Proposed Decorated Lattice-Gas Model of H/Pd(100)

Recently Tománek, Louie, and Chan[1] performed an *ab initio* total-energy calculation for H on the Pd(100) surface. On the basis of their results they interpreted the adsorption behavior of this system within a lattice-gas model. We here note that this model is equivalent to the Ising model, that consequently the phase diagram is known exactly, and that the thermodynamics of the model are inconsistent with results derived from experiment. In the proposed model H can adsorb on the fourfold hollow and bridge sites of Pd(100) with a positive binding-energy difference, $E_b - E_h$, of 0.42 eV. The only interaction between H's is an infinite repulsion between neighboring occupied bridge and hollow sites. This is just a decorated lattice-gas model. Since many such models can be mapped onto the Ising model, they have been much studied.[2] In this example, one can associate the occupation of the hollow sites with Ising spins and sum over the configurations of bridge sites, leading to a nearest-neighbor interaction

$$J = k_B T \ln\{1 + \exp[(\mu - E_b)/k_B T]\}/4$$

and a field $h = (\mu - E_h - 8J)/2$. At low temperatures there is a line of coexistence, corresponding to $h = 0$, between a sparse "hollow-site" phase and a dense "bridge-site" phase. The exact T-coverage phase diagram is shown in Fig. 1.

In the light of the model, Ref. 1 interprets the apparent observation[3] of H coverages, θ, above one monolayer (ML) as evidence that the coexistence region is seen. However, there is no sign in the experiment of the discontinuities in the adsorption isobars, as shown in Fig. 1, characteristic of coexistence. {The experimental temperatures were much less than $T_c = (E_b - E_h)/k_B \ln[(7+5\sqrt{2})/2]$.} Reference 1 concluded agreement with experiment by comparing the model isosteric heat of adsorption, E_{ad}, with experiment. Figure 2 shows the actual θ dependence of the contribution of E_{ad} due to the configurational degrees of freedom of the model for a $T < T_c$. It is qualitatively different from the experimental curve, which is approximately linear for deduced $\theta > 1$ ML. Tománek, Louie, and Chan have subsequently agreed[1b] that the simple model discussed here does not explain the experimental data above 1 ML.

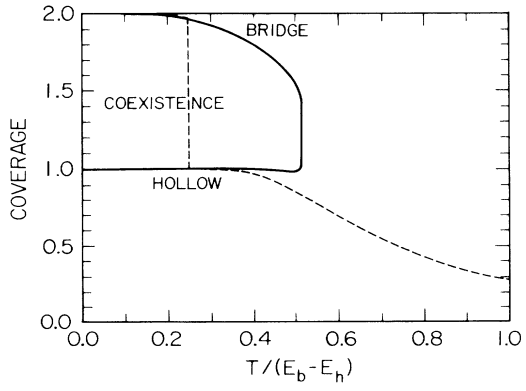

FIG. 1. Phase diagram of the model. Typical isobar (dashed line) estimated with use of transfer matrices on semi-infinite strips.

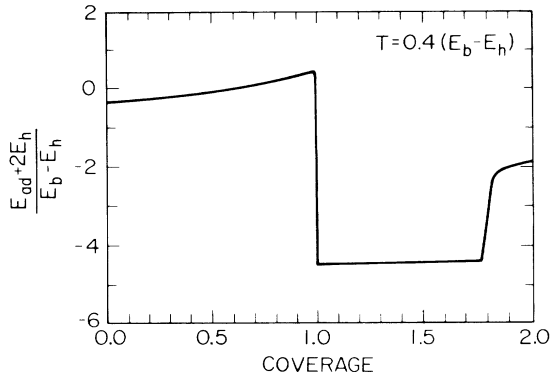

FIG. 2. Coverage dependence of E_{ad} of the model, computed as was isobar in Fig. 1.

For the energies (but including the H_2 dissociation energy) quoted in Ref. 1, the *total* overlayer energy of the perfect hollow-site monolayer is less than that of the saturated bridge-site overlayer. Thus the calculation suggests that coverages above 1 ML due to bridge-site occupation would not occur under the experimental conditions. Given the difficulties in the determination of absolute H coverages and the possibility of other complications (e.g., defects, subsurface occupation), this prediction might be correct. Also the proposed model is only one of many (lattice-gas) parametrizations that can account for the $T = 0$ overlayer energy (including lateral interactions) at 1 and 2 ML. The presence of modest H-H interactions, i.e., a configurational dependence of the total energy, could produce qualitative changes in behavior. Thus the failure of the model to explain experiment in no way impugns the total-energy calculation of Tománek, Louie, and Chan, but does highlight the limitations of the resulting information.

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Received 6 April 1987
PACS numbers: 68.45.Ax, 05.50.+q, 73.20.Hb, 82.65.Dp

[1a]D. Tománek, S. G. Louie, and C.-T. Chan, Phys. Rev. Lett. **57**, 2594 (1986), and **58**, 287(E) (1987).

[1b]D. Tománek, S. G. Louie, and C.-T. Chan, private communication.

[2]For a similar transcription see I. Syozi and H. Nakano, Prog. Theor. Phys. **13**, 69 (1955); for a review of the use of similar decorated lattice-gas models in fluid systems see J. C. Wheeler, Annu. Rev. Phys. Chem. **28**, 411 (1977).

[3]R. J. Behm, K. Christmann, and G. Ertl, Surf. Sci. **99**, 320 (1980).