Critical exponents of the H–W(011) system

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The order-disorder phase transitions that occur in submonolayer films of hydrogen adsorbed on the (011) face of tungsten have been investigated by the low-energy-electron-diffraction method. It is shown that the temperature dependences of the intensities of the superstructure reflections of the $p(2\times 1)$ and (2×2) adsorption phases can be described by a power law in a fairly broad region near the critical point. This region is several times broader than the region over which the transition point is smeared as a result of the finiteness of the dimensions of the surface region investigated by the low-energy-electron-diffraction method. The data obtained clearly indicate that the order–disorder transition in the coating region $\theta = 0.44$–0.80 is a second-order phase transition. The values of the critical exponent of the order parameter are determined, and are found to be equal to 0.13 ± 0.04 for the $p(2\times 1)$ structure and 0.25 ± 0.07 for the (2×2).

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INTRODUCTION

The low-energy-electron-diffraction (LEED) method is a powerful means of investigating surface structure, in particular, the superstructures formed by the atoms of an absorbate.[1] The phase transitions that occur in the adsorbed films, including order-disorder phase transitions, which can be first- or second-order transitions, can be investigated by studying the dependence of the intensity of the superstructure reflections on temperature and the degree of coating. Of greatest interest are detailed investigations near the transition point. In the case of second-order phase transitions, the system is described by a set of critical indices. The LEED method allows us to find, in particular, the value of the critical exponent of the order parameter. Thus, in Ref. 2 Estrup discusses this question in connection with the choice of a model for the description of the order-disorder transition in hydrogen films on the (001) face of tungsten. But no specific measurements of the critical indices have thus far been performed by the LEED method. In this paper we determine the critical exponent of the order parameter for the order-disorder phase transitions that occur in submonolayer hydrogen films on the (011) face of a tungsten crystal.

The special interest in this system has been aroused by the following circumstance. Hydrogen on the (011) face of tungsten forms three ordered structures[3]: $p(2\times 1)$ when the degree of coating $\theta=\frac{1}{2}$, (2×2) for $\theta=\frac{3}{2}$, and (1×1) for $\theta=1$. The symmetry of the first two structures is such that they can be described by one and the same Hamiltonian with different parameter values. Even more curious is the fact that the symmetry of this Hamiltonian admits of a continuous dependence of the critical exponents on the parameters (e.g., the degree of coating). Such a symmetry is a rare exception, and all the systems that have so far been investigated have demonstrated the universality of the critical exponents[4] (i.e., the absence of a continuous dependence on a parameter).

EXPERIMENT

The measurements were performed with a low-voltage (10–100 eV) electron-diffraction camera made of glass (Fig. 1). The tungsten crystal 1 was cut in the form of a $4\times 6\times 0.5$ mm plate parallel to the (011) face to within ~10′, ground and polished mechanically, further polished electrochemically, and mounted on a leg 2, which could be filled during the measurements with liquid helium or another thermostated medium. This allowed us to either cool the sample right down to $T=5$ K, or, by passing current through it, heat it to a temperature higher than the temperature of the bath in the leg: usually to $T\approx 2300$ K. Such heating turns out to be sufficient for the purpose of cleansing the sample of most of the impurities, except carbon. The latter was removed through oxidation,[5] for which purpose there was an oxygen source in the instrument.

To obtain adsorbed hydrogen films, we used a hydrogen source in the form of a titanium helix[3] saturated with hydrogen. The gas supplied by it was 98% pure. The degree of coating θ was estimated from a set of structural-analysis, adsorption-kinetics, and work-function-variation data to within ~10%.

To avoid diffraction-pattern distortions caused by the passage of current through the sample, the measurements requiring elevated temperatures (in comparison with the temperature of the bath in the leg) were performed immediately after the current had been

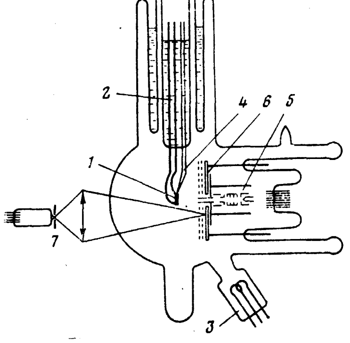

FIG. 1. Schematic drawing of the experimental setup. 1) sample; 2) leg with liquid helium; 3) hydrogen source; 4) thermocouple; 5) electron beam; 6) luminescent screen; 7) telescopic photometer.

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switched off during the period of spontaneous cooling of the sample, a period which was long enough for the establishment of equilibrium conditions to be possible. To measure the intensity, the diffraction reflection was projected with the aid of a photographic lens from the screen of the electron-diffraction camera onto the entrance diaphragm of a photomultiplier, whose output signal was amplified and fed to an $X-Y$ recording potentiometer through one input. To the second input of the potentiometer was fed the voltage potential of a VR-5/VR-20 thermocouple, 4, connected with the sample. The diaphragm of the photomultiplier cut out the central part of the reflection at roughly the half-intensity level.

An electron-stimulated disordering occurs in the hydrogen films at a sufficiently low temperature.[2] In order to prevent this process from affecting the results of the superstructure-reflection-intensity measurements at low temperatures (below the self-annealing temperature of the films), we employed the pulsed measurement regime: the electron beam was unblocked only for ~5 sec, which is significantly shorter than the characteristic time of the electron stimulated disordering process (several minutes).

Figure 2 shows the temperature dependence of the superstructure-reflection intensity, measured for different degrees θ of hydrogen coating. The curves have a low-temperature section where the intensity varies slowly and a section in the region of the critical temperature where the intensity falls off sharply. All the curves are normalized to the intensity value in the saturation region. An anomaly of the diffraction patterns corresponding to the $p(2\times 1)$ and (2×2) structures consists in the fact that all the superstructure reflections of the first structure go over into the system of superstructure reflections of the second.

In order to distinguish between the θ regions in which these phases exist, we show in Fig. 3 the experimental θ dependences of the intensity in the low-temperature region for the following two types of superstructure reflections: $(\frac{1}{2}, 0)$, which is common to both phases and $(0, \frac{1}{2})$, which is characteristic of only the (2×2) phase. Clearly, only the $p(2\times 1)$ phase exists in the $\theta = 0.3-0.6$ region, whereas the two phases can coexist when $\theta > 0.6$.

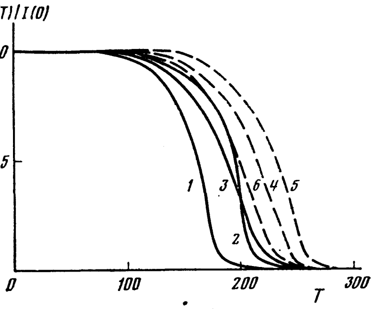

FIG. 2. Temperature dependence of the superstructure-reflection intensity. The continuous curves are for the $(\frac{1}{2}, 0)$ reflection; the dashed curves, for the $(0, \frac{1}{2})$ reflection. The degrees of coating are: 1) 0.44; 2) 0.51; 3) 0.58; 4) 0.71; 5) 0.75; 6) 0.80.

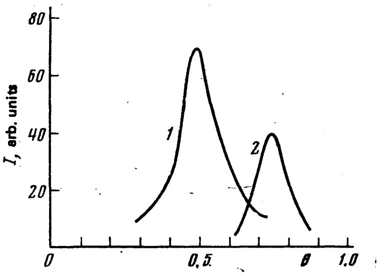

FIG. 3. Dependence of the superstructure-reflection intensity on the degree of coating at $T = 5$ K; 1) $(\frac{1}{2}, 0)$; 2) $(0, \frac{1}{2})$.

THE CRITICAL EXPONENTS

The dependence $I(T)$ has, in the vicinity of the critical point, significantly different characters in the cases of first- and second-order phase transitions. In the first case the intensity varies discontinuously, in the second, according to the law

$$I=I_0[(T_c-T)/T_c]^{2\beta}, \tag{1}$$

where I_0 is some constant, T_c is the transition temperature, and β is the exponent of the order parameter. Let us determine the type of $I(T)$ dependence corresponding to the experimental data obtained. But first we should make the following observation.

In reality the dependence (1) can describe the experimental data only in a region not too close to the transition point. This is due to the finiteness of the investigated section of the surface. There are at least two factors limiting the size of the investigated region. The first one is the instrumental resolution of the electron-diffraction camera. The characteristic dimension—the so-called coherence length—has a value of the order of 100 Å. The second factor is the imperfection of the substrate. Here estimates yield a somewhat greater characteristic dimension for the homogeneity region, namely, a dimension of the order of 300 Å. In a finite-sized region both the temperature of the system and the concentration of the adatoms fluctuate. Both of these factors lead to a situation in which the transition temperature in the finite system fluctuates. It is clear that the transition temperature in formula (1) can only be determined to within the amplitude of its fluctuations in the finite region. The data obtained in experiment are results averaged over a large number of such bounded regions. It is reasonable to assume that the transition-temperature fluctuations have a Gaussian distribution. In this case the experimental data can be described with the aid of the formula

$$I=\frac{I_0}{(2\pi)^{1/2}\Delta t}\int_{T-T_c}^{\infty}\left(\frac{T_c-T+t}{T_c+t}\right)^{2\beta}\exp\left\{-\frac{1}{2}\left(\frac{t}{\Delta t}\right)^2\right\}dt. \tag{2}$$

Here the quantity Δt characterizes the transition-temperature "smearing" width. This method of describing the experimental data has been used by Horn *et al.*[6] to determine from x-ray structural analysis data the critical exponent β for the phase transitions occurring in submonolayer films of krypton on exfoliated graphite.

Figure 4 shows in logarithmic coordinates the dependences $I(T)$, i.e.,

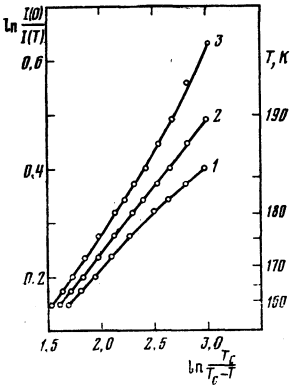

FIG. 4. Temperature dependence of the intensity of the $(\frac{1}{2}, 0)$ superstructure reflection in logarithmic coordinates for $\theta = 0.51$ and different values of the adjustable parameter T_c: 1) 196; 2) 200; 3) 204 K.

$$\ln[I(0)/I(T)], \quad \ln[(T_c-T)/T_c],$$

for $\theta = 0.51$ and different transition-temperature values ($T_c = 196$, 200, and 204 K); since the exact transition-temperature is determined in the course of the analysis of the data with the aid of the formula (1), the transition temperature is an adjustable parameter. It can be seen that the experimental data in the interval of T from $T_c - 40$ K to $T_c - 10$ K are well described by the dependence (1) for the case in which $T_c = 200$ K (which corresponds to a straight line in logarithmic coordinates). This broad temperature region of power-law decreases of the intensity allows us to determine with confidence the exponent β, T_c, and the constant I_0. Indeed, if we describe the dependence $I(T)$ by the formula (2), which is valid for a broader temperature range, we obtain a satisfactory agreement with experiment with practically the same values of β, T_c, and I_0. This is demonstrated by Fig. 5, which shows experimental points and curves computed with the aid of the formula (2) in the range from $T_c - 40$ K to $T_c + 10$ K, using for the adjustable parameters of the formula (2) the following optimum values:

$$\beta=0.13\pm0.04, \quad T_c=201\text{ K}, \quad \Delta t=8\text{ K}, \quad I_0=1.28$$

for the $p(2\times1)$ structure and

$$\beta=0.25\pm0.07, \quad T_c=247\text{ K}, \quad \Delta t=10\text{ K}, \quad I_0=1.82.$$

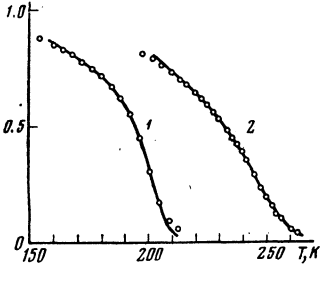

FIG. 5. Experimental data (points) on, and the result of the approximation with the aid of the formula (3) (continuous curves) for, the temperature dependence of the superstructure-reflection intensity for: 1) $\theta = 0.51$ and 2) $\theta = 0.75$.

for the (2×2) structure.

Notice that in the high-temperature region the experimental values for the reflection intensity slightly exceed the theoretical values. This additional contribution can be ascribed to scattering by the order-parameter fluctuations.

The dominant contribution to the error in the determination of β is made by the uncertainty in the transition temperature. The order of magnitude of the relative error is determined by the ratio of the quantity Δt to the temperature interval in which the exponent β is determined. Using the values obtained for Δt, let us estimate the characteristic dimension L of the investigated region, and compare it with the value given by the experimental conditions (the width of the coherence region of the electron-diffraction camera, the dimension of the homogeneity region of the substrate). As the second-order-transition point is approached, the order-parameter-fluctuation-correlation length r_c, which characterizes the dimension of the ordered region, increases. In an unbounded system, r_c tends to infinity, as the transition point is approached, according to the law

$$r_c \propto a\left(\frac{|T_c-T|}{T_c}\right)^{-\nu}. \tag{3}$$

Here a is the lattice constant and ν is the critical exponent of the correlation length. For the estimates we can use the value found for the two-dimensional Ising model ($\nu = 1$).

The power-law behavior predicted[4] for all the quantities will be observed only when $L > r_c$. In a region of finite dimensions $L < r_c$, the temperature fluctuations, according to theory,[4] are of the order of $T - T_c$. This means that the phase transition is smeared out in the temperature range in which the correlation length exceeds the dimension of the investigated region ($L < r_c$). Using these arguments, we easily obtain an estimate for L:

$$L \sim a(T_c/\Delta t)^{\nu}.$$

Substituting the numerical values, we obtain the value $L \sim 75$ Å. This value agrees quite well with the standard estimate (100 Å) for the coherence length (the dimension of the investigated region) of the electron-diffraction camera.

As has already been noted above, besides the temperature fluctuations, the fluctuations in the degree of coating make a contribution to the smearing out of the phase transition. This contribution may turn out to be substantial when the transition temperature strongly depends on the degree of coating. Indeed, in a finite system the particle-number fluctuation $\Delta N \sim N^{1/2} = L\theta^{1/2}/a$, from which we easily find that

$$\Delta T_* \sim \frac{\partial T_c}{\partial \theta}\frac{a\theta^{1/2}}{L}.$$

Substituting the numerical values $\theta = 0.5$, $a = 3$ Å, $L = 100$ Å, and

$$\partial T_c/\partial\theta \sim (T_{c1}-T_{c2})/(\theta_1-\theta_2)$$

[the subscripts 1 and 2 correspond to the $p(2\times1)$ and

(2×2) structures], we obtain the estimate $\Delta T_c \sim 4$ K. This value is of the same order of magnitude as the experimental value for Δt. Thus, the estimates made show that the observed smearing of the phase transition can indeed be explained by the finiteness of the sample dimensions.

One of the most important results of the theory of phase transitions is the assertion that the critical exponents are universal constants.[4] This means that the exponents are uniquely determined by the dimensionality and symmetry of the system, and not by the magnitudes of the parameters of the system's Hamiltonian. The available experimental data for a large number of different three-dimensional systems confirm this conclusion.[4] Nevertheless, as has already been noted above, there are occasions when theory predicts a violation of the universality, i.e., when it predicts a continuous dependence of the exponents on a parameter. This result was first obtained by Baxter[7] for an exactly soluble model, and Kadanoff and Wegner[8] have shown that such behavior of the indices is due to the special symmetry of the system. Both the $p(2\times 1)$ and (2×2) structures experimentally observed in the work possess the required symmetry.

It is most convenient to carry out the analysis of the symmetry properties on the basis of the Landau expansion. It turns out that the same Hamiltonian describes both structures [$p(2\times 1)$ and (2×2)], although with different parameter values, the Kadanoff and Wegner's investigation[8] of the parameter dependence of a critical exponent was carried out with precisely such a Hamiltonian. This Hamiltonian has the form

$$H=\int d^2x\{(\nabla\varphi_1)^2/2+(\nabla\varphi_2)^2/2+\tau(\varphi_1{}^2+\varphi_2{}^2)/2+\lambda_1(\varphi_1{}^4+\varphi_2{}^4)+\lambda_2\varphi_1{}^2\varphi_2{}^2\}. \tag{4}$$

Here $\tau=(T-T_c)/T_c$ and λ_1 and λ_2 are constants. The order-parameter components φ_1 and φ_2 correspond to density waves propagating along the $\langle 1\bar{1}1\rangle$ and $\langle\bar{1}\bar{1}1\rangle$ directions with periods equal to twice the lattice constants of the substrate in these directions. The $p(2\times 1)$ structure is described by that phase of the Hamiltonian (4) in which only one of the components, φ_1 or φ_2, is nonzero, which corresponds to a density wave along the $\langle 1\bar{1}1\rangle$ or $\langle\bar{1}\bar{1}1\rangle$ direction. This phase exists in the $\lambda_1>0$, $\lambda_2>2\lambda_1$ region. The (2×2) structure corresponds to that phase of the Hamiltonian (4) in which both of the components φ_1 and φ_2 are nonzero and equal in absolute value. This phase exists in the $\lambda_1>0$, $\lambda_2<2\lambda_1$ region. A more detailed discussion of the question of the form of the Landau expansion for the system under investigation can be found in Ref. 9.

As shown in Ref. 8, the critical exponents are continuous functions of the parameter λ_2. This means that the indices of the $p(2\times 1)$ and (2×2) phases for the stoichiometric degrees of coating $\theta=\frac{1}{2}$ and $\theta=\frac{3}{4}$ should differ from each other, since these degrees of coating correspond to different values of the parameter λ_2. Indeed, the experimental values given above for the exponents differ by a factor of two. The problem of the character of the variation of β as we go (continuously or jumpwise) from $\theta=\frac{1}{2}$ to $\theta=\frac{3}{4}$ cannot, unfortunately, be uniquely solved on the basis of the β data obtained in this work for the indicated intermediate coating region because of the insufficient accuracy with which the values of β were determined in this region. In Table I we present the values of the exponent β and of T_c (as well as the errors made in their determination) obtained for the $\theta=0.44-0.80$ coating region by processing the data of Fig. 2 according to the earlier described procedure.

TABLE I. The critical exponent β of the order parameter and the transition temperature T_c and the width Δt of the region over which it is smeared for different degrees θ of coating for H—W(011).

θ	β	T_c, K	$\Delta t/T_c$	θ	β	T_c, K	$\Delta t/T_c$
0.44	0.13±0.06	170	0.06	0.70	0,25±0.12	233	0.08
0.51	0.13±0.04	201	0.04	0.75	0.25±0.07	247	0.04
0,58	0.25±0,12	207	0,06	0.80	0.25±0,12	222	0.06

The investigation of the temperature dependences of the superstructure reflection intensity, carried out by the LEED method on submonolayer films of hydrogen adsorbed on the (011) face of a tungsten crystal, has established that we can confidently determine the order of the order-disorder phase transition under the existing characteristic—of this experiment—conditions (as determined by the degree of perfection of the substrate and the coherence width of the electron beam, characteristics which impose limitations on the dimensions of the surface region that can be investigated). For the system under consideration this transition is of second order. The order parameter's critical exponent characterizing this transition has for the two adsorbed phases of one and the same system values differing by a factor of two, which is unusual when compared with the available data on three-dimensional objects, for which the index β has quite close values (about $\frac{1}{3}$). Since this case is for the present unique, a systematic investigation of other objects having a similar symmetry is of interest. Of the already investigated systems, O–W(011) films satisfy the symmetry requirements. But the reflection intensity's temperature dependence given in Ref. 10 for the $p(2\times 1)$ phase exhibits an exponential, and not a power-law variation in a broad range of temperatures in the vicinity of the transition point, i.e., the phase transition is apparently greatly smeared.

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