

# Two-dimensional hydrogen and deuterium lattices on the (011) face of tungsten and their thermal and electron-stimulated disordering

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The low-energy electron diffraction method is used to study in the temperature interval 5–500 K the atomic structure of hydrogen and deuterium films on the (011) face of tungsten, and their thermal and electron-stimulated disordering. Hydrogen and deuterium form identical two-dimensional lattices,  $p(2 \times 1)$ ,  $(2 \times 2)$  and  $(1 \times 1)$  in the atomic phase and  $p(2 \times 2)$  and  $p(2 \times 1)$  in the molecular phase, upon adsorption on a substrate cooled to 5 K. Heating to  $\approx 60$  K transforms the molecular phase irreversibly into atomic. The thermal disordering of the atomic H and D lattices proceeds in the same manner within experimental accuracy. When the atomic lattices are disordered by electron stimulation an appreciable isotopic effect is observed, viz., the rate of disordering of the D films is smaller by an approximate factor 5 than that of the H films. Restoration of order in films disordered by electron irradiation requires activation energies 0.20 eV for the  $p(2 \times 1)$  lattice and 0.35 eV for the  $(2 \times 2)$  lattice. The possibility of quantum (tunneling) surface diffusion in molecular films is considered, as well as in atomic films with  $p(2 \times 1)$  structure.

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The physical and physico-chemical properties of adsorbed hydrogen films—the lightest adsorbate—attracts much interest.<sup>1</sup> In Refs. 2 and 3 we have described two-dimensional hydrogen lattices on the (011) face of tungsten, as well as their thermal and electron-stimulated disordering. In this paper we present more detailed information on the phase diagram of hydrogen films, and also the results of similar experiments with deuterium films on the (011)W face. Special attention is paid to revealing the mobility of the adatoms H and D at low temperatures, with an aim at finding quantum surface diffusion of adatoms.

## EXPERIMENTAL PROCEDURE

To study the structure of the surface we used the low-energy electron diffraction (LEED) method. The two-dimensional lattices of the films were determined from an analysis of the geometry of the diffraction patterns. The order-disorder transitions in two-dimensional crystals of adsorbed hydrogen and deuterium were studied by measuring the temperature dependences of the intensity  $I(T)$  of the superstructure reflections. At low temperatures, at which disordered films induced by the electron beam incident on the surface are observed, the intensity was measured in a pulsed regime, to prevent a substantial lowering of the intensity during the measurement time. A number of other details concerning the procedure used to measure  $I(T)$  are given in Ref. 3. We investigated also electron-stimulated disordering of films. This was done by recording the changes of the intensity of the superstructure reflections. The procedure is described in greater detail in Ref. 4. To determine the coverage  $\theta$  we used data on the structure analysis and on the measurements of the work function, which could be compared with the known dependence of the work function on the coverage.<sup>1</sup> The changes  $\Delta\phi$  of the work function were determined by the method of contact potential difference (the Anderson variant). To increase the reliability of the estimates of  $\theta$ , ac-

count was taken also of the adsorption kinetics, which was investigated in detail earlier for similar experimental conditions (at an adsorption temperature  $T_a = 135$  K) in Ref. 5. According to Ref. 5, the sticking coefficient of the hydrogen on the (011) face of tungsten varies like  $(1 - \theta)^2$ , and this leads to the following law for the dependence of the coverage on the absorption time  $t$ :

$$\theta / (1 - \theta) \propto t. \quad (1)$$

The investigations were carried out in a glass electron diffractometer whose construction made it possible to cool the samples with liquid helium.<sup>3</sup> The procedure used to prepare the substrate and to construct the hydrogen source are also described in Ref. 3. The deuterium source did not differ in construction from the hydrogen source. The purity of the hydrogen and the deuterium sources was verified with a mass spectrometer in a separate installation. Admixtures of other gases in the hydrogen did not exceed 2% in hydrogen and 3% in deuterium (in the case of the  $H_2$  and  $H_D$  molecules—not more than 2%).

## ATOMIC STRUCTURE OF FILMS

The electron-diffraction patterns of the hydrogen and deuterium films adsorbed on the (011) tungsten surface are identical, so that everything stated above on the hydrogen film structure pertains also to a deuterium films. Figure 1 shows electron diffraction patterns observed at different adsorption conditions, and Fig. 2 shows the models of the two-dimensional lattices.

Depending on the adsorption temperature  $T_a$  or on the annealing temperature  $T_{ann}$ , hydrogen can be adsorbed on the (011) face of tungsten in a weakly bound (apparently, molecular) state ( $T_a \lesssim 66$  K) and in a strongly bound atomic state ( $T_a \gtrsim 66$  K).<sup>6</sup> To obtain an atomic phase that is thermodynamically balanced, in most of our experiments we annealed the films, which were adsorbed at  $T_a = 77$  K, at

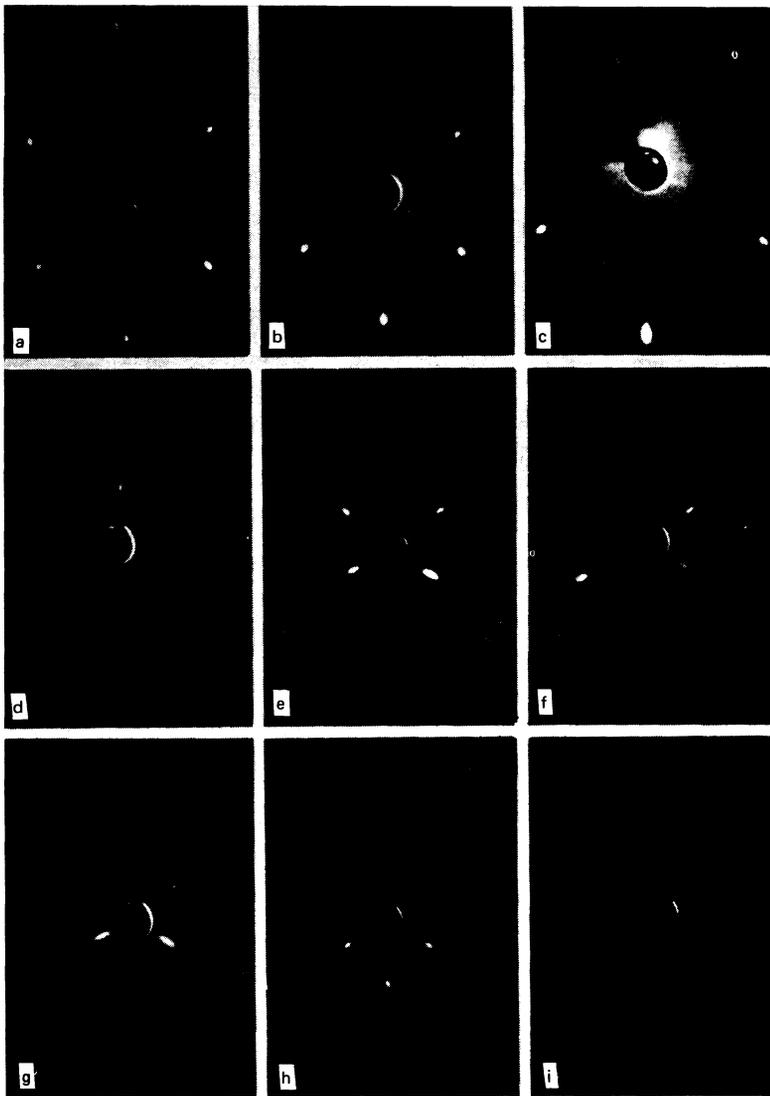


FIG. 1. Electron diffraction patterns of submonolayer hydrogen films and deuterium films adsorbed on the face (011) of tungsten, for various  $\theta$ ,  $T_{\text{ann}}$  (in K), and  $E$  (in eV): *a* - 0; 5; 34; *b* - 0.5; 120; 64; *c* - 0.3; 200; 37.6; *d* - 0.5; 5; 22.1; *e* - 0.5; 120; 21.4; *f* - 0.3; 200; 19.9; *g* - 0.75; 5; 22.1; *h* - 0.75; 160; 18.8; *i* - the same as *h*, after EDM for 2 minutes ( $E = 22.1$  eV, current density  $5 \times 10^{-4}$  A/cm<sup>2</sup>). Observation temperature 5 K.

$T_{\text{ann}} = 120\text{--}200$  K, after which the temperature was lowered to  $T = 5$  K at which the measurements were performed. The atomic hydrogen films obtained in this manner are characterized by three types of consecutively alternating two-dimensional lattices with different coverages  $\theta$  ( $\theta = 1$  corresponds to a film having one hydrogen atom per tungsten atom).

At  $\theta \leq 0.5$ , the films grown have the structure  $p(2 \times 1)$  shown in Fig. 2a. Domains of two mirror-symmetry orientations are produced on the surface, as can be seen from the presence of superstructure reflections of both  $(1/2, 0)$  and  $(1/2, 1/2)$  type (see Figs. 1b and 1e). The superstructure reflections appear first at  $\theta \approx 0.3$  in the form of doublets (splitting in the  $\langle 001 \rangle$  direction, see Figs. 1c and 1d). This can be due to the existence, in this coverage region, of antiphase domains with boundaries directed transverse to the  $\langle 001 \rangle$  axis and repeating with a period  $\sim 30$  Å (estimated from the splitting of the reflections).

At  $0.5 < \theta < 0.75$ , the film becomes denser by changing from a  $p(2 \times 1)$  into a  $(2 \times 2)$  structure with a nonprimitive

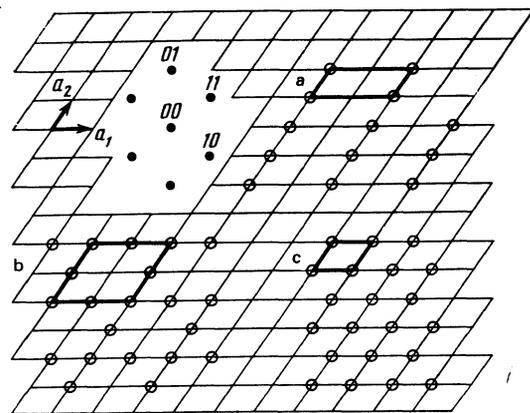


FIG. 2. Models of two-dimensional lattices of fundamental adsorption phases: *a* -  $p(2 \times 1)$ ; *b* -  $(2 \times 2)$ ; *c* -  $p(1 \times 1)$ . The grid drawn by thin lines is the lattice of the substrate with basis vectors  $a_1$  and  $a_2$ ; the thick lines show the elementary cells of the film, the circles show its lattice sites. The system of designation of the LEED reflections  $\{h, k\}$ , shown by dark circles, corresponds to designations of the directions coinciding with the vectors  $\{h a_1^{-1}, k a_2^{-1}\}$ .

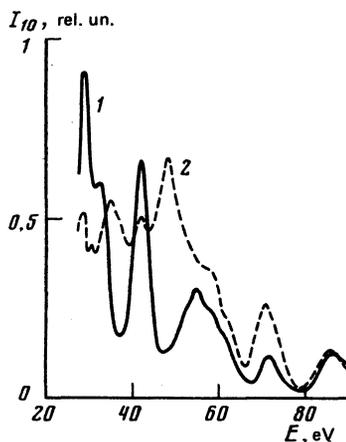


FIG. 3. Intensities for the reflections (1,0): 1—clean substrate; 2—coated with hydrogen film at  $\theta = 1$ .  $T = 5$  K.

unit cell containing three adatoms (Fig. 2b), while at  $0.75 < \theta < 1$  a transition to a  $p(1 \times 1)$  structure is observed (Fig. 2c). On the diffraction pattern, at  $\theta = 1$ , the superstructure reflections vanish completely, and the pattern does not differ geometrically from that of a clean substrate. The presence of an ordered film on the surface can be deduced in this case from the difference between the energy dependences of the intensities of the main reflections  $I_{10}(E)$ , measured at  $\theta = 0$  and  $\theta = 1$  (Fig. 3). This fact indicates that the adatoms, together with the substrate atoms, participate in the coherent scattering of the electrons.

Figure 4 shows the dependences of the intensities of the superstructure reflections  $I$  and of the work function  $\varphi$  on the time of hydrogen or deuterium adsorption (these dependences are the same for both adsorbates). Judging from the time intervals necessary to reach the maximum of the reflection intensities from the structures  $p(2 \times 1)$  and  $(2 \times 2)$ , the adsorption kinetics is satisfactorily described by expression (1). The plot of  $\varphi(t)$  shows three sections, each of which corresponds to the growth of a definite adsorption phase.

If a complete monolayer of hydrogen with structure  $(1 \times 1)$  is first adsorbed on the surface at  $T_a = 77$  K, and the

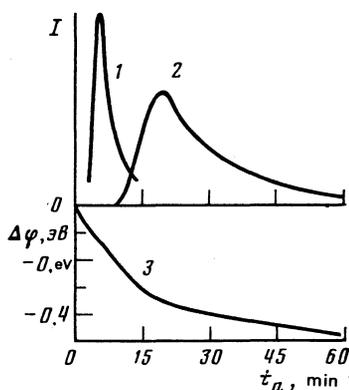


FIG. 4. Dependences of the intensity of the super-structure reflections: 1 —  $(1/2, 1/2)$  for the phase  $p(2 \times 1)$ , 2 —  $(0.1/2)$  for the phase  $(2 \times 2)$ , as well as the changes of the work function (3) vs the time of adsorption of hydrogen (at  $T_a = 77$  K and for annealing every 3 minutes at  $T_{ann} = 200$  K).

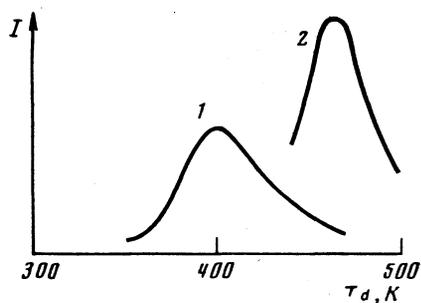


FIG. 5. Dependence of the intensity of the super-structure reflexes: 1— $(0.1/2)$  for the phase  $(2 \times 2)$ ; 2 —  $(1/2, 1/2)$  for the phase  $p(2 \times 1)$  on the desorption temperature in the case of heating in steps of 20 K in one second.

sample temperature is then increased in steps (of 20 K, we obtain plots of the intensities of the reflections of the structures  $(2 \times 2)$  and  $p(2 \times 1)$  vs the desorption temperature  $T_d$ , which are shown in Fig. 5 (the intensity was measured after cooling the sample every time to 5 K). These plots reflect the fact that different phases replace one another as the desorption of the hydrogen progresses:  $(1 \times 1) \rightarrow (2 \times 2) \rightarrow p(2 \times 1)$  clean surface. Comparing the  $I(T_d)$  curves with the thermal desorption spectra for the system H + W(011) (Ref. 1), we can conclude that the  $p(2 \times 1)$  lattice corresponds to a strongly bound phase  $\beta_2$ , while the  $(2 \times 2)$  lattice (and possibly also  $(1 \times 1)$ ) corresponds to a more weakly bound but also chemisorbed phase  $\beta_1$ .

In mixed films of hydrogen and deuterium, the same structures are produced at the corresponding combined coverages. In those cases when films with a multiple ratio of the hydrogen and deuterium concentrations were deposited, e.g., coverages  $\theta = 0.5$  with H:D = 1:1 and  $\theta = 0.75$  with H:D = 2:1, no evidence of any additional superstructure as a result of the difference between the properties of the isotopes was observed.

In addition to the electron-diffraction patterns pertaining to the films balanced by annealing (see Figs. 1b, c, d, e, h), we obtained also electron-diffraction patterns for films adsorbed on a cooled substrate at  $T_a = 5$  K (Figs. 1g, h). Although, judging from the broadening of the reflections, in non-annealed films the structure is not as perfect as in annealed ones, the basic types of the lattices could be clearly determined. The sequence of the structures with increasing degree of coverage is in this case substantially different: initially  $(2 \times 2)$  (see Fig. 1d), next  $p(2 \times 1)$  (see Fig. 1g), followed by  $p(1 \times 1)$ . In the course of annealing of these films it was possible to observe a paradoxical inversion of the electron diffraction patterns. Thus, the electron diffraction pattern (Fig. 1d) corresponding to the  $(2 \times 2)$  structure is transformed into the one shown in Fig. 1e and corresponding to the  $p(2 \times 1)$  structure; conversely, the electron diffraction pattern (Fig. 1g) of type  $p(2 \times 1)$  is transformed into an electron diffraction pattern (Fig. 1g) of type  $(2 \times 2)$ .

It appears that these changes of the electron-diffraction patterns are connected with dissociation of the adsorbed molecules when the film is heated,<sup>6</sup> i.e., with a transition from molecular to atomic lattices. In our experiments, in contrast to Ref. 6, we observed no total desorption of the

molecular phase even prior to the transition of this phase into atomic. On the contrary, in the course of heating one could observe the appearance of LEED pictures typical of the atomic phase. We propose that the first low temperature phase is  $p(2 \times 2)$ , which constitutes a lattice of molecules at a coverage  $\theta_m = 0.25$  (the subscript "m" pertains to the molecular phases). It gives the same diffraction pattern as the atomic phase at  $\theta = 0.75$  (Fig. 2b). Upon dissociation of the molecules, the number of particles on the surface is doubled and a transition to the atomic phase  $\theta = 0.5$  is observed. Actually in this case  $\theta < 0.5$ , inasmuch as partial evaporation accompanies the dissociation.<sup>6</sup>

The other low-temperature phase,  $p(2 \times 1)$ , can correspond to a lattice of molecules at  $\theta_m = 0.5$ . It appears that dissociation and partial desorption of the molecules also take place when it is heated, so that the atoms remaining on the surface form a  $(2 \times 2)$  lattice corresponding to an atomic coverage  $\theta = 0.75$ .

The presence of order in films adsorbed at  $T = 5$  K points to the existence of a certain surface mobility of the  $H_2$  and  $D_2$  molecules under these conditions. A significant argument favoring this statement is the interesting fact that annealing in the temperature region  $T_{\text{ann}} < 66$  K, in which, according to Ref. 6, the adsorbed hydrogen molecules still do not dissociate, does not improve substantially the sharpness of the reflections. On the basis of the available data it is difficult to determine unequivocally whether this mobility is of quantum origin. One cannot exclude the possibility that the establishment of the order can take place directly in the course of the very adsorption act when the adsorption energy is dissipated. It is possible also that an important role is played by the fact that the adsorbed gas is at room temperature.

## PHASE TRANSITIONS

In Refs. 2 and 3 are given the temperature dependences of the intensity of the superstructure reflections  $I(T)$  for the system  $H + W(011)$ . Figure 6 shows  $I(T)$  plots for the atomic phases of deuterium and mixed H/D films. Within the limits of the possible measurement errors, the curves for identical

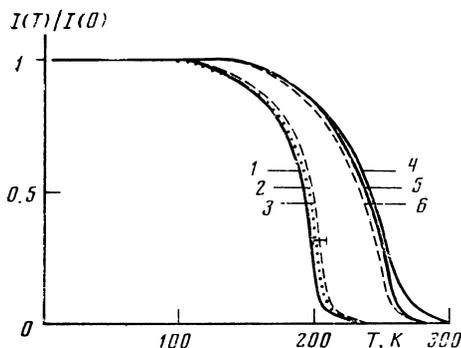


FIG. 6. Temperature dependences of the intensities of the superstructure reflections at different coverages  $\theta$ : 1, 2, 3 — 0.51; 4, 5, 6 — 0.75. Curves 1–4—for the reflections  $(1/2, 1/2)$ ; 5, 6—for  $(0, 1/2)$ .  $E = 22$  eV. The solid lines show the curves for the system  $D + W(011)$ , the dashed lines—for  $H + W(011)$ . Dotted—for the mixed film 50%  $H + 50\%$   $D$ . The horizontal segment is the experimental scatter of the curves relative to the  $T$  axis.

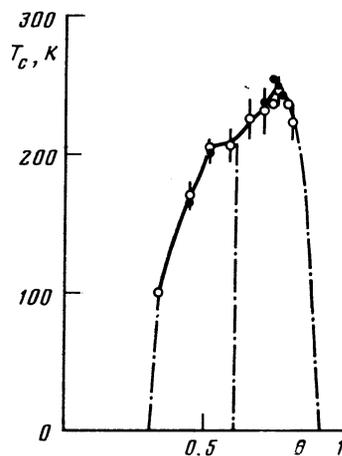


FIG. 7. Dependence of the order-disorder transitions temperature on the coverage (light circles—for hydrogen films, dark—for deuterium) and regions of existence of ordered structures  $p(2 \times 1)$  and  $(2 \times 2)$  (dash-dot lines). Vertical strokes—smeared transition temperatures.

coverage but different isotopic composition of the adsorbate coincide. Thus, no isotopic effect is observed in this phenomenon. The following arguments can be advanced concerning this result.

If the potential wells on the surface are separated by a noticeable barrier (and this is precisely attested to by the estimates given below), the presence of weak quantum tunneling, which is typical of particles that are heavy compared with electrons, such as hydrogen, cannot substantially influence the Debye-Waller factor.

In addition, we call attention to the following interesting circumstance. At  $T > \omega/2$  ( $\omega$  is the fundamental frequency of the adatom oscillations) the argument of the exponential in the Debye-Waller factor goes to its classical limit  $\sim (\Delta k)^2 T / m\omega^2$ , where  $\Delta k$  is the change of the electron momentum. However, for one and the same interaction potential,  $m\omega^2$  does not depend at all on the mass, so that at the indicated values of  $T$  there is no isotopic effect in the Debye-Waller factor. It appears that it might really manifest itself only in the order-disorder transition temperature, but it should be strongly suppressed by the fact that the transition temperatures are relatively high.

Figure 7 shows a plot of  $T_c(\theta)$ , where  $T_c$  is the order-disorder transition temperature. The values of  $T_c$  were determined by a procedure described in Ref. 3. The thermal ordering of the deuterium films, just as that of the hydrogen films,<sup>3</sup> proceeds via a second-order phase transition, and the critical exponents of the order parameter depend on  $\theta$ .

Figure 7 shows also the limits of the region of existence of the  $p(2 \times 1)$  and  $(2 \times 2)$  structures at  $T < T_c$ . Within the framework of the LEED method used in this paper, we succeeded in determining not the total phase diagram, i.e., the regions of existence and possibly coexistence of each of the phases, but only of the limits of the regions where the structures  $p(2 \times 1)$  and  $(2 \times 2)$  appear (respectively the left and the right dash-dot lines) and where the  $(2 \times 2)$  structure vanishes (the right-hand dash-dot line). It was noted above that a probable cause of the splitting of the LEED reflections,

which is observed in a narrow region of coverages near  $\theta \approx 0.3$ , is the formation of antiphase domains. Thus, the left-hand boundary of the phase-ordering region is apparently a line of a first-order phase transition. The splitting of the LEED superstructure reflections of the LEED vanishes at  $T \approx 100$  K, which is possibly in fact the tricritical point on the phase diagram, i.e., the point at which the order of the phase transition changes.<sup>7</sup>

The successive formation of the lattices  $p(2 \times 1)$  and  $(2 \times 2)$  agrees with the conclusions of Braun<sup>8</sup> that the interaction between the hydrogen atoms is of alternating-sign. We note that oxygen atoms make up on the same (011) surface of tungsten exactly the same series of lattices as H and D; a reduction of these data also leads to the conclusion that the interaction in the adsorbed film is of alternating sign.<sup>9,10</sup>

### ELECTRON-STIMULATED DISORDER

As shown in Ref. 2, when its surface is bombarded with slow electrons a hydrogen film goes over partially or fully into a nonequilibrium disordered state, i.e., electron-stimulated disorder (ESD) takes place. This manifests itself in a weakening or total vanishing of the superstructure reflections (Fig. 1i). The most interesting feature of this process is its "zero-threshold" character: the ESD is observed starting with extremely small-thermal-velocities of the electrons incident on the surface. It is important to emphasize that to observe ESD the sample must be maintained at a sufficiently low temperature,  $T \lesssim 30$ – $60$  K, so as to prevent formation of structure defects by the electrons.

Under identical experimental conditions, deuterium films become disordered much more slowly than the hydrogen films (Fig. 8). In all other respects the ESD process proceeds in the same manner in both isotopes: the  $(2 \times 2)$  phase becomes completely disordered (the intensity of the reflections decreases with time exponentially), whereas the disordering of the  $p(2 \times 1)$  phase practically stops at the level  $I/I_0 \approx 0.6$ ; the initial ESD rate for the  $p(2 \times 1)$  phase is less than for the  $(2 \times 2)$  phase; with increasing current, and also with increasing electron energy in investigated interval  $E = 0$ – $50$  eV, the ESD velocity increases.

Using the data on the initial ESD rate, we can determine the cross section  $\sigma$  of this process.<sup>4</sup> At  $E = 20$  eV, the largest

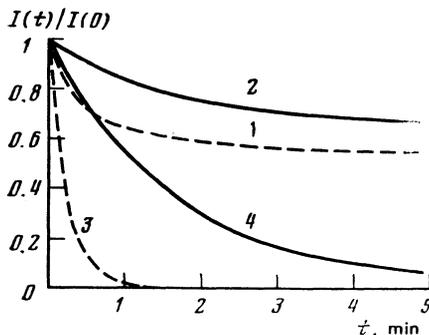


FIG. 8. Damping of the superstructure reflexes for EDM  $T = 5$  K,  $E = 22$  eV. 1, 2—the reflection  $(1/2, 1/2)$  for the phase  $p(2 \times 1)$ ; 3, 4—reflection  $(0, 1/2)$  for the phase  $(2 \times 2)$  1, 3 hydrogen films 2, 4—deuterium.

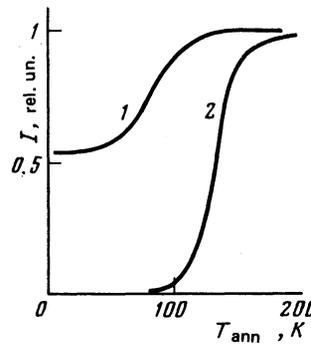


FIG. 9. Change of the intensity of the superstructure reflections: 1 —  $(1/2, 1/2)$  for the phase  $p(2 \times 1)$ , 2 —  $(0, 1/2)$  for the phase  $(2 \times 2)$ —upon annealing of hydrogen films after EDM (heating in steps of 20 K for one second).

value  $\sigma \approx 10^{-17}$  cm<sup>2</sup> is obtained for hydrogen films with  $(2 \times 2)$  structure. This is approximately double then for the  $p(2 \times 1)$  phase. In deuterium films, the corresponding cross sections are smaller by a factor 4–5.

In principle, electron bombardment can produce in hydrogen and deuterium films, besides ESD, also desorption.<sup>11</sup> This process, however, is much less effective ( $\sigma \approx 10^{-19}$  cm<sup>2</sup>), and is not observed in practice at the electron-beam parameters used in the present paper (in most experiments  $E \leq 22$  eV and the current density is  $\sim 10^{-4}$  A/cm<sup>2</sup>) at the times of electron action on the film (several minutes). Its absence was monitored against the constancy of  $\Delta\phi$  and against the restoration of the intensity following repeated repetition of ESD–annealing cycles.

We can propose several hypothetical mechanisms of the ESD, each of which ensures a zero-threshold character of the ESD process and the observed isotopic effect.

First, the process can begin with changes of the electron shell of the adatom—either as a result of temporary trapping of the incident electron on the adatom affinity level, or as a result of removal (or excitation) of the electron that couples the adatom to the substrate. We recall that even an electron that is at rest inside the sample has, relative to the Fermi level, an energy equal to the work function, approximately 5 eV in our case. On the other hand, the levels of the bond of H with W(011) lie 2.8–4.0 eV below the Fermi level,<sup>12</sup> so that the indicated energy is sufficient to remove (transfer to the Fermi level) the bond electrons. Since the changes of the electron shell take place in accordance with the Franck-Condon principle, the adatom nucleus turns out to be in a non-equilibrium position and begins to move and acquire a kinetic energy whose value depends on the lifetime of the excited state. Obviously, to project the atom onto an "incorrect" center on the substrate, i.e., to produce a Frenkel' pair, this energy must be not less than the amplitude of the potential relief of the substrate. The probability of acquiring the required energy decreases with increasing mass of the adatom, and this, just as in the case of electron-stimulated desorption,<sup>11</sup> explains qualitatively the observed isotopic effect.

Another possibility is direct excitation, by the incident electron, of adatom vibrations (such transitions are observed, in particular, in the spectroscopy of the characteristic energy losses of slow electrons with high resolution<sup>13,14</sup>).

In the case of D, the number of the vibrational level necessary for the EDM will be larger, and this will lower the probability of the process.

To give preference to one of the foregoing mechanisms, it is necessary to investigate in detail the change of the EDM cross section with change of electron energy. At any rate, the adatoms are apparently on high vibrational levels of a mode perpendicular to the surface—above the barrier for surface diffusion. The lifetime in this state, judging from the relation between the frequency and width of the peak in the spectrum,<sup>13,14</sup> amounts to not less than 10 periods of the oscillations, which is sufficient not only for a jump over into the nearest vacant adsorption center, but also for migration over several centers.

At  $T = 5$  K, a frozen disordered state was preserved for not less than several hours, without revealing any symptoms of relaxation, this being evidence of the absence of noticeable mobility of the adatoms under these conditions.

The order in the films could be the restored only by heating to much higher temperatures. This is illustrated by Fig. 9, which shows the change of the intensities of the superstructure reflections as a result of annealing. Using the values of the annealing temperature needed to restore the order in the film, we can obtain an elementary estimate of the corresponding activation energies  $E_d$ . In this case we obtain a value 0.20 eV for the  $p(2 \times 1)$  lattice and 0.35 eV for the  $(2 \times 2)$  lattice.

It is interesting to note that irradiation by slow electrons ( $E \lesssim 50$  eV) of the molecular phase of hydrogen and deuterium, which is produced upon adsorption on a substrate cooled to 5 K, does not yield an observable EDM effect: either the cross section of this process for molecules is too small, or else they have a certain mobility sufficient for rapid annealing of the defects produced by the electrons. Since the molecules are less strongly bound to the surface than the atoms, the activation energy of the surface diffusion for  $H_2$  and  $D_2$  should apparently be less than for H and D.

## DISCUSSION OF RESULTS

The foregoing results offer evidence that at  $T \approx 5$  K no noticeable surface diffusion of hydrogen adatoms on W(011) is observed. Taking into account the obtained values of the activation energy, we can easily establish that the actual width of the band for two-dimensional tunneling of the adatoms of hydrogen is very low.<sup>15</sup> Any defects on the surface will disrupt the band, so that tunneling of the hydrogen calls for involving the phonons, and in the upshot the result appears natural.

At the same time, the observed picture of the electron-stimulated disorder does not contradict the hypothesis that, at least in the  $p(2 \times 1)$  phase, the kinetics of the recombination of the interstitial adatoms and vacancies can have a quantum tunneling character (in this case phonon emission should take place, and the low temperature does not impose any restrictions). The low activation energy for migration in the case of the  $p(2 \times 1)$  phase allows us to assume that during the observation time the interstitial adatom can tunnel to a vacancy situated in the immediate neighborhood. However,

if the adatom moves away from the vacancy, there is no time for the recombination to take place. With increasing number of defects, the recombination probability increases, so that the initial decrease of the intensity of the reflections should give way with time to saturation on a finite level, as is indeed observed in the case of the  $p(2 \times 1)$  phase. The substantially higher activation energy in the case of the  $(2 \times 2)$  phase corresponds to a longer lifetime of the interstitial atom even in the immediate vicinity of the vacancy. This should lead to a disorder of the type observed in experiment for the  $(2 \times 2)$  phase.

Within the framework of an alternative interpretation, we can assume that at a lower activation energy the interstitial atom traverses during the instant of creation larger distances and retains for a longer time an excess energy sufficient for classical surmounting of the barrier in recombination.

As for the less strongly bound molecular phase, there are a number of facts that offer evidence in favor of the presence of quantum surface diffusion. One must note first of all the absence of electron-stimulated disordering in this phase and the fact that the sharpness of the reflection is not improved by annealing up to  $T_{\text{ann}} = 66$  K (at higher temperatures the molecular phase becomes atomic). Even this conclusion, however, calls for confirmation by additional experiments.

It should be noted that the result of the present paper contradict the deductions of Di Foggio and Gomer,<sup>16</sup> according to which the atoms H and W(011) have below 140 K a noticeable mobility on account of tunneling. We recall that this conclusion was drawn in Ref. 16 on the basis of an analysis of the temperature dependences of the noises of the field-emission current from the (011) face of tungsten covered with hydrogen. The authors connect the noises with film-density fluctuations due to the presence of adatom mobility. It seems to us, however, that the passage of the field-emission current itself can strongly disturb the action of the film. For example, tunneling of an electron from a virtual level of an adatom should transfer the adatom for a certain time to a nonequilibrium state, and this can in principle induce adatom mobility which is not connected with the tunneling of the adatom itself. Furthermore, the experiments are being performed under conditions when a strong electric field  $\sim 10^7$  V/cm exists at the surface.

A possible manifestation of quantum mobility of H on Ni(111), consisting of a lower (than expected) intensity of the superstructure reflexes, was reported also in Ref. 17. This conclusion, however, is based not on direct facts, but on a theoretical estimate of the quantity  $E_d$ , according to which it amounts to  $\sim 10^{-2}$  eV. In our experiments, however, as indicated above, we obtained  $E_d = 0.2\text{--}0.35$  eV.

One of the shortcomings of the LEED method, as well as of other methods of investigating a surface by using electrons and photons, is the influence of the probing beam on the state of the investigated object, in particular the electron-stimulated desorption, dissociation, and others. Fortunately, these processes are effective in by far not all the adsorption systems. However, experiments with adsorbed films of lithium,<sup>4</sup> as well as the results presented in this paper, show that even films that are stable in practice to electron-stimu-

lated desorption, can become disordered under the influence of electrons. This phenomenon must be taken into account primarily for films whose atoms have a low mass. Thus, no EDM was observed when working with strontium and oxygen films. Although by itself the EDM effect is in most cases undesirable, an investigation of the kinetics of the transition of a film into thermal equilibrium state after EDM provides a convenient means of investigating the mobility of atoms in the same instrument in which the film structure is being investigated.

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