

it. The resulting randomness in occupying top and subsurface sites would contribute a small increase in the LEED background intensity and reduce the intensity of the extra spots but would not alter the general observation of two $\sqrt{3} \times \sqrt{3} R$ 30° patterns.

We have also measured the intensity of the extra spots as a function of temperature, Fig. 2, at various exposures. The curves are labeled sequentially starting with the lowest exposure and ending with the highest: "a"(0.12 L), "b"(0.4 L), "c"(0.5 L), "d"(0.65 L), and "e"(0.8 L). The uppermost curve, d, is for an optimal $\theta = 2/3$ coverage and shows a clear point of inflection at approximately 105 K, which is a suitable measure of the critical temperature.¹¹ At higher or lower exposures, curves e and c, respectively, the point of inflection occurs at lower temperatures and the intensity is lower. Curve b corresponds to still lower exposure and has even less intensity and a lower critical temperature. Finally, curve a corresponds to an optimal coverage for the primitive $\sqrt{3} \times \sqrt{3} R$ 30° structure namely $\theta = 1/3$. Cooling with liquid helium⁷ shows the point of inflection occurs below 90 K, i.e., below the temperature range accessible with liquid ni-

trogen. Thus it is possible to plot out an experimentally determined phase diagram. The result compares favorably to the theoretically generated phase diagram using the embedded atom method.¹

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Summary Abstract: Studying surface phase transitions with probes of short range order

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In surface science there are many probes which are, as a practical matter, sensitive only to short range order at the surface. Limitations on "instrumental resolution" tend to place LEED in this category. Given the great variety of phase transitions on surfaces which are of both theoretical and practical importance, it would be desirable to apply these widely available techniques to their study. Usually, however, phase transitions are described in terms of vanishing order parameters or diverging correlation lengths. Measurement of these quantities generally requires a probe of long range order. As we have recently pointed out,^{1,2} however, probes of short range order can be used to study the singularity associated with the energy (or entropy) which occurs at phase transitions. (Similar observations have been made by others,³⁻⁵ particularly regarding measurements of conductivity.^{3,4}) In fact, the probe will show the same singularity as the energy, viz. $|T - T_c|^{1-\alpha}$, where α is the specific heat exponent, if the probe is not sensitive to the phase of the order parameter.^{1,2,6} By this insensitivity we mean that the probe cannot distinguish between the different degenerate ground states of the ordered phase. [e.g., LEED cannot distinguish the two ground states of a $c(2 \times 2)$ overlayer on a

square substrate, but polarized LEED can tell whether a ferromagnetic overlayer is spin up or spin down.]

The singularity arises because near a second-order transition, a phase-insensitive correlation function $\Gamma(T)$ can be expanded as

$$\Gamma(T) = a_r + b_r^\pm |t|^{1-\alpha} + c_r t + \dots, \quad (1)$$

where $t \equiv (T - T_c)/T_c$. For a single component ($n = 1$) order parameter (Ising) system, the two-site correlation $\langle n(\mathbf{O})n(\mathbf{R}) \rangle$ behaves in this manner. For $n \geq 2$, Eq. (1) is still obeyed above T_c by $\langle n(\mathbf{O})n(\mathbf{R}) \rangle$, but below T_c only by phase-insensitive combinations such as

$$\Gamma(\mathbf{R}, T) \equiv \sum_{\mathbf{R}'} \langle n(\mathbf{R}')n(\mathbf{R} + \mathbf{R}') \rangle$$

for overlayers having the point group symmetry of the adsorption sites [e.g., $(\sqrt{3} \times \sqrt{3})R$ 30° on a triangular lattice but not (2×1)] (cf. Ref. 6). In this framework, a first-order transition could be described as "infinitely sharp," i.e., $\alpha = 1$.⁷ Here b_r^+ and b_r^- have opposite sign, and their ratio is a universal constant.^{1,6,8} Phase-insensitive multisite correlation functions also exhibit this singularity. We have discussed^{1,2} how the integrated (about an order-induced extra

spot) LEED intensity should display the $|t|^{1-\alpha}$ singularity, since it can be represented by a combination of correlation functions, all of which have this singularity. (A more precise statement is that the field conjugate to the measured combination of correlation functions is irrelevant.⁶) We illustrated this point by constructing LEED patterns from Monte Carlo simulations of several lattice gas Hamiltonians.

An even simpler way to use LEED to study phase transitions is to monitor the *total* current collected by a LEED screen. Recent work by Iwasaki and Zhu⁹ at Maryland used this approach to examine the (7×7) reconstruction of the Si(111) surface. They saw a discontinuous change in the reflected current at the temperature of the phase transition. (In this procedure the current can either increase or decrease at the transition, depending on the incident beam energy, ultimately the spot positions relative to the screen horizon.) Their result is consistent with the interpretation that this is a first order transition. The abruptness of the transition seems to depend sensitively on surface preparation. This case study illustrates that even in situations where one has not isolated the Γ dependence of the measured quantity, one can look for energy-like singularities so long as one is certain that short range order is responsible for the variation.

In vibrational spectroscopies (EELS and IRAS), the dipole-dipole interaction between adsorbates often underlies the order-dependent effects on the spectrum. All interaction effects enter through the Fourier transform of a lattice sum,¹⁰ which we write as

$$\tilde{U}(\mathbf{q}, T) = \sum_{\mathbf{R}} \Gamma(\mathbf{R}, T) U(\mathbf{R}) e^{i\mathbf{q} \cdot \mathbf{R}}, \quad (2)$$

to manifest the structural and thermal dependence. Although the R^{-3} decay of $u(\mathbf{R})$ makes it long range,¹¹ the dipole interaction is still irrelevant (i.e., it does not affect critical properties) since its nonanalyticity is at the substrate reciprocal lattice vectors while the singularity associated with the phase transition occurs at the "extra spots." The situation is analogous to the irrelevance of dipolar interactions in antiferromagnets.¹² Thus $\tilde{U}(\mathbf{q}, T)$ also shows the energy-like singularity for $T > T_c$ and usually for $T < T_c$. $\tilde{U}(\mathbf{q}, T)$ and hence singular behavior appear not only in the Mahan-Lucas frequency shift formula,¹³ but also in expressions for the intensity at fixed \mathbf{q} . While previous work has considered the difference between the ordered state and a mean-field-like disordered state,¹⁰ one should also at least in principle be

able to see a singularity near the transition.

Finally, in photoemission one often deals with two-dimensional band structures. In a single-band tight-binding picture, we can write

$$E(\mathbf{k}_{\parallel}) = E_0 - \gamma(R_1) \Gamma(R_1, T) \sum^{(1)} \cos \mathbf{k}_{\parallel} \cdot \mathbf{R}_1, \quad (3)$$

where the summation extends over nearest neighbors at a separation R_1 . It is straightforward to generalize to include more distant hopping integrals $\gamma(R_i)$. Since these γ 's will decrease rapidly with R_i , the effect remains short ranged. Thus, the energy-like singularity should appear in level shifts and hence, band widths.

In summary, any probe of short-range order is expected to exhibit the energy-like singularity associated with a phase transition. We have performed Monte Carlo simulations to show that this procedure is feasible in LEED. In vibrational spectroscopies and photoemission, we show how the singularity enters the relevant formulas. We challenge experimentalists to seek out the most convenient ways to make these measurements.

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Summary Abstract: The suppression of carbon monoxide chemisorption on titanium oxide modified platinum

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The interaction of small metal particles with TiO_2 has been the subject of much recent interest. This work has been directed toward understanding the unexpected results of Tautser *et al.*,¹ who found that hydrogen chemisorption can be

suppressed when metal particles are supported on TiO_2 . This metal support effect also influences the catalytic response of the system in a positive²⁻⁴ or negative⁵ manner depending on the nature of the reaction. Early ideas on this