

Orientalional phase transitions in an adsorbed monolayer

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We demonstrate the possibility of the existence of orientational first-order phase transition in an adsorbed layer on the (011) face of a body-centered cubic crystal (such as tungsten).

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Recently both the theoreticians and the experimenters exhibit great interest in ordered systems whose subsystems are not commensurate. Well known examples that demonstrate the noncommensurability of the lattice period with the periods of the produced superstructures are charge-density waves as well as magnetic ordering in helicoidal magnets. Much attention is being paid also to phenomena in monolayers of adsorbed atoms (see the review⁽¹⁾), where frequently the structure of the monolayer has nothing in common with the substrate structure.

The character of the produced adsorbed-atom lattice is determined by two factors: the periodic potential relief of the substrate, and the interaction between the adsorbed atoms. Depending on the type of substrate, this interaction is mainly of two types. The first includes dipole-dipole repulsion of the adsorbed atoms. It is quite significant if the substrate is a metal (see⁽¹⁻³⁾ concerning the nature of the interaction and its character). The other class includes van der Waals attraction at large distances and repulsion by the outer electron shells of the adsorbed atoms at short distances. The latter interaction is typical in a monolayer on a graphite surface.⁽⁴⁾

We consider here the first class of interactions, which leads in the case of a weak potential relief of the surface to a close-packed structure of the monolayer, with a lattice constant determined by the concentration of the adsorbed atoms. The main contribution to the total energy $E = E_0 + E_1$ is made by the interaction between the adsorbed atoms

$$E_0 = \frac{1}{2} g \sum_{i \neq j} |\mathbf{r}_i - \mathbf{r}_j|^{-3}, \quad (1)$$

and their interaction with the substrate

$$E_1 = V \sum_i (\cos \mathbf{k}_1 \mathbf{r}_i + \cos \mathbf{k}_2 \mathbf{r}_i) \quad (2)$$

is regarded as a perturbation. We therefore do not take into account the higher harmonics in the periodic potential (2). The wave vectors \mathbf{k}_1 and \mathbf{k}_2 determine the structure of the substrate surface. The coordinates of the adsorbed atoms

$$\mathbf{r}_i = \mathbf{r}_i^{(0)} + \mathbf{u}_i \quad (2)$$

are the sums of their equilibrium positions $\mathbf{r}_i^{(0)}$ in the regular triangular lattice, and the displacements \mathbf{u}_i obtained by minimizing the total energy E . Substitution of (3) in (1) and (2) and allowance for the principal terms of the expansion in the displacements leads to the following expression for the total energy:

$$E = E_0^{(0)} + \frac{1}{2} \sum_{\mathbf{q}, \alpha, \beta} \epsilon_{\alpha\beta}(\mathbf{q}) u_\alpha(\mathbf{q}) u_\beta(-\mathbf{q}) - V \sum_i (\mathbf{k}_1 \mathbf{u}_i \sin \mathbf{k}_1 \mathbf{r}_i^{(0)} + \mathbf{k}_2 \mathbf{u}_i \sin \mathbf{k}_2 \mathbf{r}_i^{(0)}), \quad (4)$$

where E_0 is the unperturbed interaction energy of the adsorbed atoms,

$$u_\alpha(\mathbf{q}) = N_a^{-1/2} \sum_j u_{j\alpha} \exp(i\mathbf{q}\mathbf{r}_j^{(0)}) \quad (5)$$

is the Fourier transform of the α -component of the displacement (N_a is the total number of adsorbed atoms), and

$$\epsilon_{\alpha\beta}(\mathbf{q}) = 3g \sum_j (1 - \cos \mathbf{q}\mathbf{r}_j^{(0)}) \frac{5x_{j\alpha}^{(0)}x_{j\beta}^{(0)} - (r_j^{(0)})^2 \delta_{\alpha\beta}}{(r_j^{(0)})^7}. \quad (6)$$

The displacements obtained by minimizing the energy (4)

$$u_\alpha(\mathbf{k}_{(1,2)}) = \frac{i}{4} V N_a^{1/2} (\epsilon^{-1}(\mathbf{k}_{(1,2)}))_{\alpha\gamma} k_{(1,2)\gamma} \quad (7)$$

lead to an energy gain

$$\Delta\epsilon = \frac{1}{N_a} \Delta E = -\frac{1}{8} V^2 \left\{ k_1 \beta(\epsilon^{-1}(k_1)) \beta_\gamma k_{1\gamma} + k_2 \beta(\epsilon^{-1}(k_2)) \beta_\gamma k_{2\gamma} \right\}, \quad (8)$$

which, generally speaking, depends on the mutual orientation of the vector pair $(\mathbf{k}_1, \mathbf{k}_2)$ and the pair $(\mathbf{a}_1, \mathbf{a}_2)$ of basis vectors in the regular triangular lattice of the adsorbed atoms. We have calculated the function (8) numerically as a function of the rotation α

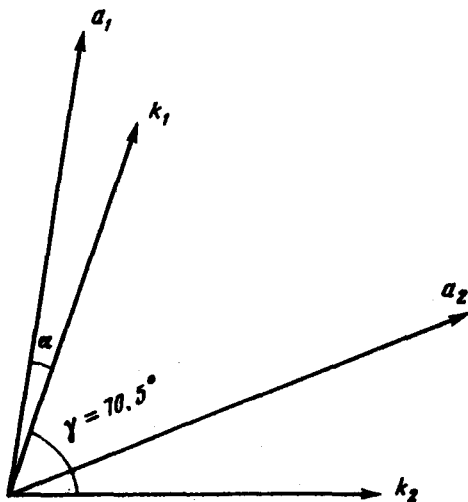


FIG. 1. Mutual orientation of the vector pairs $(\mathbf{a}_1, \mathbf{a}_2)$ and $(\mathbf{k}_1, \mathbf{k}_2)$ for the case of the (011) face of the tungsten lattice.

(see Fig. 1) for the concrete case of the (011) face of a body-centered crystal such as tungsten. The calculation was made in a wide range of adsorbed-atom concentrations $c = N_a/N$ (N is the total number of the atoms of the surface). It was found that first-order phase transitions are possible, with a jumplike change of α at the concentrations listed in Table I. Table I lists also the changes of the angle α on going from lower to higher concentrations.

TABLE I.

c	$\alpha <$	$\alpha >$
0.18	8°	20°
0.27	25°	-3°
0.47	-5°	8°
0.66	15°	25°

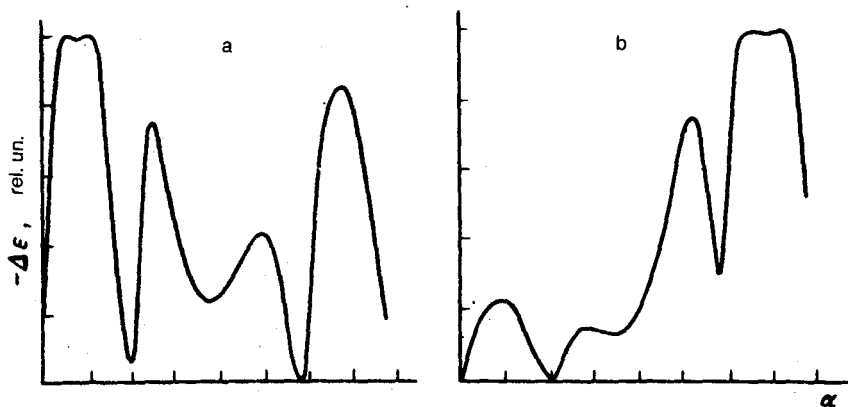


FIG. 2. Values of the function (8) for the concentrations $c=0.268$ (a) and $c=0.254$ (b).

Figure 2 shows the change of the form of the function (8) at a concentration close to $c \approx 0.27$. In experiments on the diffraction of slow electrons, an almost jumplike reorientation was observed¹⁵⁾ of the reflections produced by a cesium-atom monolayer with concentration 0.22 ± 0.03 , sputtered on the (011) face of tungsten. The angle of rotation of the adsorbed-atom lattice was close to 30° in these experiments.

It should be noted that the perturbation theory considered here breaks down if one of the adsorbed-atom reciprocal-lattice vectors approaches the vectors \mathbf{k}_1 and \mathbf{k}_2 . At concentrations determined by this condition, a one-dimensional matching of the adsorbed-atom lattice to the substrate should occur.

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