Influence of Steps on the Critical Behavior of a Two-Dimensional System: $p(2\times2)$ Oxygen on a Stepped Ru(0001) Surface

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(Received 20 March 1989)

The $p(2\times2)$ phase of oxygen on a stepped Ru(0001) surface (13 ± 2 atomic rows per terrace, steps parallel to close-packed rows) exhibits long-range order also *across* the steps and undergoes a continuous order-disorder phase transition. Critical exponents β, γ, and v were determined by LEED from the temperature dependence of LEED peak intensities and spot profiles of superstructure spots in the range $0.01 < |(T-T_c)/T_c| < 0.2$ both parallel and perpendicular to the step edges. Exponent values are close to those of the 2D-Ising class and equal for both directions.

Adsorbed monolayers are considered to represent ideal test systems for the rich variety of phase transitions in two dimensions.[1] For continuous transitions the situation should be particularly simple as critical exponents are predicted to fall into only a small number of universality classes.[2] The experimental observation, however, can be easily spoiled by the influence of defects not completely under control; their concentration is not easily reduced below 0.1% to 1%. They can strongly influence critical behavior, and even change exponents, as will be demonstrated below. Consequently, only a small number of experiments is reported in the literature,[3] with partly unexpected results[4] not interpretable within the framework of ideal lattice-gas systems.[5] Systematic experimental tests on the influences of defects are missing in 2D. Instead of shifts in T_c and rounding of the phase transition, as expected from scaling arguments[6] and corroborated by simulations[7] on finite-size systems, we show that defects do not necessarily distort ideal behavior, but can lead to interesting new physical effects.

Here we present a study of changes in critical behavior due to a specific defect, namely steps. Quite recently we demonstrated that the order-disorder phase transition of the oxygen-induced $p(2\times2)$ superstructure on a nominally flat Ru(0001) surface at a coverage θ of 0.25 relative to the substrate density is, in fact, continuous,[8,9] in agreement with the "Landau rules"[10] applied to a lattice gas. The exponents α, β, γ, and v were in good agreement with four-state Potts critical exponents.[8,9] As we observed only very small effects of corrections to scaling and of influences of defects over the temperature range accessible, we expect this system to represent an ideal candidate for systematic tests of the specific role of defects.

The surface investigated here was prepared by cutting and polishing a Ru crystal of 99.99% purity at a tilt angle of 4.0° off the (0001) plane towards the (10$\bar{1}$0) direction, thus yielding terrace edges along close-packed rows. LEED experiments were carried out at primary beam currents of 100 nA in a UHV chamber with dou-

ble Mumetal shield at a base pressure of $\leq 2\times10^{-11}$ mbar, using four-grid LEED optics with a Faraday cup movable in polar and azimuthal directions. Temperature, measured with Chromel-Alumel thermocouples, was stabilized to better than 0.1 K and could be ramped up and down linearly. Experimental details have been described in Ref. 8.

The step distribution on the surface was determined by LEED from an analysis of the (0,0) and (1,0) beam profiles of the clean surface as a function of electron energy between 40 and 500 eV.[11] We found an average terrace width of 13 atomic rows per terrace, with a width of the terrace-size distribution of ±2 atomic rows. More than 95% of the steps are monatomic steps. Details of this analysis will be presented elsewhere.[12]

Oxygen was adsorbed from the background pressure at a surface temperature of 400 K. An exact coverage of $\theta = 0.25$ was adjusted by maximizing the transition temperature.[9] After annealing to more than 800 K once, intensities and superstructure beam profiles were found to be fully reversible during temperature cycles up to 900 K at all coverages. Close to $\theta = 0.25$, *all* superstructure beams are split in the k direction normal to the step edges in addition to the integral order beams, both with the same minimum widths. Although beam splitting for superstructure beams is, in general, possible without correlations between terraces,[13] this finding is not compatible with a model of uncorrelated adsorbate ordering between adjacent terraces. Even if the terrace-size distribution and pinning to the step edges enforces correlations normal to step edges, we must assume correlations between terraces parallel to the step edges in addition. The clearest argument for correlations also normal to the steps, however, comes from the temperature dependence close to the order-disorder transition. If each terrace acts as its own subsystem, no beam splitting should be visible above T_c;[13] also, for the pinning model, correlations of critical fluctuations should end at the step edges. In contrast, we observe continuous broadening of split superstructure profiles in both directions and nearly
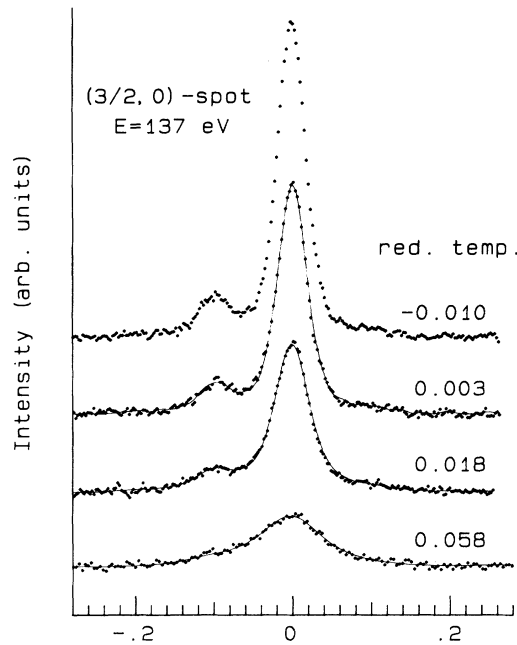
FIG. 1. Superstructure beam profiles of the $(\frac{3}{2},0)$ spot at $\theta = 0.25$ normal to the step edges at different reduced temperatures close to T_c. Lines are fits according to Eq. (1), using a low-temperature profile as an instrument function.

equal correlation lengths of critical fluctuations parallel and perpendicular to step edges up to 10 times the terrace widths (see below). Instead of convolutions of the autocorrelation functions of lattice sites and their occupation numbers[13] in real space that are characteristic for a model with statistically independent ordering on different terraces, we can quantitatively describe the temperature-dependent changes of superstructure beam profiles by a convolution in reciprocal space (see Fig. 1):

$$I(\mathbf{q}_{\parallel}) = I_{\text{lattice}}(\mathbf{q}_{\parallel}' - \mathbf{q}_{\parallel}, q_z) g(\mathbf{q}_{\parallel}) W(\mathbf{q}_{\parallel}),\qquad(1)$$

with I_{lattice} the Fourier transform of a site correlation function including steps and terraces, and $g \sim F(\langle \psi(\mathbf{R}_{\parallel}) \times \psi(\mathbf{R}_{\parallel}') \rangle)$, the Fourier transform of the autocorrelation function of the order parameter. W contains broadening due to the instrument. In Eq. (1) it is assumed that the adsorbate occupies the same sites as on a flat surface, with the substrate modified by steps and terraces, and a fixed relationship for the adsorbate layer on different terraces. The implicit assumption of Eq. (1) that $\langle \psi(\mathbf{R}_{\parallel}) \psi(\mathbf{R}_{\parallel}') \rangle$ only depends on $\mathbf{R}_{\parallel} - \mathbf{R}_{\parallel}'$ should be a good approximation for correlation lengths $\xi \gg L$, the average terrace width, a situation found for most of the data shown below. A detailed investigation of the exact form of those correlations is under way.[12]

Transition temperatures were determined from peak intensities of superstructure LEED spots at constant coverage as a function of temperature, using the points of inflection which correspond to the maximum in specific
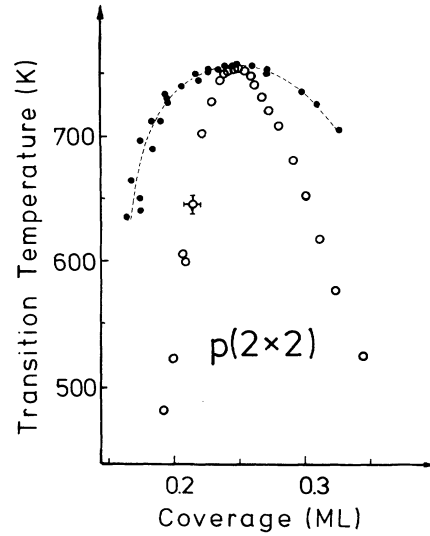

FIG. 2. Comparison of the phase diagram of oxygen adsorbed on a nominally flat (open circles) and on a stepped Ru(0001) surface (filled circles) with 13 ± 2 atomic rows per terrace, as described in the text.

heat.[14] A comparison of the phase diagrams on the flat (open circles)[15] and stepped surfaces (filled circles) is plotted in Fig. 2 showing a very small influence of steps: Within the uncertainties of absolute reading between different thermocouples (± 3 K at this temperature) there is virtually no influence of steps on T_c of the order-disorder transition at a coverage of 0.25. Only at coverages different from optimal $p(2\times2)$ order do steps seem to stabilize order and to increase T_c.

In order to avoid Fisher renormalization[16] only the maximum in T_c is used for the determination of critical exponents. The critical exponents β, γ, and ν were determined by parametrizing the structure function $g(\mathbf{q}_{\parallel},t)$ by a δ function to describe long-range order, which decays $\sim (-t)^{2\beta}$, and an isotropic Lorentzian centered at the superstructure spot position q_0 with amplitude $\chi_0 \sim |t|^{-\gamma}$ and half-width $\xi^{-1} \sim |t|^\nu$,[17,18] yielding the proper scaling form for small $\xi(q-q_0)$ and small t.[19]

Neglecting short-range-order fluctuations below T_c, the peak intensity measured long-range order. A straight line is obtained in the range $0.02 < t < 0.4$ with slope $2\beta = 0.28 \pm 0.04$, using the raw data after division by a Debye-Waller factor. Finite-size rounding effects stronger than on the flat surface exist on this surface, and corresponding deviations from the straight line are found for $|t| < 0.02$. No deconvolution of data for $t < 0.02$ was attempted, therefore, as the main uncertainty in determining β is due to these rounding effects.

Peak heights χ_0 and widths ξ^{-1} of critical scattering above T_c parallel and perpendicular to the step edges were determined by deconvoluting the structure factor g
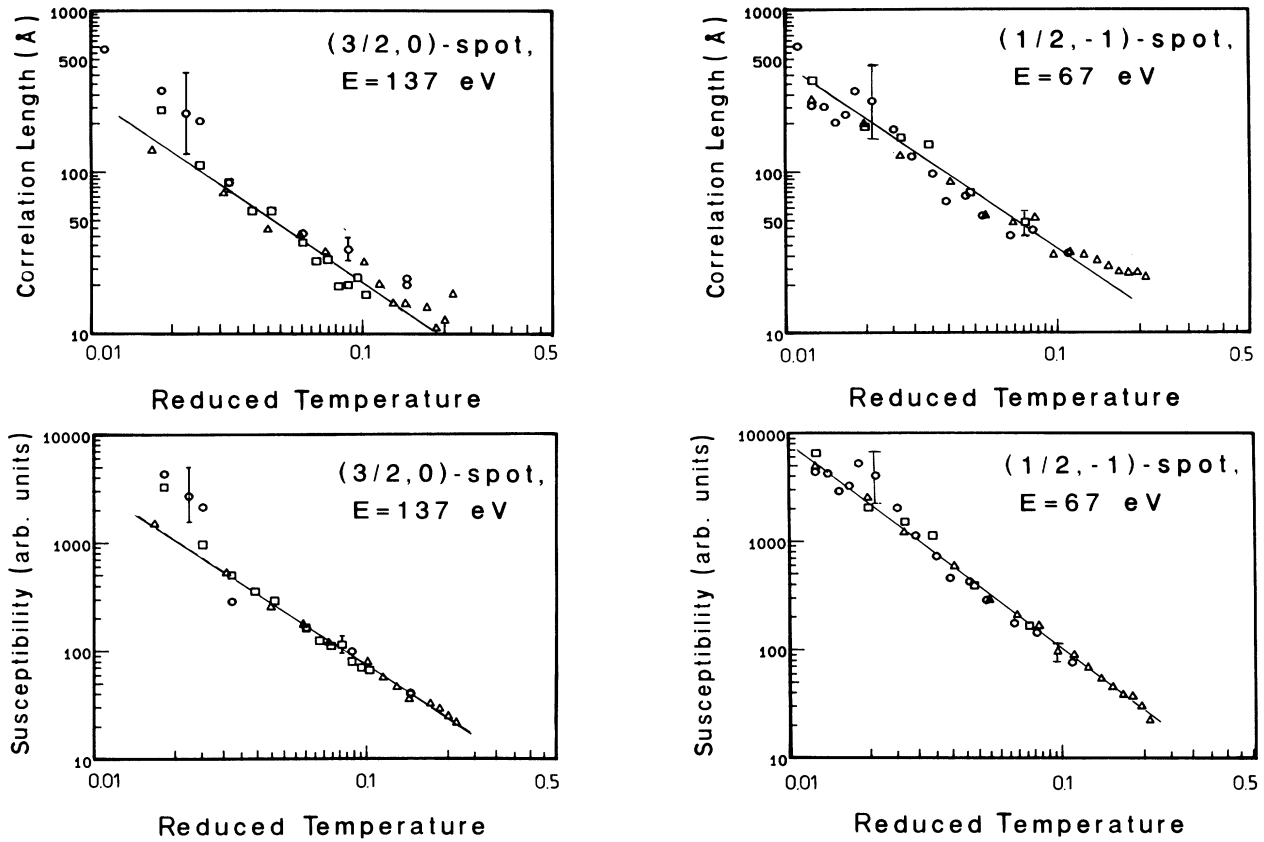
FIG. 3. Results of evaluations of peak intensities χ_0 and half-widths ξ^{-1} above T_c, after deconvolution, as a function of reduced temperature. Results on the left-hand side are measured normal to and those on the right-hand side parallel to step edges, at the energies indicated. Different symbols correspond to different experimental runs.

from the measured profiles according to Eq. (1). $(\frac{3}{2},0)$ and $(\frac{1}{2},-1)$ beams perpendicular and parallel to the step edges were measured, respectively, using low-temperature beam profiles in the directions of measurement and Gaussians in the directions perpendicular for the product $I_{\text{lattice}}W$ in Eq. (1). The beam focus was adjusted to yield transfer widths of 180 Å perpendicular to and 20% less parallel to the steps for the data shown. Inclusion of I_0 did not improve the fits in this t range.

Results of this procedure for the peak heights χ_0 and correlation lengths ξ are plotted on a log-log scale in Fig. 3. We find scaling over approximately 1 order of magni-

tude in reduced t, with exponents $\gamma_\perp = 1.65 \pm 0.1$, $\gamma_\parallel = 1.85 \pm 0.1$, $\nu_\perp = 1.1 \pm 0.15$, and $\nu_\parallel = 1.1 \pm 0.15$. For the correlation lengths a slight asymmetry is found, with the value parallel to about 30% to 50% larger than that perpendicular to terrace edges (see Fig. 3). These results clearly show that correlation of $p(2\times2)$ order extends over many terraces and does not end at a step edge. Because of correlation lengths of several hundred angstroms close to $t = 0.01$, the accuracy of the exponent determination and the observable range of scaling are mainly limited by instrument resolution at small t, and by the uncertainty in T_c.

TABLE I. Comparison of experimentally determined critical exponents with exponents of the two-dimensional Ising and four-state Potts universality classes (see Ref. 20).

| | Experiment | | | Theory | |
| | Flat surface | Stepped surface | | Ising | Four-state Potts |
		‖ steps	⊥ steps		
β	$0.085^{+0.015}_{-0.005}$	0.14 ± 0.02		0.125 $(\frac{1}{8})$	0.083 $(\frac{1}{12})$
γ	1.08 ± 0.07	1.85 ± 0.1	1.65 ± 0.1	1.75 $(\frac{7}{4})$	1.167 $(\frac{7}{6})$
ν	0.68 ± 0.03	1.1 ± 0.15	1.1 ± 0.15	1	0.667 $(\frac{2}{3})$

As seen from Table I, the changes of critical exponents on the stepped compared to the flat surface are striking and far beyond the uncertainties of determination. They are now close to exponents of the Ising class. Because of correlations between terraces the adlayer must be considered as one single system on a stepped surface, whose symmetry elements are reduced, however, from a threefold rotational axis of the flat surface to one mirror plane perpendicular to the steps at most. Within the uncertainties given, the exponents in both directions are equal, consistent with a single phase transition of the whole system. According to the Landau rules, only continuous phase transitions in the Ising class should be allowed in such a low-symmetry system in 2D,[2,10] in apparent agreement with our findings. However, $p(2\times2)$ order cannot be described with a one-component order parameter, and the Landau-rule argument does not seem to be applicable.

Concluding, we have shown that in a strongly chemisorbed system correlations between adsorbate atoms need not be limited by steps. Steps represent only a weak distortion to $p(2\times2)$ order of oxygen on $Ru(0001)$ modifying the phase diagram only slightly, and leaving the order-disorder transition still continuous. The reduced symmetry on the stepped surface, however, affects critical exponents most strongly, and Ising-type exponents result.

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