

Summary Abstract: O/Ni(111): Adlayer phases and binding sites

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Chemisorbed overlayers that manifest ordered structures are potential experimental realizations of two-dimensional cooperative phenomena. Furthermore, analysis of the phase diagrams of such systems permits the determination of the adatom-adatom and adatom-substrate interactions that produce the various phases. This is a useful check for the increasingly sophisticated calculations of such interactions that are currently being developed. In some cases symmetry considerations allow binding site determination. This extended abstract summarizes our measurements and analysis of the low-coverage oxygen layer chemisorbed on Ni(111).¹

The phase diagram as determined experimentally by LEED (plus AES to measure relative coverage) is shown in Fig. 1. The LEED system utilizes 180° hemispherical grid optics and a scanning spot photometer mounted outside the vacuum chamber.² Absolute coverage is determined based on well-established benchmarks.³ Quadrupole mass spectrometry measurements detect no thermal desorption of oxygen; however, above $T = 500$ K the oxygen concentration in the surface region is diminished, presumably by diffusion into the bulk. For an initial coverage of a half monolayer, oxygen first dissolves until a quarter monolayer remains at 700 K. Only after the temperature is raised to about 850 K does the remainder disappear. LEED is not sensitive to small amounts of NiO, but according to Holloway and Hudson,³ formation begins at the dashed line. Our work function vs coverage measurements have the first change in slope near this line, supporting their conclusion.

Two well-ordered phases are observed. Region A displays sharp (2×2) LEED spots, while B shows sharp $(\sqrt{3} \times \sqrt{3})R30^\circ$ beams.⁴ At coverages below the (long-range) (2×2) phase, the disordering characteristics with increasing temperature are reminiscent of low-coverage O/W (110).⁵ In region C there is essentially a two-phase region, with (2×2) islands immersed in a background low-density "gas"; the phase transformation occurring in crossing from region C to the "gas" amounts to island dissolution. In region D some half-order beams are broadened while others are split. The splitting starts at $\theta = 0.27$ monolayer and grows continuously to about $\frac{1}{3}$ at $\theta = 0.29$, where $\frac{1}{3}$ is a reciprocal lattice vector of the Ni surface net.

LEED intensity vs voltage calculations⁶ indicate that in the chemisorbed state, the oxygen atoms occupy the three-fold hollows on the Ni(111) surface. There are two such sites: those that would be filled by the next layer of Ni atoms (fcc sites) and those that are above the second-layer Ni atoms (hcp sites). The above-mentioned calculations were unable to distinguish

between these cases. Understanding of the LEED spot pattern of region D in the phase diagram demonstrates unambiguously that adsorption must occur in *both* types of sites. The split $(1/2, 1/2)$ beams are related by (clean) surface reciprocal lattice vectors to unsplit, highly-blurred $(1/2, 0)$ beams; thus, this LEED pattern cannot be produced by any partially ordered adlayer involving just one type of binding site.⁷ We accordingly propose that the structure in this area consists of regions of (2×2) in one type of site adjoining regions of (2×2) in the other type of site. This arrangement permits some increase in adatom density at the cost of a small increase in lateral repulsions. These regions (at finite temperature) have a distribution of sizes leading to diffuseness of the extra beams; because the average size decreases with coverage, the splitting increases.

The presence of region C in the phase diagram, i.e., the existence of (2×2) islands at coverages much lower than saturation of the (2×2) phase, indicates that the interactions which produce this periodicity are attractive. This conclusion is supported by the two-step bulk dissolution behavior described in the second paragraph.⁸

Beginning with this information and guided by tight-binding calculations of the relative strengths of the interaction,⁹ we are simulating this system with a Monte Carlo calculation of hexagonal symmetry to obtain quantitative results for the interactions. Although the calculation is not complete,

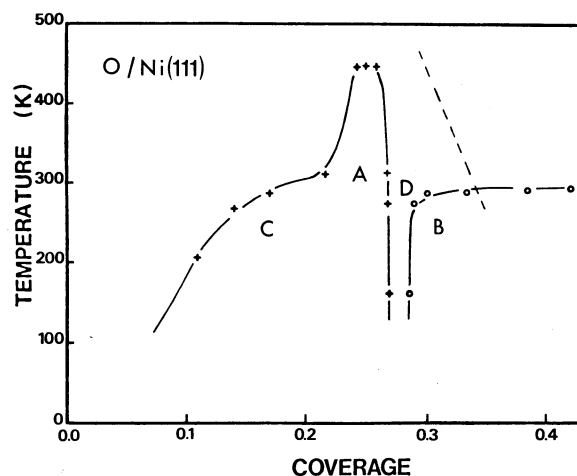


FIG. 1. Experimental phase diagram for oxygen chemisorbed on a Ni(111) surface. The dashed line suggests where the formation of nickel oxide begins (cf. Ref. 3). Regions A and C display (2×2) LEED patterns. Region B shows a sharp $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern and D gives the complex LEED pattern described in the text. In the region above C (and left of A) there is a gas of adatoms.

we have at this stage reproduced correctly all the qualitative features seen in Fig. 1. Beam profile simulations are especially useful as they provide very restrictive conditions on the interactions.¹⁰ These simulations also allow classification of the various transitions by order and universality class. Several types of critical behavior occur, including second-order order-disorder transitions, first-order island dissolution, and order-order transitions; there is also a tricritical point.

In conclusion the chemisorption system O/Ni(111) provides a realization of several interesting phase transformations. Our Monte Carlo simulation of a hexagonal net of binding sites is being used to obtain quantitative values for the significant adatom-adatom pair interactions on this surface.

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¹A complete account of this work by these authors will be published elsewhere.

²For details of our experimental arrangement, see A. R. Kortan, P. I. Cohen, and Robert L. Park, *J. Vac. Sci. Technol.* **16**, 541 (1979).

³P. H. Holloway and J. B. Hudson, *Surf. Sci.* **43**, 141 (1974).

⁴"Sharp" means as well defined as the integer-order beams.

⁵J. C. Buchholz and M. G. Lagally, *Phys. Rev. Lett.* **35**, 442 (1975); T.-M. Lu, G.-C. Wang, and M. G. Lagally, *Phys. Rev. Lett.* **39**, 411 (1977); M. G. Lagally, G.-C. Wang, and T.-M. Lu, in *Chemistry and Physics of Solid Surfaces*, edited by R. Vanselow (CRC Press, Boca Raton, 1979), Vol. II, p. 153.

⁶P. M. Marcus, J. E. Demuth, and D. W. Jepsen, *Surf. Sci.* **53**, 501 (1975).

⁷By the definition of the reciprocal lattice, the kinematic scattering intensity at points related by reciprocal lattice vectors must be identical. Multiple scattering could not produce this behavior at several energies.

⁸That is, the attractive interaction between adatoms in (2×2) configurations increases their stability on the surface, delaying their dissolution until higher temperature.

⁹T. L. Einstein, in *Chemistry and Physics of Solid Surfaces*, edited by R. Vanselow (CRC Press, Boca Raton, 1979), Vol. II, 181; P. E. Hunter and T. L. Einstein (unpublished).

¹⁰L. D. Roelofs, Robert L. Park, and T. L. Einstein, *J. Vac. Sci. Technol.* **16**, 478 (1979).