Critical Exponents of a Four-State Potts Chemisorbed Overlayer: $p(2\times2)$ Oxygen on Ni(111)

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We report the first determination of critical exponents for a chemisorbed overlayer, using low-energy electron diffraction. We examine the order-disorder transition of $p(2\times2)$ oxygen on the (111) surface of nickel. This study is the first of critical behavior of a two-dimensional system in the four-state Potts universality class. From measured diffraction-beam profiles, we extract the exponents β, γ, and ν. Discussion of disparity between our results and predicted exponents considers several possibilities, including logarithmic corrections.

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Increased understanding of two-dimensional (2D) critical phenomena has shown that second-order transitions fall into a small number of universality classes characterized by common critical exponents.[1] Since this classification depends only on the spatial dimension and the symmetry of the ordered state, it can be determined from Landau-Ginzburg Hamiltonians.[2,3] Thus the transitions of layers of adsorbed atoms on crystalline surfaces are intimately related to well-studied models.

Measurements of critical exponents, with use of calorimetry and neutron and x-ray scattering, have been reported for various physisorbed atoms on graphite or Grafoil.[4] This substrate provides the enormous surface-to-volume ratio required by the lack of surface sensitivity in these probes. The observed transition is almost always the disordering of a $(\sqrt{3}\times\sqrt{3})R30°$ overlayer, which is in the three-state Potts universality class.[5] This uniformity stems from the van der Waals origin of the lateral interactions. In chemisorption, lateral interactions are indirect and more complicated,[6] providing a richer variety of overlayers.[7] Since well-defined patterns and transitions require single-crystal substrates, one needs a strongly interacting probe such as electrons. The concomitant multiple scattering, which plagued intensity-voltage (I-V) analysis, was widely thought to make low-energy electron diffraction (LEED) unsuitable for investigating criticality. However, when the incident electron beam impinges near normal incidence (and below ~50 eV), multiple scattering *within* the adsorbed layer (which would confound extraction of exponents) is sharply reduced,[8] since electron scattering is minimal at right angles.[9,10] Moreover, the limited spatial resolution of LEED,[11] which was held also to preclude such analysis, is comparable to that of thermal neutrons.[12]

We demonstrate our procedure using the classic order-disorder transition of $p(2\times2)$ oxygen on Ni(111).[13] The transition of this frequently occurring[14] overlayer symmetry corresponds to the four-state Potts model.[3] This experiment is the first to examine a system in this universality class. The q-state Potts model is unusually intriguing at $q=4$, since for $q>4$ the transition becomes first order[15]; the essential singularity at $q=4$ (Ref. 16) leads to logarithmic corrections,[17] heightening interest but impeding analysis.

To find the critical exponents β ($T<T_c \sim 427$ K) and ν and γ ($T>T_c$) we examined the LEED beam profiles as a function of temperature. The experiments were conducted at base pressure $<10^{-10}$ Torr. The profiles were measured with a standard spherical-grid LEED optics, which was also operated as a retarding analyzer to obtain the Auger spectrum to determine the relative oxygen coverage. An optical system outside the vacuum projected a real image of the diffraction beam onto a photon counter. One cut of the angular profile of the beam was obtained by varying the incident energy to move the beam across the aperture. The equivalent angle of acceptance was 1°. Temperatures were measured by a Chromel-Alumel thermocouple and stabilized to ± 0.01 K (at 400 K) with use of a feedback circuit.

The Ni samples, nominally 99.995% pure, were zone refined to reduce the mosaic spread to less than the instrumental resolution and oriented to the (111) direction to better than 20′. Oxygen is known by LEED I-V analysis[18] to dissociatively chemisorb on Ni(111), in the threefold hollows. Marcus, Demuth, and Jepsen do not identify whether these sites are "fcc" (where the next layer of Ni atoms would bond) or "hcp" (above a Ni in the second layer). Our extensive Monte Carlo simulations[19] demonstrate that only one such site—we do not know which—is selected at fractional coverages $\theta < 0.27$, while for $\theta > 0.27$ both types of site apparently can be occupied simultaneously. Since our measurements were made at $\theta = \frac{1}{4}$, the array of binding sites has triangular, not honeycomb, symmetry. The transition is reversible, and the oxygen does not desorb from the surface.[20] While above about 500 K the oxygen does dissolve into the bulk of the crystal, below this point no T dependence in work function or Auger intensity is observed. Thus the oxygen remains on the surface and in the same type of binding site throughout the transition, realizing a 2D lattice gas.

Sixty LEED profiles were recorded between 323 and 450 K. The Debye-Waller factor was determined from the low-T dependence of the intensity at the beam center; its effects were removed by simple division of each profile by the appropriate (energy-dependent)[10] factor. We also subtracted the uniform background from thermal diffuse scattering.

The lowest-T profile, ~100 K below T_c, served as the instrument response function (IRF). Two methods were used to deconvolute it from higher-T beam profiles.[19] In the Fourier-transform method (FTM) we divided the transformed profile by the transformed IRF. (All transforms are 2D.) Alternatively, the measured beam was least-squares fit[21] to the convolution of the measured IRF and an assumed parametrized functional form for the scattered intensity.[22] Below T_c, the ideal scattered intensity near the $\frac{1}{2}$-order positions combines a δ function due to long-range order and a short-range (critical scattering) contribution,[23] which is Lorentzian in $(k\text{-}k_0)$ as the reduced temperature $t \equiv (T-T_c)/T_c$ approaches 0; k_0 is the center of the adlayer-induced spot. The δ-function contribution vanishes for $t \geq 0$. In the FTM the two contributions can be separated in Fourier ("direct") space since the long-range part gives a constant, identifiable at the profile wings. In the fit method the scattering intensity is parametrized

$$I(\vec{k}) = T(\vec{k}) \cdot \{A^2\delta(\vec{k}-\vec{k}_0) + [B^2/(\vec{k}-\vec{k}_0)^2 + w^2]\}, \quad (1)$$

where $T(\vec{k})$ is the IRF and $\cdot$ denotes 2D convolution. For each profile A, B and w are determined as functions of temperature. Then letting $G(T) = A^2(T)$, $B^{-2}(T)$, or $w(T)$, we determined the exponents $\lambda = 2\beta$ (for $t < 0$), γ, or ν, respectively, by three-parameter nonlinear least-squares fitting[21] to the functional form

$$G(T) = C_\lambda |T - T_c|^\lambda. \quad (2)$$

Alternatively, T_c could be set and only C_λ and λ fit. The choice of the data range in the fit is important and difficult. The forms (2) hold only asymptotically ($|t| \to 0$), but rounding from finite-size effects and incomplete deconvolution requires $|t| \geq 0.015$. To obtain good statistics for the fits we used $0.015 \leq |t| \leq 0.06$. This data range gives a systematic error $< 5\%$ in a determination of ν from the Ising transition.[19] The fits for ν and γ (cf. Fig. 1) gave T_c's of 153.7 and 153.9°C, respectively.

This agreement supports our choice of data range. Less data were available below T_c. The analysis for β gave a T_c 2 K greater than the other two values. When we reanalyzed using T_c pinned at 154 °C, β changed from 0.16 to 0.14, which we believe is more reliable. Thus the largest source of error in β is determination of T_c. The result is consistent with analysis for β with use of the FTM. In neither method could we determine γ' and ν' (for $t < 0$) confidently, as the profiles were rather noisy after subtraction of the long-range contribution. For $T > T_c$ the fit method was far superior because of persistent truncation oscillations in the FTM.[19]

Table I lists our results. The quoted errors combine the statistical errors suggested by the χ^2 of the fits and the sensitivity to T_c. They do not include any adjustment for systematic errors due to our choice of data range.[24] The disagreement between our exponents and accepted values[25] for the four-state Potts model are greater than

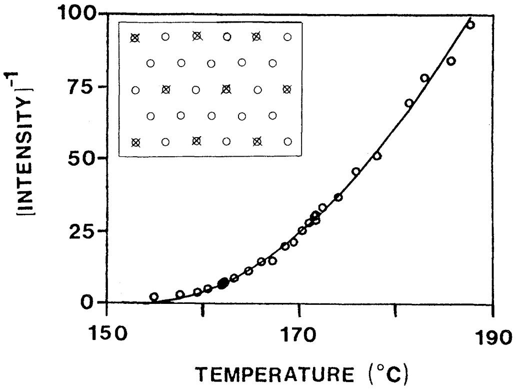

FIG. 1. Nonlinear three-parameter least-squares fit (solid line) with use of Eq. (3) of the measured inverse critical intensity (circles) vs T. The resulting exponent γ is the most discordant with the four-state Potts and "effective Potts" values. The inset illustrates the ordered phase. Circles are adsorption sites; crosses are oxygen adatoms.

TABLE I. Experimental critical exponents, their values in the Ising and four-state Potts universality classes, and effective Potts exponents due to logarithmic corrections.

Measurable	Expt.	Ising	Pure Potts	Effective Potts
Magnetization	0.14± 0.02	1/8	1/12	0.122
Susceptibility	1.9± 0.2	7/4	7/6	1.37
Correl. length	0.94± 0.10	1	2/3	0.80

the error bars of the measurement. We offer three possible explanations:

(1) The crossover to four-state Potts exponents as $|t| \to 0$ is not well understood and is not treatable within the existing Landau-Ginzburg scheme. Perhaps the Potts values become apparent only for $|t| \leq 0.015$. We are considering this question by Monte Carlo simulation.

(2) When any corrections to scaling are present, analysis with use of Eq. (2) leads to effective exponents implicitly dependent on the data range.[26] For the four-state Potts model, there are logarithmic corrections,[17] which are themselves singular as $t \to 0$:

$$
\begin{aligned}
&A \to M \sim (-t)^{1/12}[1-u_\beta \ln(-t)]^{-1/8},\\
&w^{-1} \to \xi \sim (t)^{-2/3}[1-u_\nu \ln(t)]^{1/2}, \qquad (3)\\
&B^2 \to \chi \sim (t)^{-7/6}[1-u_\gamma \ln(t)]^{3/4},
\end{aligned}
$$

and the amplitudes u_β, u_ν, and u_γ are nonuniversal. We did not include these corrections in the exponent analysis since another parameter would seriously reduce the significance of the fit. If the amplitudes are not zero, each correction has an obvious asymptotic form, e.g., $M \sim (-t)^{1/12} \times [-\ln(-t)]^{-1/8}$. The listed "effective Potts" exponents were determined by adjusting the exponent of the simple uncorrected form [here $(-t)^\beta$] to least-squares fit the asymptotic form over the t range used in the data analysis.[27] This procedure gives the most extreme effect of logarithmic corrections; thus, the entries in columns 3 and 4 of the table should bracket the experimental exponents of column 1. Although they do not, the effective exponents are closer to the experimental ones than are the "pure" exponents.

(3) The apparent agreement between our measured values and the Ising critical exponents is tantalizing. Kleban[28] showed that steps on the Ni surface, along a principal direction, lift the degeneracy of the sublattices in which the ordered state can form. Such a mechanism can lower the symmetry of this overlayer to $P2mm$. The $p(2\times 2)$ overlayer becomes a (2×1) structure in the new symmetry,[29] which lies in the Ising universality class.[2] The crossover behavior is difficult to characterize theoretically.

Random surface defects (impurities or steps) produce somewhat different effects. Consequent random interactions in the lattice gas Hamiltonian "round" the transition for positive specific-heat exponent α.[30] Random "fields" are more potent[31]: Local "moments" produce independent behavior in surrounding regions, with concomitant finite-size effects.[32] The regions' inverse size determines the degree of rounding. Both effects can cause observed exponents to deviate nonuniversally from pure values. Experiments with controlled randomness might elucidate this behavior.

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[1] In the exceptional case of "nonuniversal" transitions, the lines of varying critical exponents can be mapped onto one another. A. M. M. Pruisken and L. P. Kadanoff, Phys. Rev. B 22, 5154 (1980).

[2] E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. B 18, 2209 (1978).

[3] E. Domany, M. Schick, and J. S. Walker, Phys. Rev. Lett. 38, 1148 (1977); E. Domany and M. Schick, Phys. Rev. B 20, 3828 (1979).

[4] See, e.g., M. Nielsen, J. P. McTague, and L. Passell, in *Phase Transitions in Surface Films*, edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1980), p. 127, and references therein.

[5] S. Alexander, Phys. Lett. 54A, 353 (1975).

[6] T. L. Einstein and J. R. Schrieffer, Phys. Rev. B 7, 3629 (1973); T. L. Einstein, in *Chemistry and Physics of Solid Surfaces*, edited by Ralf Vanselow (CRC Press, Boca Raton, 1979), Vol. II, p. 181.

[7] See, e.g., G. A. Somorjai, Surf. Sci. 34, 156 (1973).

[8] Multiple scattering between an adatom and the ordered substrate is not sensitive to overlayer order, and leads to an unimportant multiplicative factor.

[9] M. Fink and J. Ingram, At. Data 4, 1 (1972).

[10] M. B. Webb and M. G. Lagally, Solid State Phys. 28, 301 (1973).

[11] L. D. Roelofs, Robert L. Park, and T. L. Einstein, J. Vac. Sci. Technol. 16, 478 (1979); Robert L. Park, J. E. Houston, and D. G. Schreiner, Rev. Sci. Instrum. 42, 60 (1971).

[12] Jens Als-Nielsen, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Gree (Academic, London, 1976), Vol. 5A, p. 87, or H. Dachs, in *Neutron Diffraction*, edited by H. Dachs (Springer-Verlag, Berlin, 1978), p. 1, and references therein. In both cases, there is considerable dependence of resolution on experimental details.

[13] C. Davisson and L. H. Germer, Phys. Rev. 30, 705 (1927).

[14] LEED $p(2\times 2)$ patterns have been observed for H, O, CO, S, or Se on Ni(111); O on Cu(111), Ir(111), or Pt(111); O or CO on Re(0001), Rh(111), or Ru(0001). Cf. Ref. 7. In some cases, particularly O on Ru, this 2×2 pattern comes from threefold-degenerate 2×1 superstructures. T. E. Madey, H. A. Englehard, and D. Menzel, Surf. Sci. 48, 304 (1975).

[15] R. J. Baxter, J. Phys. C 6, L445 (1973).

[16] B. Nienhuis, E. K. Riedel, and M. Schick, J. Phys. A 13, L31 (1980); B. Nienhuis, A. N. Berker, E. K. Riedel, and M. Schick, Phys. Rev. Lett. 43, 737 (1979).

[17] Corrections for ξ and for M are published in M. Nauenberg and D. J. Scalapino, Phys. Rev. Lett. 44, 837 (1980), and J. L. Cardy, M. Nauenberg, and D. J. Scalapino, Phys. Rev. B 22, 2560 (1980), respectively. Corrections for χ were derived by J. Bhattacharjee (private communication) and by D. J. Scalapino (private communication with J. Bhattacharjee).

[18] P. M. Marcus, J. E. Demuth, and D. W. Jepsen, Surf. Sci. 53, 501 (1975).

[19] L. D. Roelofs, Ph.D. thesis, University of Maryland, 1980 (unpublished); L. D. Roelofs and T. L. Einstein, unpublished.

[20] A. R. Kortan and Robert L. Park, Phys. Rev. B (to be published); A. R. Kortan, Ph.D. thesis, University of Maryland, 1980 (unpublished).

[21] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), p. 237.

[22] This method follows J. Als-Nielsen and O. W. Dietrich, Phys. Rev. 153, 706 (1967).

[23] M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967); H. B. Tarko and M. E. Fisher, Phys. Rev. B 11, 1217 (1975).

[24] While we implicitly used $\eta=0$, we checked (cf. Ref. 23) that, with $\eta=\frac{1}{4}$, our deduced exponents would not be affected. We could not measure η directly. Indirectly, with $\eta\equiv 2-(\gamma/\nu)$, our estimate is $\eta=0\pm\frac{1}{2}$.

[25] The values in column 3 of Table I are from the exact solution of the Baxter-Wu model, R. J. Baxter and F. Y. Wu, Phys. Rev. Lett. 31, 1294 (1973), and Aust. J. Phys. 27, 357 (1974), which is in the four-state Potts universality class.

[26] A. Aharony and M. E. Fisher, Phys. Rev. Lett. 45, 679 (1980); J. S. Kouvel and M. E. Fisher, Phys. Rev. 136, A1626 (1964).

[27] We are indebted to Norman C. Bartelt for performing this analysis.

[28] P. Kleban, to be published.

[29] We are grateful to J. F. Nicoll for helpful suggestions and insights. N. C. Bartelt is pursuing Monte Carlo tests of these ideas.

[30] Cf., e.g., A. B. Harris, J. Phys. C 7, 1671 (1974).

[31] A. Aharony, Y. Imry, and S.-k. Ma, Phys. Rev. Lett. 37, 1364 (1976).

[32] M. E. Fisher and M. N. Barber, Phys. Rev. Lett. 28, 1516 (1972).