Surface Diffraction at the NSLS

I. K. Robinson
Department of Physics
University of Illinois at Urbana-Champaign
Urbana IL 61801

The first surface x-ray diffraction experiments were made at AT&T Bell Laboratories at the end of the 1970's by Eisenberger and Marra [1], just as the final plans for the NSLS were being drafted and the construction was getting under way. These were rotating-anode-based experiments on the Ge(100) surface in which the surface structure was determined correctly. This dramatically proved the feasibility of the technique. The small signals of 1 count per second obtained were a particular limitation in an experiment where the surface itself only remained alive for a limited period because of residual gas in the vacuum system. Surface diffraction was therefore one of the visions on the horizon of new possibilities in the minds of the first PRTs to build at NSLS and several groups considered this to be one of the reasons to start thinking about synchrotron-based programs, where several orders of magnitude increases of flux would be available. The PRT groups that included surface diffraction in their original plans were from BNL Physics (X22), SUNY (then X21), IBM-MIT (X20) and AT&T (X16).

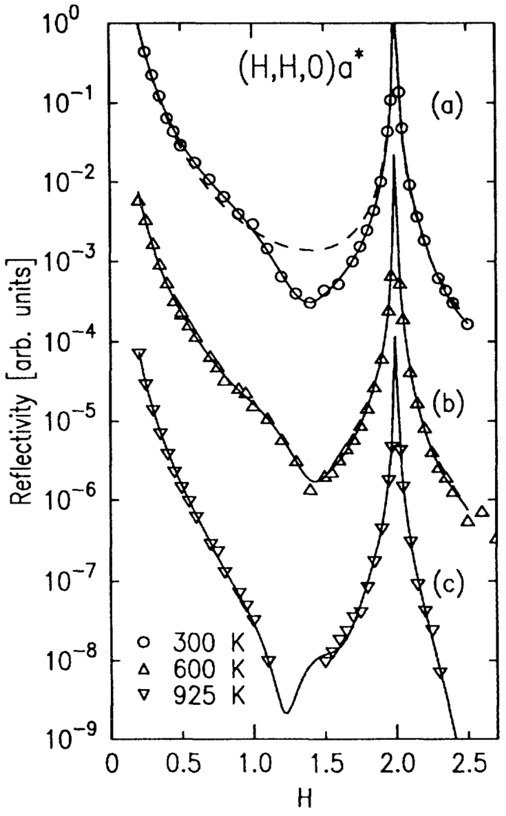

Figure 1. Specular reflectivity profile (00L crystal truncation rod) of Cu(110) measured by Helgesen et al of X22C at the three temperatures indicated [2].

Today the original groups are still active and many more have joined. Table I lists the beamlines that have developed the necessary instrumentation. It also lists the affiliations and principal investigators involved with these developments at the last count. The continuing health of the field can be gauged by the large number of new proposals to build beamlines at the Advanced Photon Source (APS) that involve equipment to carry out surface diffraction. I will not attempt to describe the details of the experimental methods, except to outline the hardware requirements and then devote the rest of this article to summarizing a number of important scientific developments in the field that all took place at NSLS in the last year.

The technique differs from traditional x-ray diffraction only in the sense that the sample environment is as bulky and complex as the diffractometer itself, so requires a rather specialized design. The sample environment is a ultra-high vacuum (UHV) system capable of 10^{-10} torr pressure, which is usually several hundred kilograms in weight. From table I it is clear that the community is divided in its choice of solutions, roughly half electing to carry the weight fully on the axes of the diffractometer, the others engineering a way to pass the precise motions through the vacuum wall to the sample inside. Some of the designs are hybrids and have been labelled somewhat arbitrarily. The diffraction measurements that inform us about the surface of a crystal are those that lie in between the Bragg reflections of the bulk crystal. The intensities are weaker typically by the ratio of the volumes of the surface to bulk regions probed (squared) or 6 to 8 orders-of-magnitude.

The thermal properties of the clean Cu(110) surface have been probed in experiments carried out by G. Helgesen et al [2] from the BNL Physics department on beamline X22C. The data, shown in figure 1, consist of X-ray reflectivity profiles as a function of temperature, extending from the origin to beyond the first Bragg peak. The bulk peaks, at H=0 and H=2 on the horizontal scale used, are substantially taller than the logarithmic vertical scale can display. Since the reflectivity function, suitably normalized, is the same as one of the crystal truncation rods [3, 4], these data were analyzed using the standard kinematic theory. The asymmetric minimum indicates that the top surface layer is contracted at all temperatures, but its inward shift with T reports that the magnitude of the contraction (relative to the lattice itself) diminishes with T, demonstrating the property of anomalous thermal expansion of the surface, in this case three times larger than the bulk.

The detailed analysis that provided the theory curves through the data of figure 1 also included a stack of layerwise thermal vibration amplitudes, also evaluated as a function of T. Clear anharmonic contributions were seen, as evidenced by the upward bending of the curve of amplitude versus T, starting about 700K for the top two layers of Cu(110). Deeper layers were found to have the same linear dependence as the bulk. These anharmonic effects amount to a three-fold enhancement in the top-layer amplitude by 920K. This study found no roughening transition in the range 300-920K, and saw only the anharmonic corrections to the classical Debye model of thermal vibration, as had an earlier He atom scattering investigation by Zeppenfeld et al [5].

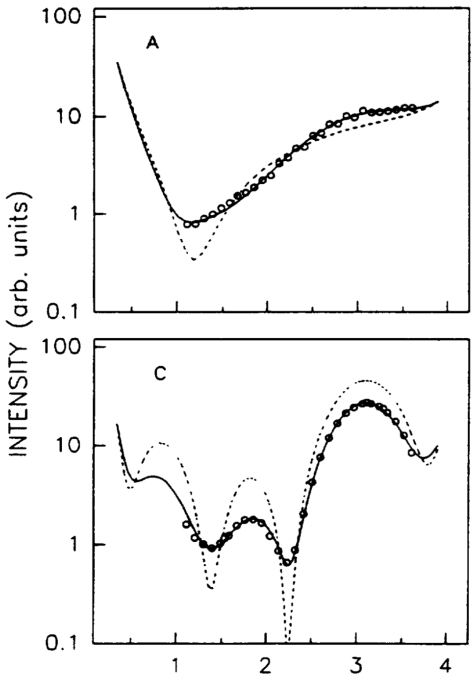

Figure 2. Specular reflectivity profile (00L crystal truncation rod) of Xe multilayers on Ag(111) measured by Dai et al of X18A at coverages of approximately 1 (top panel) and 3 (bottom panel) monolayers [6].

The structure of thin Xe films on Ag(111) was the subject of recent experiments carried out on beamline X18A, also using specular reflectivity. After the considerable technical accomplishment of cooling the substrate to 33K under UHV conditions, P. Dai et al from the University of Missouri observed the characteristic intensity oscillations associated with the growth of Xe films formed by dosing from a differentially pumped nozzle [6]. The data shown in figure 2 correspond to interruptions in the growth after approximately 1 and 3 monolayers. The curves that accurately describe the data required the adjustment of occupation parameters in multiple layers, indicating a progressively increasing roughness of the film with thickness, as might be expected if the lateral diffusion of physisorbed Xe at 33K were severely limited.

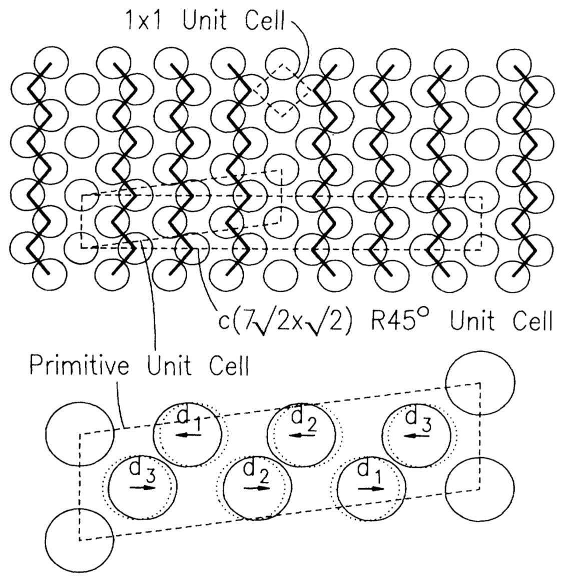

Figure 3. Structural model of the clean 7rt2xrt2 Mo(001) surface determined by Smilgies et al of X16A [7].

The structure of the clean Mo(001) surface was investigated by D. M. Smilgies et al on beamline X16A [7]. Measuring this low-temperature reconstruction with x-ray diffraction was a major tour de force because of its extreme sensitivity to hydrogen contamination; even then, it could only be studied for 8 minutes following each preparation. The structure was found to have the 7rt2xrt2 symmetry recently identified by helium scattering experiments. Figure 3 shows how this is made up of alternating striped regions that locally resemble the W(001) reconstruction, with its familiar zig-zag chain pattern of displacements. The three independent sideways displacements shown are 0.23 Å, 0.23 Å and 0.21 Å respectively, indicating a uniformly displaced structure. The value for W(001) was 0.24 Å. The similarity of Mo and W is attributed to the similarity of the 4d and 5d orbitals that are primarily responsible for cohesion in the solid.

The antiphase relationship of the stripes and the domain walls of undisplaced surface Mo atoms between them, highlighted by the dashed mirror lines in figure 3, is the feature that is novel to Mo(001). It is probably associated with a surface phonon, seen by helium atom scattering, that appears to soften upon cooling and freeze at the same temperature (120K) and same q-vector (3/7 of the <11> zone boundary) as the ordered phase. It has been proposed that this arises because of electron-phonon interactions within a charge density wave.

Surface critical exponents on Si(113) were measured in experiments carried out by D. L. Abernathy et al of MIT on beamlines X20 and X25 [8]. Si(113) was selected for these experiments because it the surface undergoes a phase transition at 959K, below which it is ordered and flat and above which it disorders continuously by introducing surface steps. What makes the phase transition interesting is that there are only two possible kinds of monatomic steps which are inequivalent to each other, so the transition has the symmetry of the 3-state chiral Potts model, about which there have been some important theoretical predictions, untested by experiment before this study.

Because of the chirality, the surface diffraction peak position is no longer tied to the 1/3-order position above the transition. The displacement in k-space, which is the incommensurablity along with the peak widths, Δx and Δy, are plotted versus reduced temperature, t, in log-log format in figure 4. All three parameters vary as power laws of t as expected, but the numerical values have considerable significance: they do not conform to the established theories depicted by the dashed lines in the figure. This question is a challenge for further theoretical study.

These four recent examples demonstrate considerable progress in the sophistication of the surface science problems being addressed over the 12 years since the first work of Eisenberger and Marra [1]. I believe it is accurate to state that more than half of the surface x-ray diffraction experiments ever performed have taken place at NSLS. Many of the results, particularly where high resolution is involved, have changed the face of the surface science field altogether. The reliable structure determinations have shown chemists that the surface affects the crystal structure not just in one layer of atoms but for many layers below. The work on two-dimensional ordering transitions has had important consequences for the corresponding theory. Best of all, there has arisen an altogether new branch of physics, which we might call `surface statistical mechanics' that concerns the thermal properties of surfaces. The x-ray diffraction experiments have stood almost alone in showing that a surface is not at all an inert slice through a bulk crystal, but has its own thermal expansion and vibration amplitudes, can have its own melting point and even has its own unique class of phase transitions, which lie between two and three dimensions, called roughening transitions.

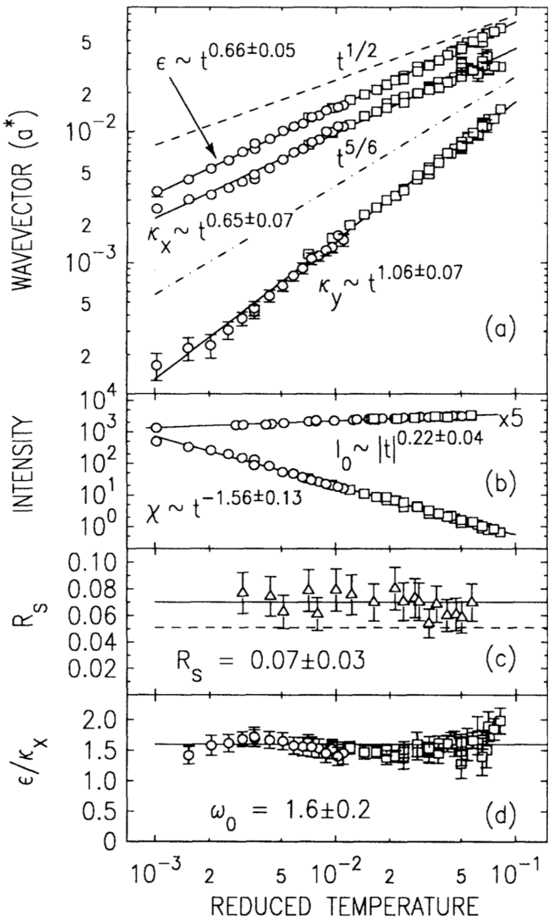

Figure 4. The incommensurablity along with the peak widths, Δx and Δy, versus reduced temperature for Si(113) above its disordering temperature. These data were measured by Abernathy et al of X20 [8].

Increasingly at NSLS, there is outside user participation in the surface x-ray diffraction facilities listed in Table I. Historically this has been relatively rare because of the difficulty of learning how to use the complex instrumentation. Brave users are seeing the advantages to their own research programs and so are becoming less intimidated. Many of these are scientist who are planning to build up programs associated with the APS, and would like to dirty their hands before sitting down to the drawing board. This certainly should be encouraged from the educational point of view, to say the least. Interested users should not hesitate to contact the individuals listed in table I about access.

References

1. P. Eisenberger and W. C. Marra, Physical Review Letters 46 1081 (1981)
2. G. Helgesen, D. Gibbs, A. P. Baddorf, D. M. Zehner and S. G. J. Mochrie, Physical Review B 48 15320 (1993)
3. I. K. Robinson in Handbook on Synchrotron Radiation, vol. III, pp 221-266, ed. D. E. Moncton and G. S. Brown (Elsevier, North-Holland, 1990)
4. I. K. Robinson, Physical Review B 33 3830 (1986)
5. P. Zeppenfeld, K. Kern, R. David and G. Comsa, Physical Review Letters 62 63 (1989)
6. P. Dai, T. Angot, S. N. Ehrlich, S. K. Wang and H. Taub, Physical Review Letters 72 685 (1994)
7. D. M. Smilgies, P. J. Eng and I. K. Robinson, Physical Review Letters 70 1291 (1993)
8. D. L. Abernathy, R. J. Birgeneau, K. I. Blum and S. G. J. Mochrie, Physical Review Letters 71 750 (1993)

TABLE I

Surface diffraction instrumentation at NSLS

Beamline	Institution	Constructed by (group of)	Design
X3	SUNY	Peter Stephens	2-circle FT
X10	Exxon	Kevin D'Amico Keng Liang	5-circle FT
X16	AT&T	Paul Fuoss Ian Robinson	5-circle FT
	AT&T	Ken Evans-Lutterodt	Portable
X18	U. Missouri	Hak Taub	Portable
X20	IBM	Paul Horn	Portable
	IBM	Glenn Held	4-circle FT
	MIT	Bob Birgeneau	Portable
	MIT	Simon Mochrie	5-circle FT
X22	BNL Physics	Doon Gibbs	4-circle FT

Notation used:
n-circle FT Static vacuum chamber with precision feedthrough (FT) is coupled to a diffractometer with n orientational degrees of freedom. 5-circle designs include additional rotation of incident beam or detector. 6-circle would include both.

Portable Vacuum chamber is mounted on diffractometer.