

New methods for determining surface structures

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Abstract

The atomic scale structure of a surface plays a central role in catalysis, defining the available sites for reactions. While there is now an extensive body of information about simple adsorption sites on metal surfaces, for other more complicated system (particularly insulators such as oxides) very little is known. We have recently been able to use classical bulk “direct methods” to determine surface structures with either surface X-ray diffraction or transmission electron diffraction. The method makes no assumptions about the surface structure and is truly *ab initio*. As a consequence, structures that one might not find or expect using simple chemical arguments can be determined if present. One recent example is the observation of a new chemical species at a surface, cyclic ozone. The basics of the approach as well as other recent results are described. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Of fundamental importance for heterogeneous catalysis is the atomic character of the surface and of chemisorbed species at a surface. For simple metals and semiconductors there is now an extensive amount of information about these, due primarily to low-energy electron diffraction (LEED) [1,2] with more recent contributions from real-space imaging methods such as scanning tunneling microscopy (STM) [3–7], atomic force microscopy (AFM) [7] or high resolution electron microscopy (HREM) [8–11]. With more complicated systems or insulators much less is known. The key point is that with a good initial model for the structure (accurate to about 0.1 Å) it is relatively straightforward to

refine highly accurate final positions, but this initial model often is pure guesswork. If the initial model is not close to the true structure, refinements will give some result but may have little real scientific value. In general there is no simple method of inverting LEED data (due to dynamical diffraction) back to approximate atomic positions. With STM and AFM not all atoms may be resolved, and it can be difficult or impossible to tell the chemical nature of “features” in the images. As such, while the images may constrain the symmetry of the structure they may not give the required estimate of the atomic positions. HREM images from surfaces are much easier to interpret, and do give atomic positions to a required level of accuracy. However, they suffer from substantial noise problems due to weak signals although this will improve in the future with the use of brighter sources.

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For bulk X-ray diffraction exactly the same issues were faced some years ago, and have been largely solved by what are called “direct methods” [12–14]. Direct methods can be broadly defined as the set of methods that provide an initial estimate of the atomic positions. As such they include Patterson-based techniques as well as (in a surface context) approaches such as photoelectron holography [15–23]. In a more crystallographic setting, direct methods are a set of mathematical techniques for determining the phases of diffracted beams given only amplitude information, the square root of the measured intensities. In general they are much more powerful than Patterson techniques and at the time of writing have been used to solve three-dimensional structures containing more than 1000 independent atoms.

Until very recently it was thought that these could not be used for surfaces. However, with due care we have recently been able to use them not just in two-dimensions [24–27] but (very recently) for full three-dimensional solutions [28]. A list of structures for which the approach has been applied to date (reviewed recently in Ref. [29]) is given in Table 1.

Table 1
List of surface structures solved by direct methods.

Structure	Data	Reference
Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°Au ^a	electron	[24]
Si(111)-(5×2) Au ^a	electron	[24]
Si(111)-(7×7) ^a	electron	[25]
Si(111)-(4×1) In	electron	[26]
Si(111)-(6×6) Au	X-ray	[30]
TiO ₂ (100)-1×3	X-ray	[31]
Si(111)-(3×1) Ag	electron	[27]
Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°Ag ^a	electron	[32]
Ge(111)-(4×4) Ag	X-ray	[33]
MgO(111)-($\sqrt{3} \times \sqrt{3}$)R30°	electron	[34]
MgO(111)-(2×2)	electron	[34]
MgO(111)-(2 $\sqrt{3} \times 2\sqrt{3}$)R30°	electron	[34]
Ni(111)-(5 $\sqrt{3} \times 2$) S ^a	X-ray	–
Cu(111)- $\begin{vmatrix} 4 & 1 \\ -1 & 4 \end{vmatrix}$ S ^a	X-ray	–
Cu(110)-p(4×1) Bi ^a	X-ray	–

^aStructures analyzed as calibration tests.

2. Methodology

The problem can be posed relatively simply. We have a set of measurements of the intensities of the diffraction spots, which can be transformed to the moduli directly. If the phases to go with these moduli were known, a simple Fourier transform would give the charge density (for X-ray diffraction) or electrostatic potential (for transmission electron diffraction). We need to find approximate values for these; even with relatively large errors of the order of 20° the Fourier transform will be close enough that approximate atom positions can be found for later refinement. Even in the simplest case such as a centrosymmetric structure (where the phase is either 180° or 360°) this sounds like an impossible task since the number of possible permutations is 2^M for M reflections. However, the phases cannot be totally random, which can be shown via many different routes all of which lead to similar conclusions. I will give here a short illustrative example, simpler than the methods normally used in practice.

Consider a material with only one type of atom. The structure factor $F(\mathbf{k})$ as a function of reciprocal lattice vector \mathbf{k} can be written as:

$$F(\mathbf{k}) = \sum_{\mathbf{r}_1} f(\mathbf{k}) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_1) \quad (1)$$

where the sum is over the positions of the atoms \mathbf{r}_1 and $f(\mathbf{k})$ is the (known) scattering from a single atom. Dividing both sides by $Nf(\mathbf{k})$ where N is the number of atoms we generate the equation:

$$U(\mathbf{k}) = F(\mathbf{k})/Nf(\mathbf{k}) = 1/N \sum_{\mathbf{r}_1} \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_1) \quad (2)$$

with $U(\mathbf{k})$ called the unitary structure factor. Looking at the real space form of $U(\mathbf{k})$ (after a Fourier transform) $u(\mathbf{r})$

$$u(\mathbf{r}) = (\mathbf{1}/N) \sum_{\mathbf{r}_1} \delta(\mathbf{r} - \mathbf{r}_1) \quad (3)$$

a set of delta functions at each of the atom sites. Since the square of a delta function is also a delta function,

$$u(\mathbf{r}) = Nu(\mathbf{r})^2 \quad (4)$$

or, in reciprocal space

$$U(\mathbf{k}) = N \sum_{\mathbf{h}} U(\mathbf{k} - \mathbf{h})U(\mathbf{h}) \quad (5)$$

Suppose that we know already the phases on the right hand side of Eq. (5) but not on the left; we can generate the phase for $U(\mathbf{k})$ straightforwardly—this is known as phase extension. Alternatively Eqs. (4) and (5) represent a set of self-consistency equations that the correct phases have to obey. For M unknown phases there are M equations of the form of Eq. (5) so, in principle, the problem is completely solved.

For a good set of three-dimensional measurements including all reflections to atomic-scale resolution (1.0–1.5 Å) the problem of obtaining solutions is (probably) more limited by available computer power than anything else. A surface represents a special case, either in two dimensions or in three dimensions. To understand this, it is important to discriminate between what, in LEED notation are called the fractional-order reflections versus the integer-order reflections. While the top atomic layers with positions different from the bulk contribute substantially to the first, for the integer-orders there are large contributions from the bulk atoms. One cannot sensibly extract the structure factor for these integer reflections when it is superimposed on this typically far larger bulk signal. A second problem is that one only has a very poor idea about how many atoms there are in the unit cell. For some material A on a substrate B, the number of A atoms might be known to an accuracy of 20% but the number of B atoms could be almost anything—this is of course an even more substantial issue in a native reconstruction. Most available programs for

bulk crystallography use the number of atoms as an input parameter and find chemically reasonable arrangements (using typical interatomic distances and bond angles for instance) which is again not going to be the same for a surface.

Of the surface data problems, the most severe is the missing reflections. Classical direct methods assume that all the strong reflections have been measured and only consider relationships between the measured reflections. (In effect, unmeasured reflections are taken to have zero intensity.) As a consequence they will (probably) fail completely if there are large, unmeasured reflections. What is needed are methods which in some fashion include estimates for the unmeasured reflections and/or work when there are not enough equations for a formal mathematical solution. Fortunately such methods already exist, and use the idea of exploiting the entropy as a functional. The best developed of these is the “maximum entropy method” [35–40] which maximizes the entropy. The approach we have developed [39] is similar, and minimizes the relative entropy [40]. Both of these are highly nonlinear and as a consequence have an in-built interpolation of the unmeasured reflections.

Using this relative entropy [39] the general approach can best be considered at a more formal level using set theory, particularly what is called “projection onto convex sets” [41–44]. The set of possible complex values with the experimentally observed moduli are one set; constraints due to the fact that the scattering comes from atoms can be considered as other sets. A global search algorithm, a genetic search in our case [45] is used to find the intersection of these sets which are feasible values for the phases. More details of the formal analysis are described elsewhere [44], and a preliminary version of the code in two-dimensions is available on the web.¹

¹ See <http://www.numis.nwu.edu/fs98>.

3. Illustrative results

As described in the introduction, to date surface structures have been solved by making reasonable assumptions about the chemical bonding and then modeling the diffraction data. This precludes cases where the bonding turns out to be more complicated (and therefore interesting) than expected. The first example is for the Ag on Si (111) 3×1 surface [27]. Fig. 1 shows the reconstructed electrostatic potential (in Fig. 1b), with the complete assignment of atomic positions shown in Fig. 1a. The two Ag sites marked on the figure are equal probability twin-related sites. Several models had been proposed in the past for the surface, but none were able to explain all the experimental data; no one guessed the real structure that at first sight appears odd. A recent theoretical analysis [46] indicates that the stability is due to a true Si=Si double bond (arrowhead in Fig. 1a), an unusual type of bonding.

A second example is the MgO (111) surface which forms a number of reconstructions upon annealing in oxygen [34]. The direct methods

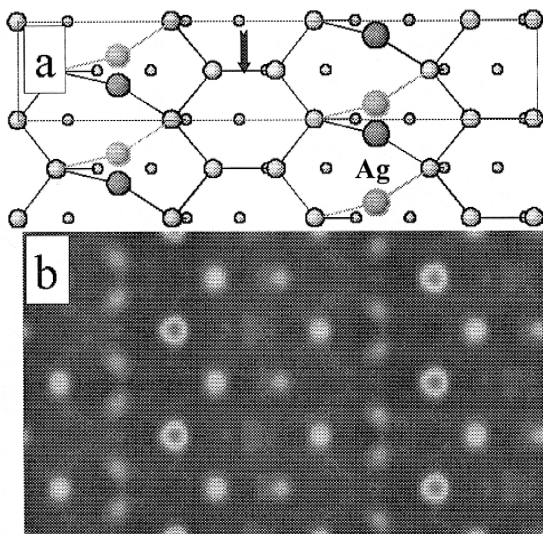


Fig. 1. Reconstructed real-space electrostatic potential in (b) with white large and the final model for the structure in (a) for the Ag on Si (111) 3×1 surface. Arrowhead in (a) is the bond that a recent theoretical calculation has suggested is a true Si=Si double bond.

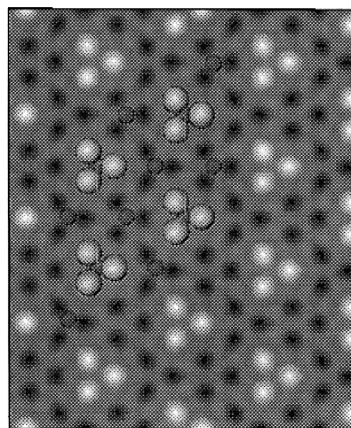


Fig. 2. Reconstructed real-space electrostatic potential for the MgO (111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface with an atomic model overlaid. The ozone trimer is believed to sit over an Mg atom, and may be negatively charged.

results shown in Fig. 2 indicate a triangular arrangement of oxygen, i.e., cyclic ozone. We believe that the cyclic form is stabilized at a surface rather than the more standard form, and this may have interesting implications for oxide catalysts.

4. Discussion

While the atomic scale structure of simple adsorbates on metals is now a relatively mature field, much less is known about more complicated materials and for oxides. The experimental tools (e.g., grazing-incidence X-ray diffraction or transmission electron diffraction) are available, and many of the oxide reconstructions are air stable. It is not clear to the author whether we currently understand enough about the structure of oxide surfaces to make reasonable deductions, and there may well be more surprises in store as more attention is paid to these technologically important materials in the future.

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