Holographic reconstruction from measured diffuse low-energy-electron-diffraction intensities

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The recent suggestion that a diffuse low-energy-electron-diffraction pattern from a disordered layer of adsorbate atoms on a crystal surface may be interpreted as a Fraunhofer hologram, from which crystallographic information may be extracted *directly*, is put to a practical test in the case of O/Ni(100). Holographic reconstruction yields an image of the Ni atoms closest to the O adsorbates. The image resolution appears sufficient for its use as a starting point for more established crystallographic techniques, to discriminate, in a preliminary search, between very different models.

Recent calculations by Saldin and de Andres[1] have suggested that the structural information present in a diffuse low-energy-electron-diffraction (diffuse LEED, or DLEED) pattern, due to a disordered layer of adsorbate atoms on a crystal surface, may be extracted directly by its interpretation as a Fraunhofer hologram. The aim of this paper is to report on the realization of this idea in practice in the case of disordered O/Ni(100).

The idea of using electron holography to generate atomic-resolution images may be traced back to the original work of Gabor.[2] He proposed forming a hologram by interfering electrons scattered from an object with mutually coherent unscattered electrons (the reference beam) from the same external source. Despite early difficulties associated with poor electron coherence lengths, work following this line remains active today.[3–6] The idea of holography with local reference waves[7] has spawned much recent theoretical and experimental work,[8–13] particularly in the field of photoelectron diffraction. The appeal of the use of standard LEED equipment for determination of the adsorption sites of atoms on surfaces by a rapid *direct* method is the impetus behind the work reported here.

The determination of the adsorption sites of atoms deposited on crystal surfaces has been the goal of many investigations by a variety of electron-diffraction techniques. Conventional LEED techniques rely on the measurement of the intensities of Bragg spots and are therefore confined to the case of ordered surfaces. During the early stages of the adsorption of atoms or molecules on a crystal surface, the adsorbates lack long-range order, as manifested by the appearance of substantial amounts of diffuse intensity between the Bragg spots. Recent work[14–16] has shown that this diffuse intensity contains information about the local adsorption sites. Up to the present, this information has been extracted by trial-and-error fitting of calculated diffraction patterns for candidate model structures with experimental data. A technique for the extraction of that information *in one step* from the experimental data would be a significant advance. A previous study of disordered O/Ni(100) adsorption system by conventional DLEED techniques used data from quite low-energy electrons (around 60 eV), at low coverages (around 15/100), and low temperatures (around 80 K). The samples were prepared following standard procedures described elsewhere.[16] As pointed out by Saldin and de Andres,[1] the reconstruction of acceptable holographic images from DLEED data requires much higher electron energies. Since the resolution of a holographic image cannot be better than approximately the wavelength of the associated radiation,[17] our measurements were performed on DLEED patterns due to electrons of energies 650, 550, 480, and 450 eV, for which the background intensities were large enough to facilitate measurement.

The basis for the subsequent holographic interpretation of DLEED patterns was provided in 1984 by Pendry and Saldin.[14] The amplitude of a DLEED pattern may be regarded as arising from a summation of all scattering paths from source to detector. All those which involve scattering from substrate atoms only give rise to the Bragg spots, since they sum destructively for all scatter-

ing directions between the Bragg spots. Thus, in order to evaluate the amplitudes detected between the Bragg spots, we may restrict our attention to just that subset of paths which involves scattering off adsorbate atoms. In the case of lattice-gas adsorption, the problem is simplified further since the DLEED pattern (away from the Bragg spots) may be regarded as the incoherent superposition of that due to a single adsorbate. Thus the DLEED amplitudes may be considered to be due to the sum of those Feynman diagrams which contain the t matrix of the adsorbate at one or more vertices. We further subdivide the above set of Feynman diagrams into those whose final vertex represents an adsorbate atom and denote their sum by R; the sums of those whose final vertex is the nearby substrate atom, i, is represented by O_i. The forms of the resulting wave fields in the far field take the form

$$R = F_o(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{1}$$

and

$$O_i = F_i(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_i)} , \tag{2}$$

where $\mathbf{k}$ is the wave vector of the detected electron. The intensity of the resulting DLEED pattern may be written

$$I(\mathbf{k}) = |R|^2 + \left[\sum_i R^* O_i + \text{c.c.} \right] + \sum_{i,j} O_i^* O_j . \tag{3}$$

In related work on photoelectron holography, Barton[8] suggested the following computer algorithm for reconstructing the amplitude $A(\mathbf{r})$ of a real-space holographic image close to the position of the adsorbate atom:

$$A(\mathbf{r}) = \int I(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\hat{\mathbf{k}} . \tag{4}$$

The efficacy of such an algorithm in reconstructing an atomic image of the immediate surrounding area of the adsorbate is dependent on two conditions: (a) that F_o and F_i have significantly slower dependence on $\hat{\mathbf{k}}$ than the exponential terms arising from path differences after the atomic scattering and (b) that $|O_i| \ll |R|$. Furthermore, it is expected that such an algorithm will not be robust against noise. If (a) is satisfied it is easy to see by substituting (1) and (2) into (3) that stationary-phase conditions predict that the first term in (3) would give rise to a peak in the reconstructed intensity at $\mathbf{r}=\mathbf{0}$, the position of the adsorbate atom, the second term at $\mathbf{r}=\mathbf{r}_i$, the positions of the substrate atoms, and the third term at $\mathbf{r}=-\mathbf{r}_i$ those of the "twin" images. If (b) were satisfied, the fourth term in (3) may be neglected. There are reasons to believe that these conditions are not unreasonable, but the acid test is to reconstruct images from real experimental data.

A measured LEED pattern from disordered O/Ni(100) for an incident electron energy of 650 eV is shown in Fig. 1. Since we are interested only in the local adsorption geometry of the O atoms, we first need to remove the Bragg spots which carry information only about the ordered substrate. We have removed those regions using a B-spline interpolation procedure.[18] There is no general way to prescribe the best method of performing this interpolation. After several different trials we have chosen a good one by visual comparison between a set of minimal reasonable fits. Then, the data were multiplied by a Hanning window function[19] to eliminate, as much as possible, the spurious high-frequency components of the Fourier transform arising from the artificial termination of the data at the edge of the detector screen. This window takes the form of a bell-shaped function that goes smoothly from zero at the boundaries to unity at the center of the screen. Its main purpose it is to avoid power "leakage" from high k values to other neighboring points, and we have found that its use improves the quality of the resulting images.

In Cartesian coordinates algorithm (4) may be recast in terms of the two-dimensional Fourier transformation

$$A(\mathbf{r}) = \int\int I(k,\hat{\mathbf{k}}) \exp[ikz(1-\hat{k}_x^2-\hat{k}_y^2)^{1/2}] \times \exp[ik(x\hat{k}_x + y\hat{k}_y)] d\hat{k}_x d\hat{k}_y , \tag{5}$$

where x and y are Cartesian coordinates in the plane of the surface, and z that perpendicular to it. The subscripts on the wave vectors $\mathbf{k}$ denote components parallel to these directions. Wei, Zhao, and Tong[10] have suggested that the above integral should be divided by the cosine of the polar angle of detection, but, in view of our subsequent multiplication by a window function, the precise form of another smoothly varying factor is of little significance. The reconstruction algorithm should be regarded as a mathematical device for extracting the atomic positions from the data, and due to the less predictable nature of our reference waves and the nonclassical nature of atomic scatterers,[12,13] an exact analogy with optical holography should not be pushed too far.

Of the four sets of measured data, our best reconstructed images were obtained from those of the two highest energies, namely 650 and 550 eV. We ascribe this to an uncertainty-principle argument: the best resolution on

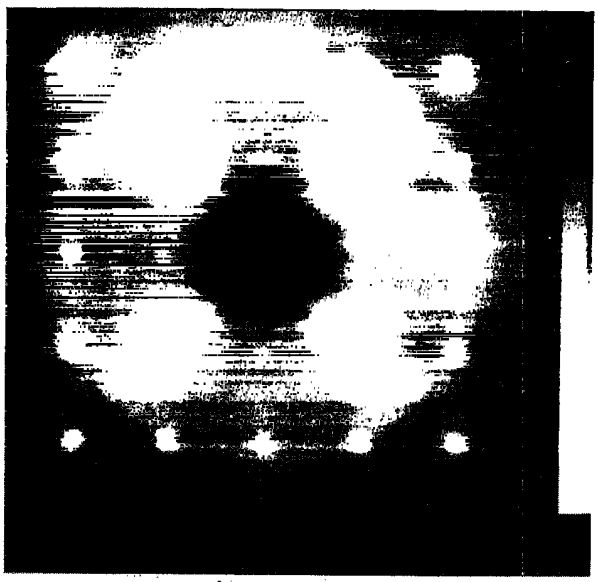

FIG. 1. Experimental LEED pattern for O/Ni(100)—disordered—at approximately 15/100 coverage, $T=80$ K, and $E=650$ eV.

the reconstructed image requires diffraction data associated with the widest range of wave vectors.[11] The sections through the images reconstructed from the DLEED data at the energies of 650 and 550 eV and representing the plane of the outermost substrate atoms are illustrated in Figs. 2 and 3. It is seen that the peaks associated with the substrate Ni atoms are more clearly reproduced at 650 eV than at 550 eV. We believe we are probably around the lower limit of the energy at 550 eV. Noise and other factors, which we thought in advance might introduce further complications, were of little significance.

A further complication may be the presence of diffuse background due to defects or inelastic processes. For standard diffuse LEED it was shown both experimentally[20] and theoretically[21] than an acceptable procedure in most of the cases was to subtract the diffuse intensities collected from the substrate. In the present case we believe this is an unnecessary (although possible) procedure. The section through the image perpendicular to the surface (Fig. 4) displays a characteristic X-shaped form, observed previously in the holographic reconstruction of Kikuchi patterns from Cu(100) surfaces.[9] Although the experiments reported here were performed at low temperatures to minimize the Kikuchi contribution to the diffraction pattern, some residual effect may be present, especially at the higher of the two energies we consider (Fig. 1).

One of the most promising features of imaging techniques based on holography is its ability to produce stereoscopic information about the surface. Currently the image resolution of this kind of technique is of the same order as that of the scanning tunneling microscope (STM). However, by its very nature, the STM is nearly blind to layers other than the outermost, and this may be of importance for chemical studies related to such technologically important processes as catalysis, oxidation, corrosion, etc. A section of the image perpendicular to the surface is shown in Fig. 4, where we have marked with crosses the position of the Ni atoms closest to the adsorbates. The quality of the image is not very good, though peaks are observed close to the expected positions of the atoms. We believe that extending the range of data collection to cover more of the backscattering hemisphere would improve the quality of the images by increasing the range of wave vectors associated with the diffraction pattern.

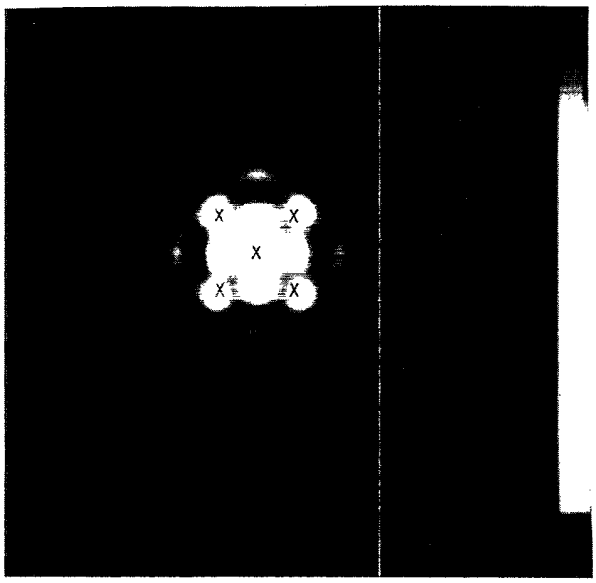

FIG. 3. Atomic-resolution holographic image for $E=550$ eV. A plane parallel to the surface passing through $z=-0.9$. The atomic positions are represented by crosses.

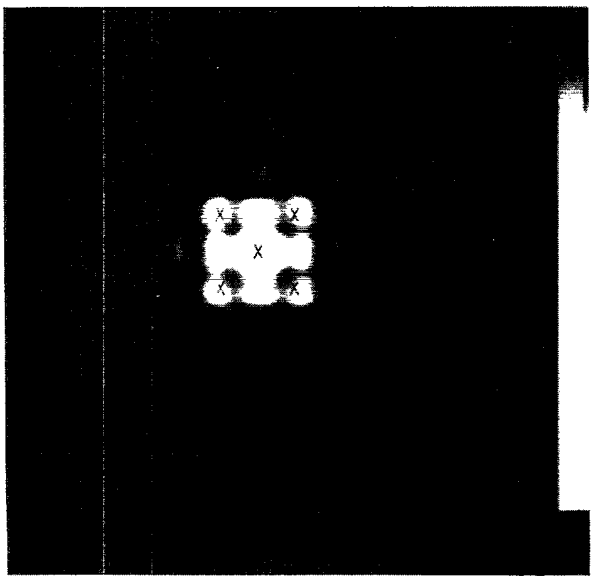

FIG. 2. Atomic-resolution holographic image for $E=650$ eV. A plane parallel to the surface passing through $z=-0.9$. The atomic positions are represented by crosses.

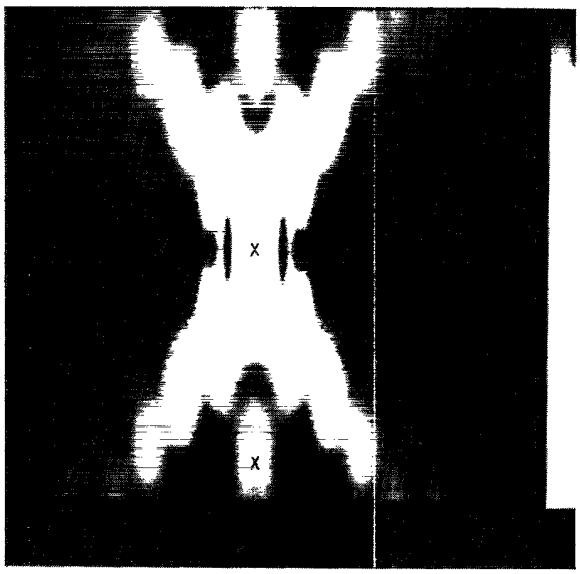

FIG. 4. Atomic-resolution holographic image for $E=650$ eV. A plane perpendicular to the surface passing through the adsorbed oxygen and two neighboring nickel atoms. The atomic positions are represented by crosses.

In conclusion, we have shown the feasibility of the *direct* reconstruction of the sites of disordered adsorbed atoms on a crystal surface by the recently proposed technique[1] of diffuse LEED holography. The range of values of the wave vector of the detected electrons is seen to be an important limiting factor of the image resolution. Nevertheless, we have been able to obtain a stereoscopic image of the surface, although the resolution in the direction perpendicular to the surface is rather low. We believe this to be not too crucial since the results of a technique of relatively low resolution may be of great value as input to a traditional "trial-and-error" search of traditional LEED, thereby helping to cut down the enormous parameter space to be explored for an unknown structure.

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[1]D. K. Saldin and P. L. de Andres, Phys. Rev. Lett. **64**, 1270 (1990).

[2]D. Gabor, Proc. Phys. Soc. London **64**, 449 (1951).

[3]J. M. Cowley and D. J. Walker, Ultramicroscopy **6**, 71 (1981).

[4]H. Lichte, Ultramicroscopy **20**, 293 (1986); Phys. Status Solidi B **151**, 214 (1988).

[5]A. Tonomura, Rev. Mod. Phys. **59**, 639 (1987).

[6]H. W. Fink, W. Stocker, and H. Schmid, Phys. Rev. Lett. **65**, 1204 (1990).

[7]A. Szöke, in *Short Wavelength Coherent Radiation: Generation and Applications,* edited by D. J. Atwood and J. Boker, AIP Conf. Proc. No. 147 (AIP, New York, 1986).

[8]J. J. Barton, Phys. Rev. Lett. **61**, 1356 (1988).

[9]G. R. Harp, D. K. Saldin, and B. P. Tonner, Phys. Rev. Lett. **65**, 1012 (1990).

[10]C. M. Wei, T. C. Zhao, and S. Y. Tong, Phys. Rev. Lett. **65**, 2278 (1990).

[11]G. R. Harp, D. K. Saldin, and B. P. Tonner, Phys. Rev. B **42**, 9199 (1990).

[12]S. Y. Tong, C. M. Wei, T. C. Zhao, H. Huang, and Hua Li, Phys. Rev. Lett. **66**, 60 (1991).

[13]S. Hardcastle, Z. -L. Han, G. R. Harp, J. Zhang, G. L. Chen, D. K. Saldin, and B. P. Tonner, Surf. Sci. (to be published).

[14]J. B. Pendry and D. K. Saldin, Surf. Sci. **145**, 33 (1984).

[15]K. Heinz, D. K. Saldin, and J. B. Pendry, Phys. Rev. Lett. **55**, 2312 (1988).

[16]U. Starke, P. L. de Andres, D. K. Saldin, K. Heinz, and J. B. Pendry, Phys. Rev. B **38**, 12 277 (1988).

[17]E. Wolf, Opt. Commun. **1**, 153 (1969).

[18]The NAG library (MK 13) was used here (The Numerical Algorithms Group Ltd., Wilkinson House, Jordan Hill Rd., Oxford, UK).

[19]W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1986).

[20]H. Ibach and S. Lehwald, Surf. Sci. **176**, 629 (1986).

[21]P. L. de Andres, P. J. Rous, and J. B. Pendry, Surf. Sci. **193**, 1 (1988).