

## Atomic-scale visualization of surfaces with x rays

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A solution to the phase problem for the case of surface crystallography is presented. By oversampling a surface diffraction pattern along the continuous crystal-truncation rods, we can iteratively recover the phases of the complex structure factors of an unknown surface atomic geometry. Simple Fourier inversion of these structure factors directly yields a three-dimensional map of the electron density in the surface region with  $\sim \text{\AA}$  resolution. This model-independent determination of atomic positions can then be used as a starting point for quantitative refinement using conventional means.

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Our knowledge of the structure of matter over a broad range of length scales is inferred from the intensity of scattered probes. For wavelike probes, the most important class of experiments is based on diffraction. In principle, the information conveyed by the diffracted radiation is sufficient to deduce in detail the structure of the object under investigation. However, the preponderance of techniques using wavelike probes measures only the scattered *intensity* in the far field, although the unmeasured *phase* of the wave contains at least as much information for the direct inversion of the scattering data.<sup>1,2</sup>

In crystallography, this loss is termed the phase problem, and has beleaguered workers seeking to unravel the structure of condensed matter since the time of the Braggs. In this paper, we present a solution to the phase problem in the case of surface crystallography. The methods used can be generalized for other problems in condensed matter physics and beyond.

The intensity of x rays scattered from condensed matter is proportional to the squared modulus of the structure factor  $F(\vec{q})$ , which itself is one coefficient of the Fourier expansion of the electron density in the sample. The Fourier coefficient is complex, but the associated phase is not detected in the experiment. Again, if the phases were known, the structure could be revealed directly by an inverse transform of the Fourier coefficients. Although the missing phase data cannot be recovered directly, the information may be supplied by other means.<sup>3</sup> In particular, with twice as many (or more) *independent* amplitude measurements as called for by the Nyquist criterion,<sup>4</sup> sufficient information is available to make the desired inversion.<sup>5</sup> Iterative algorithms have been developed to converge on this solution in other contexts.<sup>6-8</sup>

A method, then, must be found to supply additional independent measurements. For periodic systems (as in bulk crystallography), this is not possible because only a discrete set of Fourier coefficients (i.e., the Bragg peaks) will have nonzero amplitude. However, truncating the crystal to form a surface interrupts the periodicity normal to the surface. The stringency of the diffraction condition in this direction is thereby loosened, giving rise to diffuse, continuous rods of intensity.<sup>9,10</sup> Thus, a continuous range of nonzero structure factors is accessible in surface x-ray diffraction (SXR), allowing the scattered intensity to be independently sampled at

a frequency greater than that corresponding to a bulk lattice vector. This oversampling supplies the missing information needed to perform the phase recovery.

The application of oversampling to recover a structure from diffracted x-ray intensities was performed by Miao *et al.*,<sup>11</sup> who interrogated a  $\mu\text{m}$ -sized artificial object that lacked any periodicity. The diffraction pattern, which contained only diffuse intensity with a continuous distribution of wave vectors, was sampled at a frequency greater than twice that required by the size of the object. Using an iterative algorithm<sup>8</sup> similar to the one employed here,<sup>2</sup> they exploited their knowledge of the size of the object to impose a constraint in real space: the inverse Fourier transform of the experimental structure factors with trial phases must not extend in real space beyond the known size of the object. In reciprocal space, a constraint was placed on the recovered electron density by the requirement that its Fourier transform must match the experimental scattering data. Iterative application of these constraints converged on a set of phases whose corresponding electron density resembled the known object.<sup>11</sup>

Here, we show that an extension of this iterative method is able to invert measured x-ray diffraction intensities from the surface of a crystal to recover an atomic-scale visualization of the surface structure with  $\sim \text{\AA}$  resolution. The result is a model-independent way of ascertaining atomic positions on, e.g., a reconstructed or chemisorbed surface. Since conventional SXR analysis relies on refining trial atomic positions, and incorrect structural guesses are very unlikely to converge to the actual one, an important use for our method is to supply initial positions for an unknown surface. We demonstrate the efficacy of our approach by constructing a three-dimensional (3D) map of the electron density for the well-known Au(110)-(2 $\times$ 1) reconstruction. Refinement of the positions derived from this map is in quantitative agreement with previous experiments.

The algorithm used here<sup>2</sup> combines elements of the holographic approach to structure completion proposed by Szöke<sup>12</sup> with the iterative phase recovery strategy introduced by Gerchberg and Saxton<sup>6</sup> and extended by Fienup<sup>3,7</sup> and Saldin *et al.*<sup>13</sup> Briefly, in SXR, one strives to determine unknown atomic positions of the outermost layers of a sample whose bulk structure is known. For the crystal-

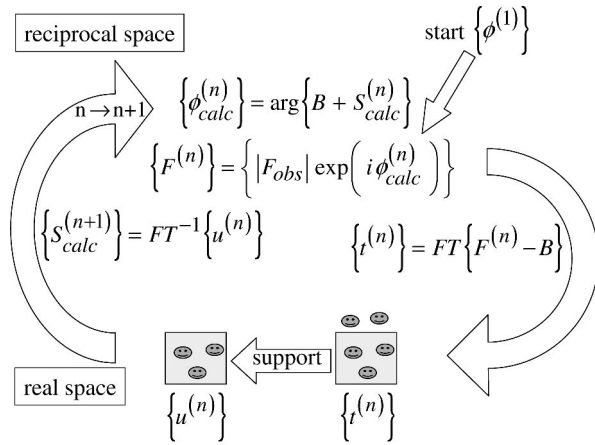


FIG. 1. Schematic flowchart of the iterative algorithm.

truncation rods<sup>9,10</sup> (CTR), which go through the Bragg spots, the signal is a superposition of calculable contributions from the known bulk structure (analogous to a holographic *reference wave*) and signals from the unknown surface structure (akin to a holographic *object wave*). The surface structural information is encoded in the interference between these signals. (For the superstructure rods, which arise from a change in lateral periodicity at the surface, there is no contribution from the bulk.)

The iterative phase recovery algorithm<sup>2</sup> is depicted in Fig. 1. Initially, a random set of phases  $\{\phi\}$  is assigned to the experimentally observed structure factor amplitudes  $\{|F_{\text{obs}}|\}$ . After subtracting the calculable bulk contribution  $\{B\}$ , a Fourier transform renders an estimate in real space of the electron density  $\{t\}$  in the near-surface region.

We next invoke a physically reasonable constraint: the surface electron density must lie within a few angstroms of the surface. Nonetheless, since we sample the scattering rods at intervals of  $\Delta q_{\perp} \approx 0.28 \text{ \AA}^{-1}$ , we are sensitive to objects of the length scale  $2\pi/\Delta q_{\perp} \approx 22 \text{ \AA}$  from the surface. In real space, we impose the constraint (spatial support) that any estimated electron density that lies more than  $8 \text{ \AA}$  from the bulk-terminating layer is set to zero,<sup>14</sup> giving an improved estimate  $\{u\}$  of the surface electron density. Next, an inverse Fourier transform of  $\{u\}$ , namely the set  $\{S_{\text{calc}}\}$  of *surface* structure factors is added to the calculated bulk contribution  $\{B\}$ . The arguments of the sums represent improved estimates of the phases  $\{\phi\}$ . A constraint in reciprocal space is then imposed by assigning these phases to the experimentally observed structure factor amplitudes  $\{|F_{\text{obs}}|\}$ , and the cycle is repeated. Thus, by alternately imposing these constraints in real and reciprocal space, we converge on a solution that is confined to the near-surface region and agrees with the experimental scattering data. We do not assume that scattering arises from atoms, but rather recover the continuous charge density. As a sensitive test of this method, we apply it to the well-known Au(110)-(2×1) reconstruction.

The structure of the Au(110)-(2×1) surface has been determined previously.<sup>15–18</sup> (See Fig. 2.) The principal structural feature is that every other row of close-packed atoms along the  $[\bar{1}10]$  direction is missing, thereby doubling the unit cell in the  $[001]$  direction. Like many metals, this sur-

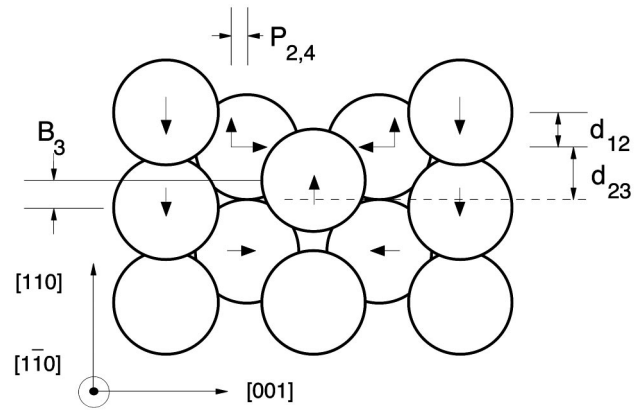


FIG. 2. Side view of Au(110)-(2×1) reconstruction. Displacements measured in experiment are indicated (not to scale). The distance  $\Delta d_{23}$  is measured to the average position of the third-row atoms (indicated by dashed line).

face exhibits an oscillatory relaxation behavior: prior experiments show negative values for the change  $\Delta d_{12}$  in the first-second layer spacing (i.e., contraction), and positive values for  $\Delta d_{23}$  (i.e., expansion).<sup>15,17,18</sup> In addition, the corrugation of the surface due to the missing rows causes distortions in the underlying layers; consistent with the symmetry of the surface, a pairing along the  $[001]$  direction has been reported for the second<sup>15,18</sup> and fourth layers,<sup>18</sup> while a buckling has been reported in the third layer.<sup>15,17</sup> The present measurements were able to detect all of these structural features, including the buckling that eluded previous SXRD measurements.<sup>18</sup>

The mechanically polished Au(110) crystal was annealed in vacuum at  $900 \text{ }^\circ\text{C}$  for 15 h to reduce the bulk mosaic spread to  $<0.04^\circ$ , and subsequently electropolished to remove the damaged and roughened surface layers. The surface was sputtered and annealed to  $430 \text{ }^\circ\text{C}$ , which is above the  $(2 \times 1) \rightarrow (1 \times 1)$  deconstruction temperature but below the surface roughening transition temperature.<sup>19,20</sup> Upon cooling to RT, a well-ordered  $(2 \times 1)$  reconstruction emerged. No contaminants were observed with Auger electron spectroscopy.

SXRD measurements were made at Beamline X22C of the National Synchrotron Light Source. The six-circle ultra-high vacuum diffractometer<sup>21</sup> was operated in the symmetrical ( $\alpha = \beta$ )  $z$ -axis mode<sup>22</sup> to access large values ( $\approx 4 \text{ \AA}^{-1}$ ) of the momentum transfer perpendicular to the surface plane  $q_{\perp}$ . Approximately 2000 surface structure factor amplitudes were measured, covering 588 nonequivalent reflections distributed along 42  $(hk)$  rods.

The corrected<sup>23</sup> data were input into the algorithm described above. Convergence was typically reached in  $<40$  iterations. Trials were initiated with random initial phases, but always converged to the same recovered electron density. A projection of the obtained 3D electron density viewed along the  $[\bar{1}10]$  direction is shown in Fig. 3. The depicted isosurfaces represent electron density at  $\approx 0.35$  of the maximum value. The recovered  $(2 \times 1)$  cell has been repeated three times to allow comparison to the bulk-terminated structure (left side) and to the final positions determined by con-

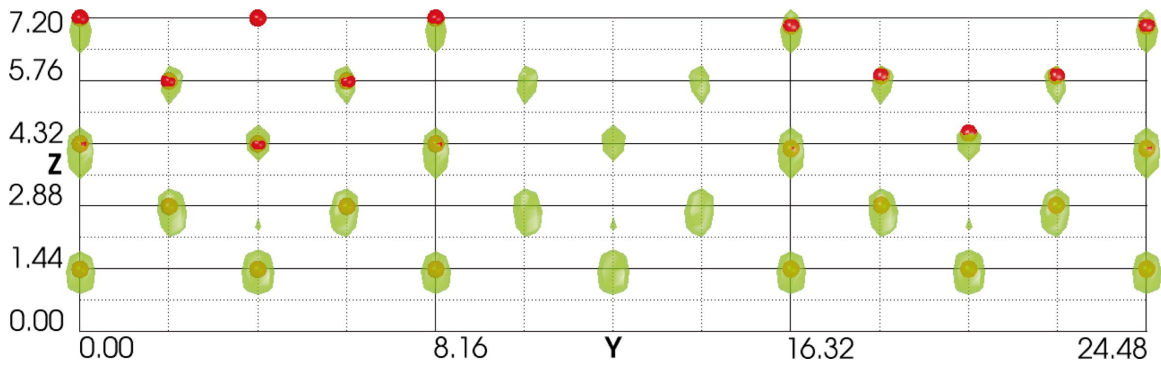


FIG. 3. (Color)  $[1\bar{1}0]$  projection of the recovered electron density. The  $(2 \times 1)$  surface unit cell is repeated three times. The balls on the left are shown at bulk-terminated locations, while those on the right are positioned according to conventional  $\chi^2$  refinement.

ventional refinement discussed below (right side).

The principal structural feature of the surface reconstruction, the missing row in the first layer, is obvious in the recovered electron density. Also, the relaxation of this layer is clearly evident in Fig. 3, as judged by the inward displacement of the remaining electron density compared to the bulk-terminated positions. Moreover, subtler features of the surface structure, such as subsurface relaxation, pairing, and buckling, are also evident. Notice that the electron density maxima in the second layer are displaced toward the center of the cell compared to the bulk-positioned spheres; this shift is consistent with the SXR D study of Ref. 18 that observed pairing in the second and fourth layers. Also, note the density maxima in the third layer are displaced alternately inward and outward compared to the bulk-positioned spheres, consistent with the third-layer buckling observed in the ion scattering<sup>17</sup> and low-energy electron-diffraction<sup>15</sup> (LEED) studies.

Beyond these naked-eye findings, we can conduct conventional refinement of the atomic positions using the electron density maxima as starting positions. The values of all of the symmetry-allowed displacements indicated in Fig. 2 have been previously determined, although no single technique was heretofore capable of determining all of them. LEED measures scattering events with large values of  $q_{\perp}$ , and hence is more sensitive to out-of-plane displacements (buckling) than to in-plane displacements (pairing), whereas the prior SXR D experiment, which could access sizable values of  $q_{\parallel}$  but only modest values of  $q_{\perp}$ , was more sensitive to pairing, but was unable to detect any buckling.<sup>18</sup> The present experiments utilized a larger range of both  $q_{\parallel}$  and  $q_{\perp}$  than the earlier SXR D study, and could therefore reliably observe both the pairing and buckling down to the fourth atomic layer. The results of our study are summarized in Table I, and are consistent with the consensus of previous determinations. Beyond these displacements, there was no statistically significant movement in the fifth or deeper layers.

The best fit to the full data set yielded a reduced  $\chi^2$  value of 2.0. This value is somewhat high, but compares favorably with the value of 2.6 found in the earlier study.<sup>18</sup> We attribute our elevated value to the difficulty of minimizing systematic uncertainties over the large span of  $h$ ,  $k$ , and  $l$  used in this study. In particular, reflections at large values of  $l$  (i.e., large  $q_{\perp}$ ) are sensitive to imperfections in the bulk. If we restrict

the  $l$  range of our data set to  $l < 1.3$ , compared to  $\approx 1$  in the previous SXR D study, we obtain a good  $\chi^2$  value of  $\approx 1.4$  with similar best-fit parameters.

Several other attempts have been made to directly extract atomic positions from SXR D and transmission electron diffraction data.<sup>24</sup> Most of these have employed the assumption of atomicity. As a consequence of this assumption, phase relations among strong superstructure reflections are expected, and have been exploited to gain some of the desired phase information.<sup>24–26</sup> Recently, Yacoby *et al.* have explored a new approach by comparing closely spaced points along a CTR. They estimate the phase of the surface structure factor by assuming that it varies only slowly along the rod,<sup>27</sup> an assumption strictly valid only if the height of the unknown surface region is small and the origin of coordinates is located near this region. Our method uses neither assumption and is therefore expected to be more robust. Moreover, our method incorporates both the CTR and the superstructure rods; approaches that use only the CTR (Ref. 27) or superstructure rods<sup>25</sup> are unable to recover the complete and unfolded surface unit cell.

The possibility of inverting a set of oversampled Fourier amplitudes (without phases) depends on the dimensionality: it has been argued<sup>5</sup> that there is no unique solution in one-dimension, but that one may be found if oversampling is possible in two (2D) and three dimensions (3D).<sup>5</sup> In the seminal works,<sup>3,11</sup> the object recovered was a 2D projection of two nonperiodic dimensions. In recent work using electron diffraction,<sup>28</sup> the 2D projection of a carbon nanotube, of

TABLE I. Summary of experimental findings for Au(110)-(2  $\times$  1).

Method	$\Delta d_{12}$ (Å)	$P_2$ (Å)	$\Delta d_{23}$ (Å)	$B_3$ (Å)	$P_4$ (Å)
LEED <sup>a</sup>	-0.29	0.07	0.03	0.24	...
MEIS <sup>b</sup>	-0.26	...	0.06	0.20	...
SXR D <sup>c</sup>	-0.32	0.05	...	...	0.05
present work	-0.28	0.05	0.01	0.29	0.04
	$\pm 0.03$	$\pm 0.01$	$\pm 0.01$	$\pm 0.03$	$\pm 0.01$

<sup>a</sup>Low-energy electron diffraction, Ref. 15.

<sup>b</sup>Medium-energy ion scattering, Ref. 17.

<sup>c</sup>Surface x-ray diffraction, Ref. 18.

one periodic and one nonperiodic dimension, was recovered using oversampling methods. Our present work shows that it is possible to recover a 3D object with just one nonperiodic dimension available for oversampling. Diffraction from a system with 2D periodicity (such as a crystal surface) gives rise to multiple rods; we suggest that although there is only one oversampled dimension, the many rods sampled constitute many interdependent, 1D Fourier transforms, and a unique phase solution exists.

The method demonstrated here can likely be applied to other systems. The principal requirement is that oversampling is allowed via a continuous distribution of scattered intensity along at least one reciprocal space dimension. In addition to the 2D surface case discussed here, liquid crystals (LC) possess this intermediate order;<sup>29</sup> thus, it seems probable that the internal structure of an unknown molecular unit that forms a LC could be determined by oversampling its diffuse intensity. This methodology might be profitably ap-

plied to biopolymers such as proteins. Rather than labor to form 3D protein crystals, whose scattered intensity is confined to Bragg spots, it may be more advantageous to impose only orientational order on the units either by forming a protein LC or by adsorbing a monolayer of protein molecules on a 2D surface.

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