Phase Diagram of Selenium Adsorbed on the Ni(100) Surface: A Physical Realization of the Ashkin-Teller Model

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We have used electron diffraction to study submonolayers of Se adsorbed on Ni(100); $p(2\times2)$, $c(2\times2)$, and disordered phases were observed and the boundaries between them located. Symmetry arguments indicate that the phase diagram belongs to the universality class of the Ashkin-Teller model and allow us to predict the critical behavior near the phase boundaries and at the multicritical point where they meet. Our lattice-gas-model calculations support these results. The predicted critical behavior, and thus the universality arguments, should be tested by additional experiments, in particular synchrotron-x-ray diffraction.

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Layers of atoms and molecules adsorbed on clean surfaces are interesting in that they may constitute physical realizations of two-dimensional (2D) models of great current interest in statistical mechanics.[1-3] Theoretical results on such models can thus provide insight into the nature of phase transitions and the topology of phase diagrams of surface structures, and theoretical predictions can be tested by performing experiments.

The Ashkin-Teller model[4] is a simple two-dimensional model for which the phase diagram is quite well known through numerous theoretical studies.[5-10] The phase diagram includes a second-order transition line of cubic xy character which splits into two Ising lines at a multicritical point.

In this Letter we report reflection high-energy electron diffraction (RHEED) measurements on the phase diagram of selenium adsorbed on the Ni(100) surface. The phase diagram includes two ordered phases with $c(2\times2)$ and $p(2\times2)$ structure, and a high-temperature 2D disordered phase. Symmetry arguments and model calculations indicate that the phase diagram belongs to the same universality class as that of the Ashkin-Teller model. The many detailed theoretical results can therefore be directly applied to this system.

Selenium was depositied from a Knudsen source and relative coverages were measured by means of Auger electron spectroscopy. The results reported here are independent of source temperature (415–485 K). RHEED measurements used 4.5-keV electrons incident at 30°. Integrated diffraction beam intensity profiles were measured as a function of selenium coverage and substrate temperature with use of a spot photometer. Details of the experiment will be presented elsewhere.

Figure 1(b) shows measurements of the integrated intensity versus coverage for the $(0,-\frac{1}{2})$ beam, which occurs only for the $p(2\times2)$ phase, and for the $(-\frac{1}{2},\frac{1}{2})$ beam, which is present in both the $p(2\times2)$ and $c(2\times2)$ phases. The $(0,-\frac{1}{2})$ intensity increases smoothly to a maximum with coverage, thereupon decreasing to the background as shown. The maximum $(0,-\frac{1}{2})$ intensity has been assigned a coverage value of $\theta=0.25$; i.e., we have assumed the surface to be completely covered with a maximally ordered $p(2\times2)$ overlayer as in previous work.[11] At $\theta=0.25$ the $p(2\times2)$ beams decrease in intensity with increasing temperature and disappear altogether for $T>500$ K. The $(-\frac{1}{2},\frac{1}{2})$ intensity also rises smoothly with increasing θ and reaches a peak at $\theta=0.5$. There is a small subsidiary maximum at $\theta=0.25$ due to the $p(2\times2)$ phase which persists up to 500 K.

The phase diagram extracted from these data is shown in Fig. 1(a). There is a disordered 2D liquid phase and two ordered phases with $p(2\times2)$ and $c(2\times2)$ symmetry. These phase boundaries were determined from inflection points in the intensity versus coverage data.[12-14] The phase boundaries separating the $p(2\times2)$ and $c(2\times2)$ phases from the disordered fluid phase are apparently lines of higher-order phase transitions. The character of the transition between the $c(2\times2)$ and $p(2\times2)$ phases cannot be

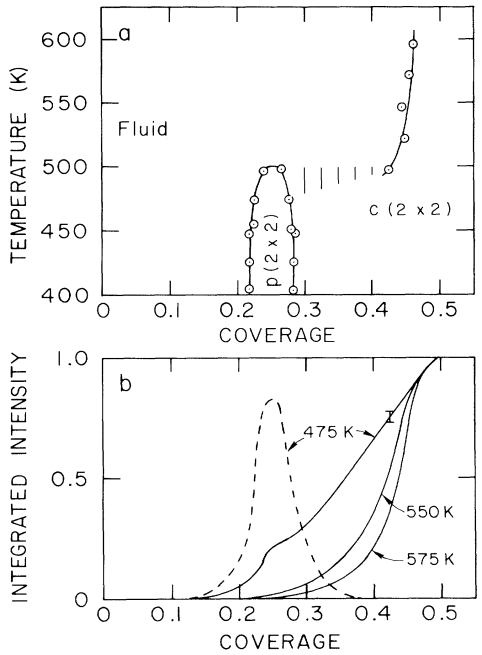

FIG. 1. (a) Experimental temperature vs Se-coverage phase diagram showing the location of continuous phase boundaries as determined from inflection points on integrated-intensity vs coverage data. (b) Integrated intensity vs Se coverage. The dashed curve is the $(0,-\frac{1}{2})$ beam and the solid curve is the $(-\frac{1}{2},\frac{1}{2})$ beam. The error bar indicates the noise level. The intensity measured at the Brillouin zone boundary has been subtracted.

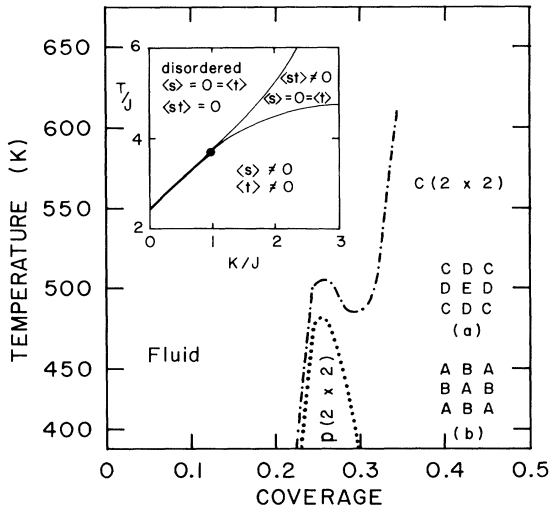

FIG. 2. Theoretical phase diagram determined by a transfer-matrix scaling calculation using parameters given in the text. The inset at the upper left is the Ashkin-Teller phase diagram determined from Eq. (1). Insets (a) and (b) show components of complex $p(2\times2)$ structure expected near the $p(2\times2)$-$c(2\times2)$ phase boundary.

determined unambiguously from the data; however, our model calculations (see below) predict it to be continuous.[15] The transition lines seem to come together at a multicritical point (as in the Ashkin-Teller model).

We now examine the connection between the Se/Ni(100) system and the Ashkin-Teller model. The philosophy to be used is that two systems belong to the same universality class and exhibit the same critical behavior if their symmetries, as expressed by the appropriate Landau-Ginzburg-Wilson Hamiltonians, are the same. Hence, to establish Ashkin-Teller critical behavior there is no need to directly relate the microscopic physical interactions to the parameters of the Ashkin-Teller model. This strategy has been advocated by Domany *et al.*[1] and used successfully, for instance, by Mukamel, Domany, and Fisher[16] to show that the phase diagrams of certain magnetic systems are realizations of the three-state Potts model. The symmetry considerations employed to this end below are based on the assumption that Fig. 1(a) is indeed the phase diagram and that there are no "intermediate" phases complicating the picture.

The Ashkin-Teller model has two Ising spins $s_i = \pm 1$ and $t_i = \pm 1$ situated as each site i on a square lattice. The spins interact through second-order and fourth-order nearest-neighbor interactions J and K,

$$H = -\sum_{\langle ij\rangle} J(s_i s_j + t_i t_j) - K\sum s_i s_j t_i t_j. \quad (1)$$

The phase diagram, Fig. 2 inset, consists of a high-temperature disordered phase and two low-temperature ordered phases. The ordered phase which is stable for small values of K has nonzero values of the order parameters $\langle s\rangle$ and $\langle t\rangle$, $\langle s\rangle = \pm\langle t\rangle \neq 0$. The ground state is fourfold degenerate corresponding to the four possibilities for choosing the signs of $\langle s\rangle$ and $\langle t\rangle$. The critical indices α, β, etc., describing the singularities of the specific heat, magnetization, etc., are continuous nonuniversal functions of K along the transition line to the disordered phase.[5,8] For larger values of K there is a mixed phase in which $\langle s\rangle = \langle t\rangle = 0$. The order parameter which becomes nonzero here is the "polarization" $\langle st\rangle$ (in Enting's notation[7]). The transition lines separating the mixed phase from the disordered phase and the other ordered phase are of Ising character. The multicritical point where all transition lines meet is a four-state Potts critical point.

For Se on Ni(100), we define order parameters as follows:

$$s = \langle s\rangle = N^{-1}\sum_{x,y}(-1)^x\langle n_{x,y}\rangle, \quad (2a)$$

$$t = \langle t\rangle = N^{-1}\sum_{x,y}(-1)^y\langle n_{x,y}\rangle, \quad (2b)$$

$$p = \langle st\rangle = N^{-1}\sum_{x,y}(-1)^x(-1)^y\langle n_{x,y}\rangle, \quad (2c)$$

where $n_{x,y}$ is the selenium-atom occupation of the Ni substrate adsorption "site" at position (x,y) and N is the total number of sites on the 2D nickel surface square lattice. Clearly $s = \pm t \neq 0$ in the $p(2\times2)$ phase. [A phase with s *or* $t = 0$ would be a striped (2×1) or (1×2) phase.] The four degenerate ground states of the $p(2\times2)$ structure correspond to the four possible choices of signs for s and t, just as for the Ashkin-Teller model. The order parameters s and t transform as a two-dimensional representation of the $4pmm$ symmetry group of the Ni(100) surface, and the phase transition belongs to the universality class of the xy model with cubic anisotropy as does the transition line in the Ashkin-Teller model.

The order parameters s and t are both zero in the $c(2\times2)$ phase, but $p = \langle st \rangle$ defined by Eq. (2c) is nonzero in this phase. The $c(2\times2)$ phase thus represents the mixed phase in the Ashkin-Teller model. The two degenerate ground states of the $c(2\times2)$ phase correspond to $p = \pm|p|$. The state with $p > 0$ can be thought of as a mixture of the states $s = t > 0$ and $s = t < 0$. The state with $p < 0$ mixes the two state with $s = -t$. The order parameter p transforms as a one-dimensional representation of the Ni(100) symmetry group and so the melting line is of Ising character. At the transition line between the two ordered phases the mixed phase decomposes into its constituents: The $p < 0$ phase may "order" into the state $s = -t > 0$ or $s = -t < 0$. This line is also of Ising character.[15]

Hence, there is a one-to-one correspondence between the symmetries of the ordered phases and transition lines for selenium adsorbed on Ni(100) and those for Ashkin-Teller model. The symmetry and universality is reflected in the phenomenological Landau-Ginzburg-Wilson expansion of the free energy in terms of the order parameters involved:

$$H = r_1(s^2+t^2) + u_1(s^2+t^2)^2 + v_1 s^2 t^2 + r_2 p^2 + Wstp + \cdots . \quad (3)$$

This Hamiltonian has the symmetry of the Ashkin-Teller model, and we thus conclude that the phase diagrams belong to the same universality class. For $r_1 < r_2$ there is a transition into the "magnetic" phase with $|s| = t \neq 0$, and the first three terms define the cubic xy model. For $r_1 > r_2$ the three order parameters are degenerate and the Hamiltonian becomes that of a 2D Heisenberg model with a third-order, anisotropy term; i.e., that of the four-state Potts model,[1,17] as it should be. The expansion is intended *only* for defining the symmetries of the various transitions and hence determining the universality classes of transitions and multicritical points. Landau "mean field" theory predictions are in general incorrect for this model.

The third-order term in Eq. (3) induces a "mixing" of order parameters in the $p(2\times2)$ phase near the $c(2\times2)$ phase boundary. Following the arguments in Ref. 1, it is easy to see that this implies that the $p(2\times2)$ phase has a complicated structure including (2×1), (1×2), *and* $c(2\times2)$ components rather than the simple $p(2\times2)$ structure with one Se atom per unit cell [see Fig. 2, insets (a) and (b)]. Equivalently, the $(-\frac{1}{2},\frac{1}{2})$ and $(0,-\frac{1}{2})$ beams are not symmetry related in this phase. This has important implications for the spatial arrangement of the overlayer atoms. Since Se atoms are too large to occupy nearest-neigbhor sites on the Ni(100) substrate all these components [or even the (2×1) or (1×2) alone] cannot be accommodated in a single unit cell simultaneously. This kind of $p(2\times2)$ structure can only occur "on average." Therefore the local order in the $p(2\times2)$ phase must undergo spatial and temporal fluctuations.

Although the Ashkin-Teller model has the correct symmetry to describe the various phases and transitions, one cannot (and need not!) relate the parameters J and K of Eq. (1) to actual physical interactions. It is, however, of interest to construct a model with physically identifiable parameters yielding a phase diagram in the same universality class as both the Ashkin-Teller model and the real Si/Ni system. To this end, we have studied a simple lattice-gas model with $n_1 = \pm 1$ representing the presence or absence of an atom at site i with interactions up to fourth nearest neighbor,

$$H = \epsilon_1 \sum_{\text{nn}} n_i n_j + \epsilon_2 \sum_{\text{nnn}} n_i n_j + \epsilon_3 \sum_{\text{3nn}} n_i n_j + \epsilon_4 \sum_{\text{4nn}} n_i n_j + \mu \sum_i n_i . \quad (4)$$

The chemical potential μ is varied to control the coverage. Because of the size of the Se atoms mentioned above, it is appropriate to take $\epsilon_1 = +\infty$ (nearest-neighbor exclusion). We utilized a transfer-matrix scaling calculation[18] using strip widths up to 6–8 (also verified by Monte Carlo calculations) for $\epsilon_2 = 1176$ K, $\epsilon_4 = 0.1\epsilon_2$, and $\epsilon_3 = 0$ which results in the phase diagram[19] shown in Fig. 2. Note that this very simple model agrees semiquantitatively with the experimental results in the region of interest, i.e., near the multicritical point. Calculated critical exponents ν and η are consistent with values expected along the critical lines, especially far from the multicritical point, but precise values are not expected with the strip widths in the range used.

Having established the connection with the Ashkin-Teller model, "universality" allows us to apply the numerous theoretical results to the physical system Se/Ni(100). This leads to specific detailed predictions about the transition lines and critical behavior: (1) The $c(2\times2)$ phase melts through a continuous Ising transition, with order-parameter exponent $\beta = \frac{1}{8}$; (2)

the $p(2\times2)$ phase melts through a continuous transition of cubic xy character with continuously varying exponents; (3) the transition line between the two ordered phases is also for Ising character. The transition lines approach a multicritical point of four-state Potts symmetry ($\beta=\frac{1}{12}$, $\alpha=\frac{2}{3}$,...)[7] along a common tangent as indicated in Fig. 2 (inset). New experiments using synchrotron radiation are planned to test these predictions and thus the underlying universality assumptions.

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