COLLOQUE DE PHYSIQUE
Colloque C7, supplément au n°10, Tome 50, octobre 1989

PHASE TRANSITIONS IN CLEAN METAL SURFACES

I.K. ROBINSON

AT and T Bell Laboratories, 600 Mountain Avenue Murray Hill, NJ 07974, U.S.A.

ABSTRACT

As temperature is changed, two entirely different kinds of structural phase transition can be seen in surfaces. The first involves reconstructed surfaces which can transform to a new structure or to a disordered state. We present x-ray data which show that W(001) undergoes such an order-disorder transition. The second class is roughening transitions from smooth at low T to rough at high T; N(113) shows this behavior. Lastly we consider the interesting case of Pt(110) which appears to have characteristics of both kinds.

RESUME

Quand on change la température, on peut trouver plusieurs classes de transitions de phase dans les surfaces. D'abord il y a les changements de reconstruction, souvent ordre-désordre. Ici nous présentons le cas de W(001), qui est un exemple typique. Le deuxième cas, Ni(113), a une transition de rugosité : la surface est plate à basse température et rugueuse à haute température. Pt(110) est un cas intermédiaire, qui a des charactéristiques soit d'ordre-désordre soit de transition de rugosité.

I. Introduction

Surface phase transitions are simple manifestations of two-dimensional (2D) critical behavior, for which a considerable quantity of theoretical work has emerged during the 1960's and 70's.[1,2] Whether or not actual surfaces, such as those prepared by traditional methods of surface science, behave in such a predictable way is an experimental question that can only be tested by careful

measurement and comparison with theory. The presence of steps and impurities in real surfaces may ultimately limit the extent of such agreement and may not always be detectable with sufficient sensitivity. In this review paper we consider three examples of phase transitions studied by x-ray diffraction and find some, but not total, consistency with appropriate theories.

The experiments used x-rays provided by synchrotron radiation sources at central facilities at SSRL and NSLS, where a large number of people are involved. The principal collaborators are E. Vlieg and A. A. MacDowell of Bell Labs; M. S. Altman and P. J. Estrup of Brown University; K. Evans-Lutterodt, J. D. Brock and R. J. Birgeneau of MIT; E. H. Conrad and D. B. Moore of U. Missouri and K. Kern of K. F. A. Julich. Without their contributions none of this work would have been possible.

II. Technique Overview

X-ray diffraction at surfaces is now a well enough established technique that it now warrants an entire conference dedicated to the subject, of which the present paper is part of the proceedings. For this reason, only details of the technique specific to the work discussed will be given.

The property of x-rays most important for phase transition work is its kinematical interaction with the surface. The shape of a diffraction peak is therefore an accurate measure of the Fourier transform of the spatial correlation function in the surface. This function is one of the quantities predicted by phase transition theory and contains much information sensitive to the details of that theory. Because a large region ($> 1\,\mathrm{mm}^2$) is usually probed and because the results require long counting times ($> 1\,\mathrm{sec}$) the ensemble- and time-averaged correlation function is relevant.

In the present work, only one diffraction peak is used. This is either a fractional-order of diffraction for a reconstructed surface [W(001) and Pt(110)] that arises only from the surface layer(s) with the broken translational

symmetry of the crystal, or else a crystal truncation rod (CTR) that arises from imperfect cancellation of the contributions of all the layers in the crystal[3] [Ni(113)]. In the former case it is the spatial correlations of the reconstruction, displacements for W(001) or missing atoms for Pt(110), that are sampled; in the latter, the argument is more subtle,[4] but ultimately shows that it is the correlations in the distribution of steps that emerges in the lineshape.

Since poorly-correlated surfaces give rise to extremely weak and diffuse diffraction peaks, intensity considerations are of the utmost importance and often limit the range of interpretable data. The ideal source would have the highest flux possible at a single wavelength, an undulator for example, with not-too-narrow bandwidth, say $\Delta E/E = 10^{-3}$ for Ge(111) monochromators.[5] This should be focused as tightly as possible onto the sample, as is achieved by a toroidal mirror.[6] Resolution is often not as necessary as it is for bulk phase transitions because even the best prepared surfaces have limited coherence, often in the range 100-1000Å but sometimes better.[4] Slits are therefore a suitable choice, with a setting of 4×10mm at 500mm distance being typical: out-of-plane resolution is less important than in-plane. The resulting resolution function is highly asymmetric[8] and this must always be taken into consideration during data analysis. Grazing incidence is useful to reduce background and to align the long direction of the resolution function with the more diffuse direction of the scattering, along the 2D rod.[8] It is not worthwhile to restrict, at the expense of intensity, the angular acceptance of the incident beam to keep its range entirely within the critical angle for total external reflection, except when the results depend on the ability to probe a variable depth of the sample.[9]

All of the samples discussed in this paper were clean metal surfaces. The preparation techniques varied considerably. W was first cleaned by annealing at moderate temperatures in O_2, then by flashing briefly to 2400K.[10] The chief surface contaminant was H arising from the residual gas which was found to stick readily and alter locally the displacements of the top layer W atoms,

thereby frustrating the reconstruction.[11] This was monitored post-facto by integration of the pressure burst upon heating at the beginning of the next cleaning cycle (two per temperature point). Ni(113) and Pt(110) were also cleaned by heating in O_2 to remove C and by Ar^+ ion bombardment to remove S[Ni] or Si and Ca [Pt]. Careful annealing was found to be important in both cases.

Data collection consisted of sequential intensities measurement along radial and transverse reciprocal space directions as a function of temperature. Interlaced scans were used to have both a small sampling interval near these peak and a wide coverage to ensure that true background levels were reached. In all three cases, a low order peak along a high-symmetry direction was selected, so that the scan directions probed independent directions of the correlation function. Data analysis consisted of lineshape fitting of both scans simultaneously to a 2D function. The peak center was adjusted in 2D to allow for possible misalignment, the chief source of which was thermal expansion of the lattice, but also (somewhat) of the sample holder.

III. The W(001) Surface

This has a $\sqrt{2} \times \sqrt{2}\,\mathrm{R}45°$ reconstruction below 230K which consists of alternating diagonal displacements of top layer atoms and smaller corresponding displacements of the layer(s) below.[10] This renders the rather open unreconstructed body centered cubic (001) face into a more close-packed configuration because the top layer atoms can "bond" together into chains. Two directions are possible and domains of each coexist. The domain size on our sample at low temperature was $\sim 200 \times 100$Å with the larger direction parallel to the chains. Our results have already been published, but will be summerized here for clarity.[12]

Upon heating, the (3/2 3/2 0) surface diffraction peak broadens in both directions. Figure 1 shows fitting parameters to the 2D Lorenzian lineshape,

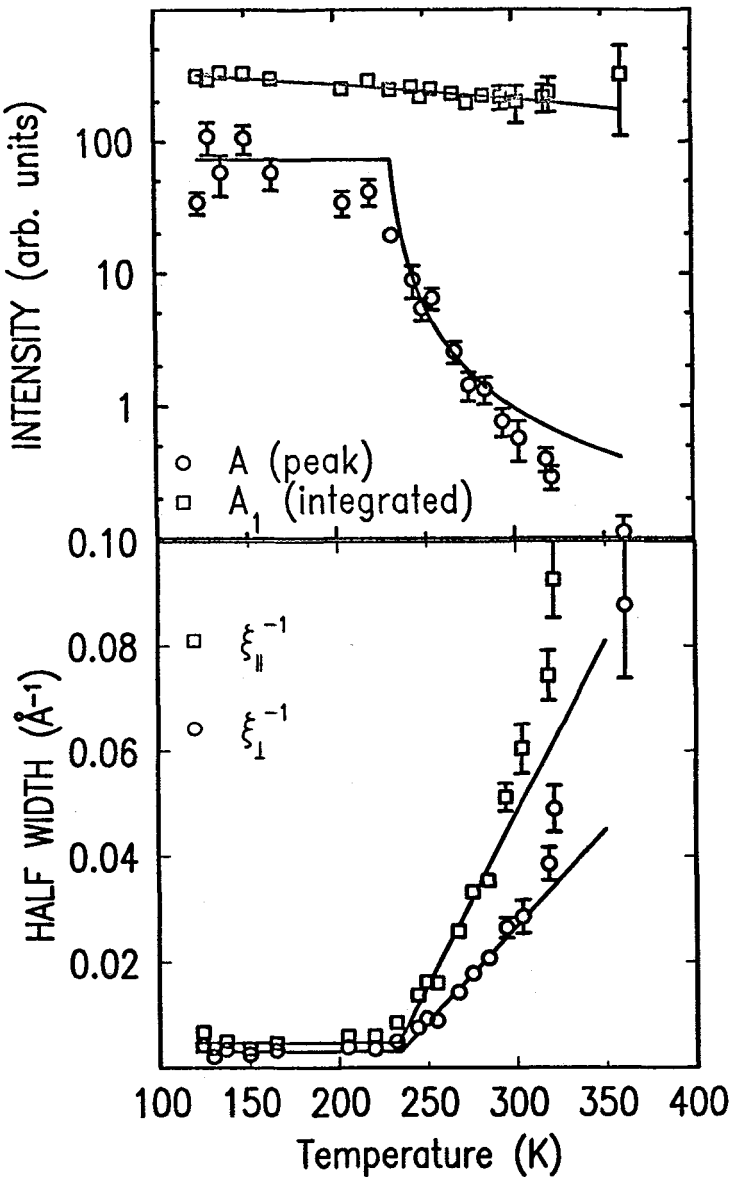

Figure 1. Fit parameters as a function of temperature for the (3/2 3/2 0) surface diffraction peak of W(001). Top panel: peak intensities A and integrated intensity A′. Bottom panel: peak widths $1/\xi$. The $\xi_{\parallel}$ direction is parallel to the momentum transfer; this corresponds to correlations perpendicular to the bonded chains of W in the ordered phase.

$$L(q_x q_y) = \frac{A}{(1 + q_x^2 \xi_x^2 + q_y^2 \xi_y^2)} \qquad (1)$$

where q_x and q_y are the deviations of momentum transfer from the center position $(Q_x Q_y) \simeq (3/2\ 3/2)$. Equation (1) was convolved numerically with the measured resolution function, which included the bimodal mosaic structure of our sample. Satisfactory fits were obtained at all temperatures as indicated by $\chi^2 \simeq 1$. Also plotted in Fig. 1 is the integral of eq. (1) over one zone of reciprocal space, A'. Whereas the peak intensity A falls precipitously at the phase transition, A' is almost constant and shows no change of slope. Since the integrated intensity is proportional to the square of the structure factor, which is itself proportional to the displacement, d (for low order reflections, such that $\vec{Q} \cdot \vec{d} \ll 1$), we conclude that the *structure is unchanged* across the transition. This is classical statistical disordering analogous to magnetic systems. This is therefore an order-disorder phase transition.[12]

Both radial and transverse widths show a corresponding increase with temperature which is approximately linear above the transition. The correlation lengths therefore obey

$$\xi \propto (T - T_c)^{-\nu} \quad T > T_c \qquad (2)$$

with $\nu \simeq 1$, the expected value for a 2D Ising model.[1] The ratio of $\xi_{\parallel}$ to $\xi_{\perp}$ is approximately constant at 0.5 for all temperatures indicating an anisotropy of the interaction between and along the bonded chains that is itself independent of domain size, showing the scaling hypothesis to be valid here.

IV. The Ni(113) Surface

This surface is not reconstructed but shows a different kind of surface phase transition called roughening. At low temperatures the surface has a regular structure consisting of terraces of (001) orientation, 1½ atomic spacings wide separated by straight monatomic steps. At high temperatures, kinks disrupt the steps which then meander and lead to a rougher surface with a larger mean

square height $<h^2>$ in the ensemble average. This is a state of lower free energy because of the configurational entropy of the many possible kink arrangements. The general trend with temperature is also understood from the entropy argument. To understand the specific behaviour of Ni(113) was the object of our study.[4]

Proceeding in the same general way as for W(001), we measured the lineshape of the first order CTR near to the point $(\bar{6}\bar{6}4)/11$ as shown in Fig. 2. The CTRs for a (113) surface are lines of diffracted intensity emanating from each Bragg point of the bulk reciprocal lattice that join together as shown. For a perfect flat surface, the intensity varies as $1/\sin^2 q_z/2$ where q_z is measured perpendicular to the surface, (113) here, in appropriate units such that it diverges at each Bragg point.[3] A rough surface *without correlations* has a modified profile.[4,7]

$$I(q_z) \propto \frac{1}{\sin^2 q_z/2} e^{-4<h^2>\sin^2 q_z/2} \tag{3}$$

Thus the greatest sensitivity to roughness $<h^2>$ is at the mid-point of the CTR, $q_z = \pi$. The point we have chosen is close to this condition and has the advantages of the grazing incidence geometry (fig. 2). Note that q_z is not simply the perpendicular component of momentum transfer; it is offset by the centering of the reciprocal lattice. Thus an in-plane measurement can still give information about the vertical structure, as it does here.

The profile of the diffraction according to eq. (3) is still an ideal δ-function. However when in-plane height correlations are present the new form is

$$I(q_x q_z) \propto \frac{1}{\sin^2 q_z/2} \sum_q e^{iq_x\xi} e^{-4<h(\xi)-h(o))^2>\sin^2 q_z/2} \tag{4}$$

where q_x represents both in-plane components of momentum transfer. We can identify the second exponential in eq. (4) as the correlation function, whose Fourier transform gives the the in-plane lineshape.

Broadening of the diffraction was indeed observed for Ni(113) at high temperatures. For the sake of quantifying the effect, without any justification,

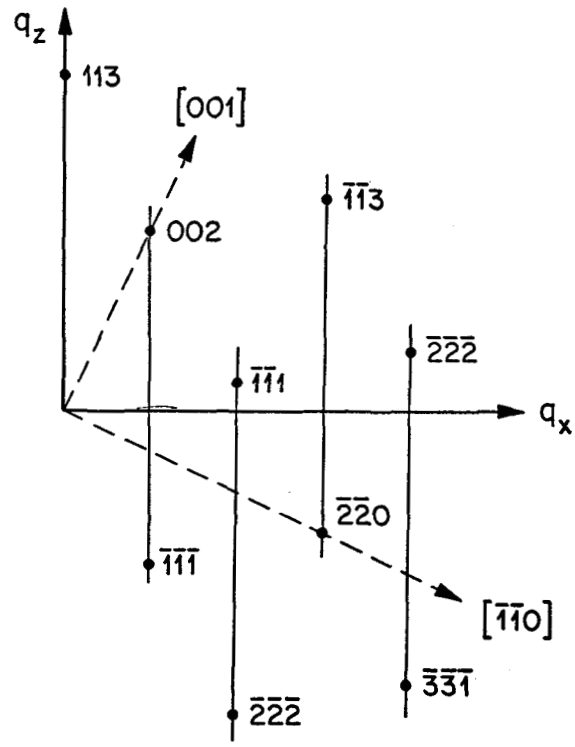

Figure 2. Reciprocal space diagram for a face-centered cubic (113) surface. q_z is along the surface normal, q_x is parallel to the surface in the directions perpendicular to the step and terrace formations. Crystal truncation rods (CTRs) emanating from each Bragg peak (dot) join up to form periodic lines of diffraction as shown.

we used eq. (1) to describe the diffraction once again convolving the known resolution function. This led to good 2D fits with $\chi^2 < 4$ for all temperatures. The width variation is shown in Fig. 3 and is somewhat analogous to the behaviour of W(001) with a dramatic rise above 750K. Here, however, the anisotropy of the diffraction, as measured by the width ratio, becomes greater with temperature. This indicates that order is lost more rapidly between the steps in the surface than along them.

Roughening is clearly apparent from the loss of intensity at this position (not shown) and is in qualitative agreement with previous work on Cu(113)[13] although no lineshape changes were seen in that study. Detailed comparison with theories of roughening is beyond the scope of this article and will be published elsewhere.[4]

V. The Pt(110) Surface

This shows the most complex behaviour of the three metals: it appears to be a case intermediate between roughening and order-disorder. Our preliminary results are partially summarized here and published elsewhere.[14]

Pt(110) has the same 1×2 missing row structure as Au(110).[15] Like Au(110) it has a phase transition in which the half-order intensity is seen to "vanish".[16,17] The peak intensity of half-order diffraction for both surfaces is shown in Fig. 4, which illustrates the similarity of the phase transitions. For the time being we will assume the analogy to be complete and regard both surfaces as the same. LEED lineshape analysis of the Au(110) phase transition has demonstrated the loss of a sharp Gaussian component in favour of a broader Lorenzian lineshape whose height is peaked slightly above the transition and whose width is a minimum there.[16] This is all in quantitative agreement with the predictions of the 2D Ising model and has been supported by Monte Carlo simulations too.[18]

However, this ignores one very important aspect of the Au(110) surface: The

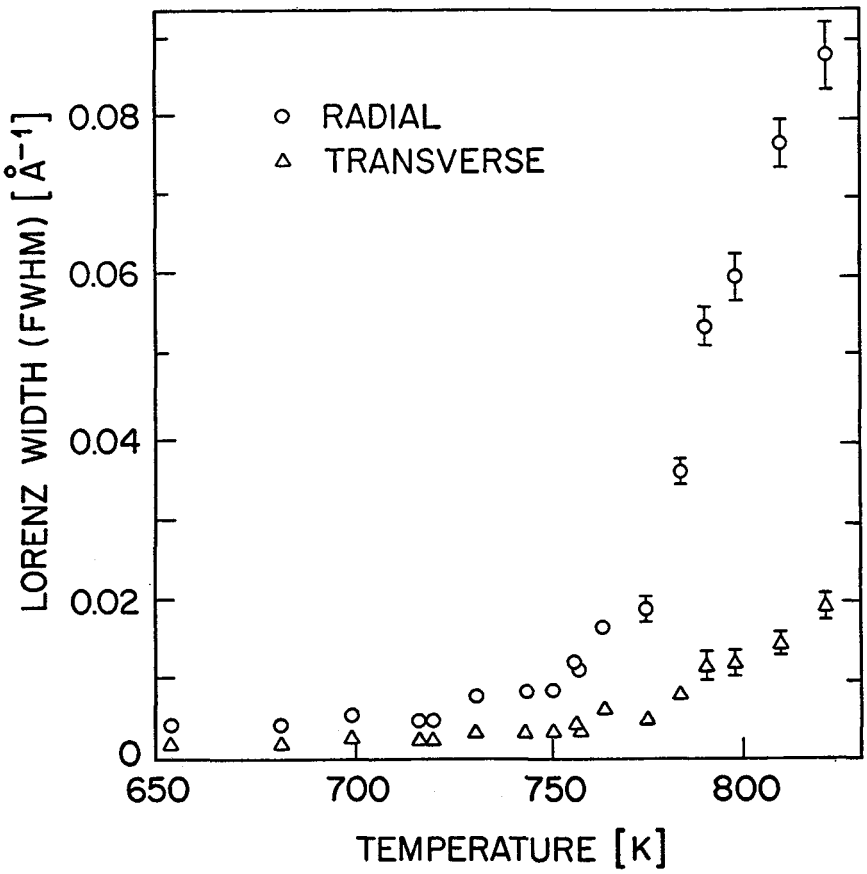

Figure 3. Fitted peak widths as a function of temperature for Ni(113) measured at $(\overline{6}64)/11$. Fits are to Lorenzians as in eq. (1) convolved with known Gaussian resolution parameters. Roughening is clearly apparent, at 715K.

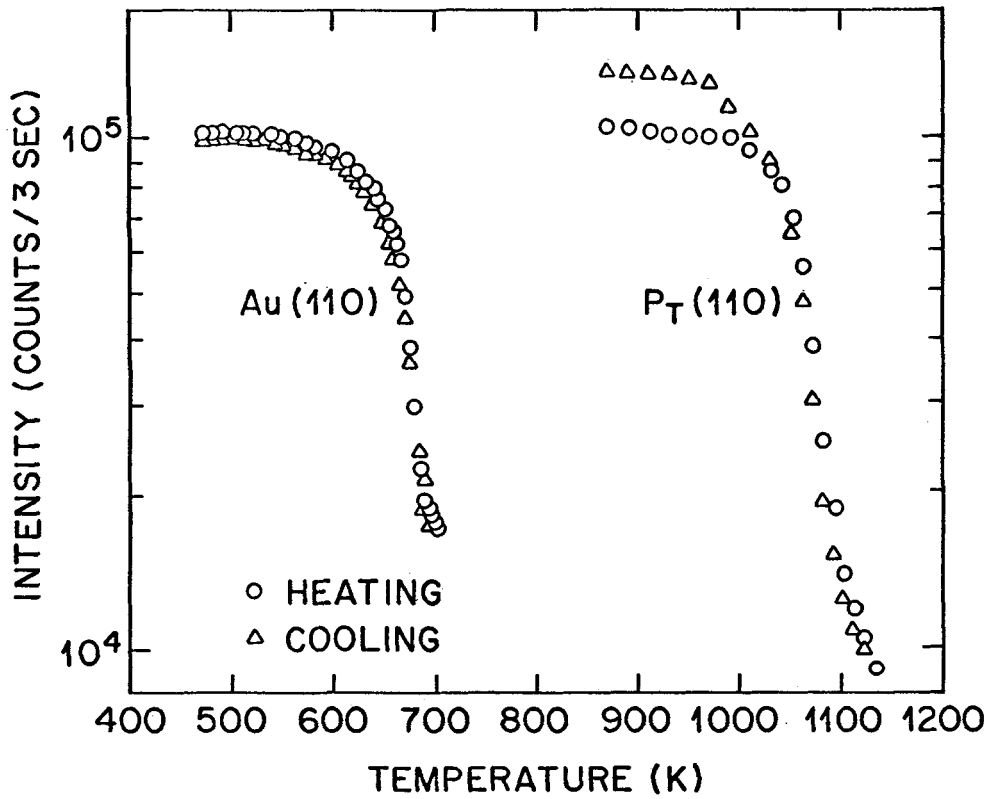

Figure 4. Comparison of the diffraction peak intensity at (1.505, 0, 0) as a function of temperature for Au(110)[17] and Pt(110). A reversible phase transition is seen. The slight gain in intensity upon cooling is probably due to sample annealing.

presence of steps. Earlier x-ray diffraction work on Au(110) found that the half-order peaks were both shifted and broadened. This was directly attributed to a distribution of monoatomic steps on the surface with a spacing of 200Å on average.[19] The LEED study saw a broad lineshape at low temperature with the same width but did not see a shift of the peak.[16] It is possible this was overlooked or obscured by nonlinearities in the optics or by dynamical effects. It is also possible that the electron energy was chosen so as to null the shift.[20] Steps are present on the Pt(110) 1×2 surface also, as the shifted peak in Fig. 5 testifies. The distribution of steps, reflected in this lineshape, changes with the preparation conditions, especially the annealing time, but was never narrower or less shifted than the example (c) shown.

At high temperature Pt(110) undergoes changes of lineshape associated with the loss of peak height shown in Fig. 4. The half-order peak becomes broader in both directions. This is similar to the uniaxial broadening of the Au(110) peak studied by LEED.[16] However, the peak shift also changes in the manner shown in Fig. 6; this was not seen in LEED.[16] To obtain these data the low temperature asymmetric lineshape of Fig. 5 was convolved with a 2D Lorenzian as in eq. (1), which includes the effects of resolution. It is clear from Fig. 6 that the density of steps, as evidenced by the shift, increases with T above the phase transition. Consequently some of its character is that of a roughening transition. If steps were the only source of disorder there would be a shift approximately equal to the half-width,[19] which is not the case here. The simple single layer Ising model cannot be a good description though. In the Monte Carlo study the reconstruction was deliberately confined to a single layer;[18] it would now be interesting to extend that work.

VI. Conclusions

X-ray lineshape analysis is clearly a useful method of characterizing surface phase transitions. Line broadening in both in-plane directions is seen in all three cases studied, with clear anisotropy. It is striking and rather alarming

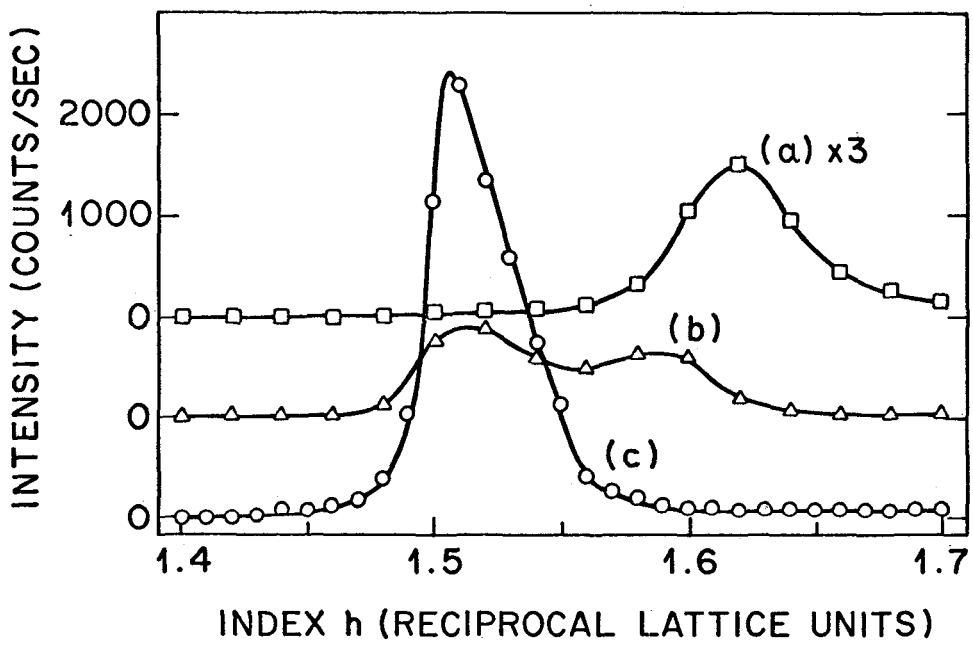

Figure 5. Lineshapes of the (3/2 0 0) surface peak for Pt(110) at different stages of preparation. The scan is radial, along (h 0 0). a) Before sputtering b) after a few hours of cleaning c) final asymptotic lineshape. The shift of the peak from the exact position at h = 1.50 is due to the presence of surface steps.[19] The magnitude of the shift relates to the step density; the overall lineshape relates to their distribution.

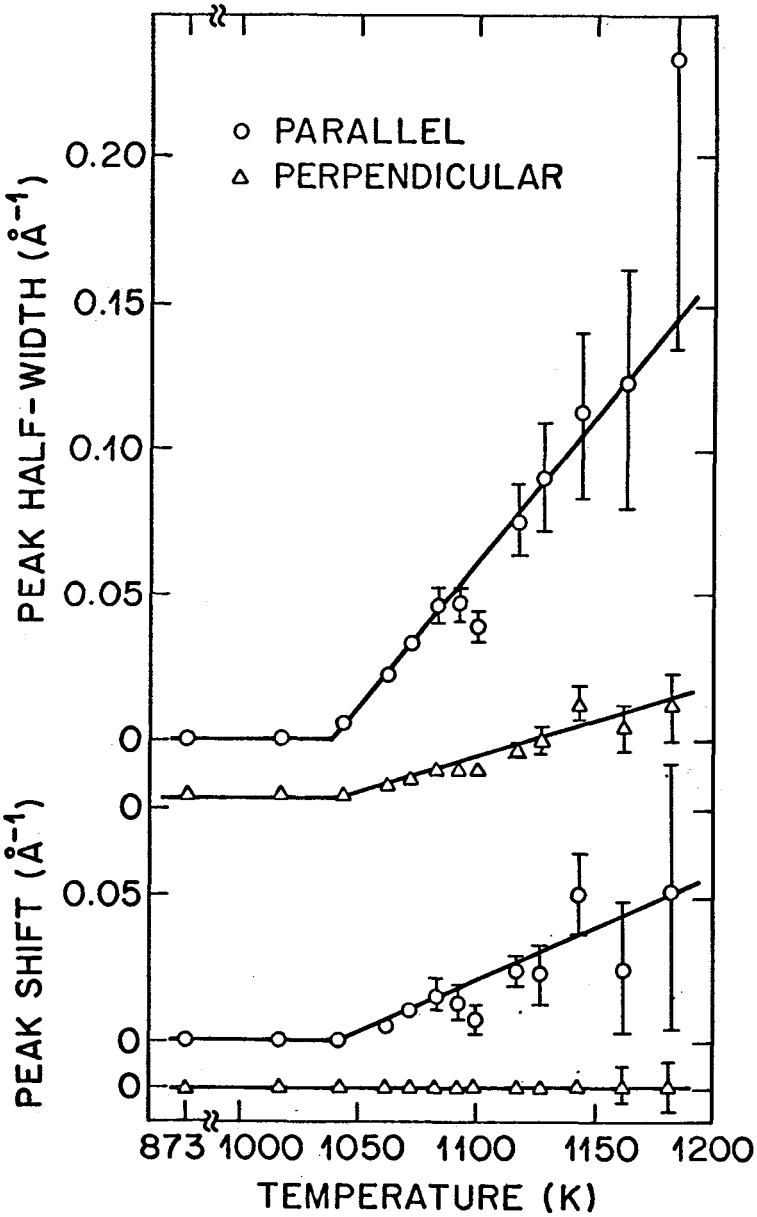

Figure 6. Fit parameters for the (3/2 0 0) surface diffraction peak of Pt(110) as a function of temperatures. The phase transition at 1040K is clearly delineated in all curves. The radial shift of the peak shows that steps appear above the transition, which therefore has the character of a roughening transition.

that roughening and order-disorder transition show qualitatively similar trends with temperature whereas these are expected to be very different. The quality of data presently available (Figs. 1, 3 and 6) is insufficient to distinguish clearly between these cases. The limitations are believed to be with the surfaces themselves, made inhomogeneous by the presence of defects and impurities. One further similarity between the three systems is the wide temperature range over which the critical behavior is seen: of order 100K, compared with $<$1K for bulk phase transitions.

The case of Pt(110) is special because roughening, due to proliferation of steps, leads to a characteristic peak shift as well as broadening. This should permit separate quantitative estimates of the extent to which its phase transition is order-disorder (within one layer) and the extent to which it is roughening (multilayer). Better data are already available and will be analyzed soon.[14]

SSRL is supported by the DOE Office of Basic Energy Sciences and NIH Biotechnology Resource Program. NSLS is supported under DOE Grant No. DE-AC012-76CH000016.

References

1. M. E. Fisher, Rep. Prog. Phys. *30*, 615 (1967).
2. H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena" Oxford Univ. Press (1971).
3. I. K. Robinson, Phys. Rev. B *33*, 3830 (1986).
4. I. K. Robinson, E. H. Conrad, D. B. Moore to be published.
5. D. E. Moncton, G. S. Brown, Nucl. Inst. Meth. *208*, 579 (1983).
6. J. A. Howell, P. Horowitz, Nucl. Inst. Meth. *125*, 225 (1975).
7. S. G. J. Mochrie, Phys. Rev. Lett. *59*, 304 (1987).

8. I. K. Robinson in "Handbook on Synchrotron Radiation" vol. 3 ed. D. E. Monctron, G. S. Brown (North-Holland, 1989).

9. H. Dosch, L. Mailander, A. Lied, J. Peisl, F. Grey, R. L. Johnson, S. Krummacher, Phys. Rev. Lett. *60*, 2382 (1988).

10. M. S. Altman, P. J. Estrup, I. K. Robinson, Phys. Rev. B *38*, 5211 (1988).

11. J. W. Chung, PhD Thesis, Brown University, Providence RI (1986).

12. I. K. Robinson, A. A. MacDowell, M. S. Altman, P. J. Estrup, K. Evan Lutterodt, J. D. Brock, R. J. Birgenean, Phys. Rev. Lett. *62*, 1294 (1989).

13. K. S. Liang, E. B. Sirota, K. L. D'Amico, G. J. Hughes, S. K. Sinha, Phys. Rev. Lett. *59*, 2447 (1987).

14. I. K. Robinson, K. Kern, National Synchrotron Light Source Annual Report (1988); K. Kern, E. Vlieg, I. K. Robinson to be published.

15. P. Fery, W. Moritz, D. Wolf, Phys. Rev. B *38*, 7275 (1988).

16. J. C. Campuzano, M. S. Foster, G. Jennings, R. F. Willis, W. Unertl, Phys. Rev. Lett. *54*, 2684 (1985).

17. I. K. Robinson, R. Feidenhans'l, M. Sauvage, National Synchrotron Light Source Annual Report (1987).

18. M. S. Daw, S. M. Foiles, Phys. Rev. Lett. *59*, 2756 (1987).

19. I. K. Robinson, Y. Kuk, L. C. Feldman, Phys. Rev. B *29*, 4762 (1984); I. K. Robinson in "Structure of Surfaces" ed. M. A. van Hove, S. Y. Tong (Springer Berlin, 1985).

20. P. Fenter, T. M. Lu, Surf. Sci. *154*, 15 (1985).