X-ray absorption anisotropy for polychromatic illumination – crystal views from inside

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Abstract

We review an atomic resolution imaging method based on the analysis of the fine structure in x-ray absorption anisotropy, which results from incident beam diffraction. For a polychromatic x-ray beam, due to the suppression of higher order diffraction fringes, x-ray absorption anisotropy patterns can be interpreted as distorted real-space projections of the atomic structure around absorbing atoms. A qualitative method for analysis of x-ray absorption anisotropy patterns is presented, based on modeling of x-ray patterns with ray-traced images calculated for clusters around absorbing atoms.

Keywords: x-ray absorption, real-space imaging, x-ray holography, electron channeling, electron backscatter and photoelectron diffraction.

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1. Introduction

The derivation of structural information from *angular* dependent absorption effects was first discussed almost 50 years ago (Cowley, 1964; Bateman and Cole, 1964). Subsequently, the x-ray standing wave method (XSW) was developed and applied for the determination of atomic sites in perfect and real crystals, at surfaces and in interfaces (Vartanyants and Kovalchuk, 2001). More recently, holographic methods based on the internal detectors principle were used for three-dimensional imaging of the structure around absorbing atoms (Faigel et al., 2007). All these methods utilize monochromatic radiation and, like standard x-ray diffraction, work in reciprocal-space. The absorption dependence can be monitored by measuring the characteristic radiation emitted after absorption processes. Thus, such methods can provide chemically specific information.

Recently, an x-ray *real-space* approach was proposed for atomic structure imaging around absorbing atoms in crystals (Korecki and Materlik, 2001), in which a broadband, polychromatic x-ray beam is used to record the absorption anisotropy pattern. Since the longitudinal coherence of a polychromatic x-ray beam is very short, the anisotropy signal shows significant values only at small angles, i.e. around inter-atomic directions. Consequently, x-ray absorption anisotropy patterns resemble electron diffraction patterns recorded in back-scattering geometries, e.g. EBSD and Kikuchi patterns (Dingley, 2004; Baba-Kishi, 2002), or in emission geometries, e.g. photo and Auger electron diffraction patterns (Seelmann-Eggeber et al., 1993; Osterwalder et al., 2000).

In this paper we discuss the basic properties of x-ray absorption anisotropy for a polychromatic illumination (XAAPI). Based on several previously reported experiments, we show the possible areas of application of this structural approach. The discussion is made without a formal mathematical approach, which was presented in Korecki et al. (2006b). Instead of this, we propose a simple geometrical approach for a direct analysis of the

experimental patterns. The experimental data are compared with ray-traced images of small atomic clusters, observed from the perspective of an absorbing atom using a fish-eye perspective.

2. Basic principles of x-ray absorption anisotropy

2.1. Origin of fine structure in x-ray absorption anisotropy

The origin of fine structure in x-ray absorption anisotropy and the scheme of its acquisition are illustrated and described in Fig. 1. As shown in this figure, the fine structure in x-ray absorption results from incident beam diffraction effects which modify the absorption coefficient of the sample.

For monochromatic illumination, absorption anisotropy can be generally described as a direction dependent modulation of the absorption coefficient (Nishino and Materlik, 1999):

$$\mu(\mathbf{k}) = \mu_0[1 + \chi_0(\mathbf{k})], \quad (1)$$

where $\mathbf{k}$ is the wave vector of the incident radiation and μ_0 is the linear absorption coefficient calculated in the absence of incident beam diffraction effects. Note that μ_0 can display some angular anisotropy due to the polarization effects (Brouder, 1990). However, in our case, this relatively slowly varying contribution will be treated as a baseline. In the first Born approximation, the anisotropy $\chi_0(\mathbf{k})$ can be written as (Adams et al., 1998):

$$\chi_0(\mathbf{k}) = -2r_0 \text{Re} \int_V \rho(\mathbf{r}) \frac{e^{ikr}}{r} e^{i\mathbf{k} \cdot \mathbf{r}} dV, \quad (2)$$

where $r_0 = 2.82 \times 10^{-5} \text{\AA}$ is the classical electron radius, $\rho(\mathbf{r})$ is the electron charge density distribution at position $\mathbf{r}$ relative to the absorbing atom and $r = |\mathbf{r}|$.

For polychromatic illumination, the absorption anisotropy becomes (Korecki et al., 2006b):

$$\chi(\hat{\mathbf{k}}) = \int_0^\infty N(k) \chi_0(\mathbf{k}) dk, \quad (3)$$

where $N(k)$ is the effective radiation spectrum sensed by absorbing atoms. Substitution of Eq. (2) into Eq. (3) gives:

$$\chi(\hat{\mathbf{k}}) = -2r_0 \text{Re} \int_V \frac{\rho(\mathbf{r})}{r} s(\theta, r) dV, \quad (4)$$

where $s(\theta, r)$ is the signal due to a point scatterer at position $\mathbf{r}$ and θ is the angle between unit vectors $\mathbf{k}$ and $\mathbf{r}$.

For a crystalline sample, it is convenient to represent $\rho(\mathbf{r})$ as a Fourier series:

$$\rho(\mathbf{r}) = \frac{1}{V_0} \sum_{\mathbf{H}} F_{\mathbf{H}} e^{i\mathbf{H}\cdot\mathbf{r}}, \quad (5)$$

where $F_{\mathbf{H}}$ is a complex structure factor and V_0 is the volume of the unit cell. In analogy with Eq. (4), the absorption anisotropy can be written as:

$$\chi(\hat{\mathbf{k}}) = -2r_0 \text{Re} \sum_{\mathbf{H}} F_{\mathbf{H}} S(\theta_{\mathbf{H}}, H), \quad (6)$$

where $S(\theta_{\mathbf{H}}, H)$ is the signal coming from a single family of lattice planes corresponding to a *pair* of reciprocal vectors $\pm\mathbf{H}$ having length H .

For many absorbing atoms, the absorption anisotropy is a properly weighted sum of χ functions from Eq. (1).

2.2. Transition from monochromatic to polychromatic illumination

The transition from monochromatic to polychromatic illumination will be demonstrated assuming a model lorentzian wave-vector spectrum $N(k)$, centered on k_0 and having a full-width-at-half-maximum (FWHM) of Δk [see Fig. 2(a)]. Signals $s(\theta, r)$ corresponding to a

single point scatterer and signals $S(\theta_{\mathbf{H}}, H)$ corresponding to a single family of lattice planes are shown for various wave-vector spectra of the incident beam. Note that, in principle, the signal $S(\theta_{\mathbf{H}}, H)$ can be calculated as a superposition of $s(\theta, r)$ signals coming from individual scatterers.

The case in which $\Delta k \rightarrow 0$ describes an almost perfect monochromatic beam, which is used in XSW or in x-ray holographic experiments. For such a beam, the anisotropy signal arising from a point scatterer is distributed over the whole sphere, whereas the $S(\theta_{\mathbf{H}}, H)$ signal is composed of two well-separated lines, which show characteristic “black/white” contrast and are located on so-called Kossel cones.

The opposite situation where $\Delta k \rightarrow \infty$ corresponds to a perfect white illumination. In such a case, the anisotropy signal $s(\theta, r)$ localizes around the inter-atomic direction and the $S(\theta_{\mathbf{H}}, H)$ signal localizes around a great circle corresponding to the projection of lattice planes. Consequently, for a perfect white illumination, the x-ray anisotropy is a simple geometric projection of atomic structure around the absorbing atoms.

Experimentally, a perfect white illumination is not feasible. The lowest ratio of $k_0/\Delta k$, which can be obtained in an experiment is on the order of one. In such a case, the localization of the signals is present; however, some remnant diffraction effects are visible.

Note that, for a sufficiently high value of Δk , i.e. that of a broad $N(k)$ spectrum, the real-space signals $s(\theta, r)$ corresponding to scatterers at different position are mutually similar. While their scales and positions change, they have the same shape. On the other hand, the exact shape of the $S(\theta_{\mathbf{H}}, H)$ signal strongly depends on the position of the absorbing atom relative to the lattice planes. This effect is discussed in the next subsection.

2.3. Planar channeling and blocking effects

In Fig. 2, $S(\theta_{\mathbf{H}}, H)$ signals were calculated for a zero offset x of the absorbing atom position relative to the lattice planes. Examples of all characteristic positions of absorbing atoms relative to atomic planes and corresponding anisotropy signals are shown and discussed in Fig. 3. The calculation was performed for a realistic polychromatic beam with $k_0/\Delta k=1/2$. For absorbing atoms located in a symmetrical position relative to the atomic planes [i.e. for $x=0$ or $x=d/2$], the anisotropy signal $\chi(\theta_{\mathbf{H}})$ is also symmetrical. For the in-plane position shown in Fig. 3(a) [$x=0$, $\text{Re}(F_{\mathbf{H}})>0$ and $\text{Im}(F_{\mathbf{H}})=0$], the absorption decreases at the center of the corresponding band. For an absorbing atom placed exactly between the planes, shown in Fig. 3(b) [$x=d/2$, $\text{Re}(F_{\mathbf{H}})<0$, $\text{Im}(F_{\mathbf{H}})=0$], absorption increases at the center of the band. For the asymmetrical position shown in Fig. 3(c) [$x=d/4$, $\text{Re}(F_{\mathbf{H}})=0$ and $\text{Im}(F_{\mathbf{H}})>0$], the band displays asymmetry.

Therefore, Fig. 3 can be used to draw a planar channeling/blocking picture of the x-ray absorption anisotropy. Note that the increase and decrease of the signals is in comparison to a constant background. Thus, for a band having zero or nearly zero intensity, the atomic packing of the corresponding lattice plane is close to the average atomic density of the crystal.

The width of the bands, 2θ , must be calculated according to diffraction theory from a generalized Bragg-Kossel condition (Korecki et al., 2006b):

$$\sin \theta = \frac{H}{2k_+} = \frac{\pi}{dk_+}, \quad (7)$$

where $k_+ = (k_0^2 + \Delta k^2/4)^{1/2}$, which for $\Delta k=0$ reduces to the ordinary Bragg condition $\lambda=2d\sin\theta$.

3. Experiments

3.1. Proof-of-principle experiment for a photodiode

The first experiment showing the real-space character of XAAPI was performed by Korecki and Materlik (2001), using an idealized detection setup. Since a very weak signal was expected in this first experiment, a Si photodiode was used as both the sample and the detector simultaneously. Photodiodes are efficient detectors not only for visible light but also for x-rays. X-rays produce high-energy photoelectrons and Compton electrons which are "thermalized" into a distribution of electron-hole pairs with energies around 3.6 eV for Si. Since a Si photodiode is a perfect crystal, it is well-suited to serve as sample and detector simultaneously. Similar EXAFS experiments with a diode were performed much earlier (Boehme et al., 1985).

The experiment was performed using a bending magnet beamline at HASYLAB. The measurements could be performed either using monochromatic x-rays (with a single crystal monochromator) or using a "white" beam. In the "white" beam mode, the direct radiation from a bending magnet passed through a thick aluminum absorber that was used to shape a broadband energy spectrum ($k_0 \sim 40$ keV, $\Delta k \sim 20$ keV). In the experiment, the diode was an ion implanted Si(111) wafer with a 7° miscut. During the experiment, the diode was rotated around two axes, and the internal photocurrent was measured to probe the absorption anisotropy.

Figure 4 compares the x-ray absorption anisotropy of the Si photodiode recorded with monochromatic and white beam illumination. The figure shows raw data; only a two-dimensional background subtraction procedure was applied to eliminate the slowly varying background. For monochromatic illumination, the main features of the anisotropy data are the sharp "black/white" lines which occur at Bragg angles. Similar patterns were interpreted using a holographic approach. For a polychromatic illumination, the anisotropy is composed of

broad bands located at great circles, which correspond to the projection of lattice planes. As shown in colorbars, the intensity of the white beam data is over one order of magnitude smaller than that of the monochromatic illumination data. For both cases, the anisotropy signals can be decomposed into elementary signals from Fig. 2.

3.2. Extinction effects

At first glance, it seems that the pattern recorded for the monochromatic beam contains much more structural information than the white beam pattern. However, the complicated net of white lines, which does not show the characteristic “black/white” contrast (note the “Y” shaped feature in the center of the pattern), is a parasitic effect. Such lines are caused by so-called extinction effects and can hinder the application of the holographic formalism as shown by Korecki et al. (2004a). Extinction effects strongly depend on the experimental geometry. It was shown that extinction effects are minimal if the scattering takes place in a symmetrical Laue geometry and *simultaneously* the escape depth of the secondary radiation is low (i.e. electron yield or fluoresce at grazing exit are recorded). Extinction effects are also negligible for very thin samples. Such virtual thin samples were used in holographic experiments with γ -rays (Korecki et al, 1997; 2004b). In γ -ray experiments, only a thin epitaxial layer enriched with specific nuclear isotopes gives rise to the total signal, whereas the substrate does not contribute to the nuclear scattering.

As will be shown in next section, white beam illumination and total electron yield detection ensure that the extinction effects are negligible. For a white beam, the scattering occurs predominantly in the forward scattering geometry, which is very close to an idealized symmetrical Laue case.

3.3. Direct access to the stereographic projection of the sample

Successive experiments were performed for real samples using total electron yield detection to probe the absorption anisotropy (Korecki et al., 2006a; 2006b; 2006c). Figure 5(a) shows the XAAPI pattern recorded for an InAs(0001) sample. Figure 5(b) indicates that the x-ray data gives direct access to a stereographic projection of the sample. While a stereographic projection of the crystal can give information about crystal symmetry (point and space group), the information content of x-ray absorption anisotropy allows for a more detailed structural analysis.

3.4. Polarity determination: fish-eye views

Figure 6 shows XAAPI patterns recorded for GaP crystals with opposite orientations. GaP crystallizes in the zinc blend structure and is a polar crystal, i.e. the crystal orientations (111) [side A] and (11-1) [side B] are nonequivalent. In addition, the absorption cross-section of Ga atoms is much higher than that of P atoms. As a result, the total electron yield, which in general does not provide chemical sensitivity, comes predominantly from Ga absorbers.

The absorption anisotropy patterns from Fig. 6 are compared with ray-traced images of small atomic clusters. These images were calculated with ray-tracing software (POV-Ray) for small clusters of spheres, arranged in the GaP structure, using principles of geometrical optics. The observation point is placed at the position of the central Ga atom, and a fish-eye perspective is used. The view-angle is the same as that of the experimental pattern, i.e. $\sim 60^\circ$. In the resulting images, Ga and P atoms are shown as dark and bright spheres, respectively. Their dimensions are proportional to the atomic number and inversely proportional to the distance from the central atom. Due to the fish-eye projection, their shapes are faintly

distorted. Note that the same fish-eye projection ($X=\theta\sin\phi$, $Y=\theta\cos\phi$) was used for the presentation of x-ray patterns.

The bands, visible in the x-ray patterns, have the shapes predicted in Fig. 3. All bands in Figs. 6(a) and 6(b) show a decrease in intensity at the center [case (a) in Fig. 3]. Thus, it can be concluded that the absorbers are located in closely packed atomic planes. The 111 bands, which form a characteristic triangle, have a small asymmetric component. This asymmetry is different for side A and side B. The difference image A-B, which enhances this asymmetric component, shows only 111 bands with a clear asymmetric shape [case (c) in Fig. 3].

All these observations can be explained by the ray-traced fish-eye images. Firstly, the decrease in intensity of the most intense bands seen in the x-ray data is due to the fact that the corresponding planes are composed solely from the heavier Ga atoms. So, one can observe an x-ray blocking effect. Secondly, fish-eye images ray-traced for different sample orientations show that the positions of the Ga atoms remain unchanged after sample reversal. The reversal of the sample alters only the positions of the lighter P atoms. Note, that P atomic planes are placed either outside the 111 triangle (for side A) or inside this triangle (for side B), whereas “empty spaces” are located on opposite sides of this triangle for both crystal orientations. This explains the experimentally observed asymmetric band shapes.

This simple analogy between experimental data and ray-traced images allows us to conclude that x-ray absorption patterns can be used for a direct visualization of crystal projections in real-space. Note that this simple qualitative approach can be followed by a quantitative tomographic approach (Korecki et al., 2006) which allows for three-dimensional imaging of crystal structure around absorbing atoms.

4. Perspectives and limitations

4.1. Determination of lattice sites

The most promising application of XAAPI is connected with the determination of atomic sites in crystals, similar to atom location by channeling enhanced microanalysis (ALCHEMI), which uses high energy electrons (Taftø and Spence, 1982), or to XSW (Cheng et al., 2003). However, in contrast with these methods, XAAPI uses a simple real-space projection approach and a kinematical formalism.

In order to show this possibility, we have simulated XAAPI patterns for a GaP crystal, assuming that absorbing atoms are impurity atoms placed either in a substitutional (Ga or P) or interstitial position at the center of unit cell. The calculation was performed for a lorentzian $N(k)$ spectrum with $k_0=25 \text{ \AA}^{-1}$ ($E_0=50 \text{ keV}$) and $\Delta k=12.5 \text{ \AA}^{-1}$ ($\Delta E=25 \text{ keV}$) according to the formalism introduced by Korecki et al. (2006b). The simulated patterns are presented in Fig. 7 together with corresponding ray-traced views, which were calculated in the same way as in Section 3.3.

The qualitative agreement of the x-ray data and fish-eye images is excellent. For the absorbing atom placed in Ga position (0,0,0), the simulated images are similar to the experimental data, which were already compared to fish-eye views.

For the absorbing atom located in P position ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), the 111-like bands show enhanced asymmetry as compared to the absorbing atom placed at the Ga site. This is caused by the fact that the heavier Ga scatterers now contribute to the band asymmetry. In addition, 010 bands show an excess of intensity, i.e. a channeling effect takes place. As shown in fish-eye views, these bands correspond to atomic planes composed of the lighter P atoms.

For the absorbing atom situated in the interstitial position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), the 111 bands, which correspond to wide “empty spaces” in the fish-eye views, are strongly enhanced.

4.2. Chemical sensitivity

The structural application of XAAPI described in the previous paragraph requires chemical sensitivity. Until now, all experiments were performed using total electron yield detection. In the future, x-ray fluorescence can be used to probe the absorption. Since the anisotropy in XAAPI is small (10^{-4} - 10^{-3}), the standard energy resolving detector accepting up to 10^6 counts/s cannot be used. Instead, a system based on polycapillary optics (Nikitina et al., 1999) coupled with a Bragg analyzer and a detector working in current mode is being developed and tested. Another solution is to use silicon strip detectors (Grybos, 2007), which at a moderate energy resolution (about 1 keV at 10 keV) can handle more than 10^8 counts/s.

4.3. Limitations

The XAAPI method provides *average* atomic structure around absorbing atoms inside the sample. Thus, absorption anisotropy can only be recorded for samples having rotational order – perfect and imperfect single crystals, multi-layers, or buried interfaces. Powders or amorphous samples are excluded. For the total electron yield detection, XAAPI provides usable information only in the case of one strongly absorbing atom (like Ga in GaP). When characteristic radiation is recorded, chemically resolved information can be, in principle, obtained. However, there are often more absorbers (even those of the same element) with non-equivalent surroundings. In such a case, XAAPI will provide an image being a linear superposition of the patterns coming from the non-equivalent sites.

XAAPI requires a broad and smooth *effective* x-ray spectrum. Any absorption edge occurring in the energetic range of this spectrum will produce sharp discontinuities and will complicate the data analysis. Therefore, for an exemplary spectrum with $E_0 \sim 50\text{keV}$ and $\Delta E \sim E_0/2$, which can be obtained using bending magnets, all absorption edges of the atoms inside the sample must lie below 20-30keV. This limits the potential applications of the

method to samples containing atoms with atomic number $Z < 50$. For hard x-ray wiggler radiation this limit can be set at $Z = 75-80$.

5. Conclusions

XAAPI is a structural tool which provides atomic resolution images of structure around absorbing atoms in a crystal. In the future, it can be used for imaging of atomic structure in thin films, buried layers and nanostructures. The anisotropy is weak and the acquisition times are on the orders of hours. However, this weak anisotropy is compensated for by the kinematical scattering which allows for easy interpretation and modeling. If the experimental problems connected with recording of the x-ray fluorescence secondary signal are solved, the method can be applied without vacuum and in the presence of strong electric and magnetic fields.

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FIGURE CAPTIONS

Fig. 1. Origin of the fine structure in x-ray absorption anisotropy. (a) Microscopic picture. Incident beam diffraction, i.e. the coherent interaction of the incident plane wave with spherical waves scattered inside the sample, results in a modification of the x-ray wave-field at sites of absorbing atoms. The resulting modulation of the absorption coefficient depends on the scattering geometry, which is determined by the sample orientation relative to the incident beam direction. (b) Macroscopic view. In an experiment, the sample is rotated relative to the incident beam direction. The absorption anisotropy pattern $\chi(\theta, \phi)$ is measured point-by-point by collecting the angle integrated secondary yield from absorbing atoms.

Fig. 2. Schematic picture of the transition from monochromatic to polychromatic illumination.

(a) Scattering geometry. Left: scatterer and absorber are located at relative distance r . θ denotes deviation from the forward scattering direction. Right: absorber is located at one of atomic planes with period $d=2\pi/H$. θ_H denotes the Bragg angle. Middle: shape and parameters of the effective $N(k)$ spectrum. (b) X-ray absorption anisotropy signal $s(\theta, r)$ calculated for constant k_0 and different widths Δk of the effective spectrum. (c) Signal $S(\theta_H, H)$ calculated for the same parameters. Note the localization of the signal around the inter-atomic direction for (a) and localization of the signal around plane projection in (b) for large Δk .

Fig. 3. Channeling/blocking picture. For a broad effective radiation spectrum, the x-ray absorption anisotropy signal $\chi(\theta_{\mathbf{H}})$ can be interpreted as a distorted geometrical projection of atomic planes. Top: schematic plots of the position of the absorbing atom relative to the atomic plane and corresponding fish-eye images calculated for observation points placed at the absorbing atom. Bottom: corresponding anisotropy signals $\chi(\theta_{\mathbf{H}})$ and their angular profiles. Panels (a), (b) and (c) correspond to different symmetrical positions and an asymmetrical position, respectively.

Fig. 4. First x-ray absorption anisotropy data recorded for polychromatic radiation: x-ray absorption anisotropy recorded for a Si photodiode. (a) Pattern recorded using monochromatic radiation at $E=15$ keV. (b) Pattern recorded using polychromatic radiation ($E_0 \sim 40$ keV, $\Delta E \sim 20$ keV).

Fig. 6. Comparison of x-ray absorption anisotropy recorded for a GaP crystal with ray-traced fish-eye images (observation point placed at the position of a Ga atom). (a) Data for side A of the crystal. (b) Data for side B of crystal (c) Left: difference image A-B. Right: auxiliary plot showing main crystal directions and planes.

Fig. 7. Determination of impurity site. X-ray absorption anisotropy patterns simulated for a GaP crystal and absorbing atoms at different lattice sites are compared with corresponding fish-eye views. (a) Absorber located at a Ga site. (b) Absorber located at a P site. (c) Absorber located in an interstitial position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$).