

SURFACE SCIENCE LETTERS

USING LEED TO STUDY SPECIFIC HEAT ANOMALIES OF  
ADSORBED OVERLAYERS \*

N.C. BARTELT and T.L. EINSTEIN

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

and

L.D. ROELOFS

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

*Physics Department, Haverford, College, Haverford, Pennsylvania 19041, USA*

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Near a second order phase boundary the leading thermal dependence of the *integrated* intensities of "extra" LEED beams is proportional to  $\mp |T - T_c|^{1-\alpha}$  for  $T \geq T_c$ , where  $\alpha$  is the specific heat critical exponent. This behavior occurs when the correlation length exceeds the characteristic length of the instrument but is less than the characteristic size of defect-free regions. We illustrate these ideas using the structure factor of a  $p(2 \times 2)$  overlayer on a triangular lattice, simulated using Monte Carlo. Similar behavior can appear in other probes of phenomena dependent solely on finite-range correlations.

There have recently been several measurements of the critical exponents of phase transitions on surfaces using low energy electron diffraction (LEED) [1-4]. The number and success, however, of such studies have been limited by the difficulty of the measurement and analysis, by the concern that multiple scattering may have a pernicious effect, and by the virtual necessity of using high resolution LEED equipment. We point out in this Letter that there is a very attractive alternative approach to studying certain critical properties of such transitions, one which focuses on short range correlations. The method has several advantages including convenience of measurement and analysis, insensitivity to multiple scattering, and no particular need for good resolution. It is based on a measurement of the *integrated* intensities of "extra" diffraction beams. Finally the critical exponent obtained with this technique, the specific

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heat exponent,  $\alpha$ , is attractive since it exhibits the largest variation between various types of continuous 2D phase transitions.

We give a brief explanation of the method and sketch its justification (a fuller treatment is deferred to a forthcoming paper [5]), demonstrate its application on the structure factor of a  $p(2 \times 2)$  order-disorder transition on a triangular lattice, and discuss the utility of this method in determining critical properties via other surface probes including electron energy loss (EELS), infrared absorption (IRAS), and core level (XPS) spectroscopies. These opportunities seem especially exciting. We hopefully await application of these probes to surface phase transitions in various universality classes.

LEED probes surface atom correlation functions like  $\langle n_0 n_r \rangle$  or  $\langle n_0 n_{r_1} n_{r_2} \rangle$ ;  $n_r$  denotes the occupation number of site  $r$  and angular brackets refer to an average over the surface. Typically, each of these finite-range correlation functions is part of the energy,  $E$ , of the surface\*. Accordingly, near  $T_c$  in a second order transition, these functions display [5] the same singularity in the temperature dependence as does  $E$ :

$$\left. \begin{aligned} \langle n_0 n_r \rangle \\ \langle n_0 n_{r_1} n_{r_2} \rangle \end{aligned} \right\} = \begin{cases} a + b_- |t|^{1-\alpha} + c|t| + \dots, & T < T_c, \\ a - b_+ |t|^{1-\alpha} - c|t| + \dots, & T > T_c, \end{cases} \quad (1)$$

where  $t \equiv (T - T_c)/T_c$  and  $\alpha$  is the specific heat exponent [6];

$$C_v = dE/dT = K_0 + K_{\pm} |t|^{-\alpha} + \dots \quad (2)$$

The constants  $a$ ,  $b_{\pm}$ ,  $c$  and  $K_{\pm}$  depend on  $r$  (or  $r_1$  and  $r_2$ ) but the ratios  $b_-/b_+$  and  $K_-/K_+$  are universal [7];  $b_-/b_+$  is the same for all correlation functions [5]. The LEED intensity evaluated at any scattering wavevector  $\mathbf{q}$  is just a weighted *finite* sum of correlation functions. (The sum does not extend to infinite  $r$  or ( $r_1$  and  $r_2$ ) because of the instrument response function [8].) Thus it displays the same  $(1 - \alpha)$  singularity:

$$I_{\pm}(\mathbf{q}; T) = A \mp B_{\pm} |t|^{1-\alpha} - Ct + \dots \quad (3)$$

More generally any measurement of short range order which is insensitive to the phase of the order parameter (sign in the Ising model) exhibits this energy-like singularity.

This straightforward observation raises two questions whose answers are related: Over what temperature range about  $T_c$  can the behavior of eq. (3) be expected? And how does one reconcile this suggestion with the picture used in analyzing X-ray [9] and neutron diffraction data [10] and in previous LEED

\* The interactions conjugate to these correlation functions are temperature-like; i.e. they do not create long range order at all temperatures. For some transitions the anisotropy of the interactions is relevant, introducing an additional competing term ( $t^{2-\alpha-\phi}$  with  $\phi > 0$ ) into eq. (1). We expect, however, the domain averaging in LEED experiments to remove this term [5].

work [1–4], where the  $T$  and  $q$  dependence of  $I$  were exploited to determine the critical exponents  $\beta$ ,  $\gamma$ , and  $\nu$ ? A detailed discussion of the answers must be based on the notion of scaling [6]. We sketch the basic ideas below, deferring complete arguments to a forthcoming paper [5].

The scaling “hypothesis” is based on the expectation that the behavior of a system near its critical point is determined by a single length scale, the correlation length for fluctuations, which diverges at  $T_c$  as

$$\xi \propto |t|^{-\nu}. \quad (4)$$

Wavevector-dependent properties such as the LEED intensity are found to depend (near  $T_c$ ) only on the dimensionless variable  $x = k\xi$ , where  $k$  is the magnitude of the displacement from the wavevector of the ordered state  $q_0$ ,  $k = |q - q_0|$ .

The LEED instrument, via its instrument response function [8,11] (a limitation of the length  $L_1$  over which the instrument resolves correlations), sets the minimum value of  $k$  which can be resolved. Denote this value by  $k_1 \approx 1/L_1$ ; then  $x_1 = k_1\xi$ . Careful analysis of the structure factor, taking scaling into account [5,6], indicates that the behavior of eq. (3) occurs when  $x_1 \gg 1$ , i.e.  $\xi \gg k_1^{-1} \sim L_1$ , when the LEED instrument is not capable of resolving the length scale on which fluctuations are occurring. In the other limit,  $x_1 \ll 1$ , one finds the sort of behavior exploited in earlier LEED experiments [1–4],

$$I(q = q_0; T) \propto \begin{cases} |t|^{2\beta}, & T < T_c, \\ |t|^{-\gamma}, & T > T_c. \end{cases} \quad (5)$$

Since  $\xi$  varies rapidly near  $T_c$ , the crossover from the behavior of eq. (3) to that of eq. (5) is quite rapid. (The crossover between the two pictures is contained in the scaling relation  $I(k_1, T) = |t|^{2\beta} Y(k_1 x_1(t))$ ). In analogy with finite size scaling, varying  $k_1$  allows one to obtain  $\gamma$ ,  $\beta$  and  $\nu$  [5]). We summarize this discussion in fig. 1, which shows the variation of  $\xi$  near a second-order transition and includes  $L_1$  and another length  $L_S$ .  $L_S$  is the characteristic size of defect-free regions on the surface. In the temperature region when  $\xi$  would exceed  $L_S$ , the sample defects prevent the continued increase of  $\xi$  and thereby round the transition. Thus region (1) gives no information about the transition. *However, the point of inflection of the intensity curve – which corresponds to the maximum of the specific heat – supplies a natural estimate of  $T_c$ .* This method of gauging  $T_c$  has been used serendipitously [12,13]. For  $L_1 < \xi < L_S$  (regions (2) and (3)) we expect the  $(1 - \alpha)$  behavior, and at  $T_{11}$  and  $T_{12}$  crossover to eq. (5) should occur.

As an example of the application of the use of integrated intensities to study second order phase transitions, we consider the disordering of the  $p(2 \times 2)$  overlayer on a triangular lattice. Our motivation for studying this transition is its relevance to the disordering of  $p(2 \times 2)\text{O}/\text{Ni}(111)$ . This system has been

studied in detail with LEED [1]. If continuous, this transition is predicted to have the same critical exponents as the 4-state Potts model; in particular,  $\alpha = 2/3$  [14]. This value is rather large ( $\alpha \leq 1$  from thermodynamic arguments [15]) and should be easily observable. We have performed Monte Carlo calculations of the structure factor for the  $p(2 \times 2)$  structure formed by nearest- and next-nearest-neighbor repulsions (with a ratio of energies of 2 : 1). The lattice size (3888 sites) was comparable to the expected average plateau size on the (111) surface used in the experiment. The structure factor,

$$S(\mathbf{q}) = \sum_r \langle n_0 n_r \rangle e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (6)$$

is what an ideal LEED instrument would measure if there were no multiple scattering. To mimic poor instrumental resolution we integrated  $S(\mathbf{q})$  12% of the way to the nearest integer position. This integrated intensity for temperatures close to the  $p(2 \times 2)$  disordering temperature (at a coverage close to 1/4) is plotted in fig. 2. Fitting these data to the form of eq. (3) yields  $\alpha = 0.62 \pm 0.06$  and  $B_+/B_- = 1.0 \pm 0.1$ . ( $A$ ,  $B_{\pm}$ , and  $T_c$  were adjusted minimize the  $\chi^2$  of the fit. The constant  $C$  was set to zero. Only data within 15% of  $T_c$  were used; data within 1% of  $T_c$  were discarded to allow for finite-size effects.) These values conform to the 4-state Potts model universality class [14,16], and demonstrate that  $\alpha$  can be conveniently determined from the integrated LEED intensity. The O/Ni(111) data show a much more rounded transition than in fig. 2,

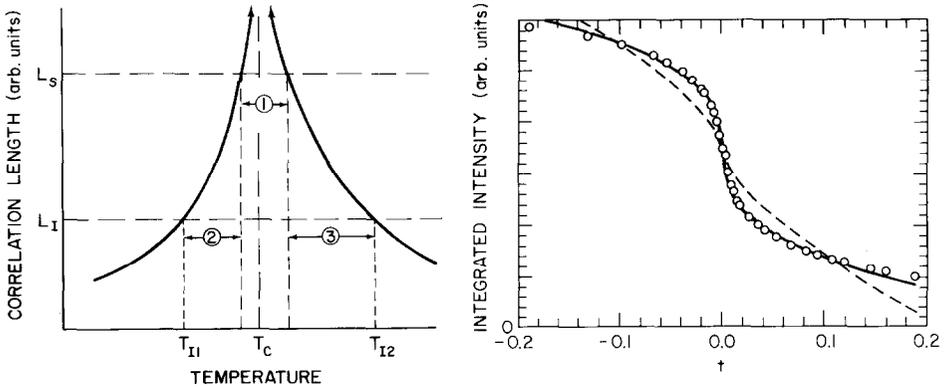


Fig. 1. Variation of the correlation length for fluctuations near a second-order transition. The significance of the various temperature regions is given in the text.

Fig. 2. Integrated kinematic intensity of half-order LEED spot from simulated  $p(2 \times 2)$  order-disorder transition (circles). The solid line is the best fit as described in the text, giving  $\alpha$  to within error of the expected 4-state Potts value of  $2/3$ . The dashed line is the best fit with  $\alpha$  fixed at  $1/3$ , the 3-state Potts value. This gives an indication of the ease of discriminating universality classes by looking at  $\alpha$ .

intimating a small positive or negative exponent  $\alpha$ . This result is consistent with the nearly Ising ( $\alpha = 0$ ) exponents  $\beta$ ,  $\gamma$  and  $\nu$  found previously [1].

There are, of course, many other probes of short-range order in surface science. If the range of detected order is large enough to observe the structural changes associated with a phase transition, then these probes too will show the energy-like singularity at the critical point. (The range of order probed need not be large. Fisher and Langer [17] long ago pointed out the presence of such energy-like singularities to explain an *electrical resistance* measurement in the vicinity of a magnetic phase transition.) To make some concrete suggestions we note for example that in EELS, the vibrational frequencies of surface atoms might be expected to depend sensitively on surface reconstructions. Indeed Willis [18] has studied the W(100) surface reconstruction induced by H adsorption near room temperature and has found easily resolved shifts in vibration frequencies correlated with the phase transitions seen using LEED [3,19]. Infrared absorption can be similarly applied. Bradshaw and Hoffmann [20] and Crossley and King [21] have found that the C–O stretch frequency depends sensitively on coverage via admolecule interactions on Pd(100) and Pt(111). Thus IRAS would seem to have sufficient sensitivity to detect overlayer order–disorder transitions and possibly to reveal the energy-like singularity. Core level spectroscopies have also been found to be sensitive to adatom interactions (see for example the XPS studies of I/Ag(111) and I/Cu(111) by DiCenzo et al. [22]) and thus can also be used to study critical behavior through the exponent  $\alpha$ .

Our point, which has been made before in other contexts [16,23,24], is: although phase transitions are defined by changes in long-range order, their critical properties, through the specific heat amplitude ratio and exponent, can be studied by *any* probe of short-range order. This statement applies also in three-dimensional systems. Nonetheless, the idea underlying eq. (3) has not, to our knowledge, been used in studies of 3D critical behavior systems, perhaps because of the availability of adequate probes of long-range order such as X-ray scattering.

We close with three comments. First, although the proposed method allows the use of low-resolution LEED equipment or even very local probes, one must nevertheless be concerned about sample quality. Finite size effects caused by impurities or steps, etc., limit the attainment of the long correlation lengths needed to produce the singularity. Secondly, in the Ising model, where  $\alpha = 0$ , there is a logarithmic singularity of the form  $B|t|(\ln|t|)$  instead of the  $|t|^{1-\alpha}$  term of eqs. (1) and (3). Finally, in most surface experiments [1,2,4] the coverage  $\theta$  of an adsorbed species is held constant while  $T$  is varied, or vice versa. The coverage is, in general, a singular function of  $T$  if the chemical potential  $\mu$  (or equilibrium vapor pressure) is fixed or of  $\mu$  if  $T$  is fixed. Hence “Fisher renormalized” [25] exponents occur if  $\theta$  (or  $T$  with fixed  $\theta$ ) is substituted for  $T$  (with  $\mu$  implicitly fixed) in eqs. (1), (3), and (5). Fisher

renormalization replaces  $\alpha$  by  $-\alpha/(1-\alpha)$ . If  $\alpha$  is positive then  $\partial I(\mathbf{q}; T)/\partial T$ , for example, will have a cusp singularity at  $T_c$  rather than a divergence, increasing the difficulty of analysis. Fisher renormalization can be avoided by studying the transition at a phase-boundary extremum, i.e.  $dT_c/d\theta = 0$ , as was done in the study of O/Ni(111) [1].

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