

Stability of low-energy electron diffraction fractional-order beam intensities and intralayer multiple scattering

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Low-energy electron diffraction (LEED) intensity measurements on adsorbed oxygen on Cu {001} at varying coverage and LEED calculations of spectra of adsorbed Al on Si {111} at several coverages show the fractional-order spectra to be remarkably independent of surface coverage. Such stability of the fractional-order spectra implies both negligible scattering between adsorbed atoms and the same substrate environment around each adsorbed atom. When such stability is found in LEED intensity measurements during adsorption experiments, the adsorbate environment can sometimes be determined by LEED intensity analysis for complicated structures and even for structures with no long-range order.

I. INTRODUCTION

Chemisorption of molecules or atoms on solid crystal surfaces leads often to ordered arrangements of adatoms in high-symmetry sites (superstructures), with periodicities equal to, or multiples of, those of the substrate surface. In many cases, particularly those involving one-quarter, one-half, or full monolayer coverage of the substrate surface by adatoms, the atomic arrangement can be determined reliably and precisely by a few techniques, foremost among which is low-energy electron diffraction (LEED).¹⁻⁴ Use of these techniques has been so far limited mostly to the end product of a chemisorption experiment. Great care is (or should be) exercised, at least in LEED experiments, to optimize the superstructure to be studied, i.e., to ensure the maximum coverage allowed by such superstructure. In LEED crystallography, intensity data are usually collected for a number of integral-order (or substrate) and of fractional-order (or superstructure) diffracted beams after optimization of the structure. Comparatively little attention has been devoted, at least in literature reports, to the evolution of a superstructure LEED pattern—and hence of the superstructure itself.

In this work we follow the superstructure LEED spectra as the superstructure evolves. We have made the noteworthy observation that in measurements on the system O/Cu {001} and in computations on the system Al/Si {111} the fractional-order spectra essentially do not change with coverage. In the first system the fractional-order spectra show quite diffuse spots, but the integrated intensity versus energy curve is measured as coverage changes. In the

second system calculations are made for a few ordered arrangements with different coverages. These observations have the intersecting consequence for LEED crystallography that adsorbate position can sometimes be determined in structures that are too complex for a complete analysis and even on a surface without long-range order.

II. OBSERVATIONS

A. Experiment

The experiment consisted of exposing a clean Cu {001} surface to low-pressure oxygen gas and observing the evolution of the LEED pattern. The Cu {001} substrate was cleaned *in vacuo* as described in an earlier publication,⁵ and the exposures to oxygen were made with the substrate at room temperature and with gas pressures of 5×10^{-7} Torr. LEED observations were made both immediately after exposure and after annealing treatments of 15 min at 450 °C. Figure 1 depicts schematically the changes in the LEED pattern with increasing exposure. Initially, we observed weak and broad intensity maxima in the center of each square characterizing the unit mesh of the substrate net [Fig. 1(a)]. With increasing exposure, these maxima coalesced into narrower maxima at the $\frac{1}{2}$ $\frac{1}{2}$ -order positions. In Fig. 1(c) the pattern can be described as $c(2 \times 2)$, or more precisely $(\sqrt{2} \times \sqrt{2})45^\circ$. Further exposure to oxygen, however, prompted the occurrence of scattered intensities at positions that ultimately characterized a $(2\sqrt{2} \times \sqrt{2})45^\circ$ pattern [Fig. 1(f)]. During this evolution,

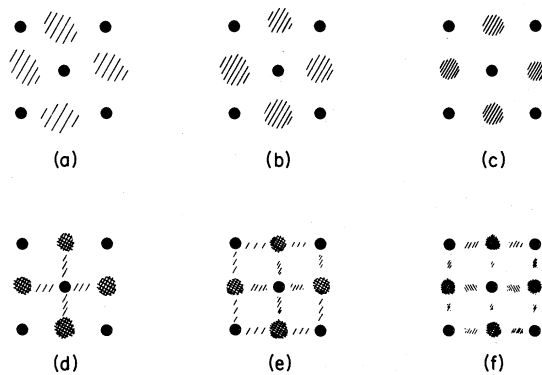


FIG. 1. Schematic changes in the LEED pattern from Cu(001) upon increasing exposure to oxygen: (a) 1×10^{-5} Torr min; (b) 2.5×10^{-5} Torr min; (c) 3.5×10^{-5} Torr min; (d) 5.0×10^{-5} Torr min; (e) 8.0×10^{-5} Torr min; (f) 13.0×10^{-5} Torr min.

the spectra (intensity versus electron energy) of the integral-order beam changed considerably, whereas those of the $\frac{1}{2}$ $\frac{1}{2}$ -order beams remained practically unaltered. Figure 2 shows the example of the 1 1 and the $\frac{1}{2}$ $\frac{1}{2}$ spectra for oxygen exposures ranging from 2×10^{-5} to 72×10^{-5} Torr min. Anneals of the substrate sharpened the LEED spots and improved the contrast but did not affect the shape of the spectra.

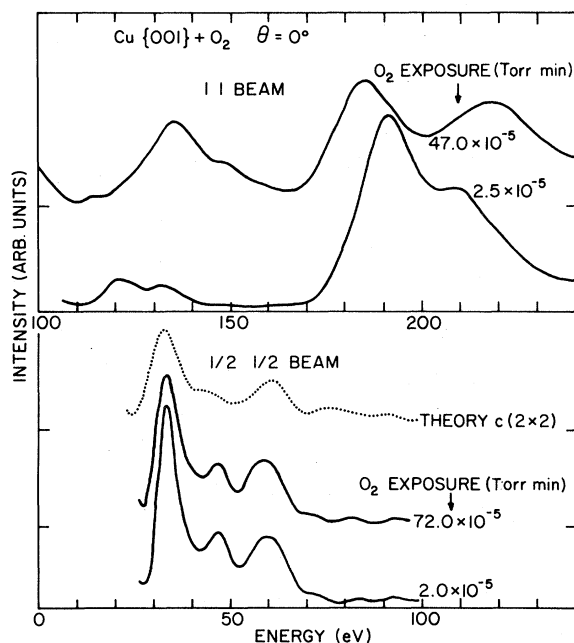


FIG. 2. Change of LEED 1 1 spectra (upper panel) and $\frac{1}{2}$ $\frac{1}{2}$ spectra with increasing oxygen exposure of a Cu(001) surface.

B. Computation

In the course of a study of the Si {111}- $(\sqrt{3} \times \sqrt{3})$ -Al structure,⁶ we calculated LEED intensity spectra for a variety of models. On two different occasions we noted that the (calculated) fractional-order spectra remained unaltered when the surface coverage was doubled, provided that the adsorbate (in this case, Al) had the same environment. On one occasion, Al was located in the so-called fcc sites (no atom underneath) with a density of one Al atom per surface unit mesh and later two Al atoms per surface unit mesh. For these two cases the integral-order spectra turned out to be different but the fractional-order spectra were almost identical. On the second occasion, the Al atoms were located in the so-called hcp sites, again with one and two atoms per surface unit mesh, respectively. Again, the calculations revealed differences between integral-order spectra and almost no change between fractional-order spectra.

III. DISCUSSION

The experimental observations in the O/Cu system, when combined with the computational results in the Al/Si system, invite the conclusion that the O atoms sit on the same sites during the evolution of the LEED pattern (Fig. 1), i.e., both in the apparent $c(2 \times 2)$ and in the final $(2\sqrt{2} \times \sqrt{2})45^\circ$ structure, and that the only quantities that change are surface coverage and periodicity of the surface structure. This stability of the fractional-order spectra requires both that the adsorbate have the same environment irrespective of surface coverage, and also that multiple scattering within the adsorbate layer be negligible. If there is no multiple scattering between adsorbates the scattered beam spectra are determined by the interference of scattered waves between one adsorbed atom and the substrate and the spectra will be the same for all atoms if all atoms have the same environment.

The stability of the fractional-order spectra may turn out to be very useful. If in the course of preparation of a surface structure the fractional-order spectra are found to be stable (as in the O/Cu case discussed above), then throughout the preparation the adatoms must maintain essentially the same environment. If meanwhile the LEED pattern indicates that structures with increasing complexity are being formed (e.g., with increasing periodicity, as in the O/Cu case discussed above) then it may be possible to determine the adatom position from the simplest of all structures observed, and claim that this position is the same in the most complicated structure as well.

We can test this claim immediately with the example of O/Cu discussed in Sec. II. The reaction of oxygen with Cu(001) was the object of several litera-

ture reports,⁷⁻¹² all concerned with either the $(2\sqrt{2} \times \sqrt{2})45^\circ$ or the $c(2 \times 2)$ structure. An investigation of the former structure, by Kono *et al.*,¹² with x-ray photoemission spectroscopy concluded that the oxygen atoms are located deep into the fourfold symmetrical hollows of the Cu {001} net, and are coplanar with the Cu atoms. We therefore made a calculation of the $\frac{1}{2} \times \frac{1}{2}$ spectrum for a $c(2 \times 2)$ structure with the oxygen atoms in the fourfold symmetrical hollows and either coplanar with, or 0.1 Å above, or 0.1 Å below, the first Cu layer. We found that the curve calculated for 0.1 Å above the Cu plane agrees quite well with experiment (Fig. 2). We claim therefore that this is the position of O even in the more complicated $(2\sqrt{2} \times \sqrt{2})45^\circ$ structure, in good agreement with the results of Kono *et al.*¹² Thus, the O atoms do not move away from the positions acquired early in the chemisorption process or go into new kinds of sites while this process unfolds. In addition, we can exclude (large) motions of the Cu atoms during adsorption if these motions do not maintain a 1×1 periodicity in the substrate, because if the Cu layer were to reconstruct, we would observe changes in the fractional-order spectra. To be sure, in our experiment we could monitor only the $\frac{1}{2} \times \frac{1}{2}$ spectra and the $\frac{3}{2} \times \frac{1}{2}$ spectra (not reported here) because in the initial stages of adsorption the intensities of the fractional-order beams are very low and difficult to measure, but the above conclusion is likely to be valid for all such beams.

A simple explanation for the weakness of multiple scattering within the adlayer is that at or near normal incidence such multiple scattering requires at least two large-angle (near 90°) scattering events between

distant scatters (the overlayer atoms are farther apart than substrate atoms), while for interlayer scattering only one such event (one backscattering) is required; also scattering cross sections for side scattering are smaller than for forward or back scattering. In the quasidynamical (QD) method of LEED intensity calculation, the still stronger assumption is made that multiple scattering can be neglected in all layers,¹³ and for weak-scattering crystals such as Si and Ge it has been established that QD and full-dynamical calculations give similar results.¹⁴ As far as overlayer systems are concerned, however, the neglect of multiple scattering in just the overlayer should have more general validity than the QD assumption. For example, the measurements of Demuth¹⁵ on O, S, Se, and Te overlayers on Ni {001} show that the $\frac{1}{2} \times \frac{1}{2}$ spectra of the $p(2 \times 2)$ and the $c(2 \times 2)$ structures for a given adsorbate are practically identical to one another, although the substrate is a strong close-packed scatterer. Hence, as in the case above, we conclude that the environment of the adsorbate was essentially the same in the two structures despite the fact that the surface coverage differs by a factor of 2. We also note that the stability of the $\frac{1}{2} \times \frac{1}{2}$ spectra holds for Te as well as O, so that neglect of multiple scattering can be valid even when the adsorbate atoms are individually strong scatterers.

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