

# Phase transitions in a monolayer on the surface of a metal

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The structures of monolayer adsorption films of the alkali-metal type which can be formed on a metal substrate, the charge state of the films, and their effect on the surface characteristics are studied theoretically. A model Hamiltonian of the Anderson type is chosen for the calculations. Electrostatic interaction between the adsorbed atoms via a free half-space is taken into account. The electron structure of a fixed adsorbed-atom lattice is determined in the Hartree-Fock approximation. A transition from a uniform distribution of charges over the atoms to a nonuniform distribution (a discrete analog of Wigner crystallization) is predicted for a certain range of parameters. A thermodynamic analysis of the monolayer carried out in the self-consistent field approximation reveals that decrease of the adsorbed-atom charge, which occurs on compression of the film results, in a phase transition of the condensation type in the charged film despite the repulsive nature of the interaction. In the two-phase region there coexist a uniformly charged phase and a phase with different density and mean charge. The latter may be distributed uniformly or unevenly. Experimental data that confirm the existence of condensation in a number of systems are discussed.

## 1. INTRODUCTION

New experimental methods for investigating the faces of single crystals coated with adsorbed films are being diligently developed in recent years (the slow electron diffraction method (SED)<sup>[1]</sup>, Auger spectroscopy<sup>[2]</sup>, mass spectrometry<sup>[3]</sup>, resonant tunneling<sup>[4]</sup>, etc.). These investigations make it possible to establish the density, structure, and charge state of the film, and also its influence on the electron-emission properties of the surface. Significant variations in the surface properties occur precisely in the case of submonolayer coatings. Great interest attaches therefore to the theoretical study of all possible structure of monolayer adsorption films and their influence on the characteristics of the surface.

It is presently impossible to calculate on the basis of a microscopic theory the properties of a surface coated with a monolayer film. We construct a model that describes reasonably the processes on the surface, and investigate this model. The parameters of the model can be obtained from experiment.

Let us describe qualitatively the state of one adsorbed atom on the surface of a metal. The discrete level of the isolated atom, owing to its interaction with the metal, smears out into a quasilevel. The electrons of the metal occupy all the quasilevel states located below the Fermi level. Let us consider the case when the work function  $\varphi_0$  of the pure metal exceeds the effective ionization potential  $I$  of the atom on the surface of the metal (Fig. 1). The adsorbed atom is then in a charged state and forms together with its electrostatic image a dipole perpendicular to the surface. If now we place alongside the first adsorbed atom a second such atom on the surface, then they will repel each other mainly in dipole-dipole fashion, up to distances larger than interatomic<sup>1)</sup>. We emphasize that when adsorbed atoms are ionized, the energy of the system is decreased because of the interaction of the adsorbed atoms with the metal and increases as a result of the electrostatic repulsion between the adsorbed atoms. The competition of these interactions can lead to a number of effects.

In a definite range of the parameters  $\tilde{E} = \varphi_0 - I$ ,  $\Gamma$  (the width of the quasilevel), and  $\theta$  (the degree of coat-

ing, or the number of atoms per unit surface area), it may be convenient to change from a homogeneous distribution of the electron density over the adsorbed atoms to an inhomogeneous distribution. The first indication of the possibility of inhomogeneous distribution of the charge seems to have been in our paper<sup>[5]</sup>. If the adsorbed atoms themselves are mobile, then a phase transition is possible and can lead to the existence of phases with different degrees of coating and different charges.

The inhomogeneous distribution of the electron density over the adsorbed atoms leads to an increase of the electrostatic repulsion energy. If this energy is high enough (in comparison with the energy of the interaction with the metal), then such a process is favored. The repulsion of the adsorbed atoms leads to a lowering of the quasilevel of an individual adsorbed atom, and consequently leads to a decrease of the charge on it, owing to the "leakage" of the electrons from the metal to the quasilevel. This is effectively equivalent to mutual depolarization of the adsorbed atoms. As shown by one of the authors<sup>[6]</sup>, the effect of mutual depolarization should lead to condensation of the charged film, in spite of the repulsive character of the interaction.

## 2. ELECTRONIC STRUCTURE OF FIXED LATTICE OF ADSORBED ATOMS

We describe the systems of interest to us (such as an alkali-metal coating on the face of a single crystal of a high-melting-point metal) by means of the following model Hamiltonian (cf. <sup>[7]</sup>):

$$H = \sum_{\mathbf{q}} \epsilon_{\mathbf{q}} \hat{n}_{\mathbf{q}} + \sum_{\mathbf{q}, \alpha} (V_{\alpha\mathbf{q}} a_{\mathbf{q}}^{\dagger} a_{\alpha} + \text{H.c.}) + E \sum_{\alpha} \hat{n}_{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} U_{\alpha\beta} (1 - \hat{n}_{\alpha}) (1 - \hat{n}_{\beta}), \quad (1)$$

where  $\hat{n}_{\mathbf{q}} = a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}}$ ,  $\hat{n}_{\alpha} = a_{\alpha}^{\dagger} a_{\alpha}$  are operators of the occupation numbers of the states of the metal  $|\mathbf{q}\rangle$  and the states  $|\alpha\rangle$ , localized on the adsorbed atom with number  $\alpha$ ,  $a_{\mathbf{q}, \alpha}^{\dagger}$ ,  $a_{\mathbf{q}, \alpha}$  is the operator for the creation (annihilation) of the corresponding states,  $\epsilon_{\mathbf{q}}$  is the band energy,  $\tilde{E} = \varphi_0 - I$  (see Fig. 1),  $V_{\mathbf{q}\alpha}$  is the matrix element of the

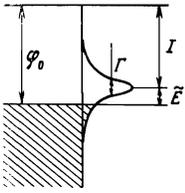


FIG. 1. Position of the quasilevel of an isolated adsorbed atom. The occupied state of the metal band and of the quasilevel are shown shaded.

transition of an electron from the atom into the metal,  $U_{\alpha\beta}$  is the energy of the electrostatic repulsion of the fully ionized adsorbed atoms, and at large distances ( $r \gg d$ ) it is equal to the dipole-dipole repulsion energy  $2e^2d^2/r^3_{\alpha\beta}$ ,  $2d$  is the dipole displacement, and  $r_{\alpha\beta}$  is the distance between the adsorbed atoms  $\alpha$  and  $\beta$ .

We have neglected in (1) the direct exchange between the adsorbed atoms, so that our analysis is valid so long as there is no metalization of the film, i.e., up to densities on the order of a complete monolayer, when the overlap of the electron shells of the adsorbed atoms takes place. The correlation energy per adsorbed atom was assumed to be large enough to be able to exclude the state with occupation numbers  $n_{\alpha} = 2$ . This approximation is analogous to the Heitler-London method.

We use for the calculations the well known Hartree-Fock method, which makes it possible to reduce the diagonalization of (1) to the problem of diagonalizing the quadratic Hamiltonian

$$H_{HF} = \sum_{\alpha} \epsilon_{\alpha} \hat{n}_{\alpha} + \sum_{\alpha, \alpha'} (V_{\alpha\alpha'} a_{\alpha}^{\dagger} a_{\alpha'} + \text{H.C.}) + E \sum_{\alpha} \hat{n}_{\alpha} + \sum_{\alpha \neq \beta} U_{\alpha\beta} (1 - n_{\alpha})(1 - \hat{n}_{\beta}) - \frac{1}{2} \sum_{\alpha \neq \beta} U_{\alpha\beta} (1 - n_{\alpha})(1 - n_{\beta}), \quad (2)$$

where  $n_{\alpha}$  is the average occupation number.

At sufficiently low temperatures, the charged adsorbed atoms become aligned into an ordered structure that varies with increasing degree of coating. In the present section we assume that the adsorbed atoms are arranged in a definite lattice (concrete calculations are given for a quadratic lattice and a one-dimensional chain) and determine the electronic structure of the adsorbed atoms as a function of the lattice (i.e., of the coating density) and other parameters.

For our purposes, it suffices to obtain the "atomic" Green's function

$$G_{\alpha\beta} = \left\langle \alpha \left| \frac{1}{\epsilon - H + i\delta} \right| \beta \right\rangle.$$

This problem can be solved exactly, since  $H_{HF}$  is quadratic. The off-diagonal terms of this matrix are due to indirect interaction of the adsorbed atoms via the metal electrons<sup>[6]</sup>. Allowance for the indirect interaction only complicates the calculations without essentially affecting the main conclusions; we therefore neglect the off-diagonal part of  $G_{\alpha\beta}$ .

The problem then reduces to diagonalization of the Hamiltonian for a single adsorbed atom in the external field produced by the charge of the surrounding adsorbed atoms. As a result we get

$$G_{\alpha\alpha} = \frac{1}{E - E_{\alpha} - \Sigma(E)}, \quad E = \epsilon + i\delta, \quad \delta \rightarrow +0, \quad (3)$$

where

$$\Sigma(E) = \sum_{\alpha} \frac{|V_{\alpha\alpha}|^2}{E - \epsilon_{\alpha}} = R(\epsilon) - i\Gamma(\epsilon), \quad (4)$$

$$E_{\alpha} = E - A + \sum_{\beta \neq \alpha} U_{\alpha\beta} n_{\beta}, \quad A = \sum_{\beta \neq \alpha} U_{\alpha\beta}. \quad (5)$$

The level density at the atom are determined by the formula

$$\rho_{\alpha}(\epsilon) = -\frac{1}{\pi} \text{Im} G_{\alpha\alpha}(E) = \frac{\Gamma(\epsilon)}{\pi} \frac{1}{(\epsilon - E_{\alpha} - R(\epsilon))^2 + \Gamma^2(\epsilon)}. \quad (6)$$

In the absence of surface levels, the quantities  $R(\epsilon)$  and  $\Gamma(\epsilon)$  vary over a bandwidth which we assume to be large in comparison with the characteristic energies ( $\bar{E}$ ,  $U_{\alpha\beta}$ ). We can then put  $\Gamma(\epsilon) = \Gamma = \text{const}$ . The dispersion relations then yield  $R(\epsilon) \equiv 0$ .

The self-consistency condition takes the form

$$n_{\alpha} = \int_{-\infty}^{\infty} \rho_{\alpha}(\epsilon) n_F(\epsilon) d\epsilon = \begin{cases} \int_{-\infty}^{-E_{\alpha}} \rho(\epsilon) d\epsilon, & T \ll \Gamma \\ n_F(E_{\alpha}), & T \gg \Gamma \end{cases}, \quad (7)$$

where  $n_F(\epsilon)$  is the Fermi distribution function, and the Fermi energy is taken to be the zero reference point.

In the general case, this is a system of transcendental equations having, as will be shown subsequently, an infinite set of solutions. Before we prove this, let us transform the system (7) into

$$E - A + \sum_{\beta \neq \alpha} U_{\alpha\beta} n_{\beta} = \varphi(n_{\alpha}), \quad (8)$$

with  $\varphi(n) = \frac{1}{2} T \ln[(1-n)/n]$  at  $T \gg \Gamma$  and  $\varphi(n) \propto \Gamma$  at  $T \ll \Gamma$ ; in particular, when  $\Gamma(\epsilon) = \text{const}$  (Lorentz shape of the quasilevel) we have  $\varphi(n) = \Gamma \cot \pi n$ . A typical form of  $\varphi(n)$  is shown in Fig. 2.

It is easily seen that the system (8) has a "homogeneous" solution  $n_{\alpha} = n$  for all parameters  $E$ ,  $\Gamma$ , and  $A$ , where  $n$  is determined by the equation

$$E - A(1-n) = \varphi(n). \quad (9)$$

Since  $\varphi(n)$ , as follows from its definition, is a monotonically decreasing function of the argument, the solution (9) is unique. It is easy to verify that  $\partial n / \partial A > 0$ , whereas  $\partial n / \partial E < 0$ . Since  $A$  increases with increasing degree of coating, we get  $\partial n / \partial \theta > 0$ , i.e., the interaction of the adsorbed atoms leads to a decrease of the charge  $f = 1 - n$ , and there exists a unique depolarization mechanism that prevails over the mutual atomic depolarization proper.

The question of the presence of other solutions of the system (a) can be answered by linearizing the system near the homogeneous solution (n),  $n_{\alpha} = n + m_{\alpha}$ :

$$\varphi'(n) m_{\alpha} = \sum_{\beta \neq \alpha} U_{\alpha\beta} m_{\beta}. \quad (10)$$

Equations (10) can be easily solved, since  $U_{\alpha\beta}$  depends on the difference of the coordinates on the given lattice of adsorbed atoms. Inhomogeneous distributions appear under the condition

$$\varphi'(n) \geq K(t_1, t_2), \quad (11)$$

where

$$K(t_1, t_2) = \sum_{\alpha} U_{\alpha\alpha} e^{i(\alpha_1 t_1 + \alpha_2 t_2)}, \quad \alpha = (\alpha_1, \alpha_2), \\ m_{\alpha} = e^{i(\alpha_1 t_1 + \alpha_2 t_2)}.$$

Since  $\min K(t_1, t_2) = K(\pi, \pi)$  (in analogy with  $K(t) = K(\pi)$  in the one-dimensional case), the first nontrivial solution of the system (10), which appears when the period  $a$  of the lattice is decreased, is the "antiferromagnetic" solution  $m_{\alpha} = \exp[i\pi(\alpha_1 + \alpha_2)]$  ( $m_{\alpha} = e^{i\pi\alpha}$  in the one-dimensional case),  $A \approx 4.8e^2d^2/a^3$  in the one-dimensional case, and  $A \approx 18e^2d^2/a^3$  in the two-dimensional case. The boundary of the region where the inhomogeneous

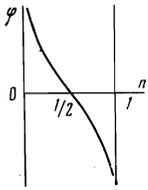


FIG. 2. Typical form of the function  $\varphi(n)$ .

ous solution exists is defined by the equation

$$\varphi'(n) = K_{min}. \quad (12)$$

Everywhere inside the region of the inhomogeneous distribution there is a solution of (8) with "antiferromagnetic" structure with occupation numbers  $n_{1,2}$  determined from the system of equations

$$\begin{aligned} E - A + \kappa A n_1 + (1 - \kappa) A n_2 &= \varphi(n_1), \\ E - A + (1 - \kappa) A n_1 + \kappa A n_2 &= \varphi(n_2). \end{aligned} \quad (13)$$

Here  $\kappa$  is the fraction of the interaction of the adsorbed atom with the adsorbed atoms from its own sublattice relative to the interaction with the entire surrounding;  $1 - \kappa$  is the same relative to the interactions with adsorbed atoms from another sublattice. The value of  $\kappa$  depends on the dimensionality of the space and on the character of the fall-off of the interaction potential  $U_{\alpha\beta}$ . Thus,  $\kappa = 0$  for the nearest-neighbor interaction and  $\kappa = 1/2$  for  $U_{\alpha\beta} = \text{const}$ ; for the dipole-dipole interaction we have  $\kappa = 1/8$  and  $\kappa = 1/2\sqrt{2}$  in the one-dimensional and two-dimensional cases, respectively.

The equation for the boundary of the region of the inhomogeneous charge distribution (12) can be represented in the form

$$\varphi'(n) = -(1 - 2\kappa)A. \quad (14)$$

The region of existence of an inhomogeneous distribution is shown in Fig. 3 in the dimensionless variables  $\delta \propto \bar{E}$  and  $\gamma \propto A$ , with  $\bar{E}$  and  $A$  made dimensionless with respect to the larger of the quantities  $T$  and  $\Gamma$ . The boundary of the region (curve 1 plus Fig. 3) is symmetrical about the line  $\delta = \gamma/2$ , as a result of the invariance of Eqs. (8) relative to the substitutions  $\bar{E} - \frac{1}{2}A \rightarrow -\bar{E} + \frac{1}{2}A$ ,  $n_{\alpha} \rightarrow 1 - n_{\alpha}$  (it is assumed that  $\varphi(n) = -\varphi(1 - n)$ ). This holds true when  $T \gg \Gamma$  as well as for any even function  $\rho(\epsilon)$ . This symmetry is analogous to the invariance of the antiferromagnetic problem relative to a change in the direction of the magnetic field.

It is easily understood that  $\varphi'(n)$  is maximal at  $n = 1/2$ , and that in order to fall into the region of existence of the inhomogeneous charge it is necessary to satisfy the inequality

$$A > \frac{|\varphi'(1/2)|}{1 - 2\kappa}. \quad (15)$$

If the quasilevel has a Lorentz shape, this means that  $e^2 d^2/a^3 > 0.9 \Gamma$  in the one-dimensional case and  $e^2 d^2/a^3 > 0.6 \Gamma$  in the two-dimensional case. If the coating makes up an incomplete monolayer, then  $d \sim a$ , i.e.,  $e^2/a \gtrsim \Gamma$ .

The system (8) determines only the possible structures of the solutions. In the region where different solutions exist simultaneously, there is realistically realized a structure with minimal energy.

Accurate to terms that are inessential in this case, corresponding to the interaction of the ions with their own images (of the type  $\theta \cdot \text{const}$ ), the energy of the monolayer is determined by the formula

$$\mathcal{E} = \sum_{\alpha} \int_{-\infty}^{\infty} \epsilon n_{\alpha}(\epsilon) \rho_{\alpha}(\epsilon) d\epsilon - \frac{1}{2} \sum_{\alpha \neq \beta} U_{\alpha\beta} (1 - n_{\alpha}) (1 - n_{\beta}). \quad (16)$$

We have used here the approximation of a broad band, in

which we can omit the term  $\int_{-\infty}^{\infty} \Delta \rho_{\mathbf{M}}(\epsilon) n_{\mathbf{F}}(\epsilon) \epsilon d\epsilon$  because

of its smallness ( $\Delta \rho_{\mathbf{M}}(\epsilon)$  is the change of the density of states of the metal as a result of adsorption of the atoms).

Cumbersome calculations show the energy of the "antiferromagnetic" distribution of the charges is smaller than the energy of the homogeneous distribution in the entire region of existence of the inhomogeneous distribution. Since the "antiferromagnetic" phase differs infinitesimally from the homogeneous phase near the boundary ( $n_1 \approx n_2 \approx n$ ), it follows from general consideration<sup>[9]</sup> that the phase transition to the inhomogeneous lattice of charges is a second-order transition. The critical transition temperature, if one exists at  $T \ll \Gamma$ , is determined from (14) by means of the expression

$$T_{cr} = \frac{2A_0}{(1 - 2\kappa)} n_0 (1 - n_0), \quad (17)$$

where  $n_0$  is the solution of (9) at a given  $E$  and maximal  $A = A_0$  (before the start of the metalization). Thus, in our case  $T_{cr} \sim A_0$ . Further investigation of (8) shows that the charge distributions of more complicated structures turn out to be stable in part of region I. In particular, inside region II of Fig. 3, the minimal energy is possessed in the one-dimensional case by a phase with three sublattices with different charges. The transition from this phase to the "antiferromagnetic" phase is of first order<sup>[9]</sup>.

We do not consider it useful to carry out a detailed investigation of more complicated structures before experiment reveals the structures of the antiferromagnetic type. The estimates given above show that there are grounds for expecting this to occur. On the SED pictures, the phase transition described above should appear as an increase of the lattice period by a factor of two in the one-dimensional case and by a factor  $\sqrt{2}$  with rotation through  $45^\circ$  in the case of a quadratic structure of the single-crystal face.

In the calculations presented so far it has been assumed that homogeneous ordering of the adsorbed atoms on the single-crystal substrate is produced and governed by external factors. In fact, the distribution of the adsorbed atoms over the substrate is of course governed also by the potential relief, as well as the electrostatic interaction between the atoms, in such a way as to ensure a minimum of the total free energy. So far, we have found electronic structures that ensure a relative minimum of the free energy at a fixed position of the adsorbed atoms. We now proceed to minimization of the total free energy.

### 3. CONDENSATION OF A CHARGED FILM

The set of different structures and transitions between them, observed in the experiment, is quite varied. This is apparently connected with the complicated character of the interaction of the adsorbed atoms with the substrate and with one another. Indeed, the presence of a potential relief of finite depth, in addition to the long-range repulsion between particles with even constant charge, makes it quite difficult to analyze the possible structures. In the limiting case of a smooth surface, a

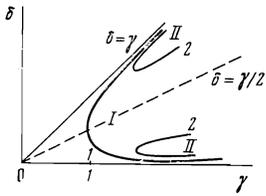


FIG. 3. Region of existence of the "antiferromagnetic" type of inhomogeneous solution (I), and of the existence of a solution with a unit cell of three atoms in the one-dimensional case (II).

monolayer of adsorbed atoms with constant charge becomes monotonically compressed when the density of the film increases, and retains an ordered structure up to temperatures on the order of the interaction temperature. In the other limiting case, the surface is a set of infinitely deep potential wells arranged in a definite sequence. The adsorbed atoms are situated only in these wells and form a lattice with a maximal period. At zero temperature, with increasing coating, the transition from lattice to lattice occurs via a set of intermediate structures with large period. At any degree of coating, the monolayer is homogeneous. Without stopping to analyze this question in detail, we emphasize only that the monolayer remains macroscopically homogeneous in both limiting cases.

In the present section we shall show that the change of the charge of the adsorbed atoms with changing density of the monolayer and the ensuing change in the interaction of the adsorbed atoms lead to a phase transition of the condensation type in the film. Thus, macroscopic regions that differ in density and in electron structure can appear in the monolayer. The free energy of the monolayer has, in the self-consistent field approximation, the form

$$F = \mathcal{E} - TS, \quad (18)$$

$$S = -\theta \ln \theta - (1 - \theta) \ln (1 - \theta), \quad (19)$$

where  $\mathcal{E}$  is determined by formula (16) and includes the free energy of the electron subsystem, the internal energy of the ion subsystem, and the energy of interaction of the two subsystems, while  $S$  is the entropy of the ion subsystem.

In the preceding section we have obtained  $\mathcal{E}(\theta)$  by assuming that the atoms at a given  $\theta$  are arranged in a lattice, and by determining the electronic structure of the film. The use of formulas (18) and (19) for the free energy presupposes that the electronic structure is preserved on the film when the arrangement of the atoms fluctuates, since the main contribution to the statistics is made by states near the homogeneous distribution of the adsorbed atoms with average density  $\theta$ . The extent to which the electronic structure is sensitive to changes in the arrangement of the atoms depends on the character of the fall-off of the interaction with increasing distance between adsorbed atoms and the number of neighbors in the lattice. Thus, if the interaction decreases infinitely slowly,  $U_{\alpha\beta} \sim \text{const}$  ( $\kappa = 1/2$ ), the fluctuations do not affect the average field and the self-consistent-field method is exact (see, e.g., [10]). In the opposite limiting case, namely the nearest-neighbor interaction ( $\kappa = 0$ ), it can be shown that even in the region of the inhomogeneous charge distribution the presence of one defect or one line of defects does not lead to a realignment of the electronic structure of the entire film. Thus, the destruction of the electronic structure occurs only when a relative area on the order of unity is filled with defects, i.e., the problem is analogous to the percolation problem. We see that even in this case the weight of the

correctly accounted-for states is large enough and we can expect the self-consistent-field method to give qualitatively correct results.

The calculations are too cumbersome to be presented here. We present several limiting cases. Let  $T = 0$  and  $\Gamma \ll \tilde{E}$ ; then the film is uniformly charged in the case  $\kappa = 1/2$  (see (14)), and its charge is determined by the following expression (it is assumed that  $U_{\alpha\beta} \propto r_{\alpha\beta}^{-3}$ , and then  $A \propto \theta^{3/d}$ , where  $d$  is the dimensionality of the space):

$$n = \begin{cases} 0, & A < E \text{ or } \theta < \theta_{\text{cr}} \\ 1 - E/A = 1 - (\theta_{\text{cr}}/\theta)^{3/d}, & A > E \text{ or } \theta > \theta_{\text{cr}} \end{cases} \quad (20)$$

where  $\theta_{\text{cr}} = (\tilde{E}/A_0)^{d/3}$  and  $A_0 = A|_{\theta=1}$ . For the film energy  $U = \mathcal{E}/\tilde{E}$  we have

$$U = \begin{cases} 1/2 \theta (\theta/\theta_{\text{cr}})^{3/d} & \theta < \theta_{\text{cr}} \\ \theta [1 - 1/2 (\theta_{\text{cr}}/\theta)^{3/d}] & \theta > \theta_{\text{cr}} \end{cases} \quad (21)$$

It is evident from this (see also curve 1 of Fig. 4) that in the region  $\theta > \theta_{\text{cr}}$  we have  $U''(\theta) \ll 0$ . This means that in the region  $\theta > \theta_{\text{cr}}$  the film is thermodynamically absolutely unstable.

At a given  $\theta > \theta_{\text{cr}}$ , the monolayer breaks up into two phases with  $\theta' < \theta_{\text{cr}}$  and  $\theta'' \approx 1$ . It is assumed, of course, that  $\theta_{\text{cr}} < 1$  (i.e., the film can be compressed in such a way that  $A > \tilde{E}$ ). At  $\kappa = 0$  (nearest-neighbor interaction only) we have

$$U = \begin{cases} 1/2 \theta (\theta/\theta_{\text{cr}})^{3/d} & \theta < \theta_{\text{cr}} \\ 1/2 \theta, & \theta > \theta_{\text{cr}} \end{cases} \quad (22)$$

and  $n = 0$  at  $\theta < \theta_{\text{cr}}$  and the film is unevenly charged at  $\theta > \theta_{\text{cr}}$ , namely,  $n = 0$  in one sublattice and  $n = 1$  in the other. As seen from (22) (curve 2 of Fig. 4), near  $\theta = \theta_{\text{cr}}$  the function  $U(\theta)$  is concave, and consequently the film is unstable, just as in the preceding case. When  $0 < \kappa < 1/2$  there are two sections on which  $U''(\theta) < 0$  (curve 3 in Fig. 4), namely at  $\theta_{\text{cr}} < \theta < \theta_{\text{cr}}(1 - \kappa)^{-d/3}$  and at  $\theta > \theta_{\text{cr}} \kappa^{-d/3}$ . We note that for a quadratic lattice and for a one-dimensional chain we have  $\kappa = (1/2)^{3/d}$ . The intermediate section  $\theta_{\text{cr}}(1 - \kappa)^{-d/3} < \theta < \theta_{\text{cr}} \kappa^{-d/3}$  is stable or metastable, depending on the value of  $\theta_{\text{cr}}$  compared with unity. With increasing width of the quasilevel, the dependence of the charge on the degree of coating becomes weaker and the effect of condensation vanishes at  $\Gamma \sim \tilde{E}$ . At  $\Gamma \ll \tilde{E}$ , the critical temperature of this transition is of the order of  $E$  and can be either higher or lower than the critical temperature of the charge transition (see (17)). Uniformly and non-uniformly charged phases coexist in the two-phase region. The  $\mathcal{E}(T)$  dependence that follows from (17) at  $T \gg \Gamma$  affects the shape of the phase coexistence curve, but does not change the order of the critical temperature. The stability-loss curve  $T(\theta)$  is determined from the equation

$$T = -\theta(1 - \theta) \mathcal{E}_{\theta\theta}''(\theta, T) \quad (23)$$

and its form coincides qualitatively with that predicted in [6]. A more detailed investigation should take into account the relief of the substrate, so as to be able to answer precisely which phases can coexist in the two-phase region.

We proceed now to compare the results obtained in the present section with experiment. Upon condensation, the monolayer breaks up into regions with different density, structure, and charge. This becomes manifest in an experiment on diffraction of slow electrons, as the coexistence of reflections from two different structures in a certain region of coatings, and when the coating is

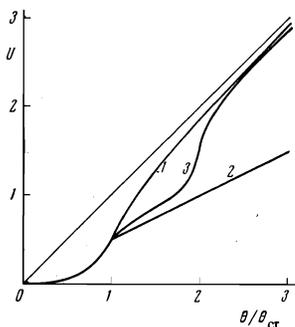


FIG. 4. Dependence of the dimensionless free energy  $U = \mathcal{E}/\tilde{E}$  on the degree of coating relative to the critical value, in the case  $T \rightarrow 0$  and  $\Gamma \rightarrow 0$ ; 1)  $\kappa = 1/2$  (infinite number of neighbors), 2)  $\chi = 0$  (nearest-neighbor interaction), 3)  $\kappa = 1/6$  (one-dimensional chain).

varied the reflections from one structure become weaker and those from the other become stronger. Such a behavior of the reflections was observed in the systems Na-W (110)<sup>[11]</sup>, Na-Ni (110)<sup>[12]</sup>, and also in the recently investigated systems Ba-Mo (110) and Ba-Cu (110)<sup>[13]</sup>. The experiments of<sup>[13]</sup> have shown that the region of coexistence of the reflections correlates with the linear section on the plot of the work function  $\phi$  against the degree of coating and with the inflection observed on the plot of the desorption energy  $q$  against the degree of coating. These facts are readily explained by the theory developed here. In the phase-transition region there coexist regions with different wave functions  $\phi'$  and  $\phi''$  and with densities  $\theta'$  and  $\theta''$ , and the area occupied by each phase depends linearly on the coating. Since the distance between electrodes is much larger than the dimensions of the regions, the experiment determines the average work function

$$\phi = \phi' \frac{\theta'' - \theta}{\theta'' - \theta'} + \phi'' \frac{\theta - \theta'}{\theta'' - \theta'}, \quad (24)$$

which depends linearly on the coating. In the phase-transition region, the free energy depends linearly on the coating, and therefore the change  $\Delta q = \partial F / \partial \theta$  of the desorption energy is constant. Measurements of the desorption energy were carried out at high temperatures  $\sim 10^3$  °K, i.e., apparently above the critical temperature, but nevertheless the characteristic singularity on this curve should remain also at these temperatures. When the temperature is increased from 77 to 300° K, the linear section on  $\phi(\theta)$  decreases, in agreement with the form obtained by us for the phase-coexistence curve.

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<sup>1)</sup>Since the electric field exists only in the space outside the metal, the interaction energy is half the energy of the usual dipole interaction.

<sup>1</sup>J. J. Lander, *Progr. Solid State Chem.* **2**, 26, 1965.

<sup>2</sup>A. U. MacRae, K. Müller, J. J. Lander and J. Morrison, *Surf. Sci.* **15**, 483, 1969.

<sup>3</sup>P. N. Tamm and L. D. Schmidt, *Surf. Sci.* **26**, 286, 1971.

<sup>4</sup>E. W. Plummer and R. D. Young, *Phys. Rev.* **B1**, 2088, 1970.

<sup>5</sup>L. A. Bolshov and A. P. Napartovich, Preprints of 3-rd Intern. Conf. on Thermionic Electrical Power Generation, G-128; Jülich, FRG, 1972.

<sup>6</sup>L. A. Bol'shov, *Fiz. Tverd. Tela* **13**, 1679 (1971) [*Sov. Phys.-Solid State* **13**, 1404 (1971)].

<sup>7</sup>P. W. Anderson, *Phys. Rev.* **124**, 41, 1961.

<sup>8</sup>T. B. Grimley and S. M. Walker, *Surf. Sci.* **14**, 395, 1969.

<sup>9</sup>L. D. Landau and E. M. Lifshitz, *Statisticheskaya fizika (Statistical Physics)*, Nauka, 1964 [Pergamon, 1971].

<sup>10</sup>J. L. Lebowitz and O. Penrose, *J. Math. Phys.* **7**, 98, 1966.

<sup>11</sup>V. K. Medvedev, A. G. Naumovets, and A. G. Fedorus, *Fiz. Tverd. Tela* **12**, 375 (1970) [*Sov. Phys.-Solid State* **12**, 301 (1970)].

<sup>12</sup>R. L. Gerlach and T. N. Rhodin, *Surf. Sci.* **17**, 52, 1969; **19**, 405, 1970.

<sup>13</sup>A. G. Fedorus and A. G. Naumovets, Yu. S. Vedula, *Phys. Stat. Sol. (a)*, **13**, 445, 1972.

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