Energy determination of synchrotron X-ray beam energy in the high energy region of 38–50 keV using powder diffraction patterns of the standard powder Si640b

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ABSTRACT

Powder diffraction patterns from SRM Si640b are used to calibrate the energy scale for two experiments using a monochromated synchrotron X-ray beam in the high energy region 38–50 keV. The energy of the beam is determined to accuracies between 0.0007% and 0.07% of the beam energy. Uncertainties in the energy scale are reduced by correcting for the zero offset angle of the monochromator crystal. Corrections of between -150 and $50\,eV$ are applied to the nominal beam energy. It is shown that systematic errors arising from the misalignment of the monochromator can lead to large systematic shifts in the beam energy.

1. Introduction

Powder diffraction is one of the most common and important techniques used with synchrotron radiation for structure determination [1]. Today's synchrotron sources can provide radiation with a very high flux across a wide and continuous range of the X-ray energies. The ability to tune the beam, however, also leads to uncertainty in the beam energy [2,3]. Powder diffraction standards are commonly used to calibrate the X-ray beam energy scale and to correct some systematic errors such as the zero offset of the 2θ angular scale of the diffractometer.

This study analyses powder diffraction patterns to determine the beam energy using the central locations of the Bragg diffraction peaks [4]. In this approach, peak central positions are used rather than whole pattern matching. This avoids the need to fit for peak broadening effects such as particle size and beam energy bandwidth. Such an approach is well suited to powder diffraction patterns generated with synchrotron radiation because of the highly symmetric nature of the diffraction peaks. While single crystal diffraction patterns have narrower and higher intensity peaks, which have higher angular resolution, the same assumption of high peak symmetry is not valid.

When measurements are made over an extended range of energies, systematic errors in the monochromator crystal alignment such as the zero offset of the crystal can lead to uncertainties in the energy scale [2]. To correct for this, absolute

measurements of the beam energy using powder patterns are made at selected energies across the energy range of the experiment. A calibration curve can then be made which allows one to interpolate and correct energies across the range of the experiment.

In this study, we used the X-ray Extended Range Technique (XERT) [5,6] to measure the X-ray mass attenuation coefficient of silver and gold across a wide range of energies [7–15]. First, the mass attenuation coefficients of silver were measured from 25 to 50 keV. Then the mass attenuation coefficients of gold were measured from 38 to 50 keV. The angle of the monochromating crystal was always rotated in the same direction when changing energy to avoid backlash. This meant that the chosen energies decreased monotonically from the highest energy, 50 keV, to the lowest energy, 25 keV. The measurements for gold and silver were made separately, so the monochromator had to be reset to the highest energy after the silver measurement. We show that the effect of resetting the monochromator and resetting its detuning led to a large offset in the energy calibration curve.

Two sets of powder diffraction patterns from the NIST Si standard reference material (SRM 640b) were used calibrate the two different experiments. In the silver experiment, 23 patterns were collected between 38 and 50 keV. In the second experiment only three powder diffraction patterns were collected in the same energy range, due to time constraints.

The energy calibration curves for the two experiments were found to give a good fit using linear models. The slope of the two lines was the same within uncertainty, proving the consistency and reproducibility of the linearity of the

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energy scale. A significant difference was found in the constant monochromator angle offset between the two calibrations. It should be noted that in XANES studies the constant offset term E_0 needs to be determined. This can lead to uncertainty in the edge region which can limit the ability to determine the speciation of the element being studied [16]. In XAFS and XANES studies the constant E_0 term of the energy calibration can be fitted in the analysis stage. The first-order term of the linear energy calibration could still lead to shifts across the spectra [2].

2. Experimental setup

Powder diffraction patterns were recorded by a scanning arm diffractometer at selected energies for the standard powder Si640b [17]. During the measurement the powder was spun in a 60 μm diameter glass capillary to average over possible crystal orientations. A sodium-iodide scintillation counter located on the detector arm of the diffractometer was scanned over a range of angles to record the Bragg peaks.

A right-angle linkage silicon (400) monochromator was used to select the nominal X-ray beam energy with a small energy bandwidth. The (400) Bragg reflection was accepted through the monochromator, as well as harmonics of higher-order reflections. Changing the angle of the monochromator changed the energy of the reflections in accordance with the Bragg equation.

A prior approximate setting of the monochromator angular scale to the beam energy allowed us to choose the nominal energy of the beam. However, the nominal beam energy chosen is usually different from the actual energy of the beam because of systematic errors such as hysteresis in the monochromator movement [9,4], and the zero offset of the monochromator crystal. To determine the correct energy using the powder diffraction standard, measurements of the beam energy are made at various values of the monochromator angle. The monochromator angle can then be calibrated against the energy.

3. Analysis

Peak central positions 2θ of the powder diffraction peaks were fitted with a Lorentzian convolved with a slit. A quadratic background model was used to correct for the background intensity. The Levenberg–Marquardt non-linear least squares algorithm was used to minimize the reduced χ^2 of the fitting model.

Miller indices were assigned to the peaks. The Bragg equation is used to determine the offset from the nominal energy δE

$$E + \delta E = \frac{hc}{2d\sin(\theta + \theta_0 + \theta_z + \theta_y)} \tag{1}$$

where θ_0 is the zero offset of the diffractometer, θ_z is the angular offset due to the horizontal misalignment of the powder and θ_y is the vertical angular offset. The horizontal and vertical angle misalignment parameters are related to the vertical and horizontal distance of the powder sample from the center of the diffractometer as

$$\delta\theta_y = \frac{\delta y}{D}\cos 2\theta \tag{2}$$

and

$$\delta\theta_z = \frac{\delta z}{D}\sin 2\theta \tag{3}$$

where δy and δz are the vertical and horizontal offsets of the powder from the center of the diffractometer. These forms of δy
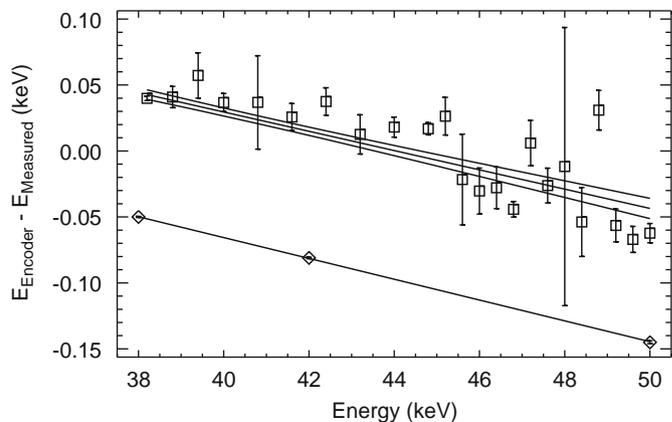
Fig. 1. The differences between measured energies and encoder energies. The values for the silver experiment are labelled as ◇ and the values of the gold experiment with □. A calibration line is fitted two both sets of data separately. The uncertainties for the second set are smaller that the first because of optimizations made to the monochromator. These changes included changing the zero angle offset of the monochromating crystal which led to a different constant fitted to the calibration line, while the slope of the line remained unchanged.
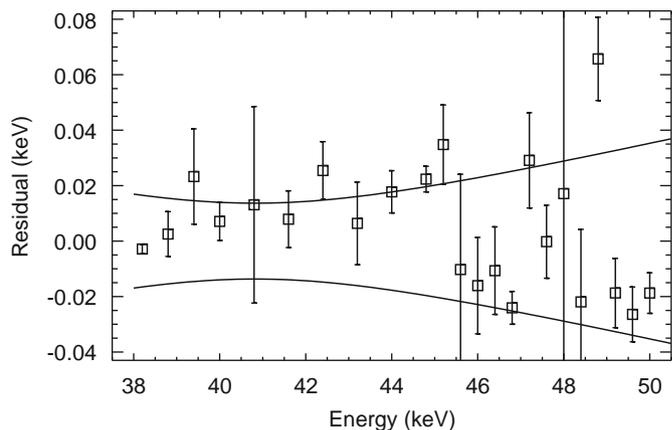
Fig. 2. Residual values of the measured energies of the first experiment from the energies fitted by the model. The residuals are consistent to within a few σ of zero.

and δz orthogonalize the components and minimize correlations between the two parameters.

Fig. 1 shows difference between the measured energy $E_{measured}$ and the energy derived from the angle recorded by the monochromator encoder $E_{encoder}$ for both energy calibrations as a function of $E_{measured}$. Both sets of data are fitted with a straight line. The two calibration lines fitted to the data in Fig. 1 had the same slopes within the uncertainty of the fitting parameters; 0.99268(77) for the first data set and 0.99211(08) for the second.

The residuals of the straight line fit are shown in Figs. 2 and 3. The residuals are within 2σ of the measurement error, indicating that the model is satisfactory. Uncertainties in the calibration line are plotted as enveloping lines. They are calculated from the covariant error matrix of the least squares fit.

The analysis of the powder diffraction patterns uses the central locations of the Bragg diffraction peaks rather than full pattern fitting used in Rietveld analysis [18]. Using peak centroid locations rather than the full pattern (including widths) has been shown [4] to avoid possible significant correlation errors of peak amplitude modelling due to broadening effects such as the particle size effect, energy bandwidth [19] and the curvature of low-angle lines [20].
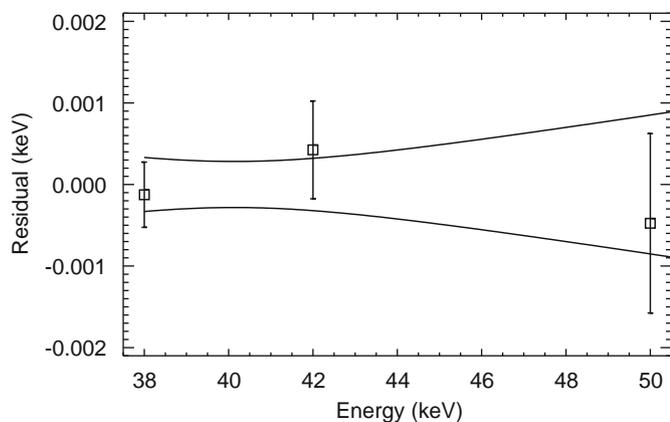
Fig. 3. Residual values of the measured energies of the second experiment from the energies fitted by the model. The residuals are within error of zero, indicating that the data was well fitted by the model.

4. Conclusion

Powder diffraction patterns of standard powders provide an important independent measurement of the energy of mono-chromated X-rays. Energy calibration of experiments carried out across a wide range of X-ray energies can correct systematic errors which would otherwise introduce large systematic shifts in the energy of the beam. The calibration scale was well fitted by a linear function. The constant offset term is important for XANES analysis, particularly for determining speciation [21]. The first order term may lead to shifts in energy affecting XAFS and XANES studies if it is not corrected [3,2].

Bragg reflections in powder diffraction studies are more symmetric than low order reflections from single crystal diffraction from the same material. This property can be used to simplify the process of energy calibration by eliminating the need to consider peak broadening processes and asymmetric peak profiles.

The linearity of the energy scale was confirmed across a wide range of energies from 38 to 50 keV. The largest source of uncertainty was the zero offset introduced into the monochro-mator angle between the two experiments. This led to a large constant offset in the energy calibration scale. To avoid introducing a large constant offset in the energy scale is a calibration is required for each experiment.

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