Intrinsic defects in adsorbed monolayers

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Structural irregularities of monolayers on a surface with a deep potential relief are examined for adatom concentrations close to 1/3 and 1/6.

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The physics of surface effects, particularly the branch dealing with the properties of adsorbed monolayers, has lately attracted special attention. In this letter we examine the properties of monolayers of adsorbed atoms (adatoms) on the close-packed face (011) of a body-centered crystal such as tungsten. Detailed information on such systems is given in a review by Bol'shov *et al.*[1]

The structure of the submonolayer film depends on the interaction energy of the adatoms, their concentration, the periodic potential relief of the substrate, and the temperature.

The interaction of adatoms in the case at hand is a dipole–dipole repulsion, whose origin is not difficult to understand. After settling on the surface, an alkali atom gives up its outer electron to the conduction band of the metal. The electrostatic image forms a dipole, which is oriented along the normal to the surface. The interaction energy of the adatoms, which is two-dimensionally isotropic, decreases with distance r as r^{-3}. Without a monolayer–substrate interaction the adatoms would form a regular triangular lattice whose interatomic distance would be determined by their concentration. Such a lattice is obviously incommensurable with the structure of the (011) tungsten face.

The potential relief of such a surface is shown schematically in Fig. 1. If the relief is "shallow" compared to the interaction energy of the adatoms, then the regular triangular lattice will be slightly modulated by the periodicity of the substrate. If, however, the relief is "deep,"[1] then the adatoms will fill the potential wells and the arrangement of the occupied wells will be regulated by the interaction of the adatoms. The optimum configuration of the filled wells can easily be determined by numerical calculation[3] if the concentration c of the adatoms, i.e., the ratio of their number M_α to the number N of minima in the potential relief of the substrate's surface, is equal to p^{-1} (p is an integer). In this case a unit cell of the monolayer lattice will contain one atom, and its area relative to a unit surface cell will be p. At other concentrations

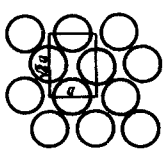

FIG. 1. The arrangement of the tungsten atoms on the (011) face. The lattice constant a is taken as unit length, and the interaction energy of adatoms separated by unit distance is adopted as unit energy.

TABLE I.

c	1/3		1/6	
a	–	1	2	3
$\epsilon_v + \epsilon_d^{(a)}$	3.159	1.803	1.728	1.795

$c = m/n$ ($m < n$ are integers), the minimum configuration of the monolayer should correspond to a regular lattice with at least m adatoms in the unit cell. Structures of this kind are commensurable with the structure of the substrate surface.

For $c \gtrsim 1/3$ mismatched structures (regular triangular) as well as some simple matched structures with $p = 3$, 4, 6, 9, 12, and 21 have been observed experimentally (see the review article[1]) by using the slow-electron diffraction method. Instead of inquiring why structures with other values of p have not been observed, we shall examine the structure of the monolayer for concentrations close to 1/3 and 1/6. Of course periodic matched structures can exist in these cases, but the unit cell must contain many atoms. The formation of lattices with large unit cells, however, requires rather low temperatures, which exponentially lengthen the migration time of the adatoms along the surface. In this situation, very simple matched structures with defects are characteristic examples. They can be vacancies in the lattice of the adatoms, adatoms which fill the free minima of the potential relief (henceforth called defects), "twins," grain boundaries, and so on. A method for calculating the energy of the vacancy–defect structure is described below.

The interaction of adatoms in the monolayer is expressed by

$$E = 1/2 \sum_{i \neq j} | \mathbf{r}_i - \mathbf{r}_j |^{-3}, \tag{1}$$

where $\mathbf{r}_i$ is the coordinate of the filled well in the periodic matched structure. All the distances and also the energy are dimensionless (see Fig. 1). By using a specific concentration which does not match $1/p$ ($p = 3.6$), we can determine the difference between the number of vacancies M_v and the number of defects M_d:

$$M = | M_v - M_d |, \tag{2}$$

$$c = p^{-1} \pm M/N. \tag{3}$$

The plus sign in Eq. (3) corresponds to the imperfect structure and the minus sign corresponds to the vacancy structure. The energy of the monolayer with a concentration close to $1/p$ is given by

$$E(c) = E(c = p^{-1}) + M_v \epsilon_v + \sum_a M_d^{(a)} \epsilon_d^{(a)} + E_{\text{int}}. \tag{4}$$

A summation over the defect type α is performed in Eq. (4) because several types of defects and only one type of vacancy can exist in the periodic lattice with a single adatom per unit cell. The interaction energy of such systems is

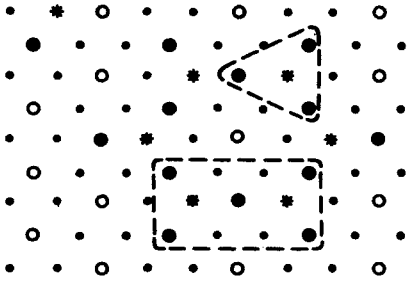

FIG. 2. Represented schematically are: the "wells" of the potential relief (·), regular structure corresponding to $c = 1/3$ (○), vacancies (●), and defects (*). A six-vacancy "molecule" coiled into a ring produces a nucleation center of the phase with $c = 1/4$. Two- and three-vacancy molecules are also isolated. Their binding energies are $\epsilon_{2v} - 2\epsilon_v = -0.128$ and $\epsilon_{3v} - (\epsilon_{2v} + \epsilon_v) = -0.102$.

$$E_{\text{int}} = \frac{1}{2}\sum_{i\neq j} |\mathbf{r}_i^{(v)} - \mathbf{r}_j^{(v)}|^{-3} + \frac{1}{2}\sum_{i\neq j} |\mathbf{r}_i^{(d)} - \mathbf{r}_j^{(d)}|^{-3} - \sum_{i,j} |\mathbf{r}_i^{(v)} - \mathbf{r}_j^{(d)}|^{-3}. \tag{5}$$

The energies ϵ_v, ϵ_d of the individual vacancies and of the defects have been calculated numerically. The results are given in Table I.

We point out here some of the main features of vacancy–defect structures.

The first peculiarity, evident from Eq. (5), is that two like objects, for example, two vacancies will repel each other. In a mutual encounter, however, they can form bound states by means of a vacancy–defect pair. In this case the effective energy of interaction of the vacancies becomes negative. Such vacancy "molecules" are characteristic of monolayers with a concentration of adatoms close to 1/3. Several simple "molecules" are shown in Fig. 2. Note the tendency to form long molecules.

At other concentrations, specifically for $c \approx 1/6$, rather than combining into molecules the individual vacancies "put on" (as in the case of a polaron) a "coat" consisting of vacancy–defect pairs. The vacancy shown in Fig. 3 contains 17 pairs in the ground state and its energy, after addition of the subsequent pairs, varies very slowly:

$$E(n+1) - E(n) \approx 3.3 \times 10^{-6}, \tag{6}$$

where $E(n)$ is the energy of the vacancy of n "cloaked" in vacancy–defect pairs. The average length of such a vacancy is enormous: $\sim 10^6\, T$, where T is the dimensionless temperature.

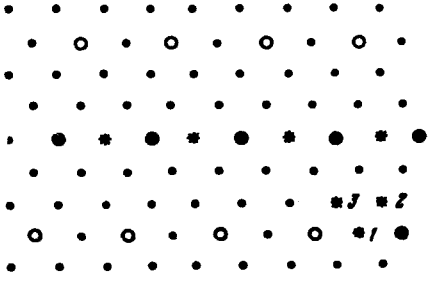

FIG. 3. The case $c = 1/6$. Symbols as in Fig. 2. A vacancy containing four vacancy–defect pairs is shown, as are three types of defects.

I have intentionally examined only concentrations close to 1/3 and 1/6, in which the collective properties of the vacancies and defects are more pronounced.

The properties of monolayers with such defects can be verified in experiments such as that of Vedula *et al.*,[4] involving the diffusion of submonolayer films. Thus "molecules" will diffuse weakly, whereas a long vacancy (Fig. 3) must migrate very fast.

The properties of monolayers with defects will be described in some detail in forthcoming papers.

[1)]A criterion for "shallow" or "deep" potential relief is given by Pokrovskiĭ and Talapov.[2]

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