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Unusual disordering processes of oxygen overlayers on Rh(111): A combined diffraction study using thermal He atoms and low-energy electrons

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The temperature-dependent behavior of the Rh(111)-(2×2)-1O phase was investigated by He-atom scattering (HAS) and low-energy electron diffraction. The adsorption system undergoes an order-disorder phase transition at $T_c = 280 \pm 5$ K, with critical exponents found to be consistent with the four-state Potts model. Beyond the phase transition the HAS specular peak intensity exhibits a strong and reversible increase. This finding points toward a reduction of the surface charge-density corrugation induced by the phase transition itself. Around 160 K, hydrogen adsorbed on the Rh(111)-(2×2)-1O surface reacts with oxygen to form water, and drives the overlayer in an out-of-equilibrium condition which is characterized by a dramatic domain-wall proliferation. [S0163-1829(97)09807-X]

I. INTRODUCTION

The Rh(111)-O system has been studied quite extensively.[1,2] In particular, the catalytic properties of this surface were widely addressed. Indeed, the extreme reactivity of this surface to CO and H_2 has to be considered its crucial characteristics. While an elucidation of the elementary reaction steps on this surface is of great importance, the extreme reactivity of rhodium has so far prevented an exhaustive and reliable characterization of the O overlayer system, most notably its temperature-dependent behavior. Several unexplained findings were reported in the literature. It was found, for instance, that the O-(2×2) structure undergoes a two-step irreversible disordering process by heating the sample above a temperature of 280 K.[2] A previous low-energy electron-diffraction (LEED) study indicated that the (2×2)-O structure becomes disordered upon electron irradiation for less than a minute.[3]

In this paper we present the results of a combined He-atom scattering (HAS) and LEED investigation on the Rh(111)-O system. These two diffraction techniques can be regarded as complementary to some extent. HAS is extremely sensitive to the presence of surface defects, and it allows us to study the surface structure in a very gentle way without introducing additional surface contaminants due to outgassing filaments. These attributes are of great importance in the study of the O-Rh(111) surface, which is easily attacked by CO and hydrogen. Moreover, the transfer width of the HAS apparatus exceeds 1000 Å, so that this technique is particularly suited for studying phase transitions. The acquisition of a complete HAS diffraction pattern, however, is quite cumbersome and time-consuming, since each point in reciprocal space has to be projected onto the aperture of the detector stage by rotating the sample. LEED, on the other hand, is capable of monitoring in parallel the complete diffraction pattern. This feature has been of great value in the study of a touchy system such as Rh(111)-O.

The present paper is organized as follows. Section II briefly describes the experimental setups used in this study. In Sec. III we report HAS and LEED results of the two distinct ordered (2×2) phases that oxygen forms on Rh(111), and compare them with the available structural models from the literature. Section IV deals with the order-disorder phase transition of the low-coverage oxygen (2×2) overlayer, while in Sec. V a transient disordering process is documented and discussed which takes place at a temperature as low as 180 K. We conclude this paper with a summary.

II. EXPERIMENT

The He scattering and diffraction measurements (Trieste) were performed with an apparatus[4] which is characterized by a fixed deflection angle of 110° and an overall angular resolution of 0.135°. The transfer width of the apparatus exceeds 1000 Å. The sample was mounted on an manipulator with six degrees of freedom and a very high angular resolution (<0.01°) that enabled us to align the surface-crystallographic directions precisely in the scattering plane, and to perform high-resolution momentum scans along particular directions. Further details of the He beam apparatus can be found in Ref. 4. The structure and the order of the surface were monitored by measuring the He beam intensity in a continuous mode using a beam energy of 19 meV, i.e., the He gas was cooled to liquid-nitrogen temperature prior to (adiabatic) expansion. The typical base pressure in the sample stage was 1.5×10^{-10} mbar. The sample could be heated up to 1150 K and cooled down to 150 K with liquid nitrogen.

The LEED measurements (Berlin) were conducted in another UHV chamber (base pressure 2.0×10^{-10} mbar during

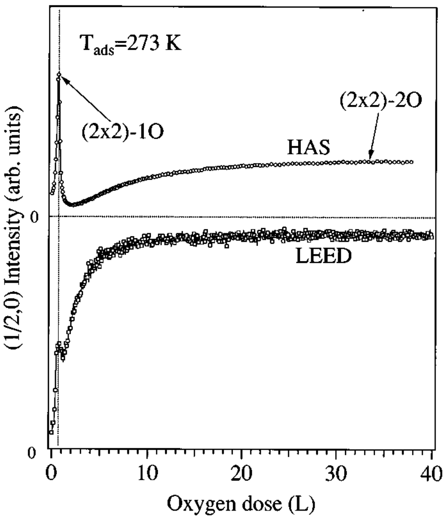

FIG. 1. He diffraction and LEED intensities of the (1/2,0) beam dependent on the O exposure. At 0.7 L oxygen a (2×2)-O phase is formed and at saturation a high-coverage (2×2)-2O phase is formed.

the measurements) equipped with facilities for Auger electron spectroscopy (AES), thermal desorption spectroscopy, and LEED. LEED intensities were measured on line with a four-grid LEED optics and a computer-controlled video-LEED system,[5] taking the integrated spot intensities from a fluorescent screen. The temperature of the Rh(111) sample could be varied from 1500 to 45 K using liquid He.

The main contaminants on the Rh(111) surface were sulfur and carbon. Sulfur could be easily removed by sputtering the sample for several minutes at 850 K with Ar (1-kV, 2-μA beam current) and subsequently flashing to 1050 K. Using HAS, the onset of annealing of defects caused by sputtering was determined to be 1020±10 K by monitoring the specular beam intensity, that increases abruptly approaching this temperature. The carbon contamination at the surface reacts to CO when exposing the sample to 2.0×10^{-7} mbar oxygen at 760 K for some minutes. To remove the surface oxygen by titration, the chamber was backfilled with 2.0×10^{-7}-mbar hydrogen at a fixed sample temperature of 750 K. This procedure ensures that no additional carbon segregated from the bulk to the surface, since the sample temperature chosen was below 800 K, the onset of carbon migration from the bulk. The cleanliness was either checked by the specular He beam intensity (Trieste) or with AES (Berlin). The same cleaning procedure was applied in both laboratories, also using the same Rh(111) sample to ensure comparable experimental conditions.

III. (2×2)-1O AND (2×2)-2O STRUCTURES

The O-Rh(111) system exhibits two ordered structures at O coverages of 0.25 and 0.50 ML, both showing an apparent (2×2) diffraction pattern. A coverage of 1 ML corresponds to a concentration of adparticles equal to that of Ru atoms in the topmost layer. In order to determine the optimum O_2 doses necessary to produce these overlayer structures, we monitored the LEED and HAS intensities of the (1/2, 0) beam as a function of oxygen dose (cf. Fig. 1). Both methods indicated the optimum (2×2)-1O structure to be prepared at an exposure of 0.7 L and 273 K. He diffraction is much more sensitive than LEED to the ordering and disordering process which is involved in the transition from the low-coverage to the high-coverage (2×2) structure. This fact explains the sharpness of the HAS (2×2)-1O feature in Fig. 1, compared to the LEED one.

A recent quantitative LEED analysis[6,7] of these oxygen phases revealed that oxygen atoms reside in both cases in the fcc-hollow site and that the (2×2)-2O is not a honeycomb (2×2) structure, but actually a (2×1)-O structure. The apparent (2×2) pattern of the (2×1) phase results from the equal presence of three (2×1) domains rotated by 120°.

IV. ORDER-DISORDER PHASE TRANSITION

The Rh(111)-(2×2)-1O system is in principle a good candidate to investigate order-disorder phase transitions. Since oxygen on Rh(111) has been shown to occupy fcc sites preferentially, from a symmetry argument one would expect to find a continuous (2×2)→(1×1) order-disorder phase transition falling into the universality class of the four-state Potts model. In fact, the order-disorder transition of the (2×2)-1O phase on Ru(0001) does belong to the four-state Potts universality class.[8] On the related Ni(111) surface, however, the classification of the order-disorder transition of the (2×2)-1O phase is still a matter of debate.[9,10] To study the order-disorder transition of the (2×2)-1O surface on Rh(111), we measured both the width and intensity of the half-order HAS peak as a function of the sample temperature. One-dimensional angular profiles of the (1/2,0) beam were collected along the direction perpendicular to $[1\bar{1}0]$. These measurements, however, were complicated by the high reactivity of the oxygen overlayer to hydrogen and CO that are inevitably present in the residual gas. In order to minimize the influence of the oxygen depletion on the peak profile measurements (in particular at temperatures above 300 K), we reprepared the optimum (2×2)-1O structure after each profile acquisition run; this could be easily accomplished by redosing oxygen until the known count rate at low temperature is restored. In doing so, the oxygen coverage could be kept constant within 1% during the series of profile measurements.

The procedure for fitting the He diffraction profiles was the following. At temperatures below the critical temperature T_c, the profiles were well described by a Gaussian function with constant widths. For temperatures above T_c, the profile was considered as a Voigt profile, i.e., a convolution of the low-temperature Gaussian function and a Lorentzian function with variable half-width. The full width at half maximum (FWHM) of the (1/2,0) spot, depending on the temperature, is summarized in Fig. 2. The half-order diffraction spot exhibits a strong broadening with increasing temperature which was fitted by a power law of the reduced temperature, i.e., $[(T-T_c)/T_c]^{\nu}$.The optimum parameters were found to be $T_c=280\pm5$ K and $\nu=0.67\pm0.01$, in excellent agreement with predictions according to the four-state Potts model ($\nu=2/3$). The critical temperature was found to be extremely sensitive to oxygen coverage: An oxygen depletion of 5% in the overlayer induced a lowering of the critical temperature by about 30 K.

Similar measurements were also performed with LEED: On cooling the (2×2)-1O from 360 to 100 K (cf. also Fig. 5,

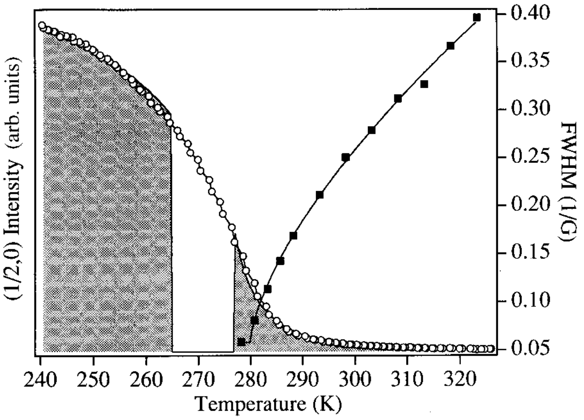

FIG. 2. Experimental (0,1/2) HAS peak intensity and width as a function of temperature (circles and squares, respectively). The fitting curves are indicated as full lines. The white area beneath the intensity best-fit curve corresponds to the temperature range $[-a,a]$ in which the finite-size effect affects the critical behavior.

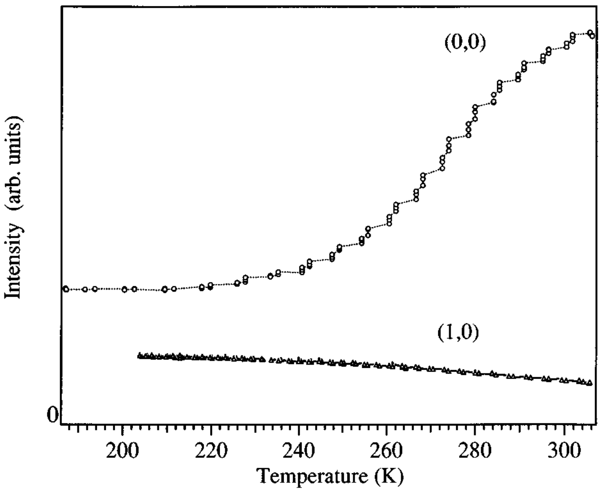

FIG. 3. He diffraction intensities of the (0,0) and (1,0) beams as a function of temperature. The specular beam intensity shows a dramatic increase upon crossing the critical temperature.

bottom panel), the LEED peak profiles were measured as a function of temperature both along the ΓM direction and perpendicular to ΓM. In both directions the analysis yields a critical exponent of $\nu=0.70\pm0.02$ and a critical temperature of 280±5 K, i.e., in nice agreement with the HAS results.

The temperature dependence of the half-order peak intensity depends on both the critical behavior of the transition and the ''Debye-Waller'' damping. Usually, it is possible to extract the Debye-Waller damping by fitting the temperature dependence of the peak in the low-temperature range. As will be shown in Sec. V, at low temperatures the Rh(111)-(2 ×2)-1O system is pushed into a transient out-of-equilibrium condition by hydrogen reaction to water. This process heavily modifies the temperature dependence of the half-order diffraction spots (see Fig. 4) and therefore precludes a reliable determination of the Debye-Waller factor. This observation forced us to use only the raw data for extracting the critical exponents β and γ. The experimental half-order peak intensity, shown in Fig. 2, was then fitted using the expression

$$I(T)=\begin{cases} A|t|^{2\beta}+B_-|t|^{-\gamma}+C_-, & t<-a \\ D, \quad |t|<a & t=\dfrac{T-T_c}{T_c} \\ B_+|t|^{-\gamma}+C_+, & t>a. \end{cases}$$

By a systematic variation of the value of a, we were able to evaluate the temperature range in which finite-size effects alter the critical behavior. The fitting procedure was repeated for different values of a, ranging from 0.01 and 0.04. It was found that the critical exponent β and γ and the critical temperature T_c do not change for $a>0.025$. The values of β and γ determined by this procedure were 0.13 ± 0.01 and 1.4 ± 0.3, respectively, while the critical temperature turned out to be $T_c=275\pm5$ K, consistent with the value found by the evaluation of the FWHM data. While the obtained value of the critical exponent ν compares very well with the one expected for a continuous phase transition in the four-state Potts universality class, i.e., 2/3, the values of β and γ deviate appreciably from the expected values (1/12 and 7/6). This disparity could be due to the Debye-Waller factor, which was not properly taken into account in the evaluation of the temperature-dependent peak intensity. On the other hand, we cannot exclude that the found values of the critical exponents β and γ may point toward an order-disorder transition different from the four-state Potts model. In particular, a finite occupation probability of non-fcc sites may change the critical behavior of the transition.

Moreover, a peculiar feature of this phase transition has to be taken in consideration. Approaching the order-disorder phase transition, all the HAS diffraction peaks are expected to decrease, due to enhanced surface disorder. This behavior is usually observed, such as for the (1×2)-Pt(110) deconstruction transition[11] and for the Rh(111)-CO($\sqrt{3}\times\sqrt{3}$)$R30°$order-disorder phase transition.[12] In Fig. 3 the temperature-dependent HAS intensities of the (1,0) and (0,0) beams are compared. The (1,0) beam suffers only a slight decrease upon passing the transition temperature, while the intensity of the specular beam dramatically increases by about a factor of 3. This behavior is completely reversible, and therefore cannot simply be explained by oxygen leaving the surface either into the bulk region or into the gas phase. It is important to notice that a similar (but less pronounced) behavior was observed by Bellman *et al.*[13] for the (2 ×2)→(2×1) phase transition of the Rh(110)-O system. A quite similar behavior was also reported by Meli *et al.*[14] for the system Ge(111)-$c(2\times8)$. The persistence of the integer-order peaks beyond the phase transition was interpreted in that case as evidence of an order-order phase transition: The high-temperature phase would accordingly display different surface corrugation, probably due to a higher degree of metallicity of the surface layer, explaining the increase of specular peak intensity. Takeuchi, Selloni, and Tosatti's calculations[15] and other experimental findings[16] predicted a metallization of the Ge(111) at high temperature, but accompanied by a complete disordering of the surface layer. In the case of the Rh(111)-(2×2)-1O system we can exclude an order-order (2×2)→(1×1) phase transition for two reasons. First, the broadening of the half-order diffraction beam profiles proves the disordered character of the high-temperature

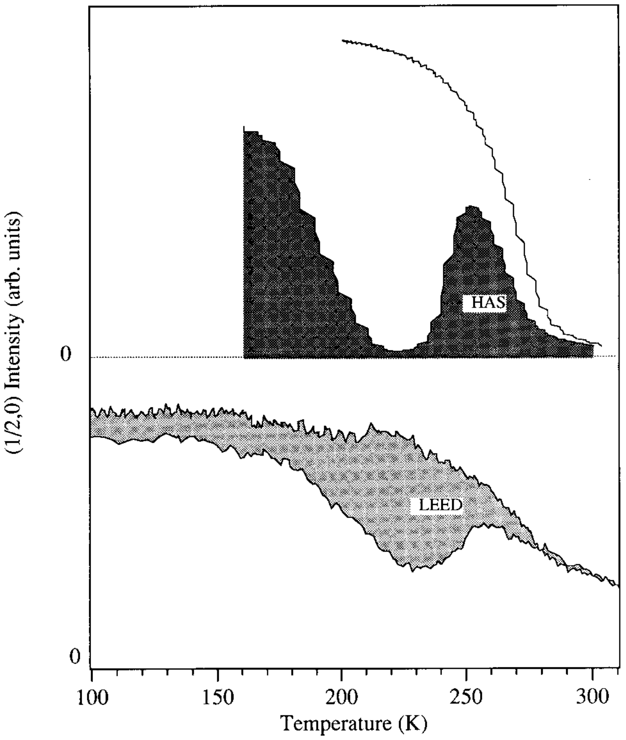

FIG. 4. HAS and LEED intensities of the (1/2,0) beam as a function of temperature. Upon heating, a distinct minimum is observed at about 230 K. The onset of the decrease in intensity is accompanied by desorption of water, while the increasing flank is related to an annealing of the O overlayer. When the (2×2)-1O surface is subsequently cooled, no such effect is observed.

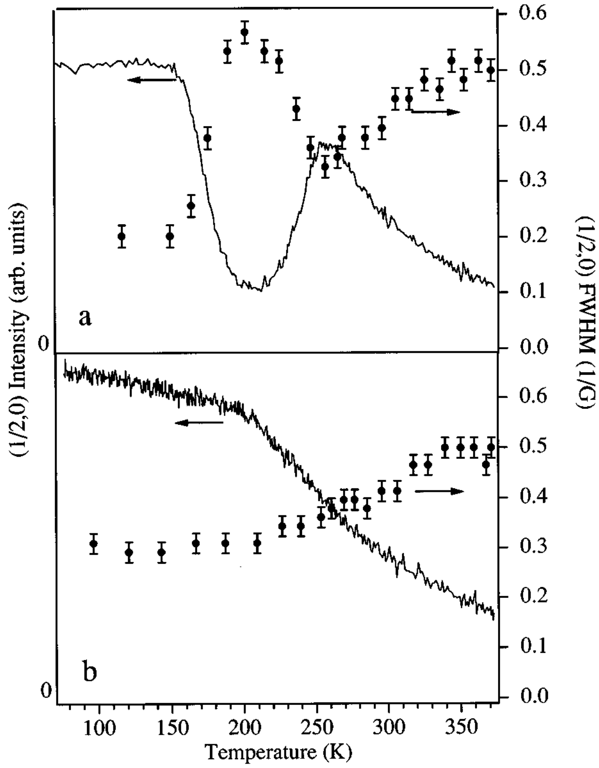

FIG. 5. In addition to the LEED intensity, the FWHM of the (1/2,0) beam of the (2×2)-1O phase was measured. Upon heating, the beam broadens substantially, and subsequently narrows again. The maximum of broadening of the (1/2,0) spot coincides with the minimum of the intensity. Upon cooling, the temperature dependence of the beam width is that expected for the ordinary phase transition. The critical temperature lowers appreciably, probably due to oxygen loss.

phase in the form of antiphase domains proliferation. Second, an ordered (1×1) surface structure is not compatible with a uniform oxygen coverage of 0.25 ML. One could speculate that (1×1) ordered domains form, leaving most (75%) of the surface uncovered. By additional O_2 dosing at 275 K, where the steep increase of the specular peak intensity occurs, one should then be able to accommodate more than 0.5 ML of oxygen on the surface. This, however, was not the case, as always the (2×2)-2O structure with global coverage of 0.5 ML appeared instead. Furthermore, we tried[7] to obtain a (1×1) oxygen overlayer on Rh(111) by dosing NO_2 at 600 K, following the procedure previously applied to the Ru(0001) surface.[17] No (1×1) structure was observed, instead a ~(7×7) coincidence pattern evolved indicating oxide formation. It was argued that the (1×1) oxygen structure on Rh(111) is energetically less favored than oxygen penetration, due to the strong expansion of the first layer Rh distance even at O coverages <0.5 ML. The increase of the specular beam intensity can therefore not be ascribed to an order-order phase transition.

One might also speculate that the closing of the (2×2) diffraction channels—due to the disordering process—could cause an increase of the specular beam. This point of view is nevertheless far from being convincing. In fact, if this were the case, the increase of the specular beam intensity should be a general feature of an order-disorder phase transition, while this is not the case. Since the disappearance of the (2×2) superstructure is associated with a disordering process, an increase of the diffuse scattering is expected, rather than an increase of the specular beam intensity. Also, it is not very likely that the (2×2) diffraction channels are really closed, since the diffraction experiments indicated a broadening of the peaks and not their disappearance.

The enormous increase of the specular peak intensity in HAS points toward a smoothing of the surface charge density induced by the disordering process. This leads to a reduction of the surface corrugation and therefore to an increase of the specular beam direction. The smoothening of the surface charge density might—but not necessarily—correspond to a kind of surface metallization. Since HAS is extremely sensitive to the outermost charge density, this change in the surface electron density might be quite small, and rather difficult to detect with other more direct techniques.

We also performed LEED *I*-*V* measurements as a function of temperature, in order to check whether the atomic geometry at the surface does change during the phase transition, i.e., top-layer relaxation, adsorption sites, etc. Since no differences between the *I*-*V* curves taken at 200 and 280 K were detectable within the experimental accuracy, the observed increase of the specular He beam intensity should be related to subtle changes in the overlayer charge density rather than to transition-induced changes of the local adsorption geometry. Remarkably, the same intensity enhancement of the specular HAS beam was observed in the order-

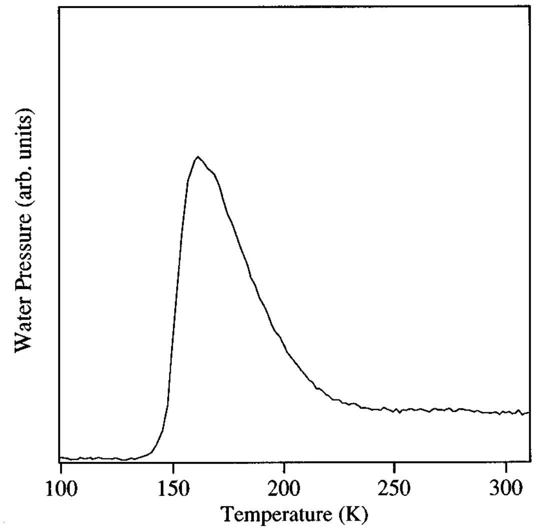

FIG. 6. TD spectrum of water from the Rh(111)-(2×2)1O surface. The TD spectrum displays a maximum around 160 K. The amount of oxygen leaving the surface due to water desorption was evaluated to be less than 5% of the (2×2)-1O structure.

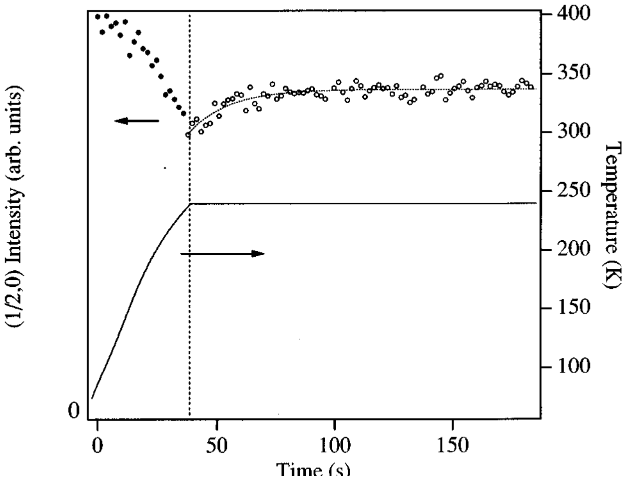

FIG. 7. Upper curve: LEED intensity of the (1/2,0) beam as a function of time during heating (filled circles) and the recovery of the ordered O overlayer at 240 K (empty circles). The full line is the best-fit curve to an exponential function of the intensity during recovery. Lower curve: the actual temperature during the measurement.

disorder phase transition of the Rh(110)-(2×2)-1O surface.[13] How this effect is correlated with an overlayer disordering process is so far not clear, so that theoretical and further experimental investigations are mandatory.

V. TRANSIENT OUT-OF-EQUILIBRIUM STATE

As mentioned in Sec. IV at low temperatures the (2×2)-1O overlayer reveals a peculiarity caused by hydrogen contamination of the surface. Figure 4 shows the temperature behavior of both the HAS and LEED (1/2,0) beam intensities. While heating the sample, the (1/2,0) beam intensity runs through a distinct minimum at 230 K that is not present during subsequent cooling. This intensity decrease was accompanied by a strong broadening of the half order profiles as seen by LEED. In Fig. 5 the FWHM of the (1/2,0) LEED beam is shown both during heating and cooling. Upon cooling, the half-order beam width decreases monotonically in the expected way, due to the ordinary phase transition at 280 K. By contrast, upon heating, the beam profile starts to broaden quite suddenly around 150 K, reaches a maximum around 230 K, and subsequently narrows. This behavior indicates that between 150 and 250 an irreversible disordering process takes place which is characterized by a substantial proliferation of antiphase domain walls in the (2×2)-1O overlayer. To further elucidate this behavior, a thermal-desorption (TD) spectrum of water (see Fig. 6) was taken. This TD spectrum indicates the formation and desorption of water at around 160 K, which points toward the presence of hydrogen as contaminant in the O overlayer. Obviously, hydrogen from the residual gas adsorbs onto the (2×2)-1O overlayer at low temperatures without reacting off the oxygen; note that cooling the sample takes about 15–30 min, and during this time hydrogen is accumulated at the surface. When the sample temperature approaches 160 K, hydrogen reacts with oxygen and forms water which leaves the surface immediately. The temperature at which the (1/2,0) beam intensity runs through a minimum varies with the amount of hydrogen adsorbed at low temperature. A quantitative evaluation of the TD spectrum reveals that the amount of oxygen leaving the surface in the form of water is less than 5% of the (2×2)-1O overlayer. It is this small quantity of water leaving the surface that causes the disordering of the O overlayer. The actual mechanism determining this disordering process is not easy to figure out. In order to gain more insight into this phenomenon, we performed the following measurements illustrated in Fig. 7. We recorded the LEED (1/2,0) beam intensity during heating up to 240 K, at which temperature the intensity reaches its minimum (full circles in Fig. 7); we then kept the temperature fixed at 240 K and monitored the (1/2,0) beam intensity as a function of time (empty circles in Fig. 7). The intensity increases with time in an exponential way, eventually recovering the value reached at the same temperature during cooling (cf. Fig. 4). This measurement clearly demonstrates that the disordered state is transient, and that the process takes place under out-of-equilibrium conditions. For each temperature between 150 and 250 K we can assume that the points in the heating curve (Figs. 4 and 5) are out-of-equilibrium states, while those of the cooling curve are the corresponding equilibrium states. It is known that defects or impurities in otherwise ordered overlayers are able to introduce both (i) a lowering of the critical temperature, and (ii) a change in the order and/or the universality class of the overlayer phase transition.[18] Furthermore, it is also conceivable that the observed transition is not continuous but of first order even without defects [case (iii)]. In the following we show that none of these effects is able to account for the observed (disordered) transient state. Indeed, a lowering of the critical temperature (from 280 to 250 K) due to a 5% depletion of the oxygen overlayer can be seen from the cooling curve. Nevertheless, case (i) is unable to explain the recovery of the ordered overlayer after domain-wall proliferation, i.e., the transient character of this process.

The discussion of case (ii) is more subtle. One might suppose that defects induce the phase transition to become of first order, displaying some hysteresis behavior. To be a first-order transition, the hysteresis has to show—as happens upon heating—a supercooling effect, i.e., the ordered phase should pertain even beyond the critical temperature, until some nucleation causes the transition to occur. By contrast in our case, the overlayer becomes disordered below the critical temperature and subsequently recovers the equilibrium-ordered phase. This phenomenon does therefore not resemble a hysteresis process typical of a first-order transition.

Case (iii) can easily be excluded since the observed hysteresis in the temperature-dependent diffraction data exhibits the wrong direction. The hysteresis should only narrow by introducing defects in the overlayer.

To understand the transient behavior, one should recall a scenario where water formation and desorption leave the overlayer in an out-of-equilibrium condition. When the rate of water desorption slows down and the temperature is sufficiently high, the surface overlayer anneals, i.e., recovers the equilibrium-ordered phase. The transient state is characterized by a domain-wall density associated with an apparently higher temperature (i.e., $T > T_c = 280$ K). This fact might provide an important clue about the mechanism. As water formation is an exothermic process, a fraction of the reaction enthalpy could be used to disorder the O overlayer locally. The thermalization of the overlayer is, of course, almost instantaneous (time scale of atomic vibrations), and is not associated with an appreciable increase of the surface temperature, but the time necessary to recover the ordered overlayer is governed by the much slower diffusion process. Moreover, even a very small fraction of the produced energy suffices to induce domain-wall proliferation, as the phase-transition temperature of this system is quite low (280 K, corresponding to about 25 meV). In order to verify the proposed mechanism, it would be desirable to apply a local probe technique such as scanning tunneling microscopy. As a final remark we note that no water formation was detected for the (2×2)-2O phase, even upon deliberate hydrogen deposition at low temperatures.

VI. CONCLUSION

A combined LEED and HAS investigation of the temperature-dependent behavior of the Rh(111)-O system was presented. The (2×2)-1O phase on Rh(111) undergoes an order-disorder transition at 280 ± 5 K. The critical parameter derived from the FWHM is compatible with the four-state Potts universality class. Along with the phase transition, an enormous increase of the HAS specular beam intensity by a factor of 3 was observed that points toward a reduction of the surface charge-density corrugation during the disordering process. The change in the surface corrugation could also affect the temperature dependence of the half-order beam intensity, which then would explain the observed deviation of the critical parameters β and γ from the expected four-state Potts values. It is also possible that this phase transition differs from the four-state Potts model, for instance, due to a finite occupation probability of non-fcc sites beyond the critical temperature. Hydrogen adsorbed on the (2×2)-1O structure at low temperatures (<150 K) reacts with oxygen to form water at about 160 K. This process drives the (2×2)-1O system into a transient out-of-equilibrium state characterized by a dramatic proliferation of antiphase domain walls. We guess that the two-step irreversible phase transition observed by Thiel and co-workers[2] might also be due to contamination by hydrogen.

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[1] D. G. Castner, B. A. Sexton, and G. A. Somorjai, Surf. Sci. **71**, 519 (1978).

[2] P. A. Thiel, J. T. Yates, Jr., and W. H. Weinberg, Surf. Sci. **82**, 22 (1979); J. T. Yates, Jr., P. A. Thiel, and W. H. Weinberg, *ibid.* **82**, 45 (1979).

[3] P. C. Wong, K. C. Hui, M. Y. Zhou, and K. A. R. Mitchell, Surf. Sci. **165**, L21 (1986).

[4] D. Cvetko, A. Lausi, A. Morgante, F. Tommasini, K. C. Prince, and M. Sastry, Meas. Sci. Technol. **3**, 997 (1992).

[5] H. Over, H. Bludau, M. Skottke-Klein, W. Moritz, G. Ertl, and C. T. Campbell, Phys. Rev. B **45**, 8638 (1992).

[6] K. C. Wong, W. Liu, and K. A. R. Mitchell, Surf. Sci. **360**, 137 (1996).

[7] S. Schwegmann, H. Over, V. De Renzi, and G. Ertl, Surf. Sci. (to be published).

[8] P. Piercy and H. Pfnür, Phys. Rev. Lett. **59**, 1124 (1987).

[9] L. Schwenger, C. Voges, M. Sokolowski, and H. Pfnür, Surf. Sci. **307-309**, 781 (1994).

[10] Z. Li, X. Liang, M. L. Stutzman, J. A. Spizuoco, S. Chandavarkar, and R. D. Diehl, Surf. Sci. **327**, 121 (1995).

[11] M. A. Krzyzowski, P. Zeppenfeld, C. Romainczyk, R. David, G. Comsa, K. E. Kuhnke, and K. Kern, Phys. Rev. B **50**, 18 505 (1994).

[12] H. Over, S. Schwegmann, G. Ertl, D. Cvetko, V. De Renzi, L. Floreano, R. Gotter, A. Morgante, M. Peloi, F. Tommasini, and S. Zennaro, Surf. Sci. (to be published).

[13] A. Bellman, D. Cvetko, A. Morgante, M. Polli, F. Tommasini, V. R. Dhanak, K. C. Prince, and R. Rosei, Surf. Sci. **281**, L321 (1993).

[14] C. A. Meli, E. F. Greene, G. Lange, and J. P. Toennies, Phys. Rev. Lett. **74**, 2054 (1995).

[15] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. **72**, 2227 (1994).

[16] S. Modesti, V. R. Dhanak, M. Sancrotti, A. Santoni, B. N. J. Persson, and E. Tosatti, Phys. Rev. Lett. **73**, 1951 (1994).

[17] C. Stampfl, S. Schwegmann, H. Over, M. Scheffler, and G. Ertl, Phys. Rev. Lett. **77**, 3371 (1996).

[18] L. Schwenger, K. Budde, C. Voges, and H. Pfnür, Phys. Rev. Lett. **73**, 296 (1994), and references therein.