Diffuse LEED and Surface Crystallography

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Diffuse low-energy-electron diffraction measurements at 46 eV for a disordered O/W(100) surface at 120 K have been interpreted by theory to give the local geometry of the oxygen atoms. This first application of the technique shows that phonon scattering does not prevent interpretation of data, and demonstrates sensitivity to surface geometry comparable with that in conventional LEED experiments on ordered surfaces. R factors for the optimum geometry are very low, indicating a highly reliable determination. The prospects for the use of this technique in a whole range of situations previously inaccessible to LEED are thereby opened.

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A knowledge of the surface crystallography is one of the most important inputs to the understanding of a surface. In recent years low-energy electron diffraction has established itself as one of the foremost surface structural techniques for ordered surfaces.[1-4] When disorder is present electrons are scattered out of the discrete beams that characterize diffraction from an ordered surface, a situation with which conventional theories cannot cope, thus closing a whole range of systems to LEED analysis. At the same time experimental diffuse LEED intensities contain a wealth of structural information. In the case we consider here, of a disordered adsorbate on a nearly perfect substrate, each electron contributing to the diffuse LEED pattern has scattered at least once from an adsorbate atom and therefore the diffuse intensities have concentrated within them information about the local environment of the adsorbate. In this respect there is an analogy with surface extended x-ray-absorption fine-structure (SEXAFS) experiments[5-9] which have been so successful in the elucidation of local structure at surfaces. In fact, a recently proposed theory of diffuse LEED[8,9] shows that the central process is precisely a SEXAFS event but one in which the electron has been introduced by an electron gun rather than by ejection of a core electron. Thus in principle the technique has the virtues of SEXAFS. In fact it has some advantages over SEXAFS because by variation of the incident angle of the electrons many independent data sets can be gathered and hence a richer mass of structural data is available for analysis. In contrast a SEXAFS experiment has at the most three data sets corresponding to the three polarizations of the x-ray beam.

Despite these advantages to the technique, doubts have remained about its experimental feasibility. Perhaps the major reservation is that in addition to the elastic diffuse scattering, many inelastic processes contribute to the diffuse wave field and separation of these contributions[10] can be an elaborate and time-consuming process in the case of phonon contributions. It is important that before we can regard diffuse LEED as a structural technique, it must be shown to work for a carefully controlled system. This paper reports for the first time experimentally measured diffuse LEED data compared with theoretical calculations. The R factor is extremely good with a value for R_P of 0.13 at optimum which compares favorably with the best conventional structural analyses.[11-18] Good sensitivity to the structural parameters is seen and we feel that the way has been opened for serious consideration of this new structural technique.

The W(100) surface was prepared according to prescriptions in the literature.[19] The well-known LEED spectra could be reproduced for the unreconstructed surface at room temperature. In order to reduce the thermal diffuse background and to avoid ordering of the adatoms, oxygen was made to adsorb at a low temperature of about 120 K. Unfortunately W(100) reconstructs below room temperature, and therefore adsorption of oxygen was allowed to an extent that the reconstruction was removed as indicated by the disappearance of extra spots. Consequently, a considerable amount of oxygen must cover the unreconstructed surface though no coverage measurement was performed. On the one hand, this increases the level of the diffuse intensities, but on the other hand it also increases adatom-adatom scattering, a feature so far not included in our theory. Fortunately much of the adatom-adatom effects can be cancelled by use of the Y function,[20] defined by

$$Y(E,\mathbf{k}_p)=L^{-1}/(L^{-2}+V_{0i}^2),$$

where $L=I^{-1}\,dI/dE$, and $I(E,\mathbf{k}_p)$ is the reflected intensity and V_{0i} is the imaginary part of the potential, for comparison with experiment as was suggested earlier[8] and is demonstrated below. Since for long-range correlations the intensity can be written as a product of form factor, I_0, and structure factor, S_M,

$$I(E,\mathbf{k}_p,\mathbf{k}_p')=I_0(E,\mathbf{k}_p,\mathbf{k}_p')S_M(\mathbf{k}_p-\mathbf{k}_p'),$$

the logarithmic derivative and hence the Y function are completely independent of S_M because of the absence of energy dependence in S_M. Multiple scattering between adatoms distorts this simple picture, but this

is in any case assumed small in our theory.

The diffuse intensities were measured by a computer-controlled TV method as described in detail in an earlier paper.[3,21] A low-noise TV camera views the luminescent LEED screen, with its diffuse pattern, from outside the ultrahigh-vacuum equipment. The pattern can be displayed at a monitor, Fig. 1(a). The video signal is simultaneously given to the processing computer via an interface. Through the computer's keyboard the size and position of a rectangular electronic window can be chosen, within which the intensities are wanted. The interface horizontally integrates the intensities within the window and delivers the result to the computer line by line. In the present experiments the window was a long, narrow slit resulting in the almost ideal vertical line profile through the pattern. The width of the window was $\frac{1}{24}$ of the distance between the 00 and 10 beams at 46 eV.

When the transfer of the window intensity to the computer is completed, the window can be shifted to another position as determined by the software. In the present experiments 24 windows were measured at 46 eV relative to the muffin-tin zero, between the 00 and 10 beams. So the reciprocal unit mesh is covered by a data grid of 24×24 points. From this the intensity distribution as displayed in Fig. 1(b) was constructed, cutting away the beam intensities of the substrate. Because of the sample holder and the limited screen extension, not all of the unit mesh could be measured as can be seen in Fig. 1(b). There is some background intensity even in the dark part of the pattern, e.g., at the sample holder and beyond the screen edge. This is mainly due to the camera dark level and was subtracted prior to the calculation of the logarithmic derivative and the Y function.

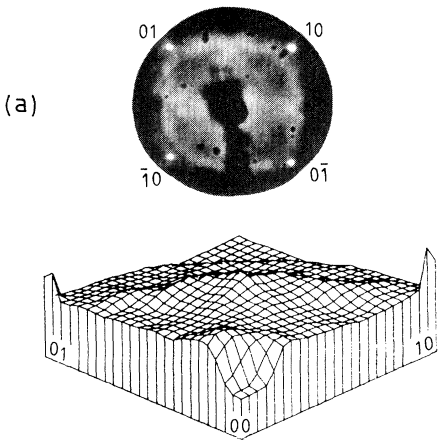

FIG. 1. Diffuse LEED intensities for O/W(100). (a) Experimental diffraction pattern for 46 eV. (b) Perspective graphical representation of the diffuse intensity distribution in the upper quarter of the photograph (a).

The whole measuring procedure works in real time according to the intrinsic TV times. So one single window is measured within the time for one TV half frame, i.e., 20 msec (European norm). In the original data the geometric structure of the wire grids can be seen. These are positioned in front of the LEED screen in order to repel inelastically scattered electrons. Therefore, the measured profiles were smoothed to an appropriate extent. The influence of screen defects [see Fig. 1(a)] was also removed by local smoothing. For the calculation of the Y function, all data had to be taken at at least two energies, in this case 46 and 48 eV relative to the muffin-tin zero. As the reciprocal space contracts on the LEED screen with increasing energy, the higher-energy data had to be reextended to the scale of the lower energy prior to calculation of the logarithmic derivative. The data handling required and more details of the measurement will be reported in a separate paper.[22]

Calculation of the diffuse low-energy-electron diffraction intensities proceeds in three steps.[8] First, we use a conventional LEED calculation to evaluate all electron paths up to the first collision with the disordered overlayer. Only an ordered surface is seen by this part of the scattering. Next we sum all events beginning with the first scattering from the adsorbate atom and ending with the last. It is this part of the calculation that resembles the theory of SEXAFS because it concerns a spherical outgoing wave being backscattered by the atoms surrounding the adsorbate. A cluster calculation is used in this step, the same one that is used in the theory of x-ray appearance near-edge structure.[23,24] The final step is calculation of all scattering events subsequent to the electron leaving the adsorbate atom for the last time. As in step 1 only an ordered surface is perceived by the electron in this step and conventional LEED programs are used but for a different value of parallel momentum, that corresponding to the appropriate point in the diffuse pattern.

The accuracy of this procedure has been demonstrated by comparison with a perturbation calculation,[9] the beam-set neglect method, developed by Van Hove, Lin, and Somorjai.[25]

Our calculations were performed for the two energies of 46 and 48 eV relative to the muffin-tin zero, to enable the Y function to be calculated. These energies correspond to 41 and 43 eV relative to the Fermi level. The imaginary part of the optical potential, V_{0i}, was taken to be -4 eV and five phase shifts were used to describe atomic scattering. In the conventional LEED part of the calculation, 37 beams were used in the multiple-scattering calculations, and in the cluster calculation a maximum angular momentum $l = 13$ was used.

Figure 2(b) shows the experimental Y function,

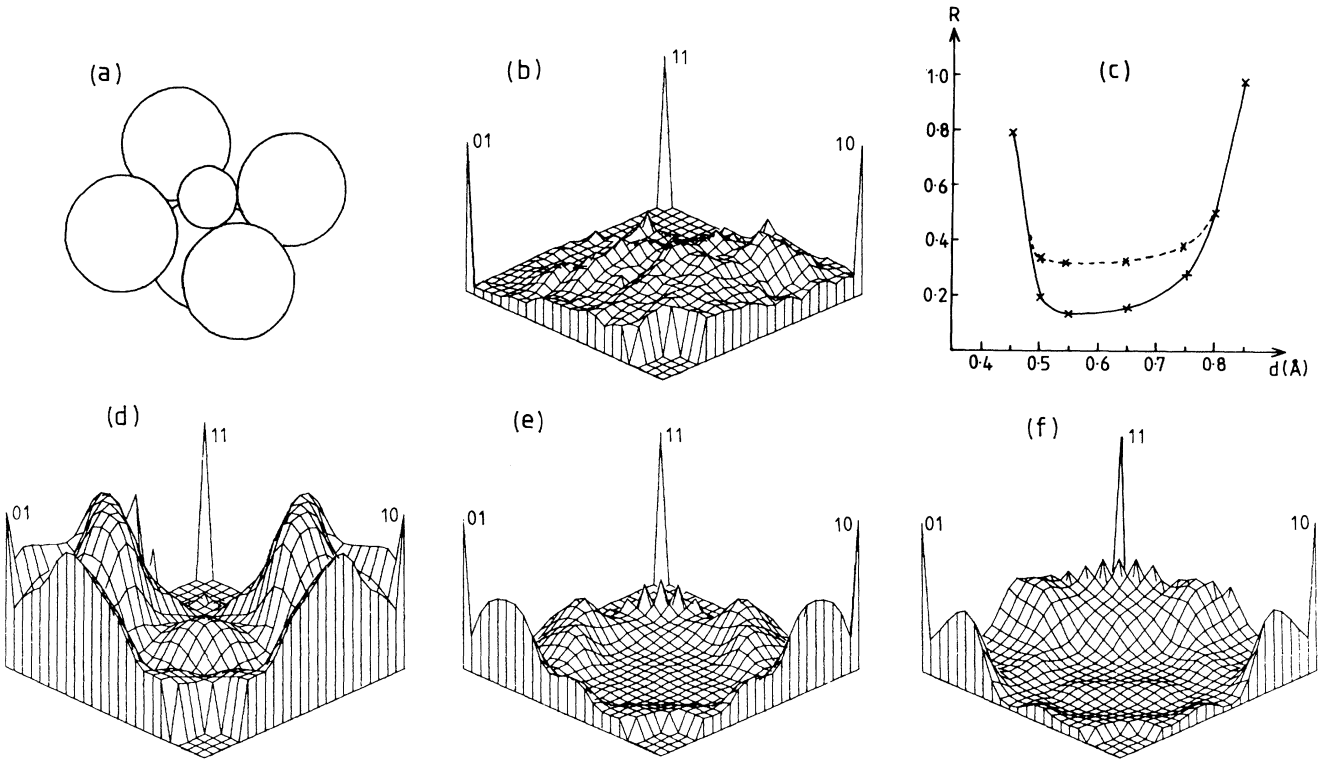

FIG. 2. Comparison of measured and calculated Y functions. (a) Perspective atomic model of the fourfold hollow site on W(100), in which the oxygen atom (small sphere) is believed to be adsorbed. Large spheres represent the tungsten atoms. (b) Experimental Y function calculated from diffuse intensity distributions at 46 and 48 eV after subtraction of a background level measured at the screen edge. The spikes at the positions of the 10, 01, and 11 Bragg spots join the minimum possible, -3.4, and maximum possible, $+3.4$, values of the Y function. Regions not available for measurement, i.e., at the sample holder and beyond the screen edge, are set to the negative maximum value, -3.4, but not included in the R-factor calculation in (c). (c) the reliability factor, R, comparing experimental and theoretical intensities as d is varied in the latter. A minimum is seen around the hard-sphere value of $d = 0.54$ Å. The solid line corresponds to an experimental Y function calculated after background subtraction from the original intensities; the broken line corresponds to no background subtraction. (d),(e),(f) The corresponding theoretical Y functions for $d = 0.45$, 0.55, and 0.65 Å, respectively. Regions not available for measurement are set to the negative maximum value as in (b).

compared in Figs. 2(d)–2(f) with the calculations for various positions of the oxygen atom in the fourfold hollow site at heights of 0.45, 0.55, and 0.65 Å, respectively, above the tungsten layer below. We did not try the bridge sites, nor the atop positions, considering them to be improbable for this system. We note that the patterns change quite markedly even for these small displacements. The absolute value of the Y function is important and it is clear that Fig. 1(e) agrees with experiment better than the other spacings. This qualitative conclusion is confirmed by a calculation of the R factor shown in Fig. 2(c). The importance of using the Y function to eliminate the effects of spurious oxygen-oxygen correlation from the data is demonstrated by reference to Fig. 3 which shows the theoretical intensities calculated for $d = 0.55$ Å. Reference to Fig. 1(b) shows little agreement between the intensities, indicating that in this system there exists strong correlation between oxygen sites which must be eliminated before meaningful comparison can be made with theory. This effect was anticipated in the earlier theoretical paper.[8]

Our conclusion is that oxygen sits in the fourfold hollow sites on a tungsten (100) surface at 0.55 ± 0.1

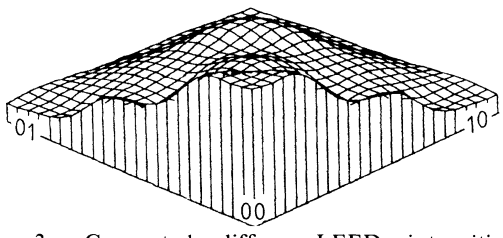

FIG. 3. Computed diffuse LEED intensities for O/W(100) for $d = 0.55$ Å.

Å above the last tungsten layer. This site is compatible with the radius of the oxygen atom and compares with the nitrogen-on-tungsten system which has been analyzed by conventional LEED: Nitrogen also sits in the fourfold hollows at a distance of 0.49 ± 0.06 Å.[26]

Of greater importance in the present context is that the feasibility of using diffuse low-energy-electron diffraction to determine surface geometry has been demonstrated. We have shown that (1) the phonon background does not seem to interfere with experiment-theory comparison, at least when the specimen is cooled to liquid nitrogen temperatures; (2) use of the Y function for experiment-theory comparison eliminates spurious correlations between adatoms which are not taken account of in the theory; (3) the method shows good sensitivity to the geometry of the adsorbate; (4) R factors obtained at the optimum geometry are amongst the lowest obtained for LEED systems.

We would point out that the present work makes only modest use of the power of the technique. The entire structure determination is based on the data available at only two electron energies; hence there is the potential for extension to complex systems, where a much larger data set would be needed to find the geometry. The way would appear to be open for extensive application of the method to a wide variety of adsorbate systems.

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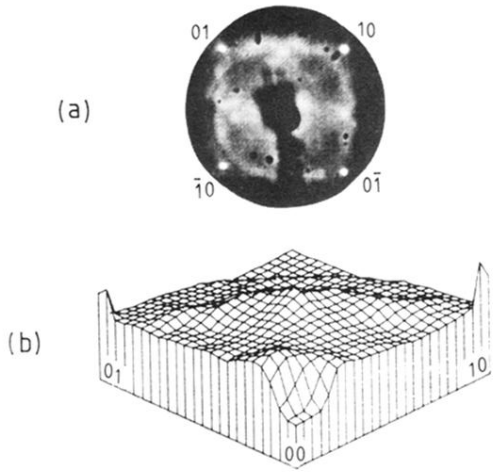

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