

## Direct reconstruction of three-dimensional atomic adsorption sites by holographic LEED

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We report on the application to measured data of an algorithm for holographic low-energy electron diffraction (LEED), which overcomes the two most important limitations of the technique to date: the “searchlight” effect, which tends to highlight only atoms forward scattered by the adsorbates, and the distorting effects on diffuse LEED intensities due to possible long-range order among the adsorbates. The only experimental input required is a set of the most reliably measured diffuse LEED patterns from normally incident electrons. The algorithm is applied to a set of 11 measured diffraction patterns from a K/Ni(001) surface. A fully three-dimensional image is reconstructed from these data by compensating for the anisotropy of the reference wave by an appropriate scattered-wave kernel. [S0163-1829(96)00936-8]

### I. INTRODUCTION

Although low-energy electron diffraction<sup>1</sup> (LEED) is one of the most important probes of surface crystallography, it has been somewhat hampered by its usual methodology for extracting structural information from experimental data. Conventionally, data are simulated for various model structures and fitted by means of a trial-and-error procedure. The problems in such a procedure are twofold: (i) the computer time requirements for the calculation of LEED spectra from even a single structure (particularly one with low symmetry) and (ii) the sheer number of different structures that need to be examined. Considerable progress has been made in the last decade in dramatically reducing the time requirements (i), especially by the technique of tensor LEED.<sup>2</sup> However, it is difficult to see any solution to problem (ii) in the case of complicated structures, since the number of structures that need to be evaluated scales exponentially with the number of structural parameters to be determined.<sup>3</sup>

In an attempt to address problem (ii) attention has been devoted towards the possibility of developing more *direct* methods for LEED.<sup>3,4</sup> In this context an idea that has shown

some real promise is that of holographic LEED.<sup>5</sup> When atomic adsorbates form a disordered lattice gas on a crystal surface, it has been suggested<sup>5</sup> that a holographic reconstruction algorithm should be able to recover the local crystallography of the adsorbates from the resulting diffuse LEED (or DLEED) intensities<sup>6,7</sup> found between the Bragg spots from the substrate scattering. The basic idea is that all electrons contributing to the DLEED intensity must have propagation paths that include at least one scattering by an adsorbate (since the ensemble of adsorbates form the only disordered part of the surface). Thus the DLEED intensity may be regarded as arising from a set of spherical waves emerging from each of the adsorbate atoms, suggesting a close analogy with a diffraction pattern formed by photoelectrons emitted from the adsorbates. In the latter case, the propagation paths leading directly from the emitter to the detector have been identified with a reference wave, while those involving subsequent scattering by a substrate atom have been regarded as object waves, allowing a holographic interpretation of the diffraction pattern.<sup>8-10</sup> In DLEED, those propagation paths leading directly from the last scattering by an adsorbate to the detector play the role of a reference wave, while those

associated with subsequent scattering by a substrate atom are identified with object waves.

As in the case of photoelectron holography, the holographic interpretation of a DLEED pattern suggests the possibility of the recovery of the relative positions of adsorbate and nearby substrate atoms *directly* from a diffraction pattern by some form of computer reconstruction algorithm. Given the limited range of measurable data on a single DLEED pattern, and the relative ease with which different DLEED patterns from electrons of different energies may be recorded, it was suggested from the beginning<sup>5</sup> that data from many such patterns could profitably be combined to produce reconstructed images of higher quality. A particularly successful multienergy reconstruction algorithm has been proposed by Barton.<sup>11</sup> A similar algorithm has been applied by Tong and co-workers to photoelectron holography,<sup>12</sup> and holographic LEED.<sup>13</sup> In the latter case, promising results were obtained from a disordered K/Ni(100) surface of a 5% coverage.<sup>14</sup> Due to the pronounced forward scattering by the adsorbate, only those substrate atoms strongly illuminated by electrons forward scattered by the adsorbate atoms were reconstructed, a phenomenon termed a “searchlight” effect.<sup>13,14</sup> This is somewhat disappointing since one of the main appeals of holography is its ability to reconstruct fully three-dimensional images.

Since the “searchlight” effect arises from the anisotropy of the reference wave, an idea might be to compensate for this anisotropy in analogy with work in Auger and photoelectron holography. In diffuse LEED, however, one is faced with the additional difficulty that the reference wave (i.e., that which leaves the adsorbate for the last time, after all prior multiple scattering with the substrate), is itself determined by the very structure being sought. In this paper we describe how this problem may be overcome. We will show how a fully *three-dimensional* image of the near-neighbor scatterer atoms may be reconstructed from diffraction patterns due to just *normally incident* electrons.<sup>15</sup> Such diffraction patterns are the most reliably measured, since they allow the averaging of symmetry-related sectors of the patterns, thus improving the signal-to-noise ratio and overcoming possible inhomogeneities on the fluorescent screen as well as residual sample misalignments.

## II. THEORY

The reconstructed amplitude  $B(\mathbf{r})$  at a point specified by the position vector  $\mathbf{r}$  relative to an adsorbate atom on the surface is calculated by the equation<sup>15</sup>

$$B(\mathbf{r}) = \int \int \left( \int K(k_{\perp}, \mathbf{k}_{\parallel}; \mathbf{r}) \chi(k_{\perp}, \mathbf{k}_{\parallel}) e^{-i(kr - k_{\perp}z)} dk_{\perp} \right) \times e^{i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}} d^2\mathbf{k}_{\parallel}, \quad (1)$$

where  $\mathbf{k}_{\parallel}$  and  $k_{\perp}$  are the components of the wave vector  $\mathbf{k}$  of a detected electron parallel and perpendicular to the surface,  $z$  is the component of  $\mathbf{r}$  perpendicular to the surface,

$$\chi(k_{\perp}, \mathbf{k}_{\parallel}) = \frac{H(k_{\perp}, \mathbf{k}_{\parallel}) - H_{av}(\mathbf{k}_{\parallel})}{H_{av}(\mathbf{k}_{\parallel})} \quad (2)$$

is a function constructed from the measured diffraction-pattern intensities  $H(k_{\perp}, \mathbf{k}_{\parallel})$ , with

$$H_{av}(\mathbf{k}_{\parallel}) = \frac{\int H(k_{\perp}, \mathbf{k}_{\parallel}) dk_{\perp}}{\int dk_{\perp}}. \quad (3)$$

Thus the measured intensities  $H(k_{\perp}, \mathbf{k}_{\parallel})$  enter the reconstruction algorithm (1) only via the function  $\chi$ , which enhances the contrast of the oscillations in  $H(k_{\perp}, \mathbf{k}_{\parallel})$ , without affecting their periodicities. A practical advantage of replacing  $H$  by  $\chi$  in the integrand of (2) is that the latter function would tend to filter out unwanted smooth background contributions to a measured DLEED pattern from, e.g., thermal diffuse scattering. A unique feature of this normalization is that perturbing effects on the diffraction patterns due to any residual long-range order are also divided out during the construction of the  $\chi$  function. This is essential since the holographic interpretation of diffuse LEED intensities is dependent on the assumption that each of the adsorbates acts as a source of electrons effectively incoherent relative to all other adsorbates (as they are naturally in the case of core-level photoelectron diffraction). In DLEED this is strictly valid only in the very low-coverage limit of a true lattice-gas adsorbate layer. Any residual long-range order among the adsorbates at higher coverages is manifested by a structure-factor term  $S(\mathbf{k}_{\parallel})$  which modulates the DLEED intensities. As the  $\chi$  function is formed by the ratios of intensities at particular values of  $\mathbf{k}_{\parallel}$ , it hence eliminates the contributions of the structure factor and makes higher-coverage data accessible for the holographic reconstruction.

The kernel  $K$  [somewhat analogous to the *scattered-wave included Fourier transform* (SWIFT) kernel of photoelectron holography<sup>16,17</sup>] is taken to be of the form

$$K(k_{\perp}, \mathbf{k}_{\parallel}; \mathbf{r}) = \left( \frac{|f_a(\mathbf{K}_0^+ \cdot \hat{\mathbf{r}})| + C}{r} \right)^{-1}, \quad (4)$$

where  $f_a$  is the scattering factor of an adsorbate atom,  $\mathbf{K}_0^+$  the wave vector of the incident electrons, and  $\hat{\mathbf{r}}$  the unit vector in the direction of  $\mathbf{r}$ . The effect of the kernel is to compensate for the “searchlight” effect mentioned earlier. This is done by correcting for the anisotropy of the holographic reference wave, consisting of a contribution  $f_a$  from the forward-scattered incident beam, as well as a new feature, the constant  $C$ , approximating the effect of the back-scattering of electrons previously diffracted by the substrate (see Fig. 1). Some earlier work by Hu and King<sup>18</sup> applied to the Bragg spot intensities<sup>19</sup> from a surface with an ordered adsorbate layer also used a kernel somewhat similar to our  $K$  in their reconstruction algorithm. A difference is that their kernel omitted the term  $C$ , and showed no evidence of the type of fully three-dimensional reconstruction described below.

## III. EXPERIMENTAL DATA

We reexamine a subset of the DLEED data from a K/Ni(001) surface, measured and analyzed with an earlier generation of reconstruction algorithm.<sup>14</sup> In the present work, instead of using data from two directions of incidence of the electron beam as previously, we use only those diffraction patterns from normal electron incidence onto the surface. Furthermore, we employed the data from just 11 different patterns of electron energies in the low range from 90 to 150 eV, in which they may be measured most reliably,

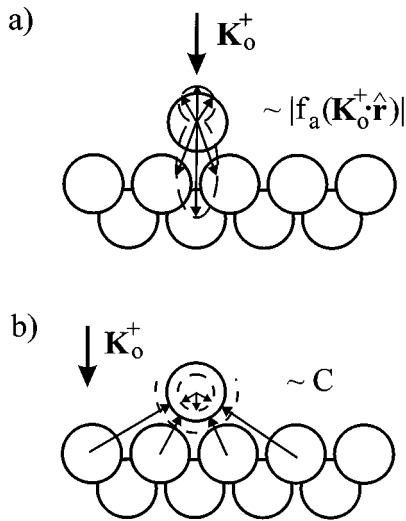


FIG. 1. Schematic diagram of the two contributions to the reference wave from the adsorbate atom: (a) the direct scattering of the incident wave by the adsorbate atom, represented by the modulus of the strongly forward-peaked atomic scattering factor  $|f_a(\mathbf{K}_0^+ \cdot \hat{\mathbf{k}})|$ ; (b) the backscattering by the adsorbate of the waves previously reflected back from the substrate, represented by the isotropic term  $C$ .

and in which the perturbing influence of thermal diffuse scattering is minimized.

As with all DLEED experiments, a considerable amount of care needs to be taken to filter out extraneous signals to access the true DLEED intensities. The contributions of thermal diffuse scattering are minimized by performing the experiments at a temperature of 90 K, and by subtraction of data additionally measured from the clean surface at each energy under consideration.<sup>20,21</sup> The latter procedure also removes the influence of static defects in the substrate. Figure 2 shows four of the 11 diffraction patterns used in the present work, following this background subtraction process. The patterns shown have also been subject to fourfold rotational averaging, using data from just the three quadrants not containing the shadow of the electron gun. A strong angular variation of the DLEED intensities is observed in each of the four patterns, as found in previous computer simulations for the analogous case of O/Ni(001).<sup>15</sup> A similarly pronounced energy dependence of the intensities, for a particular value of the component of the detected electron wave vector parallel to the surface ( $\mathbf{k}_{\parallel}$ ), is seen in the middle panel. This intensity vs energy ( $I/E$ ) curve corresponds to a position equivalent to that of an imaginary  $(\frac{1}{4}, \frac{1}{2})$  Bragg spot.

The effect of a disordered adsorbate layer on a surface is generally to redistribute intensity from the substrate Bragg spots to the diffuse part of the diffraction pattern between the Bragg spots. As a result, a subtraction pattern of the form just mentioned will tend to produce the diffuse intensity distribution we require, except in the immediate vicinity of the Bragg peaks. Visual inspection suggested that the Bragg spots were contained within a circle of radius equal to about a fifth of the interspot spacing, and therefore the intensities within these areas were subsequently set to zero.

It should also be borne in mind that experimental measurements of the diffuse intensities are made as functions of detector *angles*. An interpolation procedure is required to

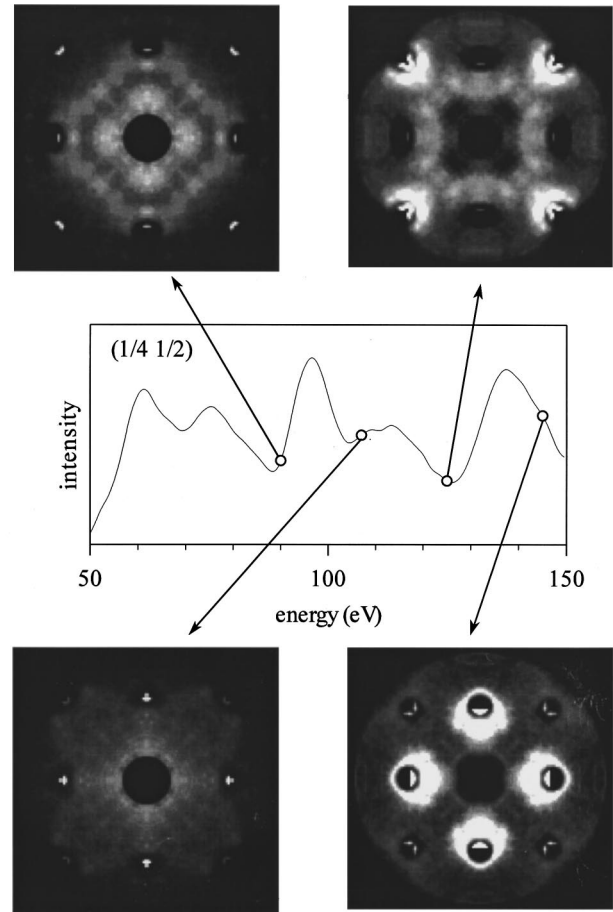


FIG. 2. Diffuse LEED patterns of a K-covered Ni(001) surface (coverage equal to 0.05) measured at the energies 95 (upper left), 107 (lower left), 125 (upper right), and 145 eV (lower right). The diffraction patterns were background subtracted by the corresponding intensities of the clean Ni(001) surface and fourfold symmetrized after the removal of the gun shadow. The variation of diffuse intensity with energy at the position corresponding to a hypothetical  $(\frac{1}{4}, \frac{1}{2})$  Bragg spot is shown in the middle panel.

assign DLEED intensities to a *common*  $\mathbf{k}_{\parallel}$  grid for all electron energies, as required for the construction of the  $\chi$  function. An advantage of such an *energy-independent*  $\mathbf{k}_{\parallel}$  grid is that the resulting diffuse intensities  $H$  as functions of  $k_{\perp}$ , for a particular  $\mathbf{k}_{\parallel}$ , tend to be continuous since, by construction, they stay away from the vicinity of the Bragg spots at all energies.<sup>15</sup>

#### IV. HOLOGRAPHIC RECONSTRUCTION

We applied this procedure to the 11 measured diffuse LEED patterns due to normally incident electrons on a disordered adlayer of 5% coverage of K/Ni(001). A striking three-dimensional image of a form similar to those from the earlier theoretical simulations<sup>15</sup> is reconstructed, as displayed in Fig. 3. The value of the constant  $C$  used in the present work was 3.4 Å, somewhat higher than for the previous simulations for the different (oxygen) adsorbate. This might be expected, due to the different atomic scattering factor of K, and thermal vibrations of the K atom on the surface may also affect the optimum value of this constant. As in the case of the theoretical simulations,<sup>15</sup> the value of  $C$  could be var-

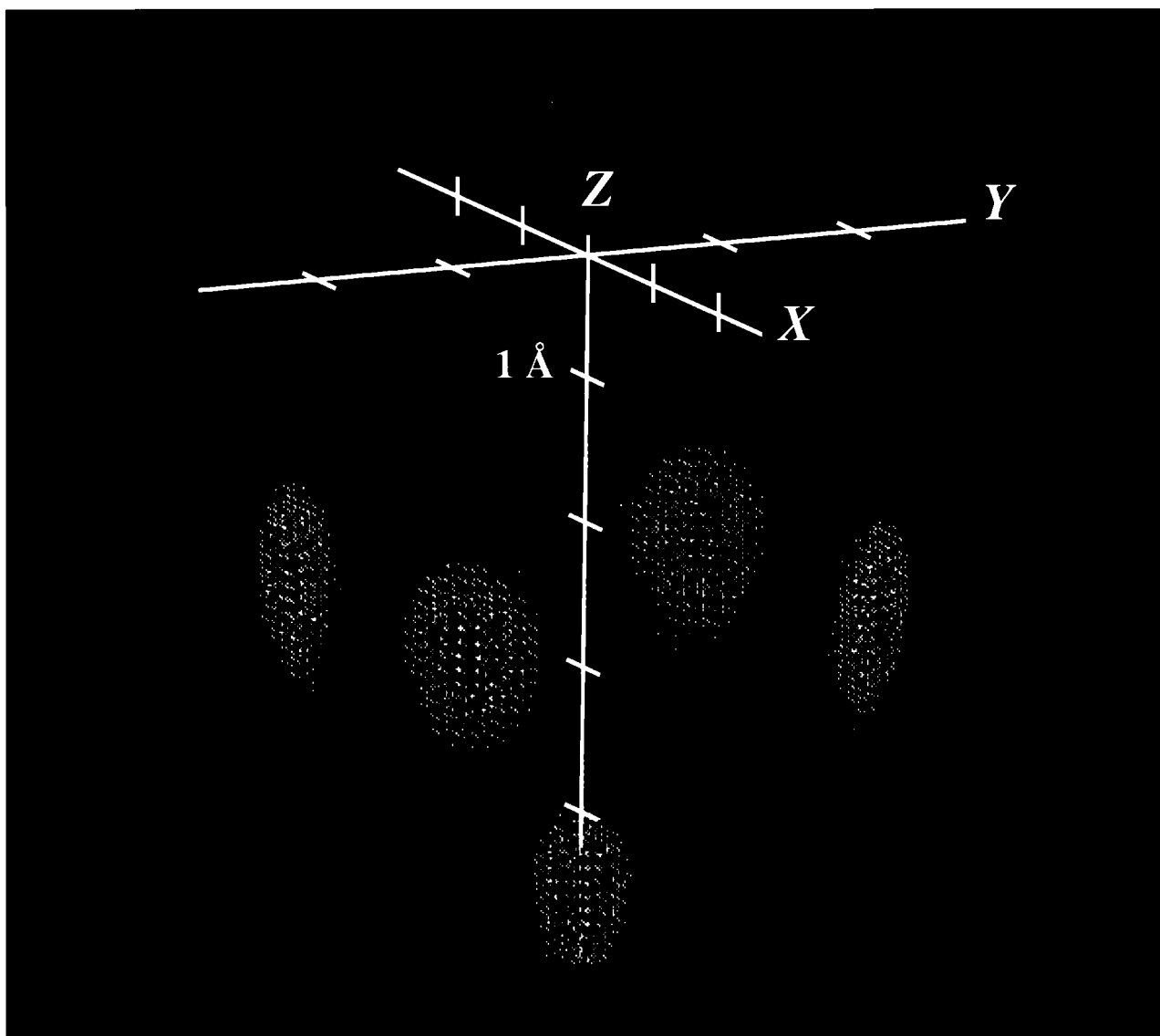


FIG. 3. Three-dimensional image reconstructed from 11 measured DLEED patterns due to electrons of energies ranging from 90 to 150 eV, normally incident on the K/Ni(001) surface. The Cartesian axes  $x$  and  $y$  define a plane parallel to the surface, and the  $z$  axis the outward surface normal. The intensity at each voxel is represented by a sphere whose radius is proportional to the intensity, and whose color varies from blue for the lower values through green to red for the higher ones. The higher intensities correspond to the reconstructed positions of the nearest substrate Ni atoms relative to a K atom (at the coordinate-system origin) adsorbed on a fourfold hollow site.

ied over quite a wide range with no significant degradation of the image.

In terms of the Cartesian system of axes of Fig. 3, a previous conventional LEED study<sup>22</sup> of the same surface had concluded that the positions of the nearest-neighbor substrate atoms to the adsorbate were to be found at  $(x,y,z)$  coordinates relative to the adsorbate of  $(1.25, 1.25, -2.72)$  in Å, together with its three companions related to it by fourfold rotations about the  $z$  axis. The nearest atom to the adsorbate in the second substrate layer was found at the position  $(0.0, 0.0, -4.4)$ , also in Å. It will be seen from Fig. 3 that the red centers of all five of these atoms are reconstructed close to these expected positions, and allow unambiguous identification of the adsorption site.

## V. CONCLUSIONS

In this paper we have described the latest advances in the technique of holographic LEED, which allow the reconstruction of a most striking three-dimensional image of the local adsorption geometry from a minimal amount of the most reliably collected data. This has been achieved by using the scattered-wave kernel  $K$  (4) in the integral (1) to cancel out the anisotropy of the *reference* wave. We have discussed the procedure to be followed in the collection of the experimental data and how to overcome any residual long-range order effects with the filter function  $\chi$ . This feature may indeed be the crucial step responsible for the particularly high quality of the reconstructed image in Fig. 3. It also opens the way for the future use of DLEED data from higher adsorbate

coverages than the present 5%, to further enhance the signal-to-noise ratio.

The quality of our reconstructed image compares favorably with any achieved to date by photoelectron holography, while obviating the need for a synchrotron radiation source. Even though in recent years Kikuchi holography has seen significant progress, it is still troubled by the problem of potentially overlapping atom images, as every surface atom acts as a reference-wave source. In contrast, diffuse LEED holography is able to focus uniquely on the atomic structure

around the adsorbates and seems therefore to be one of the most promising approaches to direct surface crystallography.

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