Au(110) (1×2)-to-(1×1) Phase Transition: A Physical Realization of the Two-Dimensional Ising Model

J. C. Campuzano, M. S. Foster, G. Jennings, and R. F. Willis
Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

and

W. Unertl
Physics Department, University of Maine, Orono, Maine 04473
(Received 12 December 1984)

We report the first measurements of the critical exponents of a phase transition at the surface of a clean metal, the Au(110) (1×2) ↔ (1×1) transition. The exponents β, γ, and ν and the amplitudes were measured by LEED and place the phase transition in the two-dimensional Ising universality class. The critical scattering is observed to peak *above* T_c, signaling the breakdown of the Ornstein-Zernike theory, and is in numerical accord with predictions of Fisher and Burford.

PACS numbers: 64.60.Fr, 61.14.Hg, 68.20.+t

The prediction[1,2] that continuous order-disorder phase transitions can be classified into a small number of universality classes, each one determined by quantities which are not system specific, such as the interaction range, the symmetry of the ordered phase, and the dimensionality of space, implies that some universality classes exist only in two dimensions. While this has prompted many studies of physisorbed and chemisorbed overlayers,[3] many metals and semiconductors also show phase transitions at their surfaces which do not occur in the bulk. The purpose of this Letter is to report the measurement of the critical exponents of a phase transition which occurs on the surface of a clean metal, and fits the two-dimensional (2D) Ising universality class.

Specifically, we present a study of the phase transition which occurs on the surface of Au(110). At room temperature on a carefully prepared surface, there is double periodicity in the (11) direction, and hence a (1×2) LEED pattern which has been ascribed to a missing row structure.[4] For tempertures greater than ~700 K, the $\frac{1}{2}$-order spots disappear and an apparently primitive (1×1) structure is observed. It has been suggested[4,5] that the high-temperature phase is disordered in the "lattice gas" sense, that is, the top-layer atoms are randomly placed on the surface rather than aligned in rows, but remain in the same type of site as in the ordered structure. From symmetry considerations, Bak[6] has predicted that the transition might belong to the 2D Ising class. Our high-resolution LEED measurements of the critical exponents confirm that this is indeed the case.

It has been demonstrated[7] that LEED is an ideal technique for studying surface phase transitions. It has high surface sensitivity, and the short interaction times allow every configuration of the system to contribute independently to the diffracted beams. The major drawback of LEED is the limited resolution of conventional diffractometers. We have overcome this limitation with a new kind of high-resolution LEED diffractometer[8] which has a sufficiently narrow response in $\mathbf{q}$ space compared with the experimental peak width that we are able to extract directly the structure function[9]

$$S(\mathbf{q},T)=I(T)\delta(\mathbf{q}-\mathbf{q}_0)+\chi(\mathbf{q}-\mathbf{q}_0,T)/\chi^0(T), \quad (1)$$

where $I(T)\delta(\mathbf{q}-\mathbf{q}_0)$ is the long-range order, $\chi(\mathbf{q}-\mathbf{q}_0,T)$ are the fluctuations in order (short-range order), $\chi^0(T)$ are the fluctuations of a random noninteracting system, and $\mathbf{q}$ is the momentum transfer of the electrons. For the Au(110) (1×2) structure, $\mathbf{q}_0=(h2\pi/a,k\pi/a)$. In LEED, multiple scattering is always present, but one still obtains a structure function of the form (1) provided that one is dealing with correlation lengths larger than the inelastic mean free path of electrons in the sample, in which case the multiple-scattering contribution will be small. For most elements, the inelastic mean free path is of the order of 4–10 Å for electrons of 20 eV. Furthermore, Roelofs *et al.*[7] pointed out that scattering at right angles is at a minimum for metals in the energy range used. Then, if the electrons are incident normal to the surface, multiple scattering in the plane of the surface will be further minimized.

The experiment consists of measuring the $\frac{1}{2}$-order beam profiles, given by the structure function (1). The profiles were obtained with normal-incidence electrons of 20 eV by the scanning of a Faraday cup along the (11) direction. Because of the limited extent of the ordered (1×2) regions on the Au(110) sample (as explained below), the Faraday-cup aperture was increased to admit $\Delta q \sim 0.010$ Å^{-1}, in order to improve the signal-to-noise ratio. The measured profiles were then corrected for this finite aperture by following the

procedure of Als-Nielsen.[9,10]

The 99.995%-pure Au crystal was cut to expose the (110) face with an accuracy of 0.5°. Only coarse mechanical polishing was employed, as Au is very soft and excessive working results in a high concentration of defects. The crystal was electropolished and cleaned *in situ* by ion bombardment. No traces of contamination were observed by Auger spectroscopy. The temperature of the sample was controlled to a relative stability and precision of $\Delta T/T \simeq 10^{-4}$, although the absolute temperature accuracy is only ± 5 K.

Figure 1 shows some typical high-resolution profiles of the $(1, -\frac{1}{2})$ beam at temperatures (a) above, (b) near, and (c) below T_c. The peak intensities of the $\frac{1}{2}$-order beams show no hysteresis as a function of temperature. According to Eq. (1), to obtain the long-range order and fluctuations we least-squares fit functions corresponding to $I(T)$ and $\chi(\mathbf{q}-\mathbf{q}_0, T)$ to the measured profiles,[9] after the Debye-Waller effect has been divided out. For $T \ll T_c$, there are no fluctuations χ and the beam profiles are dominated by $I(T)$. It can be seen that the $\frac{1}{2}$-order beams [Fig. 1(c)] have twice the full width at half maximum of the integral-order ones [Fig. 1(d)]. This is because the average size of the (1×2) domains on the surface is limited to ~ 150 Å. Similar values have been obtained by grazing-incidence x-ray measurements.[11] It should again be emphasized that this value depends greatly on sample preparation,[5,11] although this limited long-range order is probably inherent to the missing-row structure.[4,5] The upper bound imposed on the long-range order broadens $I(T)$ from a δ function to a Gaussian function. The width of the Gaussian function can be uniquely determined by fitting to the measured low-temperature profiles. Nearing T_c, fluctuations start to appear, and the profiles can no longer be fitted with a Gaussian alone. Fisher and Burford[12] have derived an expression for the fluctuations,

$$\chi(\mathbf{q}-\mathbf{q}_0, T) = \text{const} \times (\kappa^2 + \phi^2 k^2)^{\eta/2}/(\kappa^2 + \psi k^2),$$

where $\mathbf{k} = \mathbf{q} - \mathbf{q}_0$, κ is the inverse of the effective correlation length, and ϕ and ψ are slowly varying functions of T with values near T_c of $\phi = 0.03$ and $\psi \simeq 1$. Because in our sample the correlations are limited to ~ 150 Å, $\kappa^2 >> \phi^2\mathbf{k}^2$, and the expression above simplifies to $\text{const} \times \kappa^{\eta}(\kappa^2 + \mathbf{k}^2)$, which is of Lorentzian form. (Note that this does not imply that $\eta = 0$.) The measured profiles are fitted very well over the whole zone $(0.25 < k < 0.75)$ by the sum of a Gaussian (of constant width) and a Lorentzian.

After subtracting the background elastic scattering to account for $\chi^0(T)$, we obtain the critical exponents λ and the amplitudes A_λ by fitting the different components with asymptotic power laws of the form

$$A_\lambda |1 - T/T_c|^{\lambda}, \tag{2}$$

and varying T_c for best fit. The exponent β describing the decay of the long-range order is obtained by fitting the height of the Gaussian, Fig. 2, line *a*, giving $T_c = 649.75 \pm 1.5$ K (relative error), $A_\beta = 1.79 \pm 0.09$, and $\beta = 0.13 \pm 0.022$; the theoretical predictions are $\beta = 0.125$ and $A_\beta = 1.22$. The amplitudes are not universal,[13] and therefore cannot be directly compared

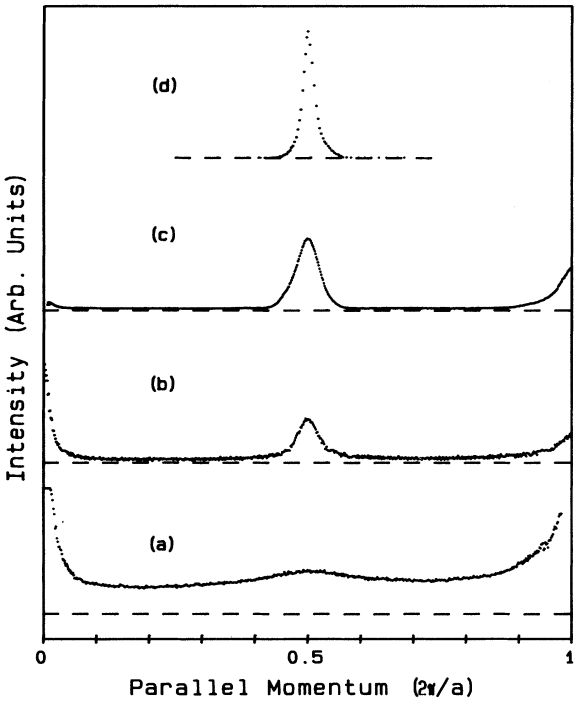

FIG. 1. Intensity profiles of the $(1, -\frac{1}{2})$ beam along (11) at (a) 756 K, (b) 658 K, and (c) 340 K. (d) (1,0) beam profile along (11) at 340 K. $T_c = 649.75$ K. Background intensity is indicated by a dashed line.

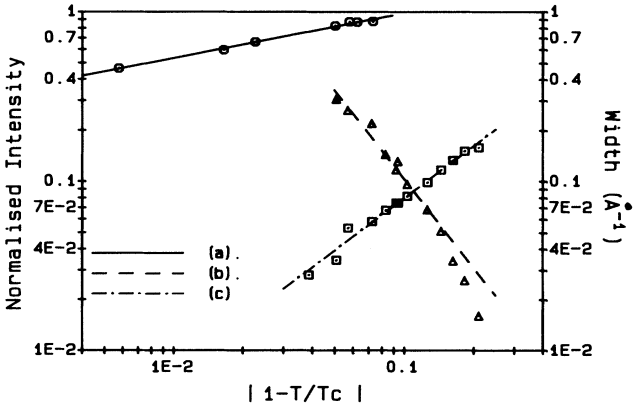

FIG. 2. Fits of the Gaussian height (circles), the Lorentzian height (triangles), and the Lorentzian width (squares).

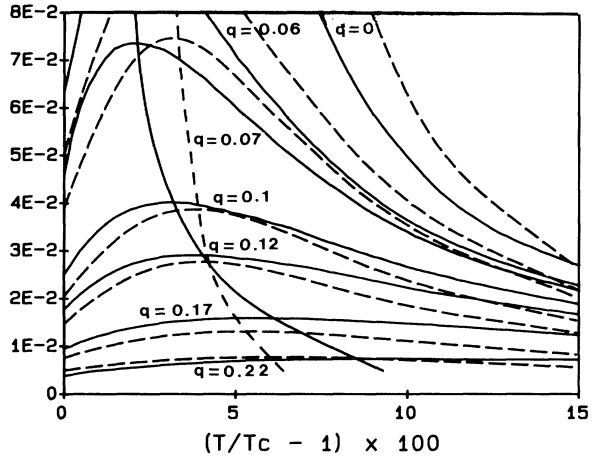

FIG. 3. Plot of the fluctuations (dashed curve) and the theoretical result of Fisher and Burford (Ref. 12) (solid curve) for fixed values of momentum transfer. The locus of the maxima for the curves are also indicated by corresponding lines.

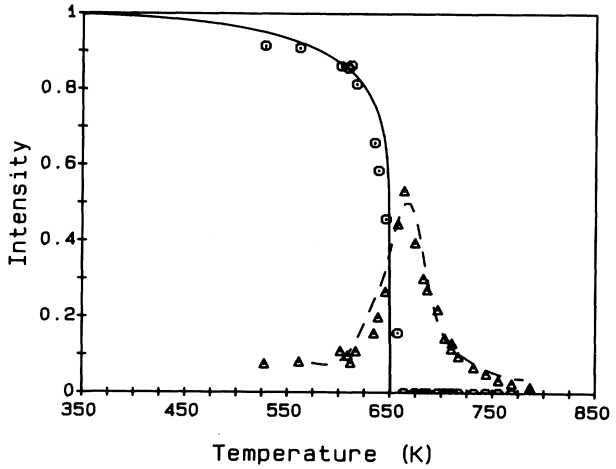

FIG. 4. Plot of the long-range order (circles) and Onsager's theoretical result (Ref. 15) (solid curve); the fluctuations (triangles) and Fisher and Burford's result $\chi = \kappa^{\eta-2}$ with measured values of κ (dashed curve).

to the predictions of Fisher.[13] When fitting the height of the Lorentzian to obtain the exponent γ which describes the divergence of χ as $T \rightarrow T_c^+$, care in the selection of the temperature interval to be used is necessary. For T very close to T_c, χ does not diverge because of the limited size of ordered regions. For T far from T_c, the asymptotic power-law definition of γ, Eq. (2), is not valid. Using data points in the range $0.09 < 1 - T_c/T < 0.15$, Fig. 2, line *b*, we obtain $\gamma = 1.75 \pm 0.03$. The predicted value is $\gamma = 1.75$. For $t > 0.15$, the data no longer follow the asymptotic behavior (Fig. 2, line *b*). The exponent ν describing the growth of κ is obtained by fitting the width of the Lorentzian, Fig. 2, line *c*, giving $\nu = 1.02 \pm 0.02$ and $A_\nu = 0.8 \pm 0.1$. The predicted values are $\nu = 1$ and $A_\nu = 0.43$.[12] Surprisingly, κ follows power-law behavior up to $t = 0.23$, a much wider range than $I(T)$ and $\chi(k,T)$. Our results bear striking resemblance to the neutron-scattering results of Samuelsen[14] on Rb_2CoF_4, which behaves as a two-dimensional antiferromagnet away from T_c. In this case, the power-law behavior of the magnetization, susceptibility, and inverse correlation length is over the same range of temperatures as that in Au(110).

Fisher and Burford[12] predicted that χ should peak above T_c, as a consequence of the breakdown of the "classical" Ornstein-Zernike theory.[13] In Fig. 3 we compare their numerical calculations of the variation of scattering intensity versus temperature for fixed wave vector (see Fig. 10, Ref. 12) (solid curves), with our measured values (dashed curves). There is good agreement with the theory, although in the data, the shift of T_c vs $\mathbf{q}$ is not quite as pronounced as predicted. However, χ clearly peaks *above* T_c. The discrepancy between theoretical and experimental shift probably arises from the finite aperture of our detector.

In Fig. 4 we plot the theoretical result of Fisher and Burford[12] $\chi(0,T) = \text{const} \times \kappa^{\eta-2}$ using our measured values of κ and $\eta = 0.25$. A worse fit is obtained with $\eta = 0$, more than one standard deviation away, in accordance with the measured value of γ and the scaling laws, strongly suggesting that $\eta \neq 0$, again as predicted. For comparison, we also plot Onsager's exact solution for the long-range order.[15] Some slight rounding in the decay of the long-range order can be seen. This rounding, due to finite-size effects, causes the disagreement between the theoretical and experimental values of β.

We conclude that these results place the Au(110) $(1\times2) \rightarrow (1\times1)$ phase transition in the 2D Ising universality class. Some exponents, such as β for example, do not vary significantly between some 2D universality classes. But we have measured three exponents independently, which cannot simultaneously be reconciled with those of other classes (particularly the measured value of ν). Although the concept of universality is strictly a theoretical one, the similarities between the Au(110) and Rb_2CoF_4 phase transitions are revealing.

We thank British Petroleum for an Extra-Mural Research Award, and D. Thouless and M. Shick for helpful discussions. One of us (M.S.F.) thanks the Science and Engineering Research Council for a studentship.

[1]K. Wilson, Sci. Am. **241**, No. 2, 140 (1979).

[2]S. k. Ma, *Modern Theories of Critical Phenomena* (Benjamin, Reading, Mass., 1976).

[3]*Phase Transitions in Surface Films,* edited by J. G. Dash and J. Ruvalds, Nato Advanced Institute Series No. 51 (Plenum, New York, 1980); *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, Amsterdam, 1980); Proceedings of a Symposium on Statistical Mechanics of Adsorption, edited by M. W. Cole, F. Toigo, and E. Tosatti, Surf. Sci. **125** (1983).

[4]H. Wolf, H. Jagodzinski, and W. Moritz, Surf. Sci. **77**, 265 (1978).

[5]J. C. Campuzano, A. M. Lahee, and G. Jennings, Surf. Sci. (to be published).

[6]P. Bak, Solid State Commun. **32**, 581 (1979).

[7]L. D. Roelofs, A. R. Kortan, T. L. Einstein, and R. L. Park, Phys. Rev. Lett. **46**, 1465 (1981).

[8]J. C. Campuzano, M. S. Foster, and R. F. Willis, to be published.

[9]J. Als-Nielsen, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 5a.

[10]In our case, the deconvolution of the finite detector aperture does not affect the values of the critical exponents; it only affects the values of the amplitudes.

[11]I. K. Robinson, Phys. Rev. Lett. **50**, 1145 (1983).

[12]M. E. Fisher and R. J. Burford, Phys. Rev. **156**, 583 (1967).

[13]See M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).

[14]E. J. Samuelsen, J. Phys. Chem. Solids **35**, 785 (1974).

[15]L. Onsager, Phys. Rev. **65**, 117 (1944).