troscopies will facilitate identification of the structure of adsorbed PC and the nature of its bonds to alkali metal surfaces.

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Summary Abstract: Structure factors of two-dimensional lattice gases: Theoretical investigation of some aspects of the capability of low-energy electron diffraction to measure critical phenomena of surface phase transitions

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The possibility of measuring critical properties of adsorbed atoms (or surface reconstructions) produced initial great excitement followed by concerns about, among other issues (1) whether low-energy electron diffraction (LEED), with its attendant multiple scattering and modest resolution, would be a viable probe; (2) whether the limited size of defect-free regions would preclude a close enough approach to the critical region to obtain decent scaling and whether the obtainable effective exponents resemble the expected pure exponents; and (3) what sort of error bars and complications are realistic. To tackle these questions we undertook extensive Monte Carlo calculations of the structure factor $S(\mathbf{k},T)$—what is measured in the kinematic limit— on lattices having sizes comparable to the defect-free regions on metal crystal faces, $\sim$4000 sites. Here we present an overview of our findings,[1(a)-1(d)] illustrating the rich possibilities.

We seek general principles by looking at systems produced by simple interactions under "ideal" conditions (e.g., symmetric, periodic boundaries) to eliminate extra, system-dependent, complications. We study four systems: $(\sqrt{3}\times\sqrt{3})R\,30°$/triangular net, $p(2\times2)$/triangular net, (3×1)/centered rectangular net, and $p(2\times2)$/honeycomb net. The first two are expected to be in the universality classes of the three- and four-state Potts models, respectively. There are only two other possible universality classes commonly expected[2] for continuous melting of adatoms on a two-dimensional (2D) lattice. Of these, the Ising model has been extensively studied with analytic techniques. The other, the XY model with four- or sixfold anisotropy, has non-universal exponents; while this distinctively 2D property lends special fascination to this model, it complicates a calibrational study. The (3×1) case is an example of incommensurate melting: the peak of the critical scattering shifts (by q) with temperature T, lying at the (non-high-symmetry) wave vector associated with long-range order only at T_c. This behavior is outside the usual Landau framework.[2] The $p(2\times2)$/honeycomb case shows that a possible first-order transition can display "critical" scattering!

As noted earlier,[1(e)] by studying probes of short-range order, e.g., the *integrated intensity* of a LEED beam about an overlayer-induced extra LEED spot, one finds an energylike anomaly at T_c, i.e., a contribution $\propto t^{1-\alpha}$. Here α is the specific heat exponent and $t\equiv|T-T_c|/T_c$. Subsequently,[1(a)] we presented a detailed analysis, including the effect of anisotropic corrections to scaling and explicit examples for $(\sqrt{3}\times\sqrt{3})\,R\,30°$ and $p(2\times2)$ overlayers on triangular nets, checking sensitivity to the integration radius and to the cutoff near T_c (necessitated by finite-size rounding). Analytic results for the Ising model are also given. Since α varies considerably between universality classes (in contrast to the long-range-order exponent β), it is noteworthy that one can measure α with a scattering experiment. Moreover, unlike in the diffraction limit (correlation length $\xi <$ characteristic instrument length), in this low-resolution limit one need not take into account the instrument response function.

Worries about the effects of multiple scattering have long cast a shadow over the use of LEED to measure critical properties. In the preceding scheme, such concerns are blatantly eliminated because the multisite correlation functions that might be introduced also have the characteristic energy-like anomaly. Moreover, we recently pointed out[1(f)] that even in the diffraction limit, multiple scattering should be viewed as a length effect which only changes (and not necessarily increases) the amplitudes of previously existing corrections to scaling of the extra LEED spots.

In the diffraction limit high resolution is desirable. As noted, we calculated

$$S(\mathbf{k},T) = \langle|\Sigma_{\mathbf{R}} n_{\mathbf{R}} e^{i(\mathbf{k}+\mathbf{k}_0)\mathbf{R}}|^2\rangle, \quad (1)$$

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where $\mathbf{k}_0$ is the center of an extra spot. The phenomenological theory of second-order phase transitions predicts

$$S(\mathbf{k},T) = a_1 t^{-\gamma} X_{\pm}(a_2 t^{-\nu}|\mathbf{k}|) \quad (2)$$

for small $t = |T - T_c|/T_c$ and $|\mathbf{k}|$; $X_{\pm}(y)$ are universal functions, $\xi \propto t^{-\nu}$, and the a_i's depend on specifics of the system. For all four systems,[1(b)-(d)] this scaling form is satisfied over a considerable portion of the surface Brillouin zone (SBZ), in the first two cases halfway to the SBZ center. Data within ~2% of T_c cannot be made to scale, coinciding with the onset of finite-size effects. While one can extract an effective η from the large-y limit of X, this procedure is not very accurate and, given realistic complications, is not likely to be fruitful experimentally.

We[1(b)] used log–log plots of susceptibility (χ), ξ, and order parameter (M) [squared] vs t to obtain the effective exponents γ, ν, and [2]β, respectively. The thermal cutoff near T_c was set at that value at which ξ attains one-half its maximum value; a similar cutoff results by using the smallest t at which Eq. (2) is satisfied. Above T_c straight log–log plots were obtained over slightly more than a decade of t. The exponents γ and ν were within about 10% of the known Potts values. This accuracy is poorer than obtainable by theoretical means but is comparable to the differences between 2D universality classes.[2] Below T_c, corrections to scaling were evident: it is not possible to obtain comparable straight lines. By including some account of corrections to scaling (either a linear term or the known leading power), the fit is improved for the $(\sqrt{3}\times\sqrt{3})R$ 30° but not for the $p(2\times2)$ (where there are presumably logarithmic corrections). Thus, as found in our experimental study of O/Ni(111),[3] the exponents and T_c obtained from critical scattering above T_c are more reliable than those from M, and one should not rely exclusively on the latter. The critical amplitude ratio for χ is over 40 in both cases, indicating the difficulty of observing critical scattering below T_c (again consistent with experiment[3]), even with high resolution.

The differences between the lattice gas models and their higher-symmetry Potts counterparts are reflected in the anisotropies of the structure factor. In the $\sqrt{3}\times\sqrt{3}$ case, the lattice mandates only threefold symmetry around the corner of the SBZ (k_0 here). This deviation from circular symmetry is related to a cubic gradient term in the Landau–Ginzburg–Wilson (LGW) Hamiltonian, known to be irrelevant, with correction-to-scaling exponent $\frac{5}{6}$.[4] Analysis of the asymmetry is consistent with this result. For the $p(2\times2)$ case, there is only twofold symmetry about the center of a side of the SBZ edge. The associated LGW term is quadratic in the gradient, and the analysis is more subtle. We also illustrate how quenched (fixed) impurities (act as random fields to) "destroy" (i.e., round) the transition near T_c.

In the case of the (3×1),[1(c)] we observe that $q \propto \xi^{-1}$ (over the range $0.015 < t < 0.15$), consistent with predictions.[5] However, the proportionality constant appears to change with chemical potential. Although the critical exponents are consistent with those of the three-state Potts model, the critical amplitude ratios are larger, particularly for χ. This model is closely related to the much-studied chiral (three-state) clock model. We see no sign of a floating phase, i.e., incommensuration with infinite ξ.

In the $p(2\times2)$/honeycomb case,[1(d)] judged to be first order, ξ grows large as one approaches T_c. Similar behavior is observed for the eight-state Potts model, known to be first order. The data satisfy Eq. (2) over a similar thermal range as the other transitions, and effective critical exponents compare well with those associated with a "discontinuity fixed point."[6] Thus the appearance of critical scattering cannot alone be used to exclude the possibility that a transition is first order. We also see near the odd-order integer beams critical scattering related to a possible (though zero here) binding energy difference between the two sites in the basis.

Our work suggests the rough accuracy that might be expected for systems with defect-free regions of size comparable to those present surfaces. To challenge theory, an order of magnitude improvement in size is needed. Nonetheless, it should be possible to investigate surface critical behavior with LEED; the situation is far more encouraging than many had feared.

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