X-ray standing waves technique: Fourier imaging active sites

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The X-ray standing wave (XSW) technique utilizes X-ray interference in order to lend spatial resolution to powerful X-ray spectroscopy technique such as photoelectron or X-ray fluorescence spectroscopy, the latter case demonstrated already in 1964 by Boris Batterman at Bell Labs. Later, Batterman utilized the interference field created by Bragg reflecting 17.4 keV X-rays by the (220) planes of a silicon single crystal for photo-exciting dilute dopant atoms. Recording As K-fluorescence as a function of the XSW movement, he revealed the substitutional location of the As atoms within in the unit cell of the silicon crystal. Since then, there have been numerous applications of the XSW technique (see Ref.1 and references therein). From the beginning, the majority of these dealt with unraveling the structure of highly dilute systems such as dopants and surface adsorbates.

The XSW technique, like diffraction, is a Fourier technique, but provides in addition phase sensitive and element specific information. One XSW measurement provides commonly one complex Fourier coefficient, i.e. amplitude and phase for the distribution of an elemental species under study. In a short paper, Hertel et al. published 1985 this principle of the XSW analysis and in a review of the XSW technique we expanded on this principle with focus on surface structure determination.

How to access several Fourier components of the spatial structure determination with spatial resolution down to pm. The XSW method is particularly useful for determining the lattice location of impurity atoms or dopants in a crystal or the position of adsorbates on a surface. Thus, these applications have dominated the use of the XSW technique. When using reflection from a synthetic multilayer or from an optical surface for producing the standing wave, the wavefield spacing and thus the accessible length scale can be several ten nm, allowing, however, only one-dimensional structural analysis.

In principle the movement of the XSW modulates any photon-scattering process and, e.g. Compton as well as thermal diffuse (i.e. phonon) scattering have been studied under the influence of XSW excitation. However, structure determination with spatial resolution down to pm relies on photo-excitation. The reason being that the probability for dipolar photo-excitation is proportional to the electric field amplitude precisely at the core of the atom. It is fortunate that dipolar photo-absorption is dominant even in the hard X-ray regime. In fact, even if present, multipole contributions do not impede high structural resolution. They can (and must) properly be taken into account in the XSW analysis.

The XSW technique distinguishes itself clearly from X-ray diffraction (XRD) techniques that utilize the coherent scattering from the distributed electron cloud. XRD provides high structural resolution in particular for periodic atomic arrangements, but inherently without element specificity. Interpreting measured electron densities or exploiting anomalous dispersion effects provides element specific information, although with some ambiguity. Worthy of note, while the XSW method uses a periodic medium for generating the interference field, periodicity of the system under study is not a prerequisite for its application of the XSW technique.

Besides providing phase sensitive information in Fourier space, the combination of X-ray interference with the elemental and chemical specificity of spectroscopy presents a huge advantage over element indiscriminate elastic scattering employed by diffraction techniques. This is of particular benefit when the species of interest is highly diluted and/or cannot otherwise be discriminated from a surrounding...
In the following, we will deal only with planar interference field, created by reflection or diffraction of a plane X-ray wave (and thus distinguish XSW from more general interference/holographic techniques). Furthermore, we will concentrate on the approach of the XSW technique that is most frequently used by far, providing atomic resolution in the pm range, i.e., single crystal XSW, where the XSW is created by Bragg reflection from a crystal lattice. We will discuss XSWs created by multilayer or total external reflection, but only briefly. Both of these variants have found some applications, but both offer neither sub-Å nor 3D resolution.

The XSW technique has meanwhile been reviewed many times, most comprehensively in a 2013 monograph. In addition and over the years, several topical reviews of the XSW technique have been published, such as on: surface displacements detection of crystals; formation of XSW in distorted crystals; Bragg reflection XSW under specular reflection condition; normal incidence XSW determination of adsorbate structure and Argand diagram analysis; theory and applications of XSW in real crystals; XSW studies of minerals and mineral surfaces; and very recently about surface structure determination by XSWs at a free-electron laser.

Just for the convenience of the reader we will in Sect. 2 recall some of the bare essential technical requirements and principles of the technique, but only very briefly because of the significant amount of literature available. Fourier imaging by the XSW technique, on which this review concentrates, is a more recent development and has neither been extensively used nor comprehensively reviewed so far.

In Sect. 3, we present and discuss three illustrative examples of XSW analysis. Determining the chemically active aluminum sites in the unit cell of the zeolite scolecite by classical XSW analysis using several reflections is reviewed in Sect. 3.1. Two applications of XSW imaging are described in following Sects. 3.2 and 3.3. Section 3.2 summarizes how the locations of active and counter-active Mn in the unit cell of the dilute magnetic semiconductor GaMnAs were revealed employing ≈20 Fourier components. This number is comparably large for the XSW technique but rather small compared with diffraction techniques. In contrast, Sect. 3.3 is an example of how XSW Fourier imaging, using just two reflection, provides structural information, here about the SrTiO3(001) surface sites that are active in the deprotonation of water.

2. The XSW method

In a nutshell, it is the main principle of the XSW technique to photo-excite atoms by an interference field instead of a transient wave. The generation of an XSW requires firstly a monochromatic and collimated X-ray beam, resembling an X-ray plane wave. Reflection gives rise to a second, coherent plane wave. Overlap of both results in the formation of a standing wave.

Sufficiently collimated and monochromatic X-radiation is nowadays routinely available in the form of monochromatized radiation emitted from undulators installed at third or fourth generation low emittance (see e.g. Ref. 35) synchrotron light source or free-electron laser, Figure 1 shows a schematic experimental setup for XSW measurements at a storage ring. Bragg reflection or total external reflection creates a second coherent plane wave, as schematically

Fig. 1. (Color online) Schematic of typical XSW set-up at a synchrotron radiation source. A double crystal Bragg monochromator selects the appropriate energy from the radiation of a low emittance undulator source. Typically used are liquid nitrogen cooled Si(111) crystals with a bandpass of \( \Delta E / E = 1.3 \times 10^{-4} \). Excellent heat conductivity and almost vanishing lattice expansion around 70 K of silicon are important to cope with the high heat load from the insertion device. Depending on the requirements, the bandpass is further reduced by a secondary monochromator. The beam intensity incident on and reflected from the sample is monitored. X-ray fluorescence and/or (photo)electrons from the sample are recorded by energy dispersive detectors. By tuning the angle of incidence, the sample can be “rocked” through the range of (total) reflection. More commonly, when using a multilayer or single crystal, the range of Bragg reflection is traversed at fixed angle by scanning the incident energy. The insets show schematically the formation of the XSW by the incoming and reflected beam with the propagation vectors \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \), respectively, related by the Laue equation \( \mathbf{K}_2 = \mathbf{K}_1 + \mathbf{H} \), with the diffraction vector \( |\mathbf{H}| = H = 1/d_h \) and the diffraction plane spacing \( d_h \), the (111) lattice constant in the shown case.
shown in Fig. 1 as well. The overlap of the two coherent plane X-ray waves leads to the formation of a planar X-ray interference field, i.e. an XSW. As shown in Fig. 1 for the case of Bragg reflection from the (111) planes of a diamond structure lattice, the equal-intensity planes of the standing wave are periodic with the planes giving rise to the reflection, i.e. with the diffraction planes with spacing \(d_{111} = d_{111}\) in the shown example. Diffraction planes are not necessarily lattice planes. Shown in Fig. 2 is the case of using (333) diffraction planes, i.e. diffracting from the (111) planes in third order \(m = 3\) as described by the Bragg equation \(36)\) by \(n \sin \theta_B = \frac{m \lambda}{d_{111}}\). Higher order reflection require for the same Bragg angle \(\theta_B\) an according shorter wavelength \(\lambda\), i.e. \(m\)-times higher energy. Photon wavelength \(\lambda\) and energy \(E\), are related by \(E_g = \frac{hc}{\lambda} = \lambda^{-1} \cdot 12.398\) 42 keVÅ. The use of higher order reflection is important for the XSW Fourier imaging technique since it allows one to access higher order Fourier components and thus shorter length scales.

At Bragg reflection, the periodicity of the X-ray planar wavefield is in resonance with the crystal lattice. Traversing the reflection range from low to high energy \(E\), or glancing angle \(\theta\) the resonance phase, the phase difference \(\psi\) between the exciting and reflected X-ray waves, characterized by complex field amplitudes \(E_i\) and \(E_R = A \cdot E_i^\ast\), respectively, changes by \(-\pi\) (see Fig. 3). The amplitude factor is simply \(A = \sqrt{R}\) with the reflectivity \(R = I_2/I_1\) and intensities \(I_{2,1} \sim |E_{2,1}|^2\). Consequently, passing the reflection range, the wavefield planes move inward by half the distance of the diffracting planes. \(1,37,38\) (We assume linearly polarized X-rays and the E-field vectors \(E_{1,2}\) of both waves being collinear. These two conditions simplify the experimental conduct and the data analysis significantly and are commonly employed in XSW experiments.) Reflectivity \(R\) and resonance phase \(\psi\) are shown in Fig. 3 for the cases of reflection from a mirror surface, multilayer and single crystal.

In the dipolar photo-absorption process, the X-rays are absorbed exactly at the center of atoms and the electrons are emitted without angular momentum. The dipole approximation is largely valid even for hard X-rays, which is the underlying reason of the high spatial resolution of the XSW technique. When scanning the wavefield by traversing the range of Bragg reflection in angle \(\theta\) or X-ray energy \(E\), the concomitantly recorded characteristic electron or X-ray fluorescence emission yield \(Y_A(\theta, E)\) from an atomic species A is recorded and represents the result on the XSW measurement. The shape of the yield is characteristic of the distribution of species A with respect to diffracting/reflected plane(s). The yield has the generic functional form \(Y_A(\theta, E) \sim \int \rho(r) |M_{fi}|^2 dr\), where \(M_{fi}\) is the transition matrix element for the considered photo-excitation process. In absence of multipole contributions this equation simplified
to

\[ Y_A(\theta, E_\gamma) \sim \int \rho(r) I(\theta, E_\gamma, r) \, dr. \]  

(1)

Here \( \rho(r) \) is the spatial distribution of atom species A and \( I(\theta, E_\gamma, r) \) is the wavefield intensity at position \( r \), which is a function of \( \theta \) and/or \( E_\gamma \). The case of total reflection XSW possesses the peculiarity that not only the position but also the spacing \( d_{\parallel} = \lambda/(2 \sin \theta) \approx \lambda/2\theta \) of the wavefield is a function of grazing incident angle \( \theta \). The intensity of the wavefield has the general form

\[ I(\theta, E_\gamma, r) = I_0 [1 + R(\theta, E_\gamma) + 2 \sqrt{\mathcal{R}(\theta, E_\gamma)} \cos [\nu(\theta, E_\gamma) - 2\pi \mathbf{H} \cdot \mathbf{r}]]. \]  

(2)

Employing reflection from a multilayer or a mirror surface, atomic distributions can be analyzed only in one dimension since the diffraction vector \( \mathbf{H} = \mathbf{K}_2 - \mathbf{K}_1 \) is always normal to the multilayer planes or the mirror surface, respectively. The dot product simplifies to \( \mathbf{H} \cdot \mathbf{r} = H \cdot z = z/d_{\parallel} \) where \( z \) is the direction parallel to \( \mathbf{H} \), i.e., perpendicular to the multilayer planes or the mirror surface. The large spacing of the wavefield does not allow one to obtain the sub-Å resolution, necessary for a detailed analysis of atomic structure. In case of total external reflection, the (variable) wavefield spacing \( d_{\parallel} = d_0 \approx \lambda/2\theta \) allows us to probe large length scales, which requires sufficient longitudinal coherence of the X-rays. Multilayer and total reflection XSW have been used for determining wider atomic distributions such as ions in front of electrodes and similar applications. In the following, we will not deal with these variants of the XSW technique any longer and concentrate on the most prominent case of Bragg reflection XSW.

When using Bragg reflection for generating the XSW, the result of every measurement of a particular atomic species A on or close to the surface is described by

\[ Y_A(\theta, E_\gamma) = Y_{A,0}[1 + R(\theta, E_\gamma) + 2 \sqrt{\mathcal{R}(\theta, E_\gamma)} F_A \cos [\nu(\theta, E_\gamma) - 2\pi P_A]]. \]  

(3)

The functional form is strictly speaking only correct in the absence of multipole contributions. The two parameters \( F_A \) and \( P_A \) represent the \( hkl \) Fourier component of the distribution \( \rho(\mathbf{A}) \) of atomic species A within the range of the XSW, i.e., \( F_A = F_{hkl}^A \) and \( P_A = P_{hkl}^A \), where \( [hkl] = \mathbf{H} \) is the diffraction vector characterizing the Bragg reflection used in the XSW measurement. The pre-factor \( Y_{A,0} \) is proportional to the density of species A within the range of the interference field. Schematically, \( P_A = \mathbf{H} \cdot \langle \mathbf{r}_A \rangle \), where \( \langle \mathbf{r}_A \rangle \) is the mean lattice location of the atomic species A. The expression is exact e.g. when the atomic species occupies a unique lattice site.

Quadrupole contributions can become appreciable in differential cross sections, e.g. when detecting photoelectrons within a limited solid angle and the yield function given above needs to be extended. This is meanwhile well understood and can/must be taken into account in the analysis of experimental XSW data.

Fitting the functional form given by Eq. (3) to acquired XSW scan data provides values for the three fitting parameter \( Y_{A,0}, F_A, P_A \). Reflectivity \( R \) and phase \( \nu \) are calculated using the structural data of the substrate, used for generating the XSW, using e.g. the dynamical theory of XRD or Parrat’s formalism.

With the help of acquired Fourier components, simple back transformation generates an image

\[ \rho_{A,XSW}(r) \sim 1 + \sum_{hkl} F_{hkl}^A \cos [2\pi [P_{hkl}^A - \mathbf{H} \cdot \mathbf{r}]]. \]  

(4)

of the distribution of species A within the boundaries of the unit cell of the crystal generating the Bragg reflections. These are limited in number and size with the smallest \( |\mathbf{H}| \) determined by largest diffraction plane spacing \( d_{\parallel} \). Consequently, length scales beyond the size of the substrate unit cell are not accessible. Such a projected atomic distribution, \( \rho_{A,XSW}(r) \), thus naturally exhibits the substrate periodicities, whether the real distribution does or does not have any long-range order. In short, XSW created images of the distribution display the atoms under study confined to or folded into the substrate unit cell.

3. XSW structural analysis and imaging: examples and discussion

3.1. Determining the active aluminum sites in zeolites: scolecite

Zeolites are nanoporous, crystalline aluminosilicate materials that are widely used in industry, e.g. as catalysts and gas separators, as well as for our daily life, for example, as adsorbents (e.g. cat litter) or as ion exchangers in laundry detergents. The functionality of a zeolite is basically determined by the size and connectivity of the pores and cages, the Si/Al ratio and in particular the placement of the trivalent aluminum atoms at specific sites within the unit cell. The replacement of a tetravalent silicon atom by a trivalent aluminum atom on a so-called lattice T-site creates a local negative charge, serving as binding site for cations. These are then held loosely in the pores and cages of the zeolite allowing them to be easily exchanged. This makes zeolites good cation exchangers, useful in water softening and in the removal of nuclear waste. The Si/Al ratio and the specific location of aluminum in the zeolite framework determine the kind and site of the charge-compensating cations, crucially influencing catalytic performance and chemical functionality of the zeolite, but are experimentally not easily accessible [see e.g. Ref. 45 and references therein] e.g. by XRD since the scattering density of Al and Si is rather similar. On the other hand, using XSW, the Al and Si K-fluorescence signal are clearly distinguishable.

An XSW study of the occupancy of T-sites by Al in scolecite was published in 2008. Figure 4 shows the structure of this zeolite. The figure also indicates the three different diffraction planes used for the XSW study, namely the (040), (002) and (402) reflections. An experimental set-up similar to the one shown in Fig. 1 was used, but with a compound refractive focusing lens instead of a post-monochromator. The sample crystal was mounted on a six-circle diffractometer, aligned and scanned in angle through the range of Bragg reflection. Figures 5(a)-(k) show the yield curves for Si, Al and the Ca cation for the three used reflections and a typical X-ray fluorescence spectrum from the sample [see Fig. 5(l)]. The shapes of the Al and Si curves are clearly different, proving that Si and Al do not occupy the same T-sites. Detailed analysis reveals that none of the T2...
sites are occupied by Al. Furthermore, of the four T1 sites only the sites marked by a, b in Fig. 4 are occupied by Al. For more details on the data analysis please consult the original publication.46)

3.2. Visualizing manganese in the dilute magnetic semiconductor GaMnAs

Dilute magnetic semiconductors such as Mn doped GaAs48) are under discussion for spintronic applications in device technology. The divalent Mn substitutes trivalent Ga and acts as an acceptor. The holes mediate a ferromagnetic interaction between the local moments of the open d shells in the Mn atoms.48) In the low doping limit, the Curie temperature \( T_c \) increases steadily with Mn concentration. With Mn concentration at around four percent, the Curie temperature \( T_c \) saturates at a value of around 150 K, still far from the desired room temperature, before decreasing again. The decrease in \( T_c \) was suspected to be caused by Mn occupying interstitial sites, thereby acting as donor, compensating the hole doping and suppressing p-type conductivity. Direct proof for the validity of this mechanism was missing, stimulating an XSW investigation.16)

Low temperature molecular beam epitaxy49) was used to grow 23 nm Ga\(_{1-x}\)Mn\(_x\)As thin film with \( x = 0.048 \) on a GaAs buffer layer on GaAs(001). The wafer was cleaved and two of the pieces were (i) annealed at 150 °C in air and (ii) hydrogenated in a hydrogen plasma. An as-grown and the two post-growth treated samples were investigated by the XSW technique at a insertion device beamline50) (see Fig. 1).

Fig. 4. (Color online) Structure of scolecite. (a) Six of the building units of scolecite, which form natrolite chains. The T-sites \( (T_1, T_2) \) are occupied by aluminum or silicon; oxygen atoms (shown as sticks) join the T-sites. Each building unit contains two types of T-atoms, four T\(_1\)-atoms and one T\(_2\)-atom. The T\(_2\)-atoms link the chain, whereas the T\(_1\)- and oxygen atoms of neighboring chains form larger pores. In scolecite, the chains are parallel to the crystallographic a axis. (b), (c) Projections of the atomic structure of scolecite along the three axes of the unit cell, marked by the blue rectangles in (b) and parallelogram in (c). The lattice parameters of the monoclinic unit cell are \( a = 0.6522 \) nm, \( b = 1.8968 \) nm, \( c = 0.9840 \) nm, \( \alpha = \gamma = 90^\circ \) and \( \beta = 109.97^\circ \). There are 20 T-sites per unit cell. The four T\(_1\)-sites associated with each T\(_2\)-site are labeled (a)–(d). The dashed lines denote the Bragg planes where coherent position \( P = 0 \) for the scolecite (040), (002) and (402) reflections. Taken from Ref. 46.
using an excitation energy of 10 keV, i.e. 367 eV below the Ga K-edge, and a high resolution Si(555) post-monochromator. With the samples mounted on a six-circle kappa-diffractometer 18 non-equivalent GaAs reflections were scanned in angle for each specimen while recording the fluorescence from the sample. An X-ray fluorescence spectrum is shown in Fig. 6, and four representative of the 18 XSW scans of the Mn K-fluorescence intensity in Fig. 7. Making use of the symmetry of the GaAs crystal unit cell, the 18 non-symmetry-equivalent reflections provide 50 Fourier components. Using Eq. (4), [Figs. 8(a)–8(c)] is produced, showing the reconstructed images of the Mn location \( r_{\text{Mn,XSW}} \) in the GaAs unit cell for the three investigated samples. The resolution of the image is \( \approx 0.09 \text{ nm} \), consistent with the XSW plane spacing of the highest order reflection used (\( d_{333} = 0.109 \text{ nm} \)). Figure 9(g) shows a ball-and-stick model of GaAs. Comparison with Figs. 9(a)–9(c) reveals that in all three cases (the majority of) Mn substitutes Ga. [Slight upward displacements is attributed to the \( c \) lattice constants of the (Ga,Mn)As layers being slightly larger than for the GaAs substrate.]

In addition to the intensity at the Ga-substitutional site, there are eight weaker spots at the locations of the Ga interstitial and As sites [see Fig. 9(h)]. They are more clearly visible in Figs. 9 (d)–9(f) where the contribution from the Mn Ga-substitutional site are removed from the images in Figs. 9(a)–9(c). These three edited images clearly reveal that Mn occupies, depending on the treatment, Ga and As interstitial sites, which are schematically shown in Fig. 9(h). Least square fitting the Fourier components of the Mn distribution function \( \rho_{\text{Mn}} \) to the experimental \( F_{\text{Mn}} \) and \( P_{\text{Mn}} \) reveals the Mn distribution on the three sites in the GaAs host lattice with 0.04% accuracy. The detailed description of the analysis is beyond the scope of this review and we refer to the original publication.16)

3.3. Water decomposition on SrTiO\(_3\)(001)

An important early development was the combination of the XSW technique with photoelectron spectroscopy (PES) 40 years ago, in the late 1970s by Kikuta and Takahashi.51,52) By employing PES, the technique is extended beyond

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Fig. 5. (Color online) XSW measurements determining Al location in scolecite. X-ray energy: 6 keV. (a) to (k): The XSW yields of K-fluorescence of Al, Si and Ca, normalized by off-Bragg yield [filled circles in (a)–(h)], and reflectivity (filled circles) for three reflections. The red curves are best fits to the data. The blue and green curves represent simulated yields assuming different occupation of the T-sites. (l) Typical fluorescence spectrum from the sample. For more details see Ref. 46.

Fig. 6. (Color online) X-ray fluorescence spectrum from a GaAs sample in air with a 23 nm epilayer doped with 4.8% Mn. Excitation energy 10 keV. Argon fluorescence is excited by the beam passing through air. The peaks at around 9 and 10 keV are electronic X-ray Raman scattering from Ga in the sample.
element specific investigations and chemical species can be identified owing to the "chemical shift" in the photoelectron spectra. Structure of the components with different binding energies can be analyzed individually as we pointed out in our 1993 surface science report and which was demonstrated shortly afterwards. This powerful application of the XSW technique has become meanwhile very popular in surface science and was employed very recently to study the decomposition of water.

Fuel production from water and sunlight by photoelectrochemistry using catalytically active semiconductors may represent a way to satisfy future energy needs. The principle feasibility was demonstrated by Fujishima and Honda in 1972 by the electrochemical photolysis of water at a TiO₂ electrode. The same was demonstrated for the cubic perovskite SrTiO₃ (STO) (see Fig. 10), a semiconductor with a wide, 3.1 eV band gap. STO becomes n-type conducting (and superconducting) via doping, e.g. by oxygen vacancies or Nb⁵⁺ substituting for Ti⁴⁺. Very recently, the adsorption and deprotonation of water was investigated by the XSW technique combined with PES dosing water on the Ti-oxide terminated STO(001) surface at low temperature in ultra-high vacuum (UHV).
has three components. The largest one, at a binding energy of $E_b = 530.8$ eV, originates from the oxygen atoms in the bulk of STO. The other two components at $E_b = 534.3$ eV and $E_b = 532.7$ eV arise from oxygen belonging to water and OH, i.e. deprotonated H$_2$O, respectively. Obviously, the water is not stable on the STO(001) surface.

Two XSW scans, using the STO 111 and 002 reflections close to 90° Bragg angle are shown in Fig. 10. The results of the 002 and the 111 reflections provide 1 + 4 symmetry-equivalent Fourier components that are used to construct the images in Fig. 11 of the oxygen positions of water and hydroxyl. Water adsorbs above a surface titanium atom, roughly where oxygen would be located in a continuation of the bulk lattice. Even at 200 K, the H$_2$O molecule deprotonates rapidly and the liberated hydrogen atom attaches to a neighboring oxygen surface atom, pulling it few ten pm out of the surface plane, as shown schematically in Fig. 11 on the right side. Water and hydroxyls are unstable at temperatures above 200 K and desorb rapidly, except for 0.25 ML OH that is tightly bound to the surface, as the inset in the spectrum of Fig. 9 shows. Whether the reaction products OH and H desorb individually or recombine and desorb as water is still an unsolved question.

3.4. Discussion

Over the last fifty years or so, the XSW technique has provided valuable contributions to numerous problems in condensed matter physics mostly concerning structure on the atomic level. The method is particularly useful for the investigation of dilute systems, determining lattice-locations of sparsely distributed active species that are important or crucial for electronic, magnetic or chemical properties of the material. We provided here three typical examples: unraveling the location of the active aluminum sites in scolecite, resolving the distribution of Mn dopants in GaAs and determining the adsorbate sites initiating the deprotonation of water on STO.

The investigation of scolecite also demonstrates that XSW analysis can deal with relatively complex substrate crystal structures. Furthermore, of the investigated small (natural) scolecite crystal, though comparably large ($\approx 5 \times 0.5$ mm$^2$)
for a zeolite crystal, only a sub-mm sub-grain could be used for the XSW analysis. Zeolites of practical or industrial use are powders with much smaller, μm sized crystals. That XSW measurements with atomic resolution are possible on such a microscopic scale had been demonstrated 2002 with the XSW investigation of a GaAlAs delta layer. Coined XSW microscopy, XSW formation and analysis was performed on a μm scale. A different approach for obtaining near-atomic resolution on a microscopic scale using multilayer XSW and full-field X-ray fluorescence imaging was published very recently.

In the case of Mn in GaAs, three different Mn species (Ga-substitutional, Ga-interstitial and As-interstitial) contributed to the XSW signals, clearly identified by constructing images from a large number of reflection. In many cases, using numerous reflections for creating an image is not necessary, because the species under study occupies one specific lattice site. When the coherent fraction for a hkl reflection is (close to) unity, i.e. the amplitude of one Fourier component is overwhelming, the coherent position, i.e. the phase of the Fourier component, directly provides the real space information along the spatial coordinate along [hkl]. In case of a single adsorption/lattice site, two or three measurements are sufficient to pinpoint the lattice position. However, the use of multiple reflections is indispensable in cases where atomic species that spectroscopy cannot distinguish occupy different, inequivalent sites such as in the case of Mn in GaAs, where single XSW measurements give coherent fractions significantly smaller than unity. The image produced by back transformation allows one to identify model-independently multiple sites and the following analysis by data fitting and refinement provides accurate structural data. Scanning the necessary large number of Bragg reflections is straightforward at an insertion device beamline equipped with a six-circle diffractometer. Employing higher order reflections also requires a low emittance X-ray beam of sufficiently high energy such as it was realized in case of Mn doped GaAs by using a Si(555) post-monochromator.

The analysis of the reaction of water on STO(001) is a good example for the power of the XSW technique when combined with PES by clearly distinguishing three different oxide species, isolating the oxygen 1s signal of oxygen in STO from OH and H2O and determining the surface location of the latter two. The O 1s signal from STO provided additional information about the STO(001) surface structure. Because of the high symmetry of the cubic STO substrate surface with two mirror planes, just two reflections were enough to construct images of the oxygen of OH and H2O on STO(001). However, the constructed images also demonstrate possible pitfalls in case of insufficient data because of limited Fourier coefficients. Firstly, the seeming in-plane periodicity of the images is artificial. XSW imaging does not provide information beyond the size of the substrate unit cell. Furthermore, normal to the surface, the images show the same pattern in the STO and TiO2 plane. The data do not allow one to distinguish whether the oxygen (of OH and H2O) resides slightly above the STO or TiO2 or in both diffraction planes because of the periodicity of the standing wave (Fourier components |H| < 1/αSTO are not accessible). Detailed analysis reveals that the hydroxyls are in fact occupying two positions on the surface as shown in Fig. 11, whereas the oxygen of the water molecules occupies as shown only one of the two sites. A larger range of XSW measurements or just one additional employing the STO(001) reflection could...
have remove this ambiguity immediately. The STO(001) reflection is unfortunately rather weak, because the TiO₂ and SrO planes possess about the same electron density and almost the cancel each other.

Because of imperfect STO crystals, the study was performed in backscattering geometry, using Bragg reflections close to 90°. In this case, the energy $E_{\text{bragg}} \approx 12.4/(2d_{\text{nh}})$ is dictated by $d_{\text{nh}}$, the used diffraction plane spacing. Thus, back-reflection XSW measurements, typically performed by scanning the energy $E$, a small range $\pm \Delta E$ around the Bragg energy $E_{\text{bragg}}$ necessarily need tunable synchrotron X-rays. Back-reflection XSW in combination with PES is presently the most popular application of the XSW technique in particular for analyzing adsorbate structures for surface science. In case of the STO(001) reflection, the back-reflection energy of $\approx 1.6$ keV is not accessible at many synchrotron radiation beamlines.

In the context of surface studies, it is interesting to note that the first XSW application by Cowan et al. in 1980 was an in situ investigation of a solid/liquid interface, Br adsorption on a Si(110) surface from a methanol solution. At that time, the XSW technique had not been adapted to UHV studies. Since then, other in situ XSW investigations have provided unique information about solid/liquid, especially solid/electrolyte interfaces using Bragg reflection XSW and total reflection XSW combined with X-ray fluorescence, and lately using multilayer reflection XSW combined with near ambient pressure PES. Besides the enabling the analysis of surface adsorbate structures, the XSW technique revealed details of the interface structure of thin films (see e.g. Ref. 72–73) and determined with $10^{-5}$ precision minute difference in lattice constant caused by the isotopic composition of crystalline films.

4. Conclusions and outlook

Without the application of synchrotron radiation, XSW measurements are tedious at best, but for the most interesting applications simply impossible, as for our three examples. At synchrotron radiation sources, the XSW technique can advantageously be combined with other techniques, also only enabled by the properties of synchrotron radiation.

In 2001, Kim and Kortright combined X-ray absorption spectroscopy and X-ray dichroism with XSW, Gupta et al. combined it with absorption fine structure and very recently Lin et al. excited (resonant) emission spectroscopy with the help of a XSW. In this way, complimentary structural information was added to all these techniques.

Another fascinating application of the XSW technique is the analysis of electronic structure. In the dipole approxima-

The wavefields used for the XSW technique are until now planar and periodic, solely produced by diffraction or reflection from substrates, which necessarily represent a part of the system under study. With the increasing degree of coherence of X-rays from synchrotron sources, interference fields can be created by other means. Tailored beam-splitters can generate XSWs of desired shapes and patterns and it is conceivable that technical advances will allow us to manipulate such XSWs with nm resolution or better. This may open the way to ultrahigh-resolution X-ray spectroscopy/microscopy, similar to the concept used nowadays in optical super-resolution microscopy.

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