

# Migration and phase transitions in adsorbed hydrogen films at low temperatures

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(Submitted 21 November 1984)

*Pis'ma Zh. Eksp. Teor. Fiz.* **41**, No. 1, 31–33 (10 January 1985)

The surface-diffusion coefficient is estimated for molecular hydrogen adsorbed on the tungsten (110) face at  $T \sim 5$  K;  $D \sim 10^{-13} - 10^{-14}$  cm<sup>2</sup>/s.

According to the available data,<sup>1</sup> hydrogen adsorbed on the closely packed tungsten (110) face can be in two different modifications. The low-temperature modification apparently corresponds to molecular hydrogen which is bound to the metal surface by comparatively weak van der Waals forces. An irreversible transition to the high-temperature modification occurs when  $T$  is raised to  $\sim 65$  K. Atomic hydrogen bound to the lattice by stronger chemical bonds may correspond to a new type of adsorption. Each modification forms different sequences of regular two-dimensional structures, which appear in succession as the surface density of particles changes.<sup>1,2</sup> The low-temperature modification forms the sequence of lattices  $p(2 \times 2)$ ,  $p(2 \times 1)$ , and (apparently)  $p(1 \times 1)$ . The ability to form ordered phases suggests that molecular hydrogen has a significant mobility even at liquid-helium temperature.

The mobility of molecules may be determined by the effect of the primary electron beam, which is unavoidable in work in a low-energy electron diffraction system; alternatively, this mobility may result from the release of energy at the time at which molecules become adsorbed. The migration may also involve an activation energy, since the atomically smooth (110) face probably has a rather flat potential relief. It may also be suggested that a particular combination of a small molecular mass and a weak interaction of the molecules with the lattice creates a favorable situation for the manifestation of quantum-mechanical effects in the surface migration of particles.

In the present letter we report a study of the migration and structural phase transitions in adsorbed hydrogen films. In the experiments we use low-energy electron diffraction and also the method of the static skin effect.<sup>2,3</sup> The design of the experimental vacuum chambers, the preparation of the samples, and the procedure for cleaning them have all been described previously.<sup>2,4</sup> The measurements were carried out in high vacuum ( $p \sim 10^{-10}$  Torr) at liquid-helium temperature.

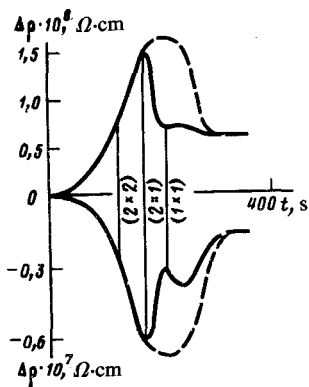


FIG. 1. Magnetoresistance of a tungsten plate versus the hydrogen-deposition time. Upper curve—Magnetic field parallel to the surface of the plate; lower curve—perpendicular.

Figure 1 shows the magnetoresistance of a thin tungsten plate versus the hydrogen deposition time,  $\Delta\rho(t)$ , for various orientations of the sample with respect to the magnetic field ( $H \sim 10$  kOe). The upper curve corresponds to the case in which the magnetic field is directed parallel to the surface of the sample, while the lower curve corresponds to the perpendicular situation. The vertical lines are the boundaries of the regions in which the  $p(2 \times 2)$ ,  $p(2 \times 1)$ , and  $p(1 \times 1)$  two-dimensional structures exist. The presence of an impurity on the surface in a small amount (0.1 of a monolayer) changes the shape of the  $\Delta\rho(t)$  curves (dashed curves) and prevents the development of the structures.

A point worthy of note is that a rotation of the plate through  $90^\circ$  around the  $C_4$  axis does not change the crystallographic orientation of the sample with respect to  $H$ . Consequently, the change in the sign of  $\Delta\rho$  (the upper and lower curves) is evidence that the observed changes in  $\rho$  stem from an effect of hydrogen on the surface scattering of electrons and are unrelated to a penetration of hydrogen into the interior of the crystal.<sup>4</sup>

The analysis in Refs. 2 and 5 shows that coherent reflections of electrons from the  $p(2 \times 2)$  lattices formed on the (110) face can give rise to a multichannel specular reflection of electrons involving electron-hole transfer between the principal parts of the Fermi surface. Such reflections would be effectively diffuse. In contrast, the coherent reflection from the  $p(2 \times 1)$  lattices is primarily specular. Finally, the reflection from the  $p(1 \times 1)$  structure, which precisely reproduces the symmetry of the (110) face, is specular for all groups of electrons. Consequently, an initial increase (or decrease, depending on the orientation of  $H$ ) in  $\rho$  may correspond to a structureless hydrogen film in which the particle density increases over time. The first structural transition to the order  $p(2 \times 2)$  state occurs in the region  $\theta < 1/4$  ( $\theta = 1$  in a monolayer) and is not accompanied by any significant change in the slope of the  $\Delta\rho(t)$  curve, apparently

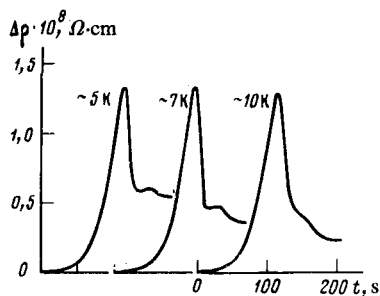


FIG. 2. Curves of  $\Delta\rho(t)$  for various sample temperatures.

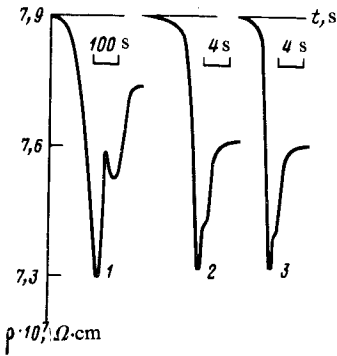


FIG. 3. Curves of  $\Delta\rho(t)$  for various hydrogen-deposition rates. The horizontal bars show the time scales for the various curves.

because both states correspond to a diffuse reflection. In contrast, the phase transition  $p(2 \times 2) \Rightarrow p(2 \times 1)$  is marked by an extremum of  $\rho$ . After the density  $\theta = 1/2$  is reached, and the entire surface is covered with the  $p(2 \times 1)$  phase, and nuclei of the  $p(1 \times 1)$  phase arise, a new extremum appears on the  $\Delta\rho(t)$  curve. It corresponds to a transition region between the two "specular" lattices  $p(2 \times 1)$  and  $p(1 \times 1)$ . The height of the final plateau is a measure of the defectiveness of specular structure  $p(1 \times 1)$ . The sequence of  $\Delta\rho(t)$  curves, obtained as the crystal temperature is raised, shows that the defectiveness of the  $p(1 \times 1)$  phase gradually decreases (Fig. 2). For the temperature  $T > 10$  K, we also see that the structural feature in  $\Delta\rho(t)$  due to the formation of the  $p(2 \times 1)$  structure is gradually erased. It can be suggested in this connection that either the  $p(2 \times 1)$  lattice does not arise at all at  $T > 10$  or the ordering of this phase requires a time longer than that over which the  $\Delta\rho(t)$  curve was recorded.

As the hydrogen flux density to the surface of the sample is gradually increased, it is easy to reach a situation in which surface relaxation, which puts the system in a state of thermodynamic equilibrium, requires a time longer than that ( $t_0$ ) required for the formation of a monolayer coverage. It can be seen from Fig. 3, which shows a series of  $\Delta\rho(t)$  curves for "fast" deposition of hydrogen ( $T \sim 5$  K, with magnetic field perpendicular to the surface of the plate), that the erasure of the structural features, which is associated with the  $p(2 \times 1)$  structure, and the increase in the height of the plateau should be attributed to more significant changes. We can draw some conclusions from these results.

Molecular hydrogen forms regular two-dimensional structures which can be observed by the method of the static skin effect. Consequently, the mobility of molecular hydrogen at  $T \sim 5$  K is not governed by the effect of the electron beam in the low-energy electron-diffraction system. The scale time ( $t_0$ ) for the formation of the structures is many orders of magnitude longer than  $1/\omega_D$ , where  $\omega_D$  is the Debye frequency. The energy release upon adsorption thus does not affect the formation of the structures. Clearly, the time  $t_0$  depends on the average number of diffusion steps, which bring the system to equilibrium, and the rate of surface migration of the particles. Using the standard expression  $D = \langle \Delta x \rangle^2 / \tau$ , and assuming that the number of elementary displacements per particle is  $\sim 10$  (Ref. 6), we find (with the values  $\Delta x \sim 3 \times 10^{-8}$  cm and  $t_0 \sim 1$  s)  $D \sim 10^{-13} - 10^{-14}$  cm<sup>2</sup>/s.

A study of the temperature and isotopic dependence of  $D$  will apparently reveal whether the diffusion of the hydrogen is classical or quantum-mechanical.

We wish to thank R. Sh. Nasyrov for furnishing the samples of clean tungsten.

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Translated by Dave Parsons

Edited by S. J. Amoretty