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

N. C. Bartelt, T. L. Einstein, and L. D. Roelofs

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

(Received 23 September 1982; accepted 12 October 1982)

PACS numbers: 68.45.Da, 68.20.+t

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(2×2) O/Ni(111) has a second order phase transition with critical exponents consistent with the two-dimensional Ising model. The Landau–Ginzberg–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, Schick1 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, 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 prefacering transformation 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 $10^6$ Monte Carlo steps/site. First order transitions have metastabilities, However, similar behavior has also been observed for the Baxter-Wu model 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 data we found the correlation length exponent $\nu$ 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 Nightingale 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 ($\nu = 0.5$) 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 ($2 \times 2$) structure. 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 Newns 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 ($2 \times 2$) orders only at temperatures less than 100 K, compared with the observed 270 K. 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.

We thank Shmuel Fishman for many useful discussions.

---

*Supported by DOE Grant #A505-79ER-10427. Computer facilities supplied by the University of Maryland Computer Science Center.

11 Department of Physics, Haverford College, Haverford, Pennsylvania 19041.


