Supplementary material (Appendices A and B) for:

"Ultra-small-angle X-ray scattering at the Advanced Photon Source"

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Appendix A: Lineshape functions for the analyzer crystal rocking curve

[All terms are defined in the main text if not defined here.]

The rocking curve, RC, produced by Bragg diffraction from a thick, perfect crystal follows the following relation:

$$R(\psi) = 1 \qquad |\psi| \le 1$$

$$R(\psi) = \left| |\psi| - \left(\psi^2 - 1\right)^{1/2} \right|^2 \qquad |\psi| > 1 \qquad \text{[A1]},$$

in which $\psi = (\vartheta - \vartheta_B)/\vartheta_D$ is a reduced angle, and $2\vartheta_D$ is the full width of the Darwin function plateau in ϑ.

For a Bonse-Hart geometry, the crystal rocking curve obtained by rotating the analyzer stage, with m monochromator reflections and n analyzer reflections, is the convolution of the individual rocking curves:

$$I(\Psi) = \int R^m_{mono}(\psi) R^n_{analyzer}(\psi - \Psi) d\psi \qquad \text{[A2]}.$$

The experimental data, however, will not strictly follow the theoretical prediction, mostly due to parasitic surface scattering and any slight misalignment. This is illustrated in **Figure A1**, in which the experimental rocking curve using Si (220) crystal optics, an X-ray energy of 11.7 keV, and with $m = n = 4$, is compared with theoretical rocking curves as calculated from dynamical diffraction theory using eqn. [A2]. The FWHM of the experimental rocking curve is 3.11", which is very close to the calculated FWHM of the rocking curve 3.09".

Since the line-shape of the experimental rocking curve is not exactly described by the Darwin function, an alternative function is needed so that the center and FWHM of the experimental curve can be precisely determined. Correct location of the center of the rocking curve affects the accuracy of the USAXS scattering profile at very low q, and the FWHM can be a convenient tool to examine, quantitatively, if a satisfactory alignment has been achieved. In addition, use of an incorrect line-shape function has a profound impact on the image contrast inside the rocking curve in analyzer-based phase contrast imaging.

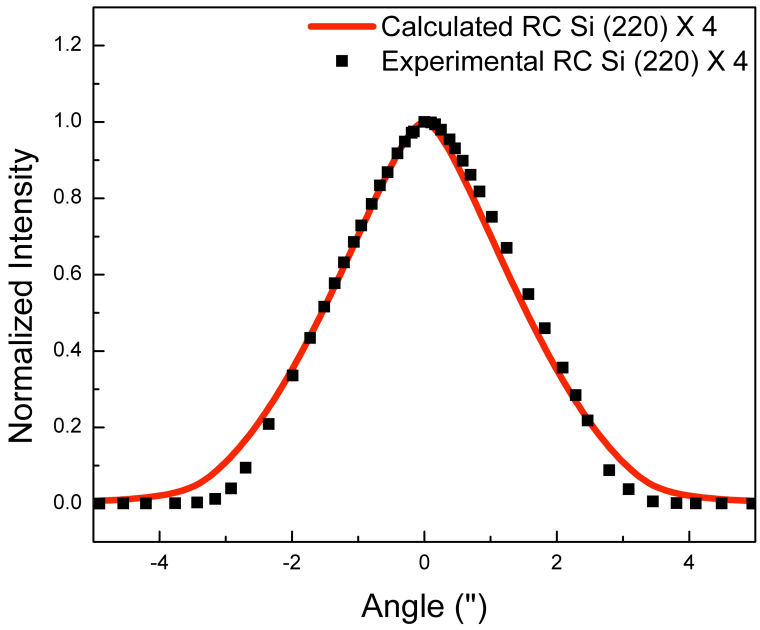

Figure A1. Comparison of theoretical perfect crystal rocking curves and the experimental rocking curve for $m = n = 4$ using a Bonse-Hart double-crystal diffractometer with Si (220) crystals in the 1D collimated USAXS mode. Measurement uncertainties on the experimental curve are smaller than the size of the symbols. The X-ray wavelength is 1.06 Å and the angle is $(\vartheta\text{-}\vartheta_B)$.

In our tests, we explored five possible line-shape functions:

1. Gaussian Function:

$$F(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-(x-\mu)^2 / 2\sigma^2\right) \qquad \text{[A3]},$$

where σ is the standard deviation, $\{2\sigma(2\ln 2)^{1/2}\}$ is the FWHM, and μ is the center of the peak.

2. Lorentzian Function:

$$F(x) = \frac{a}{\pi\left(a^2 + (x-\mu)^2\right)} \qquad \text{[A4]},$$

where $2a$ is the Lorentzian FWHM, and μ is the center of the peak.

3. Pseudo-Voigt Function:

$$F(x_1) = \eta \frac{1}{\left(1 + x_1^2\right)} + (1-\eta)\exp\left\{-(\ln 2)x_1^2\right\} \qquad \text{[A5]},$$

where $x_1 = 2(x - x_0)/w$, x_0 is the peak center, w is the FWHM (provided $\eta \ll 1$), and $0 \le \eta \le 1$ is a

normalization parameter.

4. Pearson type VII Function

$$F(x) = c\left[1 + \frac{(x-\mu)^2}{\nu a^2}\right]^{-\nu} \qquad \text{[A6]},$$

where c is a normalization constant, μ is the center, the FWHM is proportional to a, and ν decides the rate at which the tail of the peak profile falls.

5. Modified Gaussian Function

$$F(x) = a\exp\left(-\frac{1}{2}\left(\frac{|x-b|}{c}\right)^d\right) \qquad \text{[A7]},$$

where b is the peak center, the FWHM is proportional to c (> 0), and d (≥ 1) determines the fall-off rate.

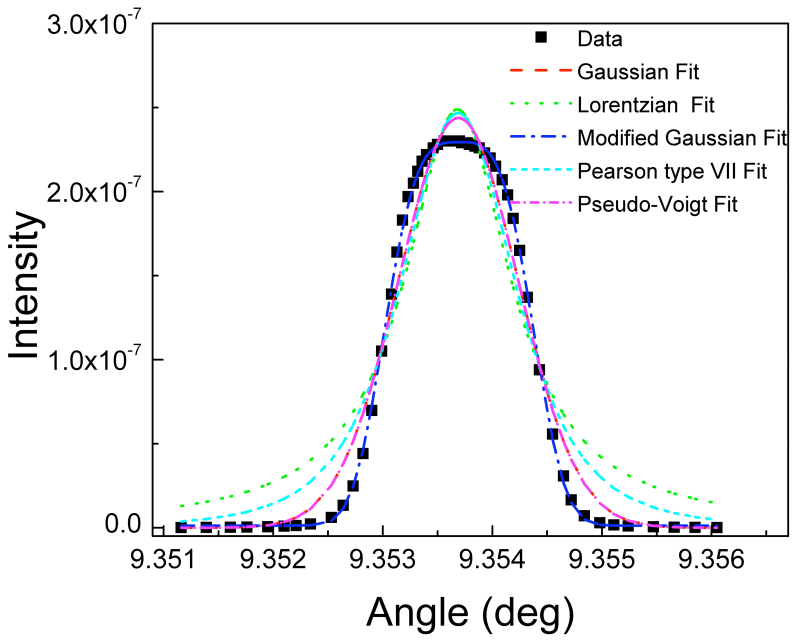

Figure A2. Numerical fits to the experimental rocking curve in the USAXS imaging mode for Si (111) crystals with two reflections with Gaussian, Lorentzian, Pearson type VII, Pseudo-Voigt, and modified Gaussian functions. Measurement uncertainties for the experimental curve are smaller than the size of the symbols. The X-ray wavelength is 1.02 Å and the angle = ϑ.

The functions were compared to an experimental rocking curve collected with Si (111) analyzer crystals. The numerical fits are shown in **Figure A2**. The modified Gaussian function clearly yields the best fit, partially due to its flexibility in having an almost flat top near the center of the peak.

Appendix B: Constraints on the minimum sample-to-detector distance and maximum allowed misalignment of the tilt angles within the analyzer stage in 1D-collimated USAXS

[All terms are defined in the main text if not defined here.]

In the alignment process for 1D-collimated USAXS, in order to achieve correct, absolutely calibrated intensity over the entire q range, requirements on the geometrical conditions must be satisfied. Here, we detail the constraints on the minimum sample-to-detector distance and on the maximum allowed misalignment of the tilt angles of the two analyzer crystals (relative to each other), which are important for the proper functioning of the 1D-collimated USAXS configuration.

(a) Minimum sample-to-detector distance:

Figure B1 shows a schematic for the minimum sample-to-detector distance determination. *SD* is the sample-to-detector distance, Θ_H is the maximum horizontal angle relative to the straight-on direction for which the detector aperture admits scattering from the sample (half the slit length in horizontal scattering angle), d is the photodiode aperture in the horizontal plane, and ϑ_R is the effective incident angle in the vertical plane at either analyzer crystal (assuming they are perfectly aligned with respect to each other) for the maximum allowed horizontal angle Θ_H. In addition, ϑ_B is the angle of incidence for Bragg reflection in the vertical plane, and *DW* is the rocking curve FWHM also in the vertical plane.

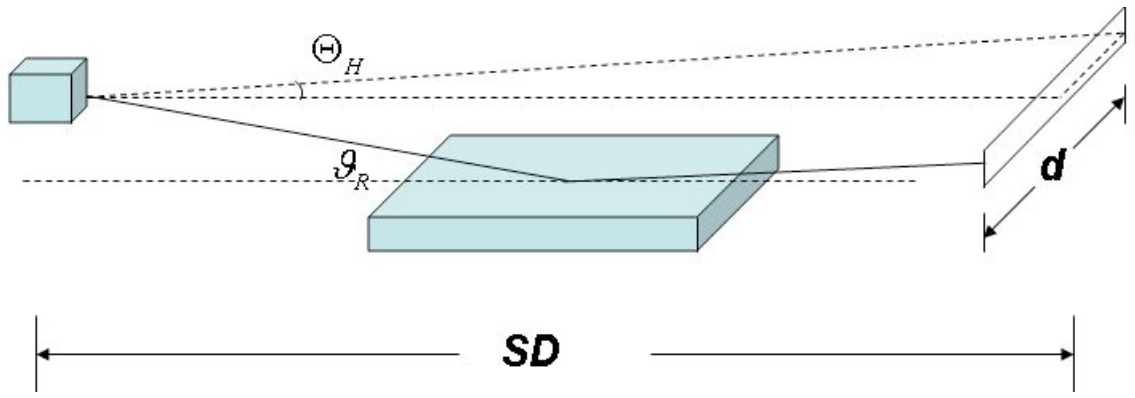

Figure B1. Schematic for the sample to detector distance determination in 1D-collimated USAXS. (Note that each point on the sample is assumed to act as a point source scatterer; so the upstream entrance slit collimation is not involved in these calculations.)

It is clear from **Figure B1** that

$$\tan\Theta_H = \frac{d}{2.SD} \qquad [B1]$$

and

$$\sin\vartheta_R = \sin\vartheta_B \sec\Theta_H \qquad [B2],$$

where for $\Theta_H = 0$, $\vartheta_R = \vartheta_B$. Inserting eqn. [B1] into eqn. [B2], we have:

$$\sin\vartheta_R = \sin\vartheta_B \sqrt{\left\{1 + \left(\frac{d}{2.SD}\right)^2\right\}} \qquad \text{[B3].}$$

Meanwhile, for an uncompromised intensity-throughput through the analyzer crystals, we require that:

$$\left|\vartheta_R - \vartheta_B\right| \leq \frac{DW}{2} \qquad \text{[B4].}$$

To illustrate how this constraint affects *SD*, we consider two examples (both with d = 5.5 mm):

(i) X-ray energy = 16.85 keV, $\vartheta_B = 11.05°$ for Si (220), $DW \approx 2"$:

following eqn. [B4], we require that: $|\vartheta_R - \vartheta_B| \leq 1.0"$, or $\vartheta_R < 11.05028°$.

This means that $\tan\Theta_H < 0.007075$ (i.e., $\Theta_H < 0.405°$), requiring $SD > 389$ mm.

(ii) X-ray energy = 11.85 keV, $\vartheta_B = 15.85°$ for Si (220), $DW \approx 3"$:

following eqn. [B4], we require that: $|\vartheta_R - \vartheta_B| \leq 1.5"$, or $\vartheta_R < 15.81042°$.

This means that $\tan\Theta_H < 0.007196$ (i.e., $\Theta_H < 0.412°$), requiring $SD > 382$ mm.

Violation of these constraints will not result in intensity loss at $q = 0$, but it will result in a reduction in the scattering intensity for q above a value for which the entire horizontal slit length should be illuminated in 1D-collimated USAXS studies. While it may be possible to set *SD* lower for the lowest X-ray energies accessible to USAXS (≈ 8 keV), a safe minimum distance is given by *SD* = 400 mm. Note that 2D-collimated USAXS does not have this constraint because the effective slit length in angle is given by the Darwin profile FWHM, which is then the effective slit width.

(b) Maximum allowed misalignment of the tilt angles between the analyzer crystals:

As described in the main text, the tilt of the analyzer crystals (perpendicular to the Bragg diffraction plane) is adjusted and optimized with a high-resolution tilt-adjusting picomotor. Nonetheless, the possibility of slight misalignment cannot be completely eliminated. If we assume that α_1 and α_2 are the misalignment of the first analyzer crystal and the second analyzer crystal in a positive sense, then $\alpha_R = \alpha_1 - \alpha_2$ is the relative misalignment of the crystal pair. For a given crystal *reflection*, the geometry and relationship between ϑ_B and ϑ_R for a general tilt misalignment angle α is the same as in eqns. [B2] and [B4] for 1D-collimated USAXS with α replacing Θ_H. Here, α is the effective tilt misalignment for the reflection,

and it is equal to 0, α_R, $2\alpha_R$, $3\alpha_R$, $4\alpha_R$, $5\alpha_R$ for the first to sixth reflections in the analyzer crystal pair, respectively. The constraint condition for α must hold for the largest tilt misalignment that arises from the last reflection in the analyzer crystal pair.

To illustrate, we again consider the two scenarios above, assuming four Bragg reflections in the analyzer:

(i) X-ray energy = 16.85 keV, $\vartheta_B = 11.05°$ for Si (220), $DW \approx 2"$:

following eqn. [B4], we require that: $|\vartheta_R - \vartheta_B| \leq 1.0"$, or $\vartheta_R < 11.05028°$.

This means that $\tan(3\alpha_R) < 0.007075$, or a maximum relative tilt misalignment $\alpha_R < 0.135°$.

(ii) X-ray energy = 11.85 keV, $\vartheta_B = 15.85°$ for Si (220), $DW \approx 3"$:

following eqn. [B4], we require that: $|\vartheta_R - \vartheta_B| \leq 1.5"$, or $\vartheta_R < 15.81042°$.

This means that $\tan(3\alpha_R) < 0.007196$, or a maximum relative tilt misalignment $\alpha_R < 0.137°$.

Violation of these constraints reduces intensity at all q, including $q = 0$, in both 1D- and 2D-collimated USAXS. However, in 1D-collimated USAXS, any tilt misalignment must be combined with the *SD* issue above. This does not involve a convolution but, depending on the sense of the relative tilt misalignment, it is an addition at one side (end) of the horizontal slit collimation and a subtraction at the other. Assuming that the individual constraints (a) and (b) are satisfied, we are concerned with the side (end) of the slit collimation where the two effects sum. We need the combined constraint to ensure no loss of scattering intensity at high q and $\tan(\Theta_H + 3\alpha_R) < 0.007075$ or 0.007196 for examples (i) or (ii) above provides the requirement. Thus, assuming $SD = 400$ mm, we have $\Theta_H = 0.394°$ and:

(i) X-ray energy = 16.85 keV: $\alpha_R < 0.0037°$ or 13.3";

(ii) X-ray energy = 11.85 keV: $\alpha_R < 0.0060°$ or 21.6".

These are extremely tight constraints for the tilt misalignment. If violated, a loss in scattered intensity at high q will result (whole collimation slit not illuminated), but not at low q. The problem can be masked if there is a compensating misalignment in the relative rotation angles of the two crystals: the situation appears satisfactory at $q = 0$ but gives a calibration failure at high q. Increasing *SD* to $SD > 450$ mm, or reducing the detector aperture d gives less stringent constraints for α_R.