

procedure was used. Simulated UPS spectra [letters (c), (d), (e), right panel of Fig. 1] utilize the double zeta plus polarization function basis set designated 6-31 G*. Structural details of the lithium surface and acetylide (C_2) units were examined by calculation using an 8 atom model of the unreconstructed bcc Li(100) surface (cluster approximation) with the minimal STO-3G basis set (data not shown). The Li_8 cluster contains 6 atoms in the first layer of the surface, 2 atoms in the second layer, and is designated $Li_8(6,2)-(100)$.

A scan of the potential energy surface for the model $C_2/Li_8(6,2)-(100)$ considered C_2 units bound on surface sites and bound within the $Li_8(6,2)$ cluster. Slices in the potential energy surface governing the structure and motion of C_2 on (100)Li near favored binding locations were then calculated. Motion of C_2 as a unit, dissociation to C atoms, relaxation of the entire lithium cluster, and relaxation of lithiums near neighbor to C_2 were some of the geometric variations considered.

Minimization of calculated total energy and agreement between observed and simulated UPS for $C_2/Li_8(6,2)-(100)$ predict a geometry with C_2 units bound below the first atomic layer of the surface. The least hindered orientation for diffusion of C_2 into the lithium lattice, a necessary process for multilayer acetylide film growth, is calculated as having the C-C axis parallel to the surface normal.

Relaxation of the *lithium cluster* in the model $C_2/Li_8(6,2)-(100)$ illustrates the use of computational methods to address a surface process that is nearly inaccessible by experiment,

metal surface rearrangement at *very low adsorbate coverage*. Surface relaxation was modeled by expansion and contraction of only the four lithium atoms near neighbor to C_2 , and of the entire $Li_8(6,2)$ cluster. *Expansion* of the four lithium atoms near neighbor to C_2 produced the most stable calculated geometric arrangement found for this model and caused the average volume per lithium to increase. This calculated result agrees with the greater than unity ratio of the volume per lithium in the carbide to the volume per lithium in the metal. *Relaxation of the lithium surface by local expansion* to accommodate C_2 adsorption below the first atomic layer of the surface is inferred to play a role in allowing multilayer carbide growth to proceed.

Different surface carbon species have previously been associated with distinct spectroscopic features such as AES line shape.² Using the lithium plus acetylene system we have associated a specific surface carbon species, acetylide, with both AES and UPS spectral data. We have also employed proven structure sensitive *ab initio* calculations to model relaxation of the lithium surface in the presence of the experimentally identified carbon adsorbate.

¹R. R. Rye, T. E. Madey, J. E. Houston, and P. H. Holloway, *J. Chem. Phys.* **69**, 1504 (1978).

²D. W. Goodman, R. D. Kelley, T. E. Madey and J. T. Yates, *J. Catal.* **63**, 226 (1980).

³J. E. Demuth, *Surf. Sci.* **93**, 127 (1980) and references therein.

Summary Abstract: (2×2) phase transitions on honeycomb lattices

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Study of the phase transitions of systems of chemisorbed atoms provides valuable insight into surface physics in at least two ways: (1) The phase diagrams of chemisorbed overlayers give information about adatom-adatom interactions. (2) Critical behavior depends sensitively on symmetry and thus provides unique information about weak symmetry-breaking effects. Here we focus on oxygen and on hydrogen adsorbed on Ni(111); each forms a (2×2) structure on the honeycomb array of (threefold symmetric) binding sites. The order-disorder transitions of these overlayers have been studied experimentally.^{1,2} We have examined these phase transitions with Monte Carlo simulations and transfer matrix scaling.

Experiment shows that $p(2 \times 2)$ O/Ni(111) has a second order phase transition with critical exponents consistent with the two-dimensional Ising model.³ The Landau-Ginz-

berg-Wilson Hamiltonian classification scheme predicts⁴ that the phase transition, if continuous, lies in the same universality class as the four-state Potts model if the crystal field E_0 (the difference in binding energy between fcc and hcp binding sites) is nonzero, and in the universality class of the Heisenberg model with corner cubic anisotropy (HCCA) if $E_0 = 0$. For certain parameters, the HCCA can have a continuous phase transition with Ising exponents. As there is no reason to suppose E_0 is zero, we expected four-state Potts exponents. On the other hand, the structure of an incommensurate phase of O/Ni(111) does indicate that E_0 is small. Hence, Schick⁵ noted the phase transition will appear to be four-state Potts-like only at temperatures very close to the critical temperature T_c . Well away from T_c it will appear Ising-like, with E_0 as the cross-over field.⁶ Schick thus suggested the experiment had been performed at temperatures

in the Ising regime.

Our work does not support this explanation of O/Ni(111) exponents. We have performed Monte Carlo simulations of the $p(2 \times 2)$ -disorder phase transition using a variety of interaction energies,⁷ which at least qualitatively reproduce the experimental phase diagram. Specifically, we took E_0 to be either small or zero. We tried several sets of interactions which a prefacing transformation⁸ indicated corresponded to an Ising-like transition in the HCCA. All of our simulations were characterized by a severe metastability between an ordered and a disordered state, which led to a double-peaked order parameter distribution. This metastability had a time scale of around 10^4 Monte Carlo steps/site. First order transitions have metastabilities. However, similar behavior has also been observed for the Baxter–Wu model⁹ (which has a continuous transition with four-state Potts exponents). In addition, our simulations of the $p(2 \times 2)$ phase transition on a triangular lattice (infinite E_0) show a similar metastability but with a time scale an order of magnitude smaller. By applying finite size scaling to the Monte Carlo data¹⁰ we found the correlation length exponent ν to be 0.72 ± 0.10 , consistent with the four-state Potts value of $2/3$. A similar study with small crystal field proved impossible because of the larger time scale of the metastability. However, by applying the transfer matrix scaling technique of Nightingale¹¹ to strips of sites two and three unit cells wide and with $E_0 = 0$, we found $\nu = 0.56$. Given the narrow strip widths considered, this number could be consistent with either a first order (" ν " = 0.5) or with a four-state Potts transition, but not an Ising transition.

Another possible explanation of the Ising exponents is that the symmetry of the surface—which determines the critical behavior—is broken by the steps which occur on any real Ni(111) surface. We tested this idea by performing Monte Carlo simulations on triangular lattices with symmetry breaking boundary conditions. A system with short range forces can only exhibit critical behavior if it is infinite in at least two dimensions. If a boundary affects bulk behavior only near the critical temperature—when the correlation length is large—the boundary is only responsible for finite size effects. We observed only finite size effects.

Hydrogen adsorbed on Ni(111) forms a honeycomb (2×2) structure.^{1,12} Since this structure is denser than the $p(2 \times 2)$, with fewer types of sites to disorder into, Monte Carlo simulations are easier to perform. The embedded cluster calculations of Muscat and Newns¹³ suggest that the nearest neighbor hydrogen–hydrogen interaction is effectively infinitely repulsive, the second neighbor interaction is weak (≤ 10 meV), while the third neighbor interaction is about 10 meV more attractive than the second neighbor interaction. Putting these interactions into Monte Carlo simulations, we find that the honeycomb (2×2) orders only at temperatures less than 100 K, compared with the observed 270 K.¹ We find a variety of different interaction parameters yield phase diagrams consistent with the experimental one due to its featurelessness and incompleteness. At half-monolayer coverage both Monte Carlo and transfer matrix scaling indicate that the order–disorder transition has the four-state Potts exponents predicted from symmetry.

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¹K. Christmann, R. J. Behm, G. Ertl, M. A. Van Hove, and W. H. Weinberg, *J. Chem. Phys.* **70**, 4168 (1979).

²A. R. Kortan and R. L. Park, *Phys. Rev. B* **23**, 6340 (1981).

³L. D. Roelofs, A. R. Kortan, T. L. Einstein, and Robert L. Park, *Phys. Rev. Lett.* **46**, 1465 (1981).

⁴E. Domany and M. Schick, *Phys. Rev. B* **20**, 3828 (1979).

⁵M. Schick, *Phys. Rev. Lett.* **47**, 1347 (1981).

⁶M. E. Fisher, *Rev. Mod. Phys.* **46**, 597 (1974).

⁷L. D. Roelofs, in *Chemistry and Physics of Solid Surfaces IV*, edited by R. Vanselow and R. Howe (Springer, Berlin, 1982), p. 219.

⁸A. N. Berker, *Phys. Rev. B* **12**, 2752 (1975).

⁹M. A. Novotny and D. P. Landau, *Phys. Rev. B* **24**, 1468 (1981).

¹⁰K. Binder and D. P. Landau, *Phys. Rev. B* **21**, 1941 (1980).

¹¹M. P. Nightingale, *Physica A* **83**, 561 (1976).

¹²E. Domany, M. Schick, and J. S. Walker, *Solid State Commun.* **30**, 331 (1979).

¹³J. P. Muscat and D. M. Newns, *Surf. Sci.* **105**, 570 (1980).