RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 2 15 JANUARY 1985

Interpretation of diffuse low-energy electron diffraction intensities

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(Received 13 November 1984)

It is shown that the diffuse low-energy electron diffraction (LEED) that occurs between sharp LEED beams can be used to determine the local bonding configuration near disordered surface atoms. Two approaches to the calculation of diffuse LEED intensities are presented for the case of lattice-gas disorder of an adsorbate on a crystalline substrate. The capabilities of this technique are most similar to those of near-edge extended x-ray absorption fine structure, but avoid the restrictions due to the use of photons.

Low-energy electron diffraction (LEED) has become one of the most powerful tools for the study of surface crystallography.[1,2] Yet so far the interpretation of experiments has been limited to well-ordered surfaces, unlike the case of some other techniques, such as surface extended x-ray absorption fine structure (SEXAFS),[3] extended appearance potential fine structure (EAPFS),[4] surface extended energy-loss fine structure (SEELFS),[5] electron energy-loss near-edge structure (ELNES),[6] angle-resolved photoelectron emission fine structure (ARPEFS),[7] and more generally angle-resolved photoelecton emission spectroscopy (ARPES).[8]

It must be regarded as a drawback of the LEED technique not to be able to interpret the diffuse scattering that is seen when the surface is disordered in some way. In particular, one is then restricted to studying adsorbates at discrete coverages corresponding to the ordered structures. Also the low-coverage limit of isolated adsorbates on a surface is then a difficult one to approach theoretically, because the unit cell (if it exists) becomes too large to handle with most current methods.[9] The same problem of large unit cells arises with saturation coverages of large molecules adsorbed on a substrate.[9] Here the molecule-substrate interaction is both the dominant and the chemically significant quantity. By contrast, the molecule-molecule interactions (responsible for any ordering) are relatively weak and chemically secondary.

In the past, Duke and Laramore[10] and Moritz, Jagodzinski, and Wolf[11] have considered the disorder problem in LEED theory with methods that have restricted applicability.

Recently a whole series of techniques have been developed,[3-8] which are local probes of surface crystallography, insensitive to any long-range ordering that the surface may have. These techniques range in theoretical complexity from SEXAFS, which is primarily sensitive to radial interatomic distances, to near-edge extended x-ray absorption fine structure (NEXAFS), which through multiple electron scattering is also directly sensitive to the direction of bonds.

It is the purpose of this Rapid Communication to point out that a LEED experiment can also be considered a local probe, and in particular that the examination of the diffuse scattering removes the requirement of long-range order.

As we shall show, the main features of a LEED pattern (sharpness and streaking of beam spots, distribution of diffuse scattering) are, to a good approximation, governed by a kinematic structure factor that depends only on the nature of the long-range order. This structure factor modulates a separable form factor representing the electron scattering (including multiple scattering) by atom clusters of size determined by the electronic mean free path. This form factor includes all the short-range structural information: layer spacings, bond lengths, bond angles.

More formally we can write the diffracted intensity in terms of a propagator T

$$I(\vec{k},\vec{k}')=|\langle\vec{k}|T|\vec{k}'\rangle|^2 , \tag{1}$$

where T can be expressed in terms of the free-electron Green's function

$$G_0(\vec{r},\vec{r}')=(4\pi)^{-1}\exp(ik|\vec{r}-\vec{r}'|)/|\vec{r}-\vec{r}'| \tag{2}$$

and the scattering amplitude t_j for the atoms j in the crystal

$$T=G_0+\sum_j G_0t_jG_0+\sum_{j,k} G_0t_jG_0t_kG_0+\dots . \tag{3}$$

This expression is quite general and describes both the coherent scattering that is confined to the discrete beams appearing as spots on the LEED screen, and the diffuse scattering that appears as a fuzzy distribution of intensity between these spots.

We now specialize to the case of a lattice-gas adsorbate on a perfectly periodic substrate and define T_c to be all the contributions to T that involve only scatterers in an ordered array. It makes no contribution to the amplitude between the discrete beams. It is possible to develop a perturbation as follows. Define T_J to be all those contributions to T that involve t_J (for the Jth disordered adsorbate) at least once, none of the other disordered adsorbates, but all possible additional scatterings from the ordered lattice. If the disordered adsorbates are sufficiently far apart we can neglect the second-order terms T_{JK} that involve t_J and t_K (corresponding to different adsorbates) at least once each. The inelastic scattering ensures that these contributions are small, and in any case, averaging over the disorder will further reduce their contribution.

Hence, we can approximate

$$I(\vec{k},\vec{k}') \simeq \left|\langle\vec{k}|T_c|\vec{k}'\rangle + \sum_J \langle\vec{k}|T_J|\vec{k}'\rangle\right|^2 . \qquad (4)$$

This approximation becomes exact in the limit that the disordered adsorbates are far apart, or more precisely, in the limit that multiple scattering between adsorbates is negligible. This is, in practice, a good approximation already whenever adsorbates are not directly bonded together, as in Ni(100)-$c(2\times2)$-O.[12]

If we are interested only in the diffuse scattering, the T_c term drops out. For lattice-gas disorder the T_J term depends on J only through a phase factor $\exp[i(\vec{k}'-\vec{k})\cdot\vec{R}_J]$, where $\vec{R}_J$ is the vector from a reference adsorbate (labeled 1) to the Jth adsorbate. Hence, the total diffuse intensity becomes

$$I_D = F(\vec{k},\vec{k}')S(\vec{k}'_\parallel - \vec{k}_\parallel) , \qquad (5)$$

where

$$F(\vec{k},\vec{k}') = |\langle\vec{k}|T_1|\vec{k}'\rangle|^2 \qquad (6)$$

and

$$S(\vec{k}'_\parallel - \vec{k}_\parallel) = \sum_J \exp[i(\vec{k}'-\vec{k})\cdot\vec{R}_J] . \qquad (7)$$

This is a very powerful result, because using it we can extract from the experiment two separate quantities: S, which tells us about any long-range order the adsorbates may have, and, of greater interest to us, F, which reflects the local structure near a single adsorbate, including all multiple scattering in that neighborhood. The separation can be effected by taking the energy derivative of I at constant $\vec{k}_\parallel$ and $\vec{k}'_\parallel$ to construct the logarithmic derivative, as S is then constant.

$$L(E,\vec{k},\vec{k}') = I^{-1}(\delta I/\delta E)|_{\vec{k}_\parallel - \vec{k}'_\parallel} = F^{-1}(\delta F/\delta E)|_{\vec{k}_\parallel - \vec{k}'_\parallel} . \qquad (8)$$

In fact we make use of a function of L

$$Y = L^{-1}(L^{-2} + V_{0i}^2)^{-1} , \qquad (9)$$

which avoids the singularities possessed by L.[13] Here V_{0i} is the imaginary part of the electron self-energy.

These ideas have some consequences for the theory. We have developed two separate approaches to disordered systems which we shall compare one with another below.

In the "cluster" approach we calculate T_1 directly, by splitting T_1 into three terms:

$$T_1 = T_b T_M T_a . \qquad (10)$$

Here T_a represents all scatterings before the electron encounters an adsorbate; since this calculation involves only atoms of the perfectly ordered substrate, it constitutes a conventional LEED calculation for a clean surface. T_M is a modified scattering factor from the adsorbate and is the sum of all scattering events that start and finish on the adsorbate, including scattering paths through the substrate. It can be evaluated in a NEXAFS-type cluster calculation[14] having the adsorbate at the center of the cluster. Finally, T_b is the sum of all events subsequent to the electron's leaving the adsorbate for the last time; this calculation again involves only atoms of the perfectly ordered substrate and constitutes a time reversed conventional LEED calculation based on the selected exit direction. The method is exact in the limit of an isolated adsorbate.

The second approach replaces the spherical-wave representation implicit in the NEXAFS-like step of the first approach by a restricted plane-wave representation (this approach generalizes the beam-set-neglect method[9]). Instead of using all possible plane waves, we use the plane wave obtained from the incident beam direction and the desired exit direction by addition of the two-dimensional reciprocal-lattice vectors of the (1×1) substrate lattice. This selection only neglects multiple scattering events of third and higher order. The three steps of the first approach can then be efficiently combined into a conventional LEED plane-wave treatment almost identical to a $c(2\times2)$ overlayer calculation.

We have applied both theoretical approaches to the calculation of diffuse intensities for a disordered layer of oxygen atoms adsorbed in hollow sites of the Ni(100) surface. Figure 1 exhibits the Y function [Eq. (9)] calculated with the first approach across the LEED screen at a kinetic energy of 2 hartrees (54.36 eV), assuming normal incidence. Figure 2 shows the same Y function obtained with the second theoretical approach. All major features are correctly reproduced in the second approach and will therefore yield essentially the same result in a structural analysis. The total integrated diffuse intensity for a disordered lattice gas of density corresponding to a monolayer coverage was found to be of the same order as the sum of the Bragg intensities from the substrate alone.

The rich structure of the patterns shows the amount of information available for structure determination even at a fixed kinetic energy. Since several theoretical quantities, which are time consuming to compute, can be reused at varying exit angles, there is an advantage in performing a structural determination at just one energy, especially with the cluster approach. But I-V curves of diffuse intensities can also be used in the same manner as I-V curves for sharp beams, most conveniently with the beam-set-neglect approach.

The developments we report here constitute an extension of the LEED technique to the class of disordered adsorbate systems. This will be important for the treatment of large molecules adsorbed at surfaces and for the monitoring of adsorbate structures as a continuous function of coverage. It also allows the examination of low-surface-diffusion adsorbates or highly reactive adsorbates which cannot be made to order. The diffuse LEED method is most akin to NEXAFS, but avoids the need for synchrotron radiation. It also removes the requirement that the adsorbate contain elements different from the substrate atoms. The multiple scattering makes it more complicated than SEXAFS, EAPFS, or SEELFS, but yields sensitivity to all bond lengths, bond angles, and layer spacings. And since the same diffraction principles underly these techniques, they should be capable of the same structural accuracy.

Other developments in hand include the ability to handle isolated defects in an otherwise periodic surface, such as substitutional or missing atoms.

On the experimental side, one must bear in mind that the observed diffuse LEED intensity contains contributions from all surface defects, not only those that one wishes to

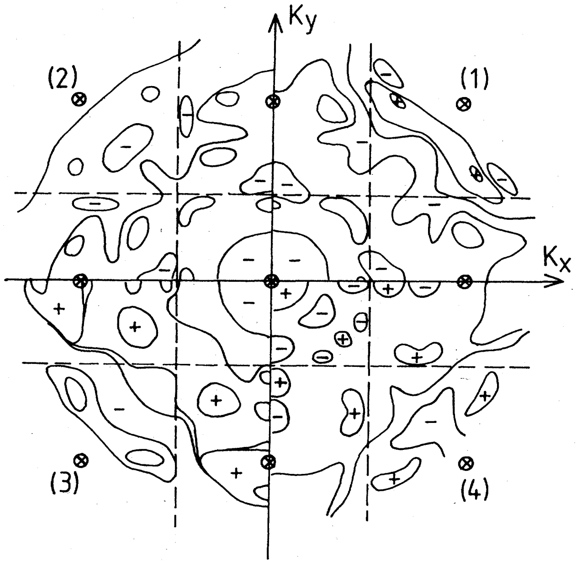

FIG. 1. Y function [Eq. (9)] across the LEED screen calculated for a lattice gas of oxygen adsorbed in fourfold symmetrical hollow sites of Ni(100) at $T=0$. The cluster approach is used. The quadrants (1)-(4) show the variation of the Y function when the O-Ni layer spacing is changed form 0.9 via 1.0 and 1.1 to 1.2 Å, respectively. The diffuse intensity distribution has fourfold rotation symmetry for each O-Ni layer spacing. Prominent positive and negative regions are denoted by corresponding signs. Circled crosses denote substrate-induced sharp spots and dotted lines denote surface Brillouin-zone boundaries (the x and y scales are slightly different).

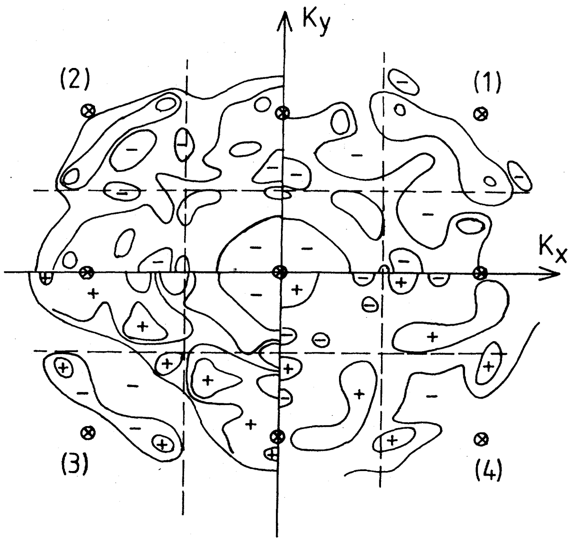

FIG. 2. Same as Fig. 1 except using the beam-set-neglect approach.

study. Paradoxically, this may therefore demand a higher initial surface perfection than in the case of ordered structures, where the singling out of the intensities of sharp beams filters out many imperfections. Also, thermal diffuse scattering becomes more influential. However, the situation is no worse than with the already well-established techniques of SEXAFS, ARPES, etc., where these effects are equally present.

Two of us (M.A.V.H. and G.A.S.) acknowledge support by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-SF00098, and the other two (D.K.S. and J.B.P.) were supported by the British Petroleum Venture Research Unit.

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