q_0)^2 + (M/2)\dot{q}^2, \tag{1}$$

where $c_{\mathbf{k}}^{+}$ and a^{+} are the respective operators of creation of an electon in a metal with momentum **k** and an electron localized on the adsorbed atom; $\hat{n}_{\mathbf{k}} = c_{\mathbf{k}}^{+}c_{\mathbf{k}}$, $\hat{n} = a^{+}a$, g is the hybridization constant; M is the mass of the adsorbed atom; q_0 is the equilibrium position of the adsorbed atom with a level occupation number n_0; ω_0 is the frequency of its vibrations about the equilibrium point at fixed n_0.

Assuming that the period of the vibrations of the adsorbed atom is large compared with the characteristic time of variation of the occupation number of the level, which is determined by its width Γ, we use, just as in Ref. 9, the adiabatic approximation. Within the framework of this approximation it is easy to obtain from (1) the average occupation number of the level

$$n = \pi^{-1}\operatorname{arcctg}\frac{\varepsilon(q_0) + \gamma(q - q_0)}{\Gamma}, \tag{2}$$

where $\Gamma = \pi g^2 N(0)$, $N(0)$ is the density of states on the Fermi level. The value of q at the equilibrium point must be determined from the adiabatic condition $\partial\langle\hat{H}(q)\rangle/\partial q = 0$. Using the known theorem of quantum mechanics, we have

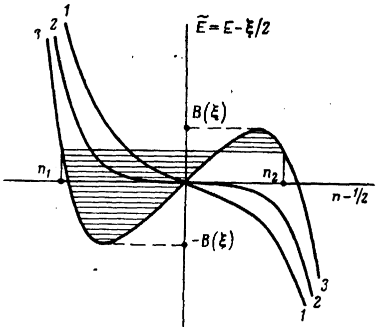

FIG. 1. Occupation number vs the position of the adsorbed-atom level: $1 - \xi < \pi$, $2 - \xi = \pi$, $3 - \xi > \pi$. The difference between the energies of states with occupation numbers n_1 and n_2 is proportional to the difference between the areas of the shaded sections.

$$\frac{\partial\langle\hat{H}(q)\rangle}{\partial q} = \left\langle\frac{\partial\hat{H}(q)}{\partial q}\right\rangle = M\omega_0^2(q - q_0) + \gamma(n - n_0), \tag{3}$$

whence

$$q - q_0 = -(\gamma/M\omega_0^2)(n - n_0). \tag{4}$$

Substituting (4) in (2) we obtain an equation for the determination of the equilibrium value of n:

$$\operatorname{ctg}\pi n = E - \xi n, \tag{5}$$

where

$$\xi = \gamma^2/M\omega_0^2\Gamma, \qquad E = \varepsilon(q_0)/\Gamma + \xi n_0.$$

It is convenient to investigate Eq. (3) by examining the dependence of $E - \xi/2$ on $n - 1/2$ (see Fig. 1). It is easily seen that at $\xi < \pi$ there is only one solution for n at a given E (one equilibrium position). At $\xi > \pi$ there are three such solutions. To assess the stability of the obtained solutions we note that (1) leads to

$$\frac{\partial\langle\hat{H}\rangle}{\partial\varepsilon} = \left\langle\frac{\partial\hat{H}}{\partial\varepsilon}\right\rangle = n(\varepsilon) - n_0. \tag{6}$$

This equation enables to compare the energies of the obtained solutions over the areas bounded by the line $E = \mathrm{const}$ and the curve of Fig. 1, and is the analog of Maxwell's rule for the transitions in question. It is easy to show also that the criterion for the stability of the equilibrium position, $\partial^2\langle\hat{H}(q)\rangle/\partial q^2 > 0$, is equivalent to $\partial n/\partial E < 0$, which in turn is the analog of the thermodynamic inequality $(\partial p/\partial v)_T < 0$. We can thus conclude that at $\xi > \pi$ and

$$|E - \xi/2| > \frac{\xi}{\pi}\arccos(\pi/\xi)^{1/2} - (\xi/\pi - 1)^{1/2} \equiv B(\xi)$$

there is one stable equilibrium position of the adsorbed atom. At $|E - \xi/2| < B(\xi)$ there are two stable positions corresponding to the minimal and maximal n at a given E. If $E > \xi/2$, then the lowest energy is possessed by the state with the minimal n. At $E = \xi/2$ the energies of both states become comparable, and the ground state is altered by the jumplike change of the occupation number and of the equilibrium position of the adsorbed atom.

We estimate now the value of ξ. We assume that the term $\gamma q\hat{n}$ in (1) appears when the electrostatic image energy is expanded in powers of the displacement. Then $\gamma \sim e^2/4R_0^2$, where R_0 is the distance between the adsorbed atom and the metal, putting $M \sim 10^5 m_e, R_0 \sim 1$ Å, $\omega_0 \sim 3 \cdot 10^{-2}$ eV, we have

$$\xi = (e^2/4R_0^2)^2 (M\omega_0^2\Gamma)^{-1} \sim 1 \text{ eV}/\Gamma$$

The same estimate is obtained if we start from the volume constants of the electron-phonon interaction $\xi \sim \lambda/N(0)\Gamma$, where λ is the dimensionless constant of the electron-phonon interaction ($\lambda \sim 0.3$). Taking the characteristic value of the state density for $W, N(0) \sim 10$ states/atom · Ry, we also obtain $\xi \sim 1$ eV/Γ. Since Γ can be of the order of tenths of an electron volt,[10] at least for levels with nonzero angular momentum, the inequality $\xi \gtrsim \pi$ is perfectly attainable, so that the aforementioned transition can occur also under real conditions.

We note that all the results described above hold true if it is assumed that $q - q_0$ is small. This is always the case of the parameter $\gamma/M\omega_0^2$ is small. Otherwise it must be taken into account that the displacement of the equilibrium position as a result of the transition considered above is $\Delta q = -(\gamma/M\omega_0^2)(n_1 - n_2)$, where $n_1 - n_2$ is the change of the occupation number of the level in the course of the transition. This is a small quantity when the constant ξ is close to its critical value $\xi_{cr} = \pi$. Therefore, when considering the transition, by choosing n_0 close to n_1 and n_2, we do not leave in fact the region where the expansion in $q - q_0$ is valid, provided only that the constant ξ is close enough to ξ_{cr}.

We note in conclusion that the hybridization constant g in (1) also depends on q. In the spirit of the adiabatic approximation, we should have written $\Gamma(q) = \Gamma(q_0)[1 + \alpha(q - q_0)]$ in (2). But if the change of the equilibrium position in the transition is $\Delta q \ll \Lambda$, where Λ is the characteristic length over which $\Gamma(q)$ changes, then allowance for the $\Gamma(q)$ dependence leads only to insignificant corrections.

§3. TRANSITION WITH DOUBLING OF THE PERIOD IN A TWO-DIMENSIONAL LATTICE OF ADSORBED ATOMS

We consider now a lattice of adsorbed atoms that interact with one another. We generalize for this purpose the Hamiltonian (1), and take into consideration the possibility of localization of the electrons on levels of different adsorbed atoms and an interaction between the adsorbed atoms in the form

$$\frac{1}{2}\sum_{i,j\neq i} U_{ij}(z/e - \hat{n}_i)(z/e - \hat{n}_j),$$

where z is the charge of the ion of the adsorbed atom. This interaction contains the energy $1/2\Sigma(z/e)\sum U_{ij}$, of the ionic core, which we shall omit from the expression for the Hamiltonian, as well as the change $-(z/e)\sum U_{ij}\hat{n}_j$, of the energy ε of the electron localized on the adsorbed atom, which we shall assume to be taken into account in ε. The energy ε defined in this manner take into account the effects of the depolarization of the adsorbed atoms and depends on the degree of coating.

We shall take into account below only one oscillation mode, corresponding to adsorbed-atom motion in a direction normal to the surface. Allowance for other vibrational modes, including both the motion of the adsorbed atoms in the adsorption plane and the vibration of the substrate ions leads only to a renormalization of the constants ξ and U_{ij} in the final result, as will be shown in § 5, and does not change substantially the conclusions of § § 3 and 4. Thus, the model Hamiltonian of the system of interacting adsorbed atom takes the form

$$\hat{H} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}} + \sum_j (\varepsilon + \gamma q_j)(\hat{n}_j - n_0) + g\sum_{\mathbf{k},j} [c_{\mathbf{k}}^+ a_j \exp(i\mathbf{k}\mathbf{R}_j) + \text{h.c.}]$$
$$+ \frac{M\omega_0^2}{2}\sum_j q_j^2 + \frac{M}{2}\sum_j \dot{q}_j^2 + \frac{1}{2}\sum_{i,j\neq i} U_{ij}\hat{n}_i\hat{n}_j. \qquad (7)$$

It is assumed that q is reckoned from a point such that the expansion in terms of q in (7) is valid in the transition region of interest to us. A similar Hamiltonian without allowance for the electron-phonon interaction was considered in connection with the problem of electronic alterations in an ordered layer of adsorbed atoms.[5] It may seem that allowance for this interaction can only cause the phonon subsystem to adjust itself to the electronic transition considered in Ref. 5, and as a result the smooth change of the occupation numbers in the course of this electronic transition, into a structure with double the period, will be accompanied by a smooth displacement of the equilibrium positions of the adsorbed atoms. Actually, however, the electron-phonon interaction leads to a number of new qualitative singularities.

In fact, it is clear that at sufficiently large ξ there should appear symptoms of the transitions considered in the preceding section. In particular, if the interaction between the adsorbed atoms is weak, a transition should take place in a narrow interval of ε, which is determined by the magnitude of this interaction, and should result in a change of the equilibrium positions and in the occupation numbers; this change should be the same for all the adsorbed atoms. It will be shown below that in the case when the adsorbed atoms are ordered on the surface of the metal, this transition goes through an intermediate phase analogous to that considered in Ref. 5, having a period twice as large as that of the initial adsorbed-atom lattice. Singularities appear also when the transition with the doubled period are considered. In contrast to the result of Ref. 5, where the indicated transition took place at a large value $\sum_j U_{ij} \equiv U \gtrsim \Gamma$, in our case it can occur also at an arbitrarily weak interaction between the adsorbed atoms, despite the fact that this interaction is in essence the cause of the transition into a state, with a charge that varies from atom to atom. In fact let $\xi > \xi_{cr}$ and assume that two equilibrium positions, corresponding to different occupation numbers, are possible for each of the adsorbed atoms if there is no interaction between them. By choosing the parameters, we can make the energy difference between these states arbitrarily small. Consequently, the energy of the phase with alternating n and q can differ little from the energy of a phase in which all adsorbed atoms have the same n and q. If we now take into account the repulsion interaction between the atoms and recognize that, as shown in Refs. 4 and 5, that this interaction contributes to the onset of structures with alternating charges of the adsorbed atoms, then it is clear that even a small U suffices to stabilize these structures.

We obtain now equations for the average occupation numbers n_j of the adsorbed atoms. We shall assume here, as before, that the displacement Δq is a slow variable. This adiabatic approximation is valid if $\xi\omega_0/\Gamma \ll 1$. The two-particle interaction $\sum U_{ij}\hat{n}_i\hat{n}_j$ will be considered in the Hartree-Fock approximation, which is valid if $U \ll \Gamma$ (see Ref. 1). Thus, we confine ourselves to consideration of two-dimensional lattices with sufficiently large distances between neighboring adsorbed atoms. Finally, we neglect the off-diagonal elements of the Green's function $G_{ij} = -i\langle Ta_i(t)a_j^+(t')\rangle$, which result from hybridization of the states of the localized and free electrons. This approximation was used also in Ref. 5. Strictly speaking, the contribution of the off-diagonal elements to the self-energy parts of the functions G_{ii}, which determine the occupation numbers n_i, is small compared with to the contribution U_{ij} if $k_F a \ll e^2/k_F\Gamma$, where a is the adsorbed-atom lattice constant. However, the equations we obtain below for the occupation numbers near the transition point are quite general in form. If a is large enough, when $|G_{ij}| \ll |G_{ii}| (i \neq j)$, allowance for the off-diagonal elements of the Green's function reduces to adding to U_{ij} the indirect interaction W_{ij}^{indir} considered in Ref. 11.

Taking the foregoing assumptions into account, we readily obtain for the diagonal elements G_{jj} the expression

$$G_{jj}^{-1}=\omega-E_j+i\Gamma\,\mathrm{sign}\,\omega, \quad E_j=\varepsilon+\gamma q_j+\sum_{i\neq j} U_{ij}n_i, \tag{8}$$

whence

$$n_j=\pi^{-1}\,\mathrm{arcctg}\,\frac{E_j}{\Gamma}. \tag{9}$$

After obtaining the equilibrium values of q_j from the adiabatic condition

$$\frac{\partial\langle \hat{H}\rangle}{\partial q_j}=\left\langle\frac{\partial \hat{H}}{\partial q_j}\right\rangle=\gamma(n_j-n_0)+M\omega_0^2 q_j=0 \tag{10}$$

and substituting them in (8) and (9), we get

$$\mathrm{ctg}\,\pi n_i=E-\xi n_i+\sum_{j\neq i}\tilde{U}_{ij}n_j, \tag{11}$$

where

$$E=\varepsilon/\Gamma+\xi n_0, \quad \xi=\gamma^2/M\omega_0^2\Gamma, \quad \tilde{U}_{ij}=U_{ij}/\Gamma.$$

At $\xi = 0$, Eq. (11) agrees with that obtained in Ref. 5. The connection between the occupation numbers and the equilibrium positions of the adsorbed atoms is given by relation (10).

Equations (11) admit of solutions with constant n_j and correspondingly constant q_j (structure I), as well as of different solutions with values of n_j and q_j that vary from point to point. When the parameters E, ξ, and U change, the structure I may turn out to be energywise unprofitable, and an alteration takes place into a state corresponding to other solutions of (11). It will be shown below that as a result of such an alteration the values of n_j and q_j can vary either smoothly or jumpwise. According to Ref. 5, a smooth alteration of structure I can terminate only in a structure with two adsorbed atoms in a unit cell (structure II with $n_j = n_1(q_j = q_1)$ or $n_j = n_2(q_j = q_2)$, depending on adsorbed-atom sublattice to which j belongs), if the minimal value of the function $U(\mathbf{k})$ (the Fourier transform of U_{ij}) is reached on the boundary of the Brillouin zone, a condition that can be ensured, for example, by monotonicity of $U_{ij} = U(|\mathbf{R}_i - \mathbf{R}_j|)$. The quantity U_{ij} is the Coulomb interaction of two charges over the surface of a metal, with allowance for the screening by the electrons of the metal. At large distances $k_F|\mathbf{R}_i - \mathbf{R}_j| \gg 1$ it takes the form

$$U(r)=\frac{e^2d^2}{r^3}+C\frac{\cos 2k_F r}{r^3}, \tag{12}$$

where the first term is the dipole-dipole interaction and the second is the result of allowance for the Friedel oscillations of the electron density.[1] The second term in (12) was obtained under the assumption that the temperature $T = 0$, the electron mean free path $\lambda = \infty$, and the Fermi surface of the substrate metal is spherical. Actually this term and its dependence on $r = |\mathbf{R}_i - \mathbf{R}_j|$ are strongly influenced by T, λ, and the shape of the Fermi surface. In principle, allowance for the indirect interaction of the adsorbed atoms via the substrate (the second term in (12), as well as W_{ij}^{indir}, Ref. 11) can cause the minimal value of $U(\mathbf{k}) + W^{\text{indir}}(\mathbf{k})$ to be reached at $k = k_0$ inside the Brillouin zone, meaning instability of structure I to a smooth alteration into a state where $n_j \sim \exp(i\mathbf{k}_0\mathbf{R}_j)$. We shall disregard hereafter this possibility and will be interested in transitions from I into II.

In this case we get from (11)

$$\begin{aligned}\mathrm{ctg}\,\pi n_1&=E-\xi n_1+\tilde{U}a_0n_1+\tilde{U}b_0n_2,\\ \mathrm{ctg}\,\pi n_2&=E-\xi n_2+\tilde{U}a_0n_2+\tilde{U}b_0n_1,\end{aligned} \tag{13}$$

where $\tilde{U}a_0 = \sum_i \tilde{U}_{ij}$ (i and j belong to the same sublattice, $\tilde{U}b_0 = \sum_i \tilde{U}_{ij}$ (i and j belong to different sublattices).

At small U, the most interesting region in which alterations are observed is the region $|\xi - \pi| \sim \tilde{U}$, $(n_{1,2} - 1/2)^2 \sim \tilde{U}$.1) Expanding the left-hand sides of the equations in (13) in powers of $\delta n_{1,2} = n_{1,2} - 1/2$ up to the cubic terms, we investigate the equations for δn_1 and δn_2. At $\xi - \tilde{U}a_0 - \pi < -\tilde{U}b_0$, Eq. (13) has only solutions with $n_1 = n_2$. In the region $-\tilde{U}b_0 < \xi - \tilde{U}a_0 - \pi < -2/3\tilde{U}b_0$, the dependence of $E - \xi/2 + \tilde{U}(b_0 + a_0)/2$ on $\delta n_1 + \delta n_2$ is shown in Fig. 2a. It is important that in this region the curve of II is monotonic. Therefore on the section $|\tilde{E}| > \tilde{E}_0(\xi, \tilde{U})$ there is one solution of (13) with $n_1 = n_2$, while on the section $|\tilde{E}| < \tilde{E}_0(\xi, \tilde{U})$ there are two solutions corresponding to structures I and II. It is easy to show, in analogy with the case for a single adsorbed atom, that the energy difference between states having the same $\tilde{E}$ can be calculated from the areas bounded by the curves I and II and $\tilde{E} = \text{const}$, recognizing that at the points of intersection of curves I and II at $|\tilde{E}| = \tilde{E}_0$ the solutions of (13) corresponding to curves I and II coincide. Thus, it is seen directly from Fig. 2 that at $|\tilde{E}| < \tilde{E}_0$ the lowest energy will be possessed by the solution corresponding to structure II. The transition from structure I to structure II with changing $\tilde{E}$ is smooth.

Curves I and II for $\xi - \tilde{U}a_0 - \pi > -2/3\tilde{U}b_0$ are shown in Fig. 2b. In this case, at $|\tilde{E}| > \tilde{E}_1$, Eq. (13) has one solution corresponding to structure I, and at $\tilde{E}_1 > |\tilde{E}| > \tilde{E}_0$ it has two stable solutions corresponding to structures I

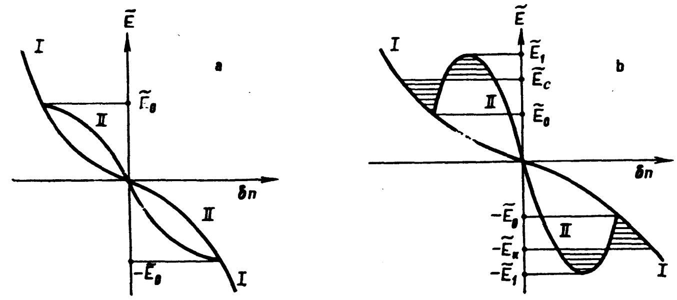

FIG. 2. Dependence of the average occupation number of the levels for structures I and II on the position ε of the adsorbed-atom level when the other parameters are fixed. Curves I and II correspond to structures I and II. $\tilde{E} = E - \xi/2 + U(b_0 + a_0)/2$ $\delta n = \delta n_1 + \delta n_2$. a) Region of smooth transitions from I to II. b) Region of first-order transitions from I to II. The areas of the shaded sections are equal.

and II. In the region $\tilde{E}_1 > \tilde{E} > \tilde{E}_c$, the lower energy is possessed by structure I, and in the region $\tilde{E}_c > \tilde{E} > -\tilde{E}_c$ by structure II, and finally at $\tilde{E} < -\tilde{E}_c$ structure I is again energywise favored. The transitions between I and II, with changing $\tilde{E}$, occur at $|\tilde{E}| = \tilde{E}_c$ and are due to the jumplike change of the occupation numbers and of the equilibrium positions of the adsorbed atoms.

We note that the transitions between I and II are possible not only in the parameter region $|\xi - \pi| \sim \tilde{U} \ll 1$ considered above, but also at $\xi - \pi \gg \tilde{U}$. In this case the interaction U_{ij} can be treated by perturbation theory. Its contribution to the energy is obviously $1/2 \sum U_{ij} n_i n_j$, where n_i and n_j are the solutions of the unperturbed problem. The occupation numbers n_i and n_j can take on values corresponding to the solutions of Eqs. (5). If we are in the parameter region where Eqs. (5) have two solutions n_1 and n_2 corresponding to states with energies $\mathscr{E}_1$ and $\mathscr{E}_2$, then two types of structures I are possible, with energies per adsorbed atom

$$\mathscr{E}_1 + {}^1/_2 \Gamma \tilde{U} (a_0 + b_0) n_1^2, \quad \mathscr{E}_2 + {}^1/_2 \Gamma \tilde{U} (a_0 + b_0) n_2^2,$$

as well as a structure II with energy

$${}^1/_2 (\mathscr{E}_1 + \mathscr{E}_2) + {}^1/_4 \tilde{U} (a_0 + b_0) \Gamma (n_1^2 + n_2^2) - {}^1/_4 \Gamma \tilde{U} b_0 (n_1 - n_2)^2.$$

Consequently, structure II has the lowest energy if the following relation is satisfied.

$$|\mathscr{E}_2 - \mathscr{E}_1 + {}^1/_2 \tilde{U} \Gamma (a_0 + b_0)(n_2^2 - n_1^2)| < {}^1/_2 \tilde{U} \Gamma b_0 (n_1 - n_2)^2.$$

This inequality can obviously be satisfied in the parameter region where $\Gamma^{-1} |\mathscr{E}_2 - \mathscr{E}_1| \sim \tilde{U} \ll 1$, $(\tilde{U} b_0 > 0)$.

§4. INSTABILITY OF STRUCTURE II TO THE ONSET OF A LONG-WAVE SUPERSTRUCTURE

The instability of phase II appears at those values of the parameters E, ξ, and U when the frequency $\omega(\mathbf{k})$ of the phonons corresponding to the vibrations of the adsorbed atoms first vanishes for one of the vibration modes a certain value $\mathbf{k} = \mathbf{k}_0$. Let us calculate $\omega^2(\mathbf{k})$, using for q_j the dynamic equations that are valid in the adiabatic approximation

$$M \ddot{q}_j = -\frac{\partial \langle \hat{H} \rangle}{\partial q_j}, \tag{14}$$

where the averaging is over the fast electron variables. If we seek the solution of (14) in the form

$$q_j = q_{1,2} + A_{1,2} \exp\{i(\mathbf{k}\mathbf{R}_j - \omega(\mathbf{k}) t)\},$$

then we get in the approximation linear in $A_{1,2}$

$$M \omega^2(\mathbf{k}) A_\alpha = \sum_{\beta, j_\beta} \left(\frac{\partial^2 \langle \hat{H} \rangle}{\partial q_{i\alpha} \partial q_{j\beta}} \right) \exp\{i\mathbf{k}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta})\} A_\beta, \tag{15}$$

where i_α is the number of the adsorbed atom in the sublattice $\alpha (\alpha = 1, 2)$. For the dynamic matrix we have

$$\frac{\partial}{\partial q_i} \frac{\partial \langle \hat{H} \rangle}{\partial q_j} = \frac{\partial}{\partial q_i} \left\langle \frac{\partial \hat{H}}{\partial q_j} \right\rangle = M \omega_0^2 \delta_{ij} + \gamma \frac{\partial n_i}{\partial q_j}. \tag{16}$$

Differentiating (9) with respect to q_j and using (8) we obtain for $\partial n_i / \partial q_j$ a system of equations that can be easily solved by changing over to Fourier components

$$T_{\alpha\beta}(\mathbf{k}) = \sum_{j_\beta} \frac{\partial n_{i\alpha}}{\partial q_{j\beta}} \exp\{i\mathbf{k}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta})\}. \tag{17}$$

Substituting (17) in (15) we obtain the dispersion equation

$$\det \| M(\omega^2(\mathbf{k}) - \omega_0^2) \delta_{\alpha\beta} - \gamma T_{\alpha\beta}(\mathbf{k}) \| = 0. \tag{18}$$

It can be shown that the condition $\omega^2(\mathbf{k}) \geqslant 0$ is equivalent to

$$D(\mathbf{k}) = \left(\frac{\pi}{\sin^2 \pi n_1} - \xi + \varphi(\mathbf{k}) \right) \left(\frac{\pi}{\sin^2 \pi n_2} - \xi + \varphi(\mathbf{k}) \right) - \psi^2(\mathbf{k}) \geqslant 0, \tag{19}$$

where

$$\varphi(\mathbf{k}) = \sum_{j_\alpha, j_\alpha \neq i_\alpha} \tilde{U}_{i\alpha j\alpha} \exp\{i\mathbf{k}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\alpha})\}, \tag{20}$$

$$\psi(\mathbf{k}) = \sum_{j_\beta, \beta \neq \alpha} \tilde{U}_{i\alpha j\beta} \exp\{i\mathbf{k}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta})\}, \tag{21}$$

and n_1 and n_2 are here the occupation numbers of the adsorbed atoms in sublattices 1 and 2. The condition $D(\mathbf{k}_0) = 0$ coincides with the condition for nontrivial solvability of the equations obtained for $B_{1,2}$ from (11) by substituting $n_{i\alpha} = n_\alpha + B_\alpha \exp(i\mathbf{k}_0 \mathbf{R}_{i\alpha})$ and linearizing with respect to B_α.

Thus, the stability limit of phase II is determined by the conditions

$$\nabla D(\mathbf{k})|_{\mathbf{k}=\mathbf{k}_0} = 0, \tag{22a}$$

$$D(\mathbf{k}_0) = 0, \tag{22b}$$

$$D(\mathbf{k}) \geqslant 0. \tag{22c}$$

We note that $D(\mathbf{k})$ can have a minimum at a point that does not lie on the boundary of the Brillouin zone, even if $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ take on extremal values only on the boundary of the zone, since (19) contains the squares $\varphi^2(\mathbf{k})$ and $\psi^2(\mathbf{k})$. This circumstance leads to a possible appearance of a superstructure in phase II even in the case when U_{ij} changes monotonically with increasing

$|\mathbf{R}_i - \mathbf{R}_j|$, and the period of the superstructure $2\pi/k_0$ depends on the parameters ξ, E, and $\tilde{U}$. The fact that one can obtain any period of the produced superstructure by a suitable choice of these parameters distinguishes this instability of phase II from the instability of phase I. In the latter case the period of the produced superstructure is determined only by the position of the extremum of the function $\varphi(\mathbf{k}) + \psi(\mathbf{k})$, and a strongly nonmonotonic dependence of the interaction $U(|\mathbf{R}_i - \mathbf{R}_j|)$ is needed to obtain a structure that differs from phase II.

Equations (22) and (13) define the surface S in the space of the parameters E, ξ, and $\tilde{U}$. This surface can be situated either in a parameter regions where the energy of phase II is less than that of phase I (phase II is stable), or in a parameter region where this phase is metastable. We shall investigate that part of the surface S which corresponds to small k_0, and obtain general cri- criteria for the onset of instability of phase II, by starting from the behavior of $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ at small k_0. The behavior of $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ at $ka \ll 1$ depends on the character of the decrease of $U(r)$ at $r \gg a$. For long-range potentials $U(r) \sim r^{-N} (N \leqslant 4)$, such as the potential (12), the expansions of $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ begin with the term $\sim|\mathbf{k}|$ (k will be reckoned hereafter in units of the adsorbed-atom lattice constant a). It can be shown that for square lattices and isotropic potentials $U_{ij} = U(|\mathbf{R}_i - \mathbf{R}_j|)$ the expansions of $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ take the form

$$\begin{aligned} \varphi(\mathbf{k}) &= \tilde{U}(a_0 + a_1|\mathbf{k}| + a_2k^2), \\ \psi(\mathbf{k}) &= \tilde{U}(b_0 + a_1|\mathbf{k}| + b_2k^2). \end{aligned} \tag{23}$$

Substituting (23) in (19) we get

$$D(\mathbf{k}) = D_0 + D_1|\mathbf{k}| + D_2k^2.$$

The conditions for the appearance of the instability (22) then take the form

$$k_0 = -D_1/2D_2, \tag{24a}$$

$$4D_0D_2 = D_1^2, \tag{24b}$$

$$D_2 > 0. \tag{24c}$$

It is seen from (19) that at small $\tilde{U}$ the dependence of $D(\mathbf{k})$ on $\mathbf{k}$ becomes substantial if

$$\frac{\pi}{\sin^2 \pi n_{1,2}} - \xi \sim \tilde{U} \ll 1.$$

It follows therefore that the phase II can become unstable only in the parameter region where $|n_1 - n_2| \ll 1$, and this occurs only if $|\xi - \pi| \sim \tilde{U}$, $(n_{1,2} - 1/2)^2 \sim \tilde{U}$. From Eqs. (24a), (24b), and (13) at small $\delta n_{1,2} = n_{1,2} - 1/2$ and at $k_0 \ll 1$ we get the shape of the curve that bounds the stability region of phase II. In terms of the variables

$$N_+^2 = \frac{\pi^3(\delta n_1 + \delta n_2)^2}{\tilde{U} b_0}, \quad N_-^2 = \frac{\pi^3(\delta n_1 - \delta n_2)^2}{\tilde{U} b_0}$$

we have

$${}^1/_6 N_-^2(A-1) = 2 - {}^3/_2 N_+^2, \tag{25}$$

where

$$A^{-1} = 2b_0(a_2 - b_2)/a_1^2.$$

The condition (24c) means that $A > 0$, and Eq. (24a) yields the dependence of k_0 of the point on the phase transition curve (25):

$$k_0 = -{}^1/_6 \frac{b_0 A}{a_1} N_-^2, \quad (a_1 < 0). \tag{26}$$

Depending on the coefficient A, the curve corresponding to (25) can lie in the region of stability or metastability of phase II. The former occurs if $A > 4/3$ (see Fig. 3). The calculation for the case of a dipole dipole interaction yields $A \approx 2.1$; $a_1 = -\pi$; $b_0 \approx 5.8$, so that the state with superstructure is the ground state of the system of atoms adsorbed on the metal surface in the region of parameters E, ξ, and $\tilde{U}$ outside the stability limit (25).

We note that in some cases allowance for the Friede oscillations (see (12)) and of the indirect interaction W^{indir} (Ref. 11) can change the values of A, a, and b_0.

An interesting feature of the resultant superstructure is that its period is not commensurate with the period of the adsorbed-atom lattice. Since the phase corresponding to the superstructure of the adsorbed-atom displacement wave is not fixed in this case (for an ideal two-dimensional atom lattice), one can expect the appearance of Goldstone excitations with an acoustic spectrum. In addition, there is also degeneracy with respect to the direction of the vector $\mathbf{k}_0$ (at small k_0), as follows from (23). We get thus an excitation branch with a small spectrum gap (determined by the $\varphi(\mathbf{k})$ and $\psi(\mathbf{k})$ expansion terms of higher order in $\mathbf{k}$, corresponding to the rotation of the vector $\mathbf{k}_0$. For nonideal surfaces with cleavages, the direction of $\mathbf{k}_0$ is determined by the direction of these cleavages.

§ 5. CONCLUSION

We used above a simplified model in which the electron-phonon interaction included only the interaction of the electrons at the adsorbed-atom level with vibrations of this atom in a direction normal to the metal surface. It is obvious, however, that it is necessary to take into account at the same time both the vibrations of the adsorbed atom along the surface, and the vibrations of the metal ions near the adsorbed atom. In the general case of the single adsorbed-atom problem it is necessary to write in (1)

$$(\hat{n} - n_0) \sum_{\varkappa} \gamma_\varkappa (q_\varkappa - q_\varkappa^0) + \frac{1}{2} \sum_{\varkappa} \omega_\varkappa^2 (q_\varkappa - q_\varkappa^0)^2, \tag{27}$$

where $q_\varkappa$ are the normal coordinates of the "adsorbed

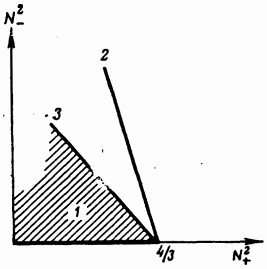

FIG. 3. Phase diagram of system adsorbed atoms: 1—curve of smooth transitions from I to II: curve of equal energies of phases I and II: $N_+^2 = 4/3 - (1/27)N_-^2$; 3—curve of onset of instability of phase II to formation of a long-wave super-structure. The shaded region corresponds to the region where a stable phase II exists in the ground state of the adsorbed atoms at $A > 4/3$.

atom + metal" system. By calculating the values of $q_\varkappa$ corresponding to the equilibrium positions, as was done earlier in § 2, and substituting them in (27) we obtain the contribution made to the self-energy part of the Green's function of the electron localized on the adsorbed atom, $\xi'\Gamma(n-n_0)$, where $\xi'=\Gamma^{-1}\sum_\varkappa \gamma_\varkappa^2/\omega_\varkappa^2$, in place of $\xi=\gamma^2/M\omega_0^2\Gamma$. The problem was thus reduced to the one considered above, and only the constant ξ changed (increased). A transition to a new state means here a shift of the equilibrium positions of both the adsorbed atom and of the neighboring metal ions.

For an adsorbed film, analogously, we have an electron-phonon interaction of the form $\sum_{\varkappa,i}\gamma_{\varkappa i}q_\varkappa(n_i-n_0)$. Accordingly we have in the self-energy part of G_{ii}

$$-\sum_\varkappa \gamma_{\varkappa i}{}^2/\omega_\varkappa{}^2(n_i-n_0)-\sum_{\varkappa,j\neq i}\frac{\gamma_{\varkappa i}\gamma_{\varkappa j}}{\omega_\nu{}^2}(n_j-n_0).$$

The first term gives a new constant ξ, and the second gives an increment to the interaction U_{ij} and to the energy ε of the localized electron. Consequently, Eqs. (11) do not change form. We note that in a model generalized in this manner for an adsorbed film, the instabilities considered in this paper lead to equilibrium-position displacements parallel to the surface. This circumstance may turn out to be important for the investigation of transitions between different mismatched adsorbed-atom lattices.

All the results obtained in this paper pertained to a lattice of adsorbed atoms on a metal surface. We wish to call attention, however, on the agreement between the experimental data cited in the Introduction for clean surfaces of the transition metals W and Mo, on the one hand, and the results of the present paper. To what degree can the employed model be used to describe the surfaces of transitions metals? Actually the structure of the d-states of transition metals in the surface layer differs greatly from the structure of the volume states, since the atoms of the surface layer are surrounded by a smaller number of neighbors. In this sense a film of some foreign metal adsorbed, say, on W does not differ in principle at all from a W film adsorbed on W, whether from the point of view of using some particular model to describe the state of the surface layer of the atoms, or from the experimental point of view.2) Observation of narrow peaks below the Fermi level in photoemission measurements on the (100) surface of W or Mo (on the same surface on which the aforementioned transition were observed), which are attributed to d-resonance of the surface atoms,[12] also favors the possibility of using our model for the description of transition metals.

The determination of the ground state of the Hamiltonian (7) for a dense nonlayer of adsorbed atoms or for a surface layer of transition metals encounters a number of computational difficulties connected, first of all, with the need for taking into account band effects, i.e., the indirect (via the "substrate") and direct exchange of electrons between the adsorbed atoms (the latter is taken into account in (7) by replacing $\sum\varepsilon\hat{n}_i$ with $\sum\varepsilon_{ij}a_i + a_j$), and second, with the correct interpretation of the interaction U_{ij}, which is larger in this case.

In some cases, however, the band effects can be neglected. In particular, as shown earlier[14] indirect exchange is insignificant if the associated level broadening is much less than its distance from the Fermi level, a statement that can obviously be made also with respect to direct exchange.

As for the interaction U_{ij}, there is no justification for taking into account in the Hartree-Fock model when $U \gtrsim \Gamma$. However, if this approximation is used, it can be shown that all the essential features of the results described below remain in force. An important circumstance is that for a sufficiently strong electron-phonon interaction the instability of the surface layer is not critical to the relation between U and Γ, and can arise for both large and small U. This gives grounds for hoping that the results will not change significantly if the allowance for the correlation effects leads only to renormalization of U_{ij}.

We consider in conclusion the possibility of experimentally observing the effects predicted in the paper for a film of adsorbed atoms. The alterations considered above take place when the positions of the levels of the adsorbed atoms change relative to the Fermi level, and also when the interaction between the adsorbed atoms changes at low temperature. The simplest way to change the energy ε is to perform the measurements in electric fields, as in electron field-emission spectroscopy. It is also possible to alter the interaction between the adsorbed atoms, as well as the position of the level ε, by varying the degree of coating. The most suitable in this case are "adsorbate + substrate" systems in which the width of the adsorbed-atom level is small enough, $\Gamma \lesssim 0.5$ eV, and this level is close to the Fermi level. Transitions can take place when this level passes through the Fermi level as a result of an applied electric field or depolarization effects when the degree of coating is changed.

It appears that the easiest way is to observe transitions between different phases I at low degrees of coating. These transitions should manifest themselves in an abrupt change of the work function following a small change of the electric field or of the degree of coating. In ordered structures of adsorbed atoms, the transition should be accompanied by two jumps of the work function, corresponding to transitions between phases I and the intermediate phase II, while in disordered structures the change of the work function will have a smoother character because of the inhomogeneous broadening of the adsorbed-atom level.

As for transitions with change symmetry of the adsorbed-atom lattice, a direct method of observing them is that of slow-electron diffraction.

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1)It must be recognized that the theory developed here is restricted to a fluctuation region whose dimensions are determined by the parameter $\omega_0/\Gamma(\xi-\pi)^{3/2} \ll 1$.

2) There are, for example, known experiments on adsorption of W on W wherein the adsorbed W is significantly electropositive.[13]

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Electrohydrodynamic instability with isotropic mechanism in cholesteric liquid crystals

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It is shown that the "dielectric" regime in cholesteric liquid crystals with negative dielectric anisotropy, as well as the newly-observed electrohydrodynamic instability in cholesteric liquid crystals with positive dielectric anisotropy, which arise in a planar texture and at voltages above the threshold of the unwinding of the cholesteric helix as well as in confocal textures, are manifestations of an isotropic instability due to electroconvective phenomena inherent in ordinary electrically conducting liquids. The role of the liquid crystal reduces to visualization of the elctrohydrodynamic currents as a result of the anisotropy of the refractive index, and to an influence exerted on the current topology by the anisotropy of the viscosity.

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When an electric field is applied parallel to the helix axis in the planar texture of a cholesteric liquid crystal (CLC), an instability appears at a certain threshold voltage, in the form of spatially-periodic deformations that are two dimensional (of the square grid type) at thickness d greatly exceeding the helix pitch $P_0 (d \gg P_0)$,[1,2] and one-dimensional at $d \approx P_0$ (Ref. 3). For CLC with positive dielectric anisotroy ($\Delta\varepsilon > 0$) the instability sets in at arbitrary external-field frequencies, whereas for CLC with $\Delta\varepsilon < 0$ it appears only below a certain critical frequency f_{cr}. This instability is similar to the Fréedericsz transition and Williams domains in nematic liquid crystals (NLC); its causes, just as in the case of NLC, are the destablizing moments of the forces induced by the field as a result of the anisotropy of the dielectric constant and (or) the anisotropy of the electric conductivity of the CLC. The threshold voltage of this instability, naturally, depends strongly on the magnitude and sign of the dielectric anisotropy, on the electric-conductivity anisotropy, and on the pitch of the helix, and is well described by the Helfrich-Hourault theory.[4–6]

For the same geometry, in CLC with $\Delta\varepsilon < 0$, and at frequencies higher than f_{cr}, deformations were observed[1,2] with a much smaller period (the analog of "chevrons" in NLC). So far, there are no published suggestions concerning the possible mechanism of this electrohydrodynamic (EHD) instability, which is called, just as in the case of NLC, the "dielectric" regime. Nor is it clear whether this mechanism is anisotropic, i.e., whether it is due to the anisotropy of the CLC properties, just as, e.g., the Helfrich-Houralt mechanism.

There is also a need for explaining the causes of the EHD instabilities observed by us in part[7] in CLC with $\Delta\varepsilon > 0$ in a planar structure and at voltages higher than the threshold of the untwisting of the cholesteric helix, and also in a confocal texture at any sign of $\Delta\varepsilon$. These cases were previously regarded as electrohydrodynamically stable.[8,9]

The present work was stimulated also by researches[10,11] that have shown that the EHD instabilities that manifest themselves in NLC in the form of "chevrons" and other patterns are caused by electroconvective motion of the liquid, and the instability mechanism is isotropic, i.e., it is not due to the anisotropy of the electric properties of the NLC.

Our present task is to show that the dielectric regime in the planar texture of CLC with $\Delta\varepsilon < 0$, and the observation of EHD instability in other textures and in CLC with $\Delta\varepsilon > 0$, can be explained with the aim of the very

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