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Second Layer Displacements in the Clean Reconstructed W(100) Surface

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X-ray diffraction is gaining acceptance in the surface science community as a method for determination of surface structure. Its biggest strength is that it is a kinematical diffraction technique, unlike LEED or atom scattering, so that intensity information may be interpreted by simple wave superposition methods, such as Fourier transformation. The field of x-ray crystallography has developed many powerful methods for finding the positions of atoms in crystals. The main disadvantage, intimately related to the kinematical approximation, is that the cross section of a monolayer is in the range 10^{-5} to 10^{-6}, so intense sources of x-rays must be used. Diffraction from the bulk can also cause background problems, but not in the study of reconstructed surfaces, where fractional-order reflections arise only from the surface layer(s), and can always be separated. Some surface structures determined recently with x-rays are InSb(111) 2×2 [1] and Au(110) 1×2 [2].

The W(100) surface reconstructs below room temperature to form a $\sqrt{2}\times\sqrt{2}$ (c2×2) structure first seen with LEED [3]. A structural model involving zig-zag displacements of the top layer in the pattern of fig 1(a) was proposed by Debe and King (DK) [4] as being the simplest structure consistent with the lower (2-fold) symmetry of the LEED pattern sometimes observed (probably stabilised by steps). This structure has been confirmed by LEED intensity analysis, giving a lateral displacement of 0.16 Å and a contraction of the top layer spacing of 6% [5,6]. Total energy calculations [7,8] support the picture as well, agreeing that the truncated-bulk surface would be unstable to this kind of distortion, either because of a soft surface mode [7] or partial covalent bond formation [8]. The phonon spectrum has also been calculated and measured [9].

We have measured the intensities of the (1/2, 1/2, $q_\perp$), (3/2, 1/2, $q_\perp$) (3/2, 3/2, $q_\perp$) and (5/2, 3/2, $q_\perp$) reflections as a function of perpendicular momentum transfer, $q_\perp$. Examples of these "rod profiles" are given in fig 2. The sample was cleaned initially by annealing in 10^{-7} torr O_2 at 1400K. Prior to each scan, the sample was flashed to 2300K

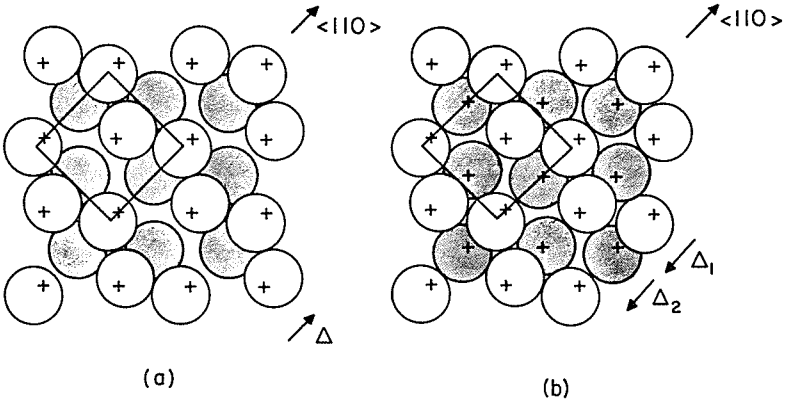

Figure 1 . (a) Model of W(100) with a single reconstructed layer. The $\sqrt{2}\times\sqrt{2}$ unit cell contains two atoms with equal and opposite displacements. (b) New model with second layer displacements.

and then cooled to 175K. The base pressure of the vacuum system was in the low 10^{-10} torr range and no detectable change of intensities with contamination was observed over the 30 minutes measurement time between flashes. A powerful 60 kW rotating anode source of x-rays (Cu K_α , 1.54 Å wavelength), pyrolytic graphite monochromator and analyser, and 4-circle diffractometer were used for the measurements. Each intensity point in fig. 2 was integrated over sample mosaic, background-subtracted, then corrected for polarisation, Lorentz factor and sample area [10]. The maximum signal observed was 14 c/s.

If the reconstruction of W(100) were confined to a single layer, as the DK model suggests, the diffraction pattern would be ideally two-dimensional: it would show a gradual decline of intensity with $q_\perp$ due to the W form factor (the finite size of the core shells) and its Debye Waller (DW) factor (thermal motion). This is shown as a dashed curve in fig. 2, and clearly does not explain the modulation observed. Instead the sinusoidal modulation, with the period of the bulk reciprocal lattice, tells us that 2 layers are reconstructed and their diffracted waves are beating against each other. The amplitude of the modulation gives us the relative contributions from the two layers. The four rods measured have modulation amplitudes ranging from 39% to 50%; to the extent that these are the same, we are informed that the four Fourier components for each layer scale together, hence that the two layers have the same structure. The phase of the modulations is such that (1/2, 1/2, 0) and (3/2, 3/2, 0) are minima, while (3/2, 1/2, 0) and (5/2, 3/2, 0) are maxima; this is only consistent with one

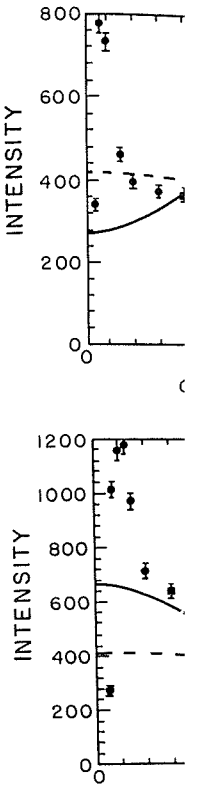

Figure 2 .(a)
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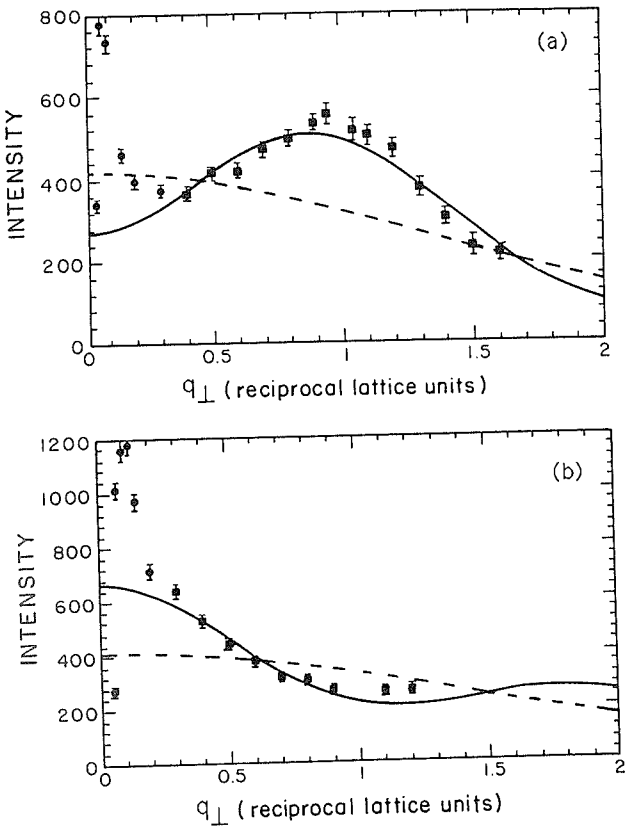

Figure 2 .(a) Intensity of the (3/2, 3/2, $q_\perp$) and (b) intensity of the (3/2, 5/2, $q_\perp$) rods of diffraction from W(100) measured at 175K. The abcissa is momentum transfer perpendicular to the surface, $q_\perp$, in units of $2\pi / a_o$ ($1.99 Å^{-1}$ for bulk W). The full curve is the result of least squares fitting; the dashed curve shows the effect of removing the second layer displacements.

registration between the layers, that of fig. 1(b), which happens to be the normal body-centred cubic arrangement of bulk W.

The single domain structure factor for this model has a particularly simple form :

$$F(h, k, q_\perp) = A_{hk} + B_{hk}\, e^{\pi i\, q_\perp} \qquad (1)$$

where the coefficients for the two layers, A_{hk} and B_{hk}, are roughly proportional to the magnitudes of the (small) displacements in the layers, Δ_1 and Δ_2 :

$$A_{hk} = (-1)^{k-1/2} \sin(h + k)\, \Delta_1$$

$$B_{hk} = (-1)^{k+1/2} \sin(h + k)\, \Delta_2$$

Thus the modulation amplitude of the intensity along the rod, $2|B/A|$, is the more or less same for all reflections, as observed. This gives us directly the ratio of the displacements in the layers, $\Delta_2/\Delta_1 \simeq 22\%$.

Also clearly visible in the rod profiles is the refraction "wiggle" at small $q_\perp$. This has a characteristic shape always seen in x-ray diffraction experiments when the incidence angle is close to the critical angle for total external reflection [11]. We used the symmetric, $\omega=0$, diffraction geometry [10] keeping the incidence and exit angles equal, which compounds the effect. We have not attempted to fit these features yet, and only considered the data points above grazing incidence.

Least-squares refinement of the structure factor (eq (1)) using the four half-order reflections then gave us the following structural parameters :

Top-layer displacement	$\Delta_1 = 0.22 \pm 0.015$Å
Second-layer displacement	$\Delta_2 = 0.044 \pm 0.015$Å
Interlayer separation	$d_{12} = 1.49 \pm 0.16$Å
Lateral DW factor	$B_{\|\|} = 0.1$Å^2
Perpendicular DW factor	$B_\perp = 3.7$Å^2

The last parameter corresponds to a vibration amplitude of 0.2Å ; we are not sure of its significance because it also includes the effects of static disorder in the form of surface roughness. The interlayer separation represents a contraction of 6% ± 10%. The fits shown in fig.2 were obtained in the structure factor calculation with these parameters. The agreement is good; the systematic part of the deviations may correspond to displacements in the third layer and below.

The existence of second layer displacements in W(100) does not alter the symmetry of the surface; indeed they might be expected from symmetry considerations, since the second layer atoms of the DK model (fig. 1(a)) lie in sites with only m point symmetry. They have been discussed in several theoretical papers [9, 12] but not seen experimentally before. With a magnitude of 20% of the top layer displacement, they are likely to make a significant modification to the calculation of total energy [7,8] of this surface. This will be

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particularly important in consideration of the relative energies of this $\sqrt{2}\times\sqrt{2}$ structure and that proposed for the H/W(100) surface with displacements along the {100} directions, in which the second-layer displacements would have a totally different symmetry.

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