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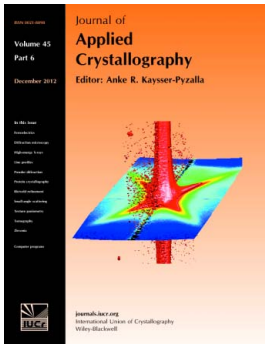

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High-energy ultra-small-angle X-ray scattering instrument at the Advanced Photon Source

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This paper reports recent tests performed on the Bonse–Hart-type ultra-small-angle X-ray scattering (USAXS) instrument at the Advanced Photon Source with higher-order reflection optics – Si(440) instead of Si(220) – and with X-ray energies greater than 20 keV. The results obtained demonstrate the feasibility of high-energy operation with narrower crystal reflectivity curves, which provides access to a scattering q range from $\sim 2 \times 10^{-5}$ to 1.8 Å^{-1} and up to 12 decades in the associated sample-dependent scattering intensity range. The corresponding size range of the scattering features spans about five decades – from less than 10 Å to $\sim$15 µm. These tests have indicated that mechanical upgrades are required to ensure the alignment capability and operational stability of this instrument for general user operations because of the tighter angular-resolution constraints of the higher-order crystal optics.

1. Introduction

Small-angle X-ray and neutron scattering (SAXS and SANS) are nondestructive techniques for measuring sample inhomogeneities on length scales ranging from ångströms to micrometres. A typical SAXS/SANS instrument makes use of a pinhole camera and an area detector at a fixed or variable sample-to-detector distance, offering a scattering vector **q** range of up to two decades and a dynamic intensity range of up to six decades. The magnitude of **q** is defined as

$$q = 4\pi \sin(\theta)/\lambda, \quad (1)$$

where λ is the X-ray or neutron wavelength and 2θ is the scattering angle. Given the fixed pixel size of an area detector, there is relatively low q sampling at low q and high q sampling at high q. At the same time, the q resolution ($q_{\rm res}$) is typically poor at low q. Pinhole SAXS and SANS cameras using multiple sample-to-detector distances can extend the q range to three decades or more, and improve both the q sampling and $q_{\rm res}$.

An extended q range (up to four decades in Å^{-1}) and extended intensity range (up to 12 decades) are major advantages of Bonse–Hart-type (Bonse & Hart, 1965) ultra-small-angle X-ray scattering (USAXS) instruments at synchrotron sources (Ilavsky *et al.*, 2009; Sztucki *et al.*, 2008) and at laboratory-based sources (Molmex Scientific, 2012). Because USAXS measurements employ a step scan, q sampling can be selected to match experimental needs. Furthermore, a typical $q_{\rm res}$ for a Bonse–Hart-type instrument, defined as the full width at half-maximum (FWHM) of the reflectivity curve of the analyzer crystal pair, is independent of q and much smaller than that for pinhole SAXS instruments. For Si(111) crystals, $q_{\rm res} \simeq 0.00019$ Å^{-1}, while for Si(220) crystals, $q_{\rm res} \simeq 0.00014$ Å^{-1}.

The parameter $q_{\rm res}$ is important because it determines the minimum q value ($q_{\rm min}$) and, thus, the largest feature size that can be meaningfully resolved by a USAXS instrument. Assuming that the minimum q required to characterize small-angle scattering features of diameter d is given by $qR_{\rm g} \simeq 1$ ($R_{\rm g}$ is the radius of gyration), the maximum $R_{\rm g}$ characterized by USAXS instruments using Si(220) optics is about 2 µm. In reality, some information is usually obtainable for larger features (possibly up to 4 µm), but the maximum size also depends on the scattering strength of the sample and may be smaller for weakly scattering samples. To resolve larger scatterer sizes using USAXS, the value of $q_{\rm res}$ must be reduced as is currently possible with ultra-small-angle neutron scattering, where the Darwin curve width of a crystal is intrinsically smaller for neutrons than for X-rays of the same wavelength (Barker *et al.*, 2005). This goal can be achieved by using higher-energy X-rays with higher-order crystal optics.

Extending the maximum size that a USAXS instrument can resolve is of great scientific and engineering importance. Many engineering materials exhibit hierarchical microstructures that span a wide range of length scales with maximum sizes in the range of 10–50 µm. Furthermore, while it is straightforward for X-ray imaging and tomography to resolve features on multi-micrometre length scales and above, it is significantly more challenging for these methods to characterize submicrometre structures. One approach for the comprehensive characterization of complex materials is to combine imaging of larger features with USAXS studies of smaller features (Barty *et al.*, 2008). For this purpose, it is required to have sufficient overlap in the measurable dimensions of these techniques so that 'normalization' of their results can be realized.

The use of higher-energy X-rays (20–30 keV) in USAXS measurements is also highly desirable as this permits greater sample thicknesses of dense materials to be accommodated or, alternatively, thicker chamber windows to be used for *in situ* measurements at higher pressures or temperatures.

The scientific needs of the USAXS user community at the Advanced Photon Source (APS) are driving the APS USAXS facility

instrumental development both to accommodate higher X-ray energy operation and to extend measurements to smaller q with a corresponding increase in the maximum measurable feature size. Here, we report the first successful experiments with the APS USAXS instrument using Si(440) crystal optics and an X-ray energy of 21.0 keV to open a path to satisfy both of these needs.

2. Experimental setup

The USAXS instrument at APS sector 15ID, operated by ChemMatCARS, is accessible to the user community through the APS general user program. It is a flexible Bonse–Hart-type instrument with several operational configurations for characterizing a wide range of materials. The most commonly used configurations are slit smeared (one-dimensional) and pinhole (two-dimensional) collimated USAXS. The slit smeared (one-dimensional) configuration used in this study is complemented by a fixed-length in-line wide-angle X-ray scattering area detector (denoted 'pinSAXS') which extends the high-q range and increases the total dynamic intensity range. The instrument receives X-rays from an APS undulator A source and Si(111) and Si(311) monochromator optics. The beamline is capable of delivering a monochromatic X-ray flux with energies between 8 and 50 keV with up to 10^{13} photons per second (at 12 keV). The USAXS instrument was limited by Si(220) optics to an energy range from 8 to 18 keV.

The currently installed optics comprise two pairs of parallel Si(220) crystals. Each crystal pair uses an even number of reflections (typically four, optionally six) (Ilavsky *et al.*, 2009). The crystal optics are in plastic enclosures containing a protective nitrogen atmosphere to keep surfaces clean and therefore reduce parasitic surface scattering. The rest of the beam path is in air, which makes the instrument accessible, flexible and easily modified to address specific experimental needs, such as installation of various environmental sample chambers (cryostats, heaters *etc.*). On the other hand, the air path significantly affects the X-ray background of the instrument and limits the instrumental sensitivity for weakly scattering samples. This is typically not an issue for studies of hard materials, such as those involved in ceramics, metallurgy, catalysis chemistry or inorganic nanoparticle assemblies.

In the current study, we utilized X-ray energies between 21 and 25 keV with Si(440) crystal optics. In practice, this was accomplished by using the second-order reflections from the Si(220) crystals. Thus, the switch between Si(220) and Si(440) optics is rapid, convenient and easily reversible. In this paper, we present results obtained using 21.0 keV X-rays.

This switch from Si(220) operated between 10 and 18 keV to Si(440) operated at 21 keV reduces the X-ray flux on the sample by a factor of 3–10. This reduction is due to multiple factors, such as undulator performance and the different energy responses of beamline optics components, collimating crystal pairs of the APS USAXS instrument, and absorption by the open air path. Despite this reduction, the X-ray flux on the sample is still of the order of 10^{12} mm^{-2} at 21 keV and satisfies the needs of most, if not all, USAXS measurements.

3. Results and discussion

Table 1 shows the calculated and measured widths of the crystal reflectivity curves for Si(220) and Si(440) channel-cut crystals at 16.8 and 21.0 keV X-ray energies. These widths are the FWHM expressed in q units of 10^{-5} Å^{-1}. The results show that, while the theoretical q_{res} value for Si(440) optics at 21.0 keV should be smaller by a factor of 3 than that of Si(220) optics at 16.8 keV, the measured value is actually reduced by a factor of ∼4. The source of this difference is currently under investigation.

Table 1
Calculated and measured FWHMs of the reflectivity curves for Si(220) and Si(440) crystals at 16.8 and 21.0 keV in q units of 10^{-5} Å^{-1}.

	Si(220)/16.8 keV	Si(440)/21.0 keV
Calculated FWHM	9.3	3.0
Measured FWHM	8.2	2.1

Fig. 1 shows the measured peak intensity profile for the instrument with no sample present (*i.e.* a 'blank' scan) as a function of q. These measurements were conducted with the minimum angular step (1×10^{-6}°). The full width of the Si(440) peak is measured in 15 steps at 21.0 keV, while the broader Si(220) peak at 16.8 keV takes 38 steps. A well defined and characterized peak intensity profile is of critical importance because it directly defines the angular position of the analyzer crystal pair corresponding to $q = 0$, and hence the accuracy of q values at small q. This profile is also used to determine the absolute calibration of the scattering intensity. While the minimum angular step of the current rotational stage appears to be adequate for operations with Si(440) crystals at 21.0 keV, future operations at higher X-ray energies present a challenge because the peak profiles have even narrower widths. A new analyzer crystal rotational stage will be required to enable reliable operations much above 21.0 keV.

Fig. 2 shows measurements of the same sample [a metal–organic framework (MOF) CO_2 solid sorbent material] using Si(220) optics with 16.8 keV X-rays and Si(440) optics with 21.0 keV X-rays. For each setup we show both the sample data profile and the associated instrumental 'blank' profile. To match the peak heights, the sample data profiles were scaled by the inverse of the sample transmissions. If we set the sample scattering intensity to blank scattering intensity ratio at three as a threshold for reliable USAXS intensity subtraction, the data show that this threshold occurs at $\sim 2.3 \times 10^{-5}$ Å^{-1} for Si(440) and at $\sim 8.0 \times 10^{-5}$ Å^{-1} for Si(220). We also note that the total data collection times are about the same when using either Si(440) or Si(220) optics.

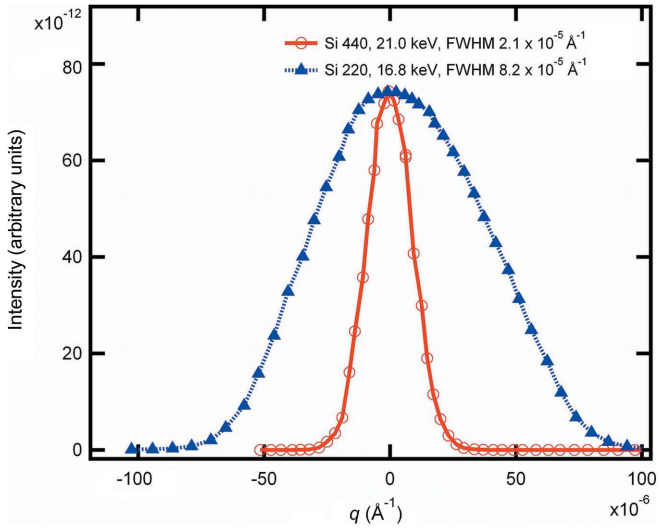

Figure 1
Measured instrument reflectivity curves using Si(220) optics at 16.8 keV and Si(440) optics at 21.0 keV.

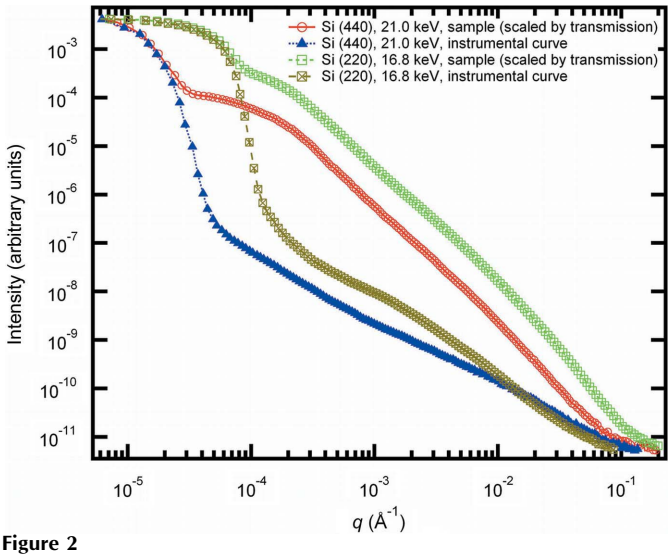

Figure 2
Comparison of USAXS measurements of a MOF CO_2 solid sorbent material using Si(440) crystals at 21.0 keV and Si(220) crystals at 16.8 keV. Sample data are scaled by the inverse of sample transmissions to match the peak heights to the instrumental curves.

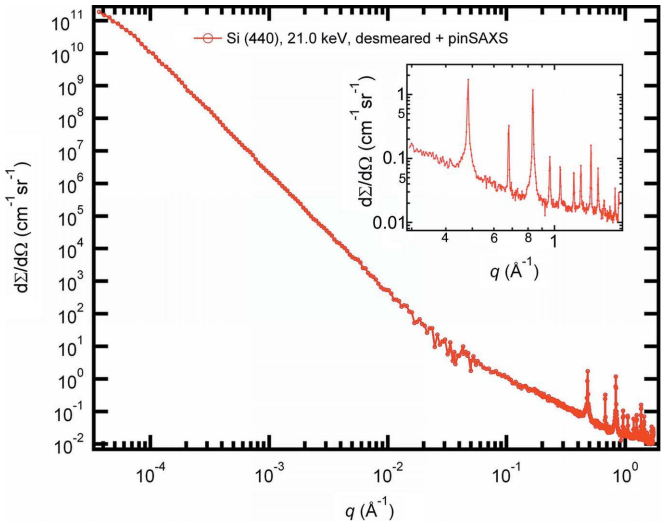

Figure 3
Example of USAXS data of a new MOF-based and zeolite-based CO_2 solid sorbent material: combined USAXS [Si(440), 21.0 keV, desmeared] with high-q scattering (fixed length pinSAXS) data.

Fig. 3 shows a combined data profile that includes USAXS data of a second MOF-based and zeolite-based CO_2 solid sorbent material measured using an Si(440)/21.0 keV setup and sector-averaged data measured using the pinSAXS detector, also with 21.0 keV X-ray energy. The total q range of these data covers nearly five decades (from $q = 3 \times 10^{-5}$ to $q = 1.8$ Å^{-1}) with a corresponding scattering intensity range of ~12 decades. One notable feature in Fig. 3 is that, for the combined data set, q_{res} and the q sampling are appropriate in the entire q range. This is best observed in the sharp diffraction peaks shown in the inset of Fig. 3, which demonstrates that both q_{res} and q sampling are sufficient.

4. Conclusions

New scientific challenges are driving USAXS instrument development towards the use of higher X-ray energies and increased dynamic ranges both in q and in the measured scattering intensity. Our data show that reliable USAXS operation with Si(440) optics is feasible. However, our results also show that the narrow width of the crystal reflectivity curve (Fig. 1) is reaching the limit that the present stage-motion precision can resolve, and the mechanics of key parts of the USAXS instrument need to be upgraded for stable high-energy USAXS operations. When completed, these upgrades will provide a new USAXS instrument with an unprecedented q range of approximately five decades and a corresponding intensity range of up to 12 decades. It also features excellent q_{res} and q sampling over its entire q range. At the same time, when this instrument is operated in the X-ray energy range of 20–30 keV, it will provide the higher penetration needed for *in situ* characterization of engineering materials in relevant sample environments. For example, the mean penetration distance through a quartz window for 21.0 keV X-rays is greater than 2 mm, compared to less than 0.25 mm for 10.5 keV X-rays. We also note that the use of Si(440) and Si(220) optics will enable a rapid switch between two X-ray energies separated by a factor of two, which allows different materials to be probed at energies more suitable for their microstructural characterization.

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