Phase transitions in an adsorbed monolayer

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Phase transitions occurring in a layer adsorbed on a metal surface are investigated within the framework of the Anderson Hamiltonian with allowance for the interaction between the adsorbed atoms (adatoms) and the electron-phonon interaction. A time-dependent functional of the free energy is obtained. It is shown that, depending on the model parameters, both first- and second-order phase transitions with a doubling of the two-dimensional adatom-lattice constant are possible, the system in question being described in one of the limiting cases by the two-dimensional Ising model with long-range antiferromagnetic interaction in a field. The temperatures at which these transitions occur are computed for different limiting cases. It is also shown that the existence of a long-wave superlattice incommensurable with the original adatom lattice is possible at low temperatures. The energy relations between the various types of superlattices and the collective excitations in them are considered.

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§ 1. INTRODUCTION

The advances that have been made in the development of experimental methods of investigating the structure of monolayers adsorbed on metal surfaces and the phase transitions that occur in them when the temperature or the degree of coating is varied (see Ref. 1 for a review) make the theoretical investigation of these phenomena essential.

Any change that occurs in the positions of the adsorbed atoms (adatoms) during phase transitions in adsorbed layers is, generally speaking, accompanied by changes in the electronic state and, in particular, the charge of the adatoms. This connection between the location of the adatoms and their electronic state may turn out to be weak in certain particular cases. Then the investigation of the energy relations between the various states of the monolayer can be performed in different limiting cases, either assuming the adatom charges to be fixed and introducing a pair interaction potential between them, or conversely, fixing the equilibrium positions of the adatoms and considering the various electron configurations (see Ref. 1 for a review of these investigations).

In an earlier paper[2] we proposed a model that takes account of the above-mentioned connection between the electronic state and the structure of a monolayer, which leads to qualitatively new distinctive features of the phase transitions that occur in adsorbed layers.

We investigated in Ref. 2 on the basis of the Anderson model Hamiltonian with allowance for the interaction between the adatoms and the electron-phonon interaction the ground state of the adsorbed layer. It was shown that different structures are realized in the ground state, depending on the parameters characterizing the model, namely the location of the electronic level of the adatom relative to the Fermi level and the constants determining the interaction between the adatoms and the electron-phonon interaction. We investigated the energy relations between the homogeneous structure, in which all the adatoms have the same charge and are located at equal distances from the surface, and the structure with a doubled lattice constant. The latter structure is comprised of two adatom sublattices differing from each other in charge and distance to the surface (in the simplest case it is assumed that the adatoms cannot undergo displacement along the surface).

It was also shown that the structure with the doubled lattice constant can turn out in some parameter region to be unstable against the appearance of a new structure in which the charges of the adatoms and their equilibrium distances from the surface in each of the sublattices vary periodically. The lattice constant of this superlattice depends on the parameters of the model, and can be arbitrarily large and, generally speaking, incommensurable with that of the original two-dimensional adatom lattice.

However, we did not consider in Ref. 2 the temperature phase transitions, as well as the energy relations between the various possible superlattices. To investigate these problems, we construct in §2 of the present paper on the basis of the model Hamiltonian proposed in Ref. 2 an effective Hamiltonian that depends only on the phonon variables. Further, in §3 we consider with the aid of this Hamiltonian the distinctive features of the temperature phase transitions that is accompanied by a doubling of the lattice constant. In particular, we show in this section that the phase transition is described in the case of a sufficiently strong electron-phonon interaction by the Ising model with antiferromagnetic interaction in an external field. In the case of a weaker electron-phonon interaction the system is not described by the Ising model. In this case the investigation of the phase transitions is performed on the basis of the Landau free-energy functional, which is derived microscopically from the effective Hamiltonian.

Section 4 of the present paper is devoted to the investigation of the various superlattices that arise in a background of the lattice with the doubled lattice constant at low temperatures. The acoustic branches of the collective-excitation (phase-oscillation) spectrum that arise in a monolayer in the presence of incommensurate superlattices are considered in §5.

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§ 2. THE EFFECTIVE HAMILTONIAN

The model Hamiltonian proposed in Ref. 2 for a system of atoms adsorbed on a metal surface has the form

$$H=H_e+H_\varphi+H_{e-\varphi},$$
$$H_e=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}n_{\mathbf{k}}+g\sum_{\mathbf{k},j}[c_{\mathbf{k}}^{+}a_j\exp(i\mathbf{k}\mathbf{R}_j)+\text{H.c.}]$$
$$+\sum_j\varepsilon(n_j-n_0)+\frac{1}{2}\sum_{i,j\neq i}U_{ij}n_in_j, \qquad (1)$$
$$H_\varphi=\frac{1}{2}M\omega_0^2\sum_j q_j^2+\frac{1}{2}M\sum_j\dot{q}_j^2, \quad H_{e-\varphi}=\gamma\sum_j q_j(n_j-n_0),$$

where $c_{\mathbf{k}}^{+}$ and a_j^{+} are respectively the operators of creation of an electron in the metal and an electron localized on the j-th adatom; $n_{\mathbf{k}}=c_{\mathbf{k}}^{+}c_{\mathbf{k}}$, $n_j=a_j^{+}a_j$; g is the hybridization constant; ε is the energy of an electron occupying the adatom level; U_{ij} is the interaction between electrons localized on different adatoms; q_i is the operator of displacement of an adatom from the equilibrium position corresponding to the level occupation number n_0; γ is the electronphonon interaction constant.

Assuming, as in Ref. 2, that the repulsion energy for electrons with oppositely directed spins, and occupying the same level, is the largest energy quantity of the problem, we exclude from consideration the states with two electrons occupying the adatom level.

For the investigation of the dynamical and statistical properties of the two-dimensional adatom lattice, it is convenient to eliminate the electronic variables and perform the subsequent analysis on the basis of an effective Hamiltonian containing only the variables q_j.

It is easy to show (see Ref. 3, Chap. 3) that the statistical sum of the system (1) can be represented in the form of a path integral over the phonon variables:

$$Z=\int\limits_{q_i(0)=q_i(\beta)}D\{q_i\}\mathrm{Sp}\left\{\exp(-\beta H_e)T\exp\left[-\int_0^\beta[H_\varphi(\tau)+H_{e-\varphi}(\tau)]d\tau\right]\right\}, \qquad (2)$$

where the trace is taken over the electron states and $\beta=(kT)^{-1}$.

Below it will be convenient for us in the calculation to shift the reference point for the adatom displacement by setting:

$$q\to q-\frac{\varepsilon}{\gamma}-\frac{1}{2}\frac{U}{\gamma}, \quad U=\sum_{i\neq j}U_{ij}$$

and redesignate

$$H_e\to H_e-\left(\varepsilon+\frac{U}{2}\right)\sum_j(n_j-n_0), \quad H_{e-\varphi}\to H_{e-\varphi}+\left(\varepsilon+\frac{U}{2}\right)\sum_j(n_j-n_0).$$

Let us set

$$Z_1=Z_0\left\langle T\exp\left[-\int_0^\beta d\tau\sum_i\gamma q_i(\tau)n_i(\tau)\right]\right\rangle, \qquad (3)$$

where

$$Z_0=\mathrm{Sp}[\exp(-\beta H_e)], \quad \langle\ldots\rangle=Z_0^{-1}\mathrm{Sp}[\exp(-\beta H_e)\ldots].$$

It is well known (see Ref. 4, Chap. 3) that the quantity $\Delta\mathcal{H}=-T\ln(Z_1Z_0^{-1})$ is the sum of closed connected diagrams in which $\gamma q_i(\tau)$ plays the role of an external field. Since we shall below be interested in small displacements q_i, let us limit ourselves to the first terms of the diagram series right up to the terms of fourth order in the "field" γq_i. At the same time, we can neglect in each order in γq_i the quadratic and higher-order terms of the expansion in the interaction U, assuming, as before in Ref. 2, that $U\ll\Gamma$, where $\Gamma=\pi g^2N(0)$ is the adatom-level width. We shall also restrict ourselves in (3) to the consideration of only the diagonal elements, G_{ii}, of the electron Green function, since allowance for the off-diagonal elements $G_{ij}(i\neq j)$ leads in the case of a fairly rare monolayer only to the addition to U_{ij} of the indirect hybridization interaction investigated in Ref. 5.

It is significant that, for our choice of reference point for q_i, the electron Green function $G_{ii}(\omega)$ possesses the property that $G_{ii}(\omega)=G_{ii}(-\omega)$, a consequence of which is the absence of a cubic term in the expansion of $\Delta\mathcal{H}$ in powers of q_i.

Using the found value of $\Delta\mathcal{H}$, we obtain from (2) the expression

$$Z=Z_0\int D\{q_i\}\exp(-\beta\mathcal{H}). \qquad (4)$$

The effective Hamiltonian has the form

$$\mathcal{H}=-\frac{\gamma}{\xi}E\sum_i q_i(0)+\frac{1}{2}M\omega_0^2\sum_{i,\omega}\left(\frac{\omega^2}{\omega_0^2}+|\omega|\frac{\xi}{\pi\Gamma}-\Delta\right)|q_i(\omega)|^2$$
$$+\frac{1}{2}M\omega_0^2\sum_{\substack{\omega,\\ i,j\neq i}}\frac{U_{ij}}{\pi\Gamma}q_i(\omega)q_j^{*}(\omega)$$
$$+\frac{\gamma^4}{12\pi\Gamma^3}\sum_{\substack{i,\omega,\\ \omega',\Omega}}q_i(\omega)q_i^{*}(\omega-\Omega)q_i(\omega')q_i^{*}(\omega'+\Omega), \qquad (5)$$

where

$$\xi=\gamma^2(M\omega_0^2\Gamma)^{-1}, \quad E=\varepsilon\Gamma^{-1}+\xi(n_0-{}^1/_2)+{}^1/_2U\Gamma^{-1},$$
$$\Delta=\frac{\xi}{\pi}-1-\frac{\pi\xi}{3}\frac{T^2}{\Gamma^2}.$$

The summation in (5) is performed over the discrete frequencies $\omega_n=2\pi nT$.

In principle, the Hamiltonian (5) contains complete information about the dynamic and statistical properties of the adatom lattice. The expression (5), exclusive of the term $\sim|\omega||q(\omega)|^2$, could have been easily derived directly from (1) by assuming the q_i to be adiabatic variables and eliminating the n_i with the aid of the adiabatic condition

$$\partial\langle H\rangle/\partial q_i=0.$$

The term $\sim|\omega||q_i|^2$ describes the nonadiabatic contribution to the lattice energy. It is important for the investigation of the dynamic properties of the system. In particular, as will be shown in §5, it determines the phonon attenuation.

The simplest approximation that allows the computation of the free energy of the various structures consists in taking into account in (4) only the extremal trajectory $\{q_i(\tau)\}$ that minimizes the functional (5). Evidently, for this trajectory, $q_i(\tau)=q_i$, and the corresponding q_i values are found from the conditions

$$\partial\mathcal{H}/\partial q_i=0. \qquad (6)$$

Using the relation

$$\varkappa_i = \gamma\langle q_i\rangle/\Gamma = \pi(1/2 - \langle n_i\rangle),$$

which follows directly from the equations of motion for the operators a_i^+, and q_i, we can easily verify that the Eqs. (6) coincide with the Eqs. (11) of Ref. 2 for $|1/2 - n_i| \ll 1$. Thus, the approximation used in Ref. 2 is equivalent to the neglect of all the q_i fluctuations.

Allowance in (4) for the τ-independent trajectories that are different from the extremal trajectories and the τ-dependent trajectories corresponds to the consideration of the thermodynamic and quantum fluctuations.

§ 3. THE PHASE TRANSITIONS WITH A DOUBLING OF THE LATTICE CONSTANT

In Ref. 2 we showed that, for $\Delta > 0$, there exists a range of values of the parameter $\tilde{E}$ where each individual adatom can have two stable equilibrium positions, q_1 and q_2, in which it possesses different occupation numbers, n_1 and n_2. This means that, for $U_{ij} = 0$, the local minima of the functional $\mathcal{H}$ correspond to configurations in which q_i can assume the two values $q_i^{(0)} = \{q_1, q_2\}$.

For $U_{ij} \neq 0$, two cases are possible. If the interaction U_{ij} is sufficiently weak, to wit, if $U(\pi\Gamma)^{-1} \equiv u \ll \Delta$, then it has no effect on the positions of the local minima q_1 and q_2, and only determines the configuration energy. On the other hand, when $u \sim \Delta$, the state of a monolayer of noninteracting adatoms having two possible equilibrium positions loses any meaning as an initial approximation.

Let us first consider the first case. Then the weak interaction U_{ij} can be regarded as a perturbation that changes the value of the functional $\mathcal{H}$ for each extremal configuration by the amount

$$\frac{1}{2} M\omega_0^2 \sum_{i,j\neq i} u_{ij} q_i^{(0)} q_j^{(0)}.$$

Thus, taking into account in (4) only the above-indicated configurations, and introducing the variables ν_i, which assume the values ± 1, we easily obtain from (4) and (5) the expressions

$$Z = Z_0 \sum_{\nu_i = \pm 1} \exp(-\beta\mathcal{H}),$$
$$\mathcal{H} = \frac{1}{2}\sum_{i,j\neq i} J_{ij}\nu_i\nu_j + h\sum_i \nu_i, \tag{7}$$

where

$$J_{ij} = U_{ij}\frac{(\varkappa_1 - \varkappa_2)^2}{(2\pi)^2}, \quad h = \frac{\Gamma}{4\pi}(\mathscr{E}_1 - \mathscr{E}_2) + U\frac{\varkappa_1^2 - \varkappa_2^2}{(2\pi)^2},$$
$$\mathscr{E}_{1,2} = -2E\varkappa_{1,2} - \Delta\varkappa_{1,2}^2 + {}^1/_6\varkappa_{1,2}^4,$$

and the quantities $\mathscr{H}_{1,2} = \gamma q_{1,2}\Gamma^{-1} = \pi(1/2 - n_{1,2})$ are the largest and smallest roots of the equation $\partial\mathscr{E}/\partial\mathscr{H} = 0$.

Above we neglected the fluctuations in q_i relative to the equilibrium position q_1 or q_2. This can be done in the case when

$$\langle(q_i - q_{1,2})^2\rangle \ll (q_1 - q_2)^2.$$

Computing the mean square fluctuation with the aid of

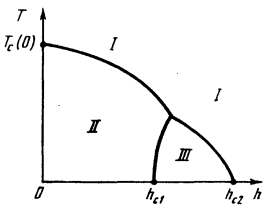

FIG. 1. Phase diagram of the system for the case of strong electron-phonon interaction: I) structure of the "ferromagnetic" type; II) structure of the "antiferromagnetic" type; III) complex structures.

(5), we obtain the condition for the applicability of the expressions (7):

$$\frac{\omega_0}{\Gamma\Delta^{1/2}}\operatorname{cth}\left(\frac{\omega_0\Delta^{1/2}}{2T}\right) \ll 1. \tag{8}$$

Thus, when this inequality is fulfilled and the electron-phonon interaction is sufficiently strong (i.e., $\Delta \gg u$), the system is described by the two-dimensional Ising model with antiferromagnetic interaction in an external field.

Qualitatively, the phase diagram of a system having a statistical sum of the form (7) is known (see, for example, Ref. 6). It is shown in Fig. 1. In the region of low temperatures $T < T_c(h)$ and weak "fields" $h < h_{c1}$ the system possesses long-range "antiferromagnetic" order, which in our language, means the presence of two adatom sublattices in which the adatom charges and equilibrium positions are different. The antiferromagnetic order disappears at $T > T_c(h)$, so that the system undergoes a second-order phase transition into the disordered phase at $T = T_c(h)$.

The characteristic values of h_{c1} and $T_c(0)$ are of the order of $\frac{1}{4}U(n_1 - n_2)^2 \sim U\Delta$. Clearly, here $T_c(0)$ should not be too high, so as not to violate the inequality (8). Substituting $T_c(0)$ into (8), we obtain $u \ll \Delta$, which was assumed in the derivation of (7).

Notice that the deviation of the interaction U_{ij} from the interaction with only the nearest neighbors leads to the possibility of the existence of complex structures at low temperatures. In particular, at $T = 0$ the transition from the phase with the doubled lattice constant into the homogeneous phase, in which all the adatoms are in the same state, occurs when h is increased from h_{c1} to $h_{c2} = \frac{1}{4}U(n_1 - n_2)^2$ by means of an infinite number of transitions, as a result of which there arise phases with an ever-increasing number of adatoms in the unit cell. The width of the region $h_{c2} - h_{c1}$ depends on the rate of decrease of the potential U_{ij} with distance, and is equal to zero for interaction with only the nearest neighbors.

Let us now consider the case when $|\Delta| \sim u$ and the problem does not reduce to the Ising model. It would be easy to compute the free energy of the system and find the phase-transition temperature T_c in the extremal approximation. In this approximation, the free energy coincides with (5), and the whole dependence on temperature is determined by the $T^2\Gamma^{-2}$ term in the expression for Δ, a term which arises simply because of the smearing of the Fermi distribution at finite temperatures. On the other hand, it is well known that the short-wave fluctuations can have a significant effect on the T_c value. In our case these fluctuations are large because of the "softness" of the individual-adatom vi-

brations, whose frequency $\omega \sim \omega_0 |\Delta|^{\frac{1}{2}}$ is low when $|\Delta| \ll 1$. Below we show that it is precisely these vibrations that determine T_c when $|\Delta| \ll 1$. In this sense the situation is very different from, for example, the Peierls transitions, where T_c is determined by the Kohn anomaly in the polarization operator, as a result of which there appears a term $\sim \ln(T/\varepsilon_F)$, instead of the electronic contribution $\sim (T/\Gamma)^2$.

To investigate the phase transition, let us construct the Landau functional, averaging it over the short-wave fluctuations. Neglecting the quantum fluctuations, and setting in (5)

$$q_i = q_0 + \frac{1}{N^{1/2}} \sum_{\mathbf{k}} q(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_i),$$

where q_0 is found from the condition $\partial \mathcal{H}^{(0)}/\partial q_0 = 0$, $\mathcal{H}^{(0)} = \mathcal{H}/q_i = q_0$ and N is the number of adatoms in the monolayer, we transform (5) into the form

$$\mathcal{H} = \mathcal{H}^{(0)} + \frac{\Gamma}{2\pi} \Big\{ \sum_{\mathbf{k}} \Omega(\mathbf{k}) |\varkappa(\mathbf{k})|^2 + \frac{2}{3} \varkappa_0 N^{-1/2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \varkappa(\mathbf{k}_1) \varkappa(\mathbf{k}_2) \varkappa^*(\mathbf{k}_1 + \mathbf{k}_2) + \frac{1}{6} N^{-1} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} \varkappa(\mathbf{k}_1) \varkappa(\mathbf{k}_2) \varkappa(\mathbf{k}_3) \varkappa^*(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \Big\}, \tag{9}$$

where

$$\varkappa_0 = \gamma q_0 \Gamma^{-1}, \quad \varkappa(\mathbf{k}) = \gamma q(\mathbf{k}) \Gamma^{-1}, \quad \Omega(\mathbf{k}) = \varkappa_0^2 - \Delta + u(\mathbf{k}),$$
$$u(\mathbf{k}) = \frac{1}{\pi\Gamma} \sum_{i \neq j} U_{ij} \exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)].$$

The free energy of the system

$$\mathcal{F} = -T \ln \int D\{\varkappa(\mathbf{k})\} \exp(-\beta \mathcal{H})$$

can be expanded in a perturbation-theory series in the nonquadratic—in $\mathcal{H}$—terms in (9), and is the sum of all the connected closed diagrams in which the role of Green's functions is played by the mean quantity

$$\langle |\varkappa(\mathbf{k})|^2 \rangle_0 = \pi T/\Gamma\Omega(\mathbf{k}),$$

while the bare vertices in which three or four Green's functions intersect are respectively $\frac{2}{3}\mathcal{H}_0 N^{-1/2} T^{-1}$, $\frac{1}{6} N^{-1} T^{-1}$ (see, for example, Ref. 7).

For $T \to T_c$, the integrals over momentum in each order of the perturbation theory diverge at momenta close to $\mathbf{k}_c = (\pm\pi, \pm\pi)$ [we assume that $u(\mathbf{k})$ is monotonic in the Brillouin zone and has a minimum at $\mathbf{k} = \mathbf{k}_c$], which leads to singularities in the second derivatives of $\mathcal{F}$ at $T = T_c$.

If, however, we split the domain of integration over $\mathbf{k}$ into the regions $|\mathbf{k} - \mathbf{k}_c| < Q \ll 1$ and $|\mathbf{k} - \mathbf{k}_c| > Q$, and first perform in all the diagrams the integration over the momenta far removed from $\mathbf{k}_c$, then we obtain diagrams containing integration just in the vicinity of $\mathbf{k}_c$ with renormalized bare vertices. The totality of these vertices determines the Landau functional. (The vertex-renormalization procedure is described in detail in Patashinskiĭ and Pokrovskiĭ's review article.[8])

Let us consider the parameter range where $|\Omega(\mathbf{k}_c)| \ll \Omega(0) \sim u$. In this case we can show that we can, in renormalizing the vertices, limit ourselves to the lowest-order perturbation theory if $T(\Gamma u^2)^{-1} \ll Q^2 \ll 1$. In

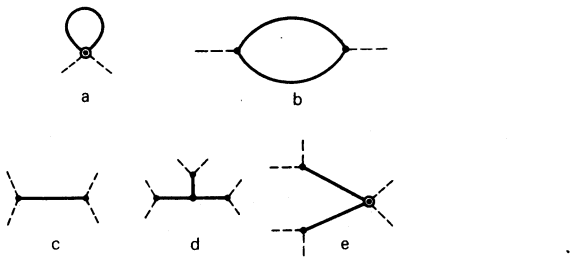

FIG. 2. Renormalization of the vertices of the free-energy functional: the heavy lines represent the correlators $\langle |\varkappa(\mathbf{k})|^2 \rangle_0$, the number of dashed lines corresponds to the order of the vertex; a point in a circle represents the bare fourth-order vertex, a heavy point the bare third-order vertex.

Figs. 2a and 2b we show the diagrams that make a contribution to the renormalization of $\Omega(\mathbf{k})$. Assuming that

$$\Omega(\mathbf{k}_c + \mathbf{Q}) \approx \Omega(\mathbf{k}_c) + cQ^2 \gg |\Omega(\mathbf{k}_c)|,$$

we can set $\Omega(k) = c|\mathbf{k} - \mathbf{k}_c|^2$ for $Q < |\mathbf{k} - \mathbf{k}_c| \ll 1$. Thus, the the two diagrams in Figs. 2a and 2b diverge logarithmically at small $|\mathbf{k} - \mathbf{k}_c|$, and therefore it is precisely this region that makes the largest contribution to the integrals when $\ln Q^{-1} \gg 1$. Finally, the renormalized $\Omega(\mathbf{k})$ has the form

$$\Omega(\mathbf{k}_c + \mathbf{k}) = \alpha(T - T_c) + ck^2, \tag{10}$$

where

$$\alpha = \left(1 - \frac{4\varkappa_0^2}{\Omega(0)}\right) \frac{\ln Q^{-2}}{4\Gamma c} \approx \left(1 - \frac{4\varkappa_0^2}{\Omega(0)}\right) \frac{\ln|\Omega(0)/\Omega(\mathbf{k}_c)|}{4\Gamma c}, \quad \Omega(\mathbf{k}_c) = -\alpha T_c.$$

The conditions $Q^2 \gg |\Omega(\mathbf{k}_c)|/c$ and $Q^2 \gg T(\Gamma u^2)^{-1}$ are equivalent to the condition $Q \gg r_c^{-1}(T)$, where $r_c(T)$ is the correlation length in the region of temperatures far from the transition point. For $T \lesssim T_c$ we have $r_c^{-2} \sim |\Omega(\mathbf{k}_c)|/c \sim |\Omega(\mathbf{k}_c)|\Omega^{-1}(0)$; therefore, we can, with logarithmic accuracy, set $\ln Q^{-2} \approx \ln|\Omega(0)/\Omega(\mathbf{k}_c)|$ in (10).

Besides the "fluctuation" diagrams containing integration over $\mathbf{k}$, and proportional to the temperature T, we should also take into account the diagrams, like those shown in Figs. 2c - 2e, that are nonzero at $T = 0$. Simple computations yield for the fourth-order vertex the value:

$$(b - h|\mathbf{k}|)N^{-1}, \tag{11}$$

where

$$b = \frac{1}{6}(1 - 6\varkappa_0^2 \Omega^{-1}(0)), \quad h = \frac{2\pi}{a_0 + b_0} \frac{\varkappa_0^2 u(0)}{\Omega^2(0)}.$$

Notice that the term proportional to the imparted momentum $|\mathbf{k}|$ arises as a result of the assumption made by us here, as well as in Ref. 2, that the interaction $U_{ij} \sim |\mathbf{R}_i - \mathbf{R}_j|^{-3}$ and, thus, decreases slowly. It should be taken into account when $|b| \ll 1$. The numerical coefficients in (11), as well as everywhere below, are defined according to the equalities (see also Ref. 2)

$$u(\mathbf{k}_c + \mathbf{k}) = \frac{u(0)}{a_0 + b_0}[(a_0 - b_0) + (a_2 - b_2)k^2], \quad k \ll 1,$$
$$u(\mathbf{k}) = \frac{u(0)}{a_0 + b_0}[(a_0 + b_0) - 2\pi|\mathbf{k}| + (a_2 + b_2)k^2]. \tag{12}$$

The sixth-order vertex given by the diagrams in Figs.

2d and 2e is equal to

$$N^{-2}d \equiv N^{-2}\frac{\varkappa_0^2}{\Omega(0)^2}\left(1-\frac{2}{3}\frac{\varkappa_0^2}{\Omega(0)}\right). \tag{13}$$

Investigating the equation for $\mathscr{H}_0$, we easily find that $d>0$ for all $\tilde{E}$, ξ, and $u(0)$. Thus, the Landau functional has the form

$$\begin{aligned} F=\frac{\Gamma}{2\pi}\Big\{&\sum_{|\mathbf{k}|<Q}[\alpha(T-T_c)+ck^2]|\Phi(\mathbf{k})|^2 \\ &+\frac{b}{N}\sum_{|\mathbf{k}|<Q}\Phi(\mathbf{k}_1)\Phi^*(\mathbf{k}_1-\mathbf{k})\Phi(\mathbf{k}_2)\Phi^*(\mathbf{k}_2+\mathbf{k}) \\ &-\frac{h}{N}\sum_{|\mathbf{k}|<Q}|\mathbf{k}|\Phi(\mathbf{k}_1)\Phi^*(\mathbf{k}_1-\mathbf{k})\Phi(\mathbf{k}_2)\Phi^*(\mathbf{k}_2+\mathbf{k}) \\ &+\frac{d}{N^2}\sum_{|\mathbf{k}|<Q}\Phi(\mathbf{k}_1)\Phi(\mathbf{k}_2)\Phi(\mathbf{k}_3)\Phi(\mathbf{k}_4)\Phi(\mathbf{k}_5)\Phi(\mathbf{k}_6)\delta\Big(\sum_{i=1}^{6}\mathbf{k}_i\Big)\Big\} \end{aligned} \tag{14}$$

where α, T_c, b, h, and d are defined in (10)–(13), $\Phi(\mathbf{k})=\mathscr{H}(\mathbf{k}_c+\mathbf{k})$, and $c=(a_2-b_2)(a_0+b_0)^{-1}u(0)$.

Let us first consider the region of the parameters where $b>0$ and $\Omega(\mathbf{k}_c)<0$. In this case, when b is not too small, we can neglect the last two terms in (14).

The Landau theory then predicts a second-order transition with a doubling of the lattice constant at $T=T_c$. Comparing the fluctuation contribution to the thermal capacity with the magnitude of the jump arising in the Landau theory, we find the temperature region in which we can neglect the fluctuations:

$$|\tau|\equiv\frac{|T-T_c|}{T_c}\gg\frac{b}{2c\alpha\Gamma}=\frac{1}{3}\ln^{-1}\left|\frac{\Omega(0)}{\Omega(\mathbf{k}_c)}\right|\frac{1-6\varkappa_0^2\Omega^{-1}(0)}{1-4\varkappa_0^2\Omega^{-1}(0)}.$$

Thus, the transition temperature computed by us is asymptotically exact at large $\ln|\Omega(0)\Omega^{-1}(\mathbf{k}_c)|$.

Now let $b<0$. In this situation, a first-order transition accompanied by a doubling of the lattice constant should, according to the Landau theory, occur at the temperature

$$T_k=(b^2/4d-\Omega(\mathbf{k}_c))\alpha^{-1}.$$

In deriving the functional (14), we neglected the quantum fluctuations. We can take them into account by replacing $\Omega(\mathbf{k})$ by $\omega^2\omega_0^{-2}+|\omega|\Gamma^{-1}+\Omega(\mathbf{k})$ in all the diagrams and, besides the integration over $\mathbf{k}$, carry out a summation over ω. It is easy to show that, if the short-wave cutoff satisfied the condition $\omega_0\Gamma^{-1}u^{-3/2}\ll Q\ll 1$, then we can, in renormalizing the vertices, limit ourselves to the lowest orders of the perturbation theory. As a result of the consideration of the quantum fluctuations, we obtain temperature-independent corrections to the vertices in (14). In particular, the correction to $\Omega(\mathbf{k}_c)$ found from the diagrams in Figs. 2a and 2b is equal in order of magnitude to $\omega_0\Gamma^{-1}u^{-1/2}$, so that the correction to T_c will be small if $\omega_0\Gamma^{-1}u^{-1/2}\ll|\Omega(\mathbf{k}_c)|$.

§ 4. THE LONG-WAVE SUPERLATTICE

Thus far, we have not taken into consideration the term proportional to $|\mathbf{k}|$ in (14). Meanwhile, the presence of this term makes the appearance of a structure whose wave vector differs slightly from the vector $\mathbf{k}_c=(\pm\pi,\pm\pi)$, which corresponds to the doubling of the lattice constant, energetically advantageous. We shall call such a structure a long-wave superlattice, bearing in mind here that it develops in a background of the original lattice with a doubled lattice constant, and that each of the two sublattices has a large lattice constant.

In this section we shall, using the functional (14), investigate the possible types of superlattices in the mean-field approximation at $T=0$. First of all, it is convenient to transform (14) with the aid of the wavelength and order-parameter scaling transformations

$$k\to\frac{2h}{c}\left(\frac{|\Omega(\mathbf{k}_c)|}{3d}\right)^{1/2}k,\quad \Phi\to\left(\frac{|\Omega(\mathbf{k}_c)|}{3d}\right)^{3/4}\Phi$$

and the energy transformation $F\to\text{const}\cdot F$ into the form

$$\begin{aligned} F=\int d^2\mathbf{r}\Big[&\operatorname{sign}\Omega(\mathbf{k}_c)\Phi^2+\beta\Phi^4+\frac{1}{3}\Phi^6\Big]+A\Big\{\sum_{\mathbf{k}}k^2|\Phi(\mathbf{k})|^2 \\ &-\frac{1}{2N}\sum_{\mathbf{k}}|\mathbf{k}|\Phi(\mathbf{k}_1)\Phi^*(\mathbf{k}_1-\mathbf{k})\Phi(\mathbf{k}_2)\Phi^*(\mathbf{k}_2+\mathbf{k})\Big\}, \end{aligned} \tag{14'}$$

where $\beta=b(3d|\Omega(\mathbf{k}_c)|)^{-1/2}$ and $A=4h^2(3dc)^{-1}$. Since we shall be interested below in the region $|b|\ll 1$, $|\Omega(\mathbf{k}_c)|\ll\Omega(0)$, $\beta\sim 1$, we can evaluate the values of h and d at the points where $b=0$ and $\Omega(\mathbf{k}_c)=0$. Then it follows from the equations for $\mathscr{H}_0$ with allowance for these conditions that

$$3d\Omega(0)=\tfrac{4}{9},\quad A=\pi^2/2b_0(a_2-b_2).$$

Notice that the functional (14′) does not contain a parameter having the dimensions of length, and equal to the lattice constant of the two-dimensional adatom lattice. In other words, the functional (14′) has been written in the continuum approximation, and does not contain terms that could describe the interaction of the structures in question with the adatom lattice. Below we shall show that the constant of the superlattice that minimizes (14′) can have any value, and that it is a continuous function of the parameters. Thus, the superlattice constant can turn out to be incommensurable with the adatom-lattice constant. In this case, when allowance is made for the terms describing the interaction with the adatom lattice (the commensurability energy), the appearance of effects connected with the interaction of the incommensurable structures is, in principle, possible.[9,10] However, since we are confining ourselves to the investigation of the long-wave superlattices, the commensurability energy is represented by terms into which the amplitudes enter with a very high power. Consequently, these terms are insignificant in the region where the value of the order parameter connected with the superlattice in question is small. This is the case at least near the thresholds of a second-order transition and in the vicinity of a first-order transition if the Φ jump at the threshold of the first-order transition is small. Thus, we exclude the commensuracility effects from consideration.

Naturally, all the foregoing equally well applies also to the commensurability effects that arise in the interaction with the metal substrate.

We shall seek the minimum of (14′) on the class of periodic superlattices:

$$\Phi(\mathbf{r})=\frac{1}{N^{1/2}}\sum_{\mathbf{k}}\Phi(\mathbf{k})e^{i\mathbf{kr}}=A_0+\sum_{\mathbf{G}'\neq 0}A(\mathbf{G}')e^{i\mathbf{G}'\mathbf{r}}, \tag{15}$$

where $\mathbf{G}'=m\mathbf{G}_1+n\mathbf{G}_2$ ($m, n=0, \pm1, \pm2\ldots$) are the reciprocal-lattice vectors of the superlattice.

Since the Hamiltonian (14′) is invariant under rotation through any angle, to the minimum of (14′) clearly correspond structures with $|\mathbf{G}_1|=|\mathbf{G}_2|=G$, the amplitudes satisfying the parity condition: $A(\mathbf{G}')=A(-\mathbf{G}')$, $\mathrm{Im}A(\mathbf{G}')=0$. The amplitudes of the harmonics $A(\mathbf{G}')$ and the quantity G are found from the conditions for extrema:

$$\partial F/\partial A(\mathbf{G}')=0, \tag{16}$$

$$\partial F/\partial G=0. \tag{17}$$

By fixing the various superlattice symmetries by prescribing the angle, θ, between $\mathbf{G}_1$ and $\mathbf{G}_2$, and investigating the system of equations (16), (17), we can find the nature of the transition into the state with a superlattice and the energy relations between the various superlattices.

Let us first of all consider the one-dimensional superlattice, which corresponds to $\theta=0$. We shall assume that the superlattice arises smoothly, so that $A(\mathbf{G}')\to 0$ in the vicinity of the stability threshold for the structure with the doubled lattice constant. Then the existence domain of the superlattice is found from the condition for the violation of the positive definiteness of the quadratic form (14′) in $A(\mathbf{G}')$ upon the neglect of all the terms of higher order in $A(\mathbf{G}')$. It is easy to show that this occurs when

$$\beta+A_0^2(1-{}^1/_4A)\leqslant 0, \tag{18}$$

the coefficient in front of $|A(\mathbf{G}')|^2$, where

$$|\mathbf{G}'|\equiv k_0=A_0^2, \tag{19}$$

vanishing at the stability threshold [which corresponds to the equality sign in (18)]. This means that, in the vicinity of the stability threshold, the superlattice is described by a near-harmonic function of wave vector $|\mathbf{G}|=k_0$. The higher-order harmonics $A_n\equiv A(n\mathbf{G})$ are quantities of higher order in smallness: $A(n\mathbf{G})\sim A^n(\mathbf{G})$.

In order to find the dependence of A_1 on the parameters β and A near the stability threshold $\beta=\beta_c(A)$, it is necessary to take into account in the equation $\partial F/\partial A_1=0$ the terms $\sim A_1^3$, as well as the terms $\sim A_0A_1A_2$, which have the same order of smallness as the A_1^3 terms. As a result of the solution of Eqs. (16) and (17) with this accuracy, we easily find with allowance for (18) that

$$A_1^2=-\frac{8|1-{}^1/_2A||\beta-\beta_c|}{7(A-{}^{12}/_7)(A-4)},\quad \beta_c=\frac{A/4-1}{|1-{}^1/_2A|^{1/2}}, \tag{20}$$

$$k_0=|1-{}^1/_2A|^{-1/2}. \tag{21}$$

For $A<2$ the superlattice is formed at $\beta>\beta_c$, while for $A>2$ the existence domain of the superlattice is the region where $\beta<\beta_c$.

The expression (20) for A_1^2 shows that the solution to Eqs. (16) and (17) that corresponds to a smooth formation of the superlattice exists only for $12/7<A<4$. Outside these limits the transition into the state with a superlattice occurs discontinuously at $\beta<\beta_c$ if $A<12/7$ and at $\beta>\beta_c$ if $A>4$. Let us recall that the parameter A is determined only by the character of the decrease of the interaction $U(|\mathbf{R}_i-\mathbf{R}_j|)$. For the dipole-dipole interaction $U\sim|\mathbf{R}_i-\mathbf{R}_j|^{-3}$, $A\approx 2.1$, so that the superlattice is formed smoothly. However, allowance for the Friedel oscillations can change the magnitude of A and, together with it, the nature of the transition. Notice that the possibility of a first-order transition in the present case is connected with the allowance for the terms $\sim A_1A_2$ in Eq. (16). Therefore, it is natural to assume that $A_2\sim A_1$ in the resulting superlattice, so that this superlattice can differ quite sharply from the harmonic superlattice.

The two-dimensional superlattices ($\theta\neq 0$) can be investigated in similar fashion. A preferred one among them is the hexagonal superlattice, which corresponds to the value $\theta=\frac{1}{3}\pi$. The fact that there are in this case three wave vectors $\mathbf{G}_1$, $-\mathbf{G}_2$, and $\mathbf{G}_2-\mathbf{G}_1$ with equal magnitudes (i.e., such that $|\mathbf{G}_1|=|\mathbf{G}_2|=|\mathbf{G}_2-\mathbf{G}_1|$) and a null resultant leads to the appearance in the equation $\partial F/\partial A_1=0$ of terms $\sim A_0A_1^2$, whereas for all other values of θ the nonlinear—in A_1—term in this equation is of the same order of smallness[1)] as A_1^3. As a result, we have from (16) and (17) for A_1 the equation

$$A_1^2f(A)+A_1\frac{(8-3A)A}{|1-{}^1/_2A|^{1/4}}=8(2-A)(\beta-\beta_c), \tag{22}$$

where $f(A)=-(60+25\cdot 3^{1/2})A^2+(336+80\cdot 3^{1/2})A-(352+64\cdot 3^{1/2})I$.

Let us first consider the case when $f(A)>0$. This, in particular, occurs in the case of a dipole-dipole interaction between the adatoms. If the sign of A_1 is chosen so that the linear—in A_1—term in (22) is negative, then Eq. (22) can have two solutions in that range of the parameters where the structure with the doubled lattice constant is still stable. Of the two the solution with the larger $|A_1|$ is the local minimum of F. When

$$\beta=\beta_c+(8-3A)^2A^2[36|1-{}^1/_2A|^{1/4}(A-2)f(A)]^{-1}$$

this minimum becomes deeper than the minimum corresponding to the structure with the doubled lattice constant, and a first-order transition into the state with a superlattice occurs, the amplitude of A_1 at the transition point being equal to

$$\Delta A_1=2(8-3A)A[3|1-{}^1/_2A|^{1/4}f(A)]^{-1}.$$

Let us note that in the case under consideration the first-order transition is due to the interaction between the harmonics $A(\mathbf{G}_1)$, $A(-\mathbf{G}_2)$, and $A(\mathbf{G}_2-\mathbf{G}_1)$, and, for small A_1, the superlattice is the resultant of three waves with wave vectors $\mathbf{G}_1$, $\mathbf{G}_2$, and $\mathbf{G}_2-\mathbf{G}_1$. A formally similar problem has been considered by McMillan[11] in connection with the phenomenological investigation of the production of charge-density waves in layered systems. It is also clear that, at least near the stability threshold $\beta=\beta_c(A)$, the hexagonal superlattice that arises via a first-order transition is energetically more advantageous than any superlattice that can arise as a result of a second-order transition, since it has a finite amplitude $A_1\neq 0$ at the stability threshold. It follows from this, in particular, that, in the case of the dipole-dipole interaction between the adatoms, the hexagonal superlattice is energetically more advantageous than the one-dimensional superlattice in the vi-

cinity of the stability threshold. However, in the presence of cleavages on the surface the energy relation can change in favor of the one-dimensional superlattice.

Now let $f(A)<0$. It can be shown that in this case all the solutions to (22) are unstable. This means that there occurs in the stability region for the structure with the doubled lattice constant a first-order transition into a superlattice state in which the higher harmonics cannot be considered to be weak.

§ 5. COLLECTIVE EXCITATIONS OF THE ACOUSTIC TYPE

As is well known, the degeneracy in energy terms of the ground state of the incommensurable superlattice with respect to uniform displacement leads to the appearance of collective oscillations with an acoustic spectrum. Let us compute the spectrum of these excitations for the case of the one-dimensional, and the two-dimensional hexagonal, superlattice. For this purpose, let us set in (15)

$$A(\mathbf{G}')=|A(\mathbf{G}')|\exp[i\varphi(\mathbf{G}')+i\delta\varphi(\mathbf{G}',\mathbf{r})],$$

where $\delta\varphi(\mathbf{G}', \mathbf{r})$ is a slowly varying function of the coordinates. Substituting (15) into (14′), expanding in terms of the small deviations

$$\delta\varphi(\mathbf{G}',\mathbf{r})=\sum_{\mathbf{q}}\delta\varphi(\mathbf{G}',\mathbf{q})e^{i\mathbf{q}\mathbf{r}}$$

and diagonalizing the obtained quadratic form, we find for the acoustic branch of the eigenvalues in zeroth order in $|A(\mathbf{G}')|$:

$$\omega^2(\mathbf{q})=s^2q^2\cos^2\alpha,$$

where

$$s^2=\frac{\pi^2}{2Ab_0(a_0+b_0)}\omega_0^2u(0)a^2,\quad \cos\alpha=\frac{\mathbf{qG}}{qG}$$

for the one-dimensional superlattice (a is the lattice constant of the original adatom lattice).

For the hexagonal superlattice there are two acoustic branches: longitudinal and transverse, for which s^2 has respectively the values:

$$s_l^2=\frac{\pi^2}{2Ab_0(a_0+b_0)}\cdot\frac{3}{4}\omega_0^2u(0)a^2,$$
$$s_t^2=\frac{\pi^2}{2Ab_0(a_0+b_0)}\cdot\frac{1}{4}\omega_0^2u(0)a^2.$$

Knowing $\omega^2(\mathbf{q})$, we can easily derive for the acoustic-type collective-excitation spectrum the expression

$$\mathscr{A}(\omega)=\omega^2(\mathbf{q}),\qquad(23)$$

where $\mathscr{A}(\omega)=\omega^2+i\omega_0^2\Gamma^{-1}\omega$ is the analytic continuation of the frequency dependence of the coefficient attached to $|q(\omega, \mathbf{k})|^2$ in the functional (5).

It can be seen from (23) that the decrement of the collective excitations in the region of small q is high. This is connected with the absence of a gap in the single-particle electron-excitation spectrum and the possibility of absorption of the acoustic-wave energy through the production of such excitations.

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[1)]It is clear from symmetry arguments that $A(\mathbf{G}_1)=A(\mathbf{G}_2)=A(\mathbf{G}_2-\mathbf{G}_1)\equiv A_1$.

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