Surface Structure Determination with X-ray Standing Waves

– A Short Tutorial –

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The X-ray Standing Wave (XSW) technique provides element specific information on surface structures and adsorbate sites by combining a diffraction based approach with spectroscopic measurements. The availability of brilliant and tunable synchrotron light has stimulated the application of this technique to a wide range of problems in surface science.

The basic principle: Bragg reflection close to $\theta_\mathrm{B} = \pi/2$

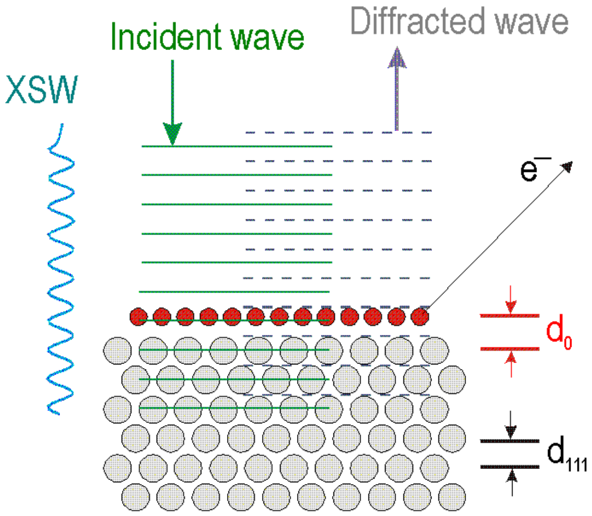

Figure 1: A standing wave with the periodicity of the substrate lattice is generated by reflection from a single crystal. By scanning the photon energy of the incident wave through the Bragg condition the XSW field above the surface changes in a characteristic way. The emitted photoelectrons or Auger electrons that are generated by inelastic scattering processes can be used as element-specific signals that reflect the position d_0 of the adsorbate atom.

The X-ray standing wave field

The XSW field is produced by the coherent superposition of the incoming plane wave with the electrical field vector $\mathbf{E}_0$ and the Bragg-reflected wave $\mathbf{E}_H$ as depicted in Fig. 1. The (normalised) spatial intensity variation $I^{\mathrm{SW}}(\mathbf{r})$ within and above the substrate is then given as

$$I^{\mathrm{SW}}(\mathbf{r}) = \frac{|\mathbf{E}_0 + \mathbf{E}_H|^2}{|E_0|^2} = 1 + \left|\frac{E_H}{E_0}\right|^2 + 2C\left|\frac{E_H}{E_0}\right|\cos(\nu - 2\pi\mathbf{H}\cdot\mathbf{r}), \tag{1}$$

where ν is the phase of the complex amplitude ratio, $E_H/E_0 = |E_H/E_0|\exp(i\nu)$, $\mathbf{H}$ the reciprocal lattice vector, C the polarisation factor ($C = 1$ for σ-polarisation; $C = \cos 2\theta_B$ for π-polarisation), and θ_B the Bragg angle.

The photon energy dependence both of ν and the reflectivity $R = |E_H/E_0|^2$ are well-known within the framework of dynamical diffraction theory: The ratio of the complex amplitudes E_0 and E_H of σ-polarised X-rays is given by [1, 2]

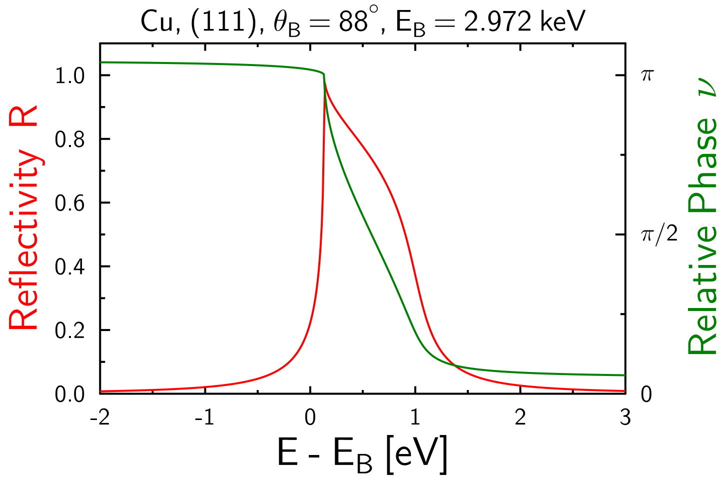

Figure 2: Theoretical energy dependence of the reflectivity R and XSW phase ν.

$$\frac{E_H}{E_0} = \sqrt{\chi_H/\chi_{\bar{H}}}\left(\eta \pm \left(\eta^2 - 1\right)^{1/2}\right) \tag{2}$$

for a symmetric Bragg reflection. Here χ_0 and χ_H are the 0th- and Hth-order Fourier components of the complex crystal susceptibility $\chi(\mathbf{r})$ which is related to the dielectric function $\epsilon(\mathbf{r})$ via

$$\chi(\mathbf{r}) = \epsilon(\mathbf{r}) - 1. \tag{3}$$

The susceptibility components[1] $\chi_{0,H}$ are calculated from the structure factor $F_{0,H}$ via

$$\chi_{0,H} = \frac{r_0\lambda^2}{\pi V_c}F_{0,H}, \tag{4}$$

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[1] Note, that for a centrosymmetric crystal, $\chi_{\bar{H}} = \chi_H^*$ and therefore $(\chi_H\chi_{\bar{H}})^{1/2} = |\chi_H|$.

where r_0 is the classical electron radius, λ the wavelength, and V_c the volume of the unit cell for which the structure factor has been derived. The complex variable η in Eq. (2), which for Bragg reflections close to $\theta_B = \pi/2$ is given by [3]

$$\eta = \frac{2(\Delta E/E_B)\sin^2\theta_B - \chi_0}{(\chi_H \chi_{\bar{H}})^{1/2}}, \tag{5}$$

is a function of the energy difference $\Delta E = E_B - E$. On the basis of these equations the reflectivity R and the phase ν can be calculated, see Fig. 2. Since the phase ν generally varies asymptotically by π when going through the Bragg condition, the X-ray standing wave field moves by half a diffraction plane spacing within this range.

The angular width W_θ of the Bragg reflection varies as

$$W_\theta \propto d_s^2 F_H \tan\theta_B, \tag{6}$$

where d_s is diffraction plane spacing. Since for Bragg angles close to $\pi/2$ the width increases strongly, crystalline imperfections (mosaicity) can be tolerated.

The electron yield in coherent and partly coherent films

As indicated in Fig. 1 the XSW technique requires measurements of the photo yield Y_p which characterises the position the atoms in the interference field. For this purpose the intensities of photo or Auger electrons are commonly used. The data are usually analysed in the so-called dipole approximation, where Y_p is proportional to the square of the electric field at the centre of the atoms and thus proportional to I^{SW} [4]. For systems with all atoms on equivalent sites (coherent case) one obtains

$$Y_p(\mathbf{r}) = 1 + R + 2C\sqrt{R}\cos(\nu - 2\pi\mathbf{H}\cdot\mathbf{r}). \tag{7}$$

Figure 3 illustrates the effect different positions $\mathbf{r}$ have on the photo yield.

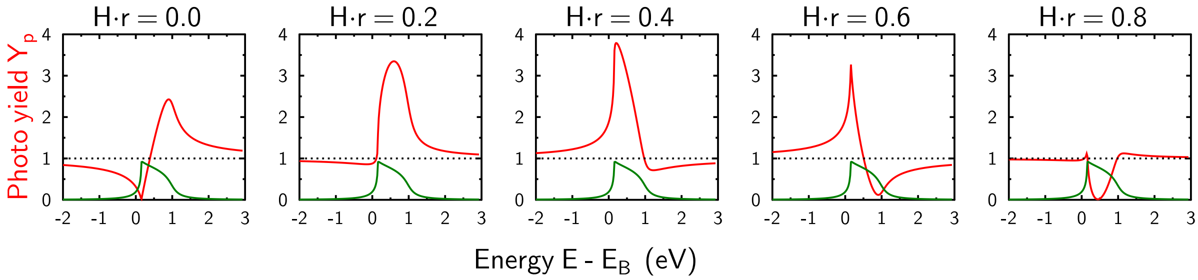

Figure 3: Theoretical normalised photo yields for different values of $\mathbf{H}\cdot\mathbf{r}$ in equation (7). The extraordinary sensitivity of Y_p to the position of the atom $\mathbf{r}$ is demonstrated.

For an (partly) incoherent system with atoms on non-equivalent sites a normalised distribution function $n(\mathbf{r})$ that describes the spread of atoms around their average lattice position has to be introduced. Equation (7) is then generalised to

$$\begin{aligned} Y_p &= \int Y_p(\mathbf{r})n(\mathbf{r})d\mathbf{r} & (8) \\ &= 1 + R + 2C\sqrt{R}\int n(\mathbf{r})\cos(\nu - 2\pi\mathbf{H}\cdot\mathbf{r})d\mathbf{r}. & (9) \end{aligned}$$

A more manageable form of this averaging equation is obtained by introducing two new parameters: the *coherent position* $P_H = \mathbf{H} \cdot \mathbf{r}$ and the *coherent fraction* f_H.

$$Y_p = 1 + R + 2C\sqrt{R} f_H \cos(\nu - 2\pi P_H). \tag{10}$$

This is the working equation for most XSW experiments since P_H and f_h contain all structural information on the specific system. The coherent position $0 \leq P_H \leq 1$ now gives the position relative to the diffraction planes, whereas the coherent fraction $0 \leq f_H \leq 1$ describes the degree of coherent order in the system.[2] Finally, the position of the adsorbate atom as depicted in Fig. 1 is given by

$$d_0 = d_{hkl}(n + P_H), \tag{11}$$

where n is an integer and d_{hkl} the substrate lattice plane spacing corresponding to the lattice vector $\mathbf{H}$.

The standing wave parameters $\mathrm{P_H}$ and $\mathrm{f_H}$

The equivalence of equations (9) and (10) can be used to explore the physical meaning of the *coherent fraction* f_H [5]. By equating both expressions we obtain a relation

$$f_H \cos(\nu - 2\pi P_H) = \int n(\mathbf{r}) \cos(\nu - 2\pi \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}, \tag{12}$$

which has to hold for any value of ν. An expansion of the cosine sums on both sides now gives

$$\begin{aligned} \cos\nu\, f_H \cos(2\pi P_H) + \sin\nu\, f_H \sin(2\pi P_H) &= \cos\nu \int n(\mathbf{r}) \cos(2\pi \mathbf{H} \cdot \mathbf{r}) d\mathbf{r} \\ &+ \sin\nu \int n(\mathbf{r}) \sin(2\pi \mathbf{H} \cdot \mathbf{r}) d\mathbf{r} \end{aligned} \tag{13}$$

As $\sin\nu$ and $\cos\nu$ are linear independent functions this relation can only be satisfied if the individual coefficients are equal, i.e.

$$f_H \cos(2\pi P_H) = \int n(\mathbf{r}) \cos(2\pi \mathbf{H} \cdot \mathbf{r}) d\mathbf{r} \tag{14}$$

$$f_H \sin(2\pi P_H) = \int n(\mathbf{r}) \sin(2\pi \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}. \tag{15}$$

Using complex numbers this can finally be summarised by

$$f_H \exp(2\pi i P_H) = \int n(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}. \tag{16}$$

Therefore the coherent fraction f_H is the first Fourier component of the distribution function $n(\mathbf{r})$ multiplied by a phase factor containing the coherent position P_H. This means by measuring photo yields for sufficiently many reciprocal lattice vectors $\mathbf{H}$ it is in principle possible to the determine the Fourier representation of the specific electron density.

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[2] This is best illustrated by considering two extreme cases: A random distribution of atoms on the surface, e.g. a thick film of molecules, with $f_H = 0$ results in $Y_p = 1 + R$, i.e. depending on the absorption $Y_p \leq 2$. A perfectly ordered ad-layer with $f_H = 1$, in contrast, amplifies the photo yield to $Y_p \leq 4$.

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