Orientational second-order phase transitions in monolayers

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The orientational second-order phase transition in a monolayer of atoms adsorbed at the surface of a metal at low temperatures is investigated.

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Novaco and McTague[1] were first to predict the existence of orientational epitaxy in submonolayers of adsorbed atoms. It was established that interaction with the substrate determines a definite orientation of the lattice of the adatoms, which is incommensurable with the substrate. Uĭmin and Shchur[2] predicted the existence of orientational first-order phase transitions consisting of steplike variations of the angle between the adatomic lattice and the substrate.

The orientational second-order phase transitions are also possible. Let us consider the substrate as a two-dimensional charge image having two-fold axes of symmetry. Consider a case when the lattice of adatoms has two axis of second order. In the symmetric phase of the axis of symmetry the substrates coincide with the axes of symmetry of the adatomic lattice. In the second-order transition the symmetry is violated and the adatomic lattice goes over the phase in which the angle between the axes of symmetry of both lattices is nonvanishing. As a result, two symmetric energy minima are produced as functions of the angle θ between the axes. Uĭmin and Shchur[2] encountered this in their numerical calculations.

The orientational phase transitions occurs when the adatomic lattice is incommensurable with the substrate; however, they are closely associated with the transitions to the commensurable phase. As Pokrovski and Talapov[3] showed, if the geometry of one lattice differs from that of the other, then a one-dimensional commensurability occurs. In the commensurable phase one of the vectors of the reciprocal lattice of the substrate coincides with a vector of the reciprocal lattice of the adatoms. But their axes of symmetry do not coincide because of the different geometry of the lattices (see Fig. 1).

A configuration with coincident axes of symmetry is often preferred at some distance from the transition (in the incommensurable phase). Therefore, as the transition approaches, the angle between the axes of symmetry forms first (orientational phase transition) and then commensurability sets in. Such orientational transitions apparently are missing in systems in which both lattices have identical geometries.

We calculated the free energy of the adatoms at lower temperatures than the Debye temperature, as a function of the angle between the lattices and also the curves for the phase transitions in the concentration-temperature plane.

The energy of interaction of the adatoms can be written in the harmonic approximation:

$$E_0 = 1/2 \sum_{\mathbf{k}} \epsilon_{\alpha\beta}(\mathbf{k})\, u_\alpha(\mathbf{k})\, u_\beta(-\mathbf{k}). \qquad (1)$$

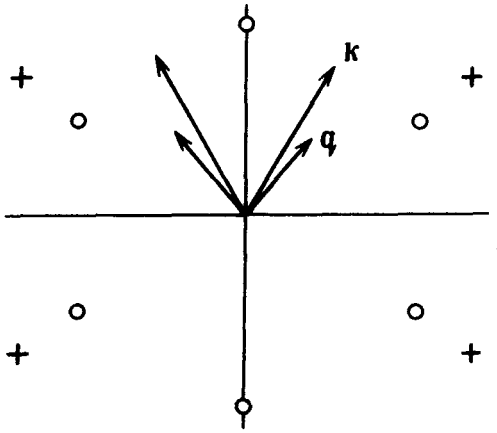

FIG. 1. Incommensurable phase in which the symmetry axes of both lattices are the same. The crosses represent substrate atoms and the open circles denote adsorbed atoms.

The energy of interaction with the substrate is regarded as a perturbation:

$$E_1 = \sum_{\mathbf{q}a} V(\mathbf{q}) \cos \mathbf{q}(\mathbf{a} + \mathbf{u}_a), \tag{2}$$

where $\mathbf{q}$ is the vector of the reciprocal lattice of the substrate and a is the vector of the adatomic lattice. A minimization of the sum (1) and (2) produces nonzero shift of the equilibrium position and an energy gain:

$$\Delta E = -1/4 \sum_{\mathbf{q}} V^2(\mathbf{q}) \epsilon^{-1}_{\alpha\beta}(\mathbf{q}) q_\alpha q_\beta \tag{3}$$

(see Refs. 1, 2, and 4).

The oscillation spectrum of the adatoms near the new equilibrium positions will be different from the oscillation spectrum of the adatoms without taking into account the interaction with the substrate:

$$\epsilon'(\mathbf{k},s) = \epsilon(\mathbf{k},s) + \sum_{\mathbf{q}} \frac{V^2(\mathbf{q})}{4} |\mathbf{q}v_{ks}|^2$$

$$\times \sum_{\nu} \frac{2|\mathbf{q}v_{q\nu}|^2}{\epsilon(\mathbf{q},\nu)} - \frac{|\mathbf{q}v_{q+k,\nu}|^2}{\epsilon(\mathbf{q}+\mathbf{k},\nu) - \epsilon(\mathbf{k},s)} - \frac{|\mathbf{q}v_{q-k,\nu}}{\epsilon(\mathbf{q}-\mathbf{k},\nu) - \epsilon_i(\mathbf{k},s)} \tag{4}$$

$s,\nu = 1, 2$ are the branches of the spectrum.

A variation of the oscillation spectrum due to the interaction with the substrate (4) changes the velocity of the sound and hence the energy of the phonon gas.

The interaction between the adatoms adsorbed on the surface of a metal is primarily a dipole-dipole interaction (see review article of Bol'shov *el al.*[5]). In this case the free energy of the phonon gas is

$$\Delta F(T) = V^2 \frac{ma^{11}}{\hbar^2 d^6} T^3 f(\theta, c), \tag{5}$$

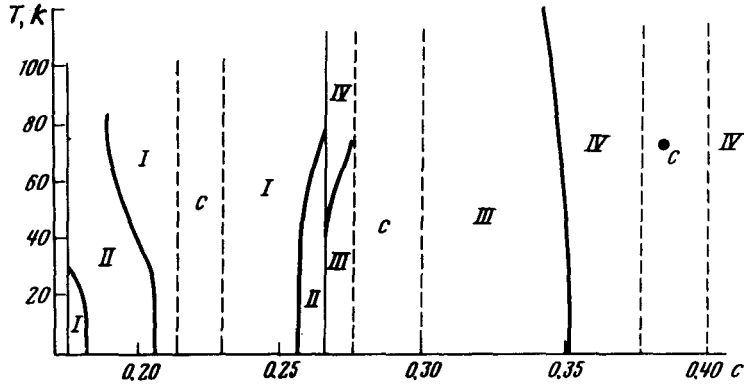

FIG. 2.

where m is the mass of the adatom, d is the dipole moment, a is the adatomic lattice constant, and T is the temperature.

We numerically calculated the $f(\theta,c)$ function for the case when the substrate is the (011) face of the tungsten and the adatomic lattice is triangular. A minimization of the sum (3) and (5) relative to the angle θ between the axes of symmetry of the lattices gives a dependence of the orientation on the concentration and temperature. The points of the phase transitions are determined according to the Landau theory. In the potential of interaction with the substrate only the first harmonics are conserved.

The phase diagram is shown in Fig. 2. In phase III (shown in Fig. 1) the axes of symmetry of the adatomic lattice coincide with those of the substrate, i.e., the angle θ, which is the order parameter, is equal to zero (symmetric phase). In phase IV, which is a phase with a spontaneously violated symmetry, the angle θ between the axes of symmetry of both lattices is nonvanishing. Phases I and II differ from phases III and IV in that their adatomic lattice is rotated 90° and they are separated by a first-order phase transition (the vertical line in Fig. 2). In phase I the axis of symmetry of one lattice coincides with that of the other and phase II is a phase in which the symmetry is violated. The angle θ between the axes in the asymmetric phases II and IV is equal to 5° and c is the commensurate phase.

The first-order phase transitions are almost temperature independent; however, the second-order phase transitions exhibit a temperature dependence (the critical concentration varies by 5% as a result of increasing the temperature from 0 to 100 K). The effect of temperature only on the second-order transitions is attributable to the fact that the free-energy of the phonon gas (5) is small compared to the energy at zero temperature (3). However, in the neighborhood of the second-order phase transition the energy at zero temperature slowly depends on the order parameter and a small temperature correction appears to be essential.

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