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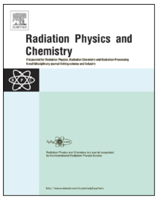

High accuracy energy determination and calibration of synchrotron radiation by powder diffraction

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HIGHLIGHTS

- Energy calibration in synchrotron environments where hysteresis is common.
- About 0.1 eV accuracies for a wide range of energy.
- Consecutive runs with the same monochromator and detuning can yield 10–20 sigma discrepancies.
- Offset errors can be critical for comparison to theory and for XANES interpretation.
- Slope errors and offset are significant for XAFS bond lengths and interatomic distances.

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ABSTRACT

Powder diffraction patterns of standard reference material LaB_6 (660a) have been used to determine the energy of a synchrotron beam across the range 7–12 keV with typical uncertainties of 0.1 eV. Diffraction peaks were recorded on X-ray image plates over a broad range of diffracting angles. Multiple systematic errors were corrected in a robust fitting procedure, providing consistent physical results. We have shown the reliability of this method and observed limitations of reproducibility due to hysteresis by repeated multiple energy calibrations. We report accuracies as low as 13 parts per million (ppm), and demonstrate the need to accurately determine the energy of the X-ray beam during experiments.

1. Introduction

The recent development in fields such as X-ray absorption fine structure (XAFS), X-ray absorption near-edge structure (XANES) and X-ray diffraction (XRD) has relied heavily on the ability to monochromate the broad band of photon energies produced by synchrotron radiation. Energy offsets can occur due to hysteresis of the monochromator motor control and from errors in the reported encoder angle of the monochromator. This becomes problematic in fields that require accurate knowledge of the beam energy.

Previous measurements of K absorption edge energies in transition metals have shown discrepancies of over 6 eV in the literature (Kraft et al., 1996). XAFS oscillations depend on the energy of the incident radiation, hence offsets in energy cause XAFS peaks to shift. More importantly, errors beyond a simple energy offset, of a linear or quadratic or more complex nature, change the dynamical bond lengths and the broadening parameters interpreted by standard XAFS analysis, and any constant offset has a large impact upon XANES interpretation. This is important in fields such as catalysis studies, which employ XAFS and XANES to determine oxidation state of different catalysts (Choi and Lee, 2000). Such analyses often involve detecting small shifts in absorption edge energies, so that energy offsets can lead to inaccurate conclusions.

XRD is a popular method for determining crystal structures. Since the angular location of diffraction peaks depends on the energy of the incident radiation, errors in the monochromator energy reading can produce large offsets in Bragg diffraction peak locations. The use of SRM's to determine photon energies is a common procedure, allowing accurate calibration of the incident beam in order to obtain accurate data (Fleming et al., 2003).

Our group has previously shown discrepancies between standard reference materials (SRMs) LaB_6 (660) and Si (640b) (Chantler et al., 2004) and calibrated the relative lattice spacing

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through analysis of the physical broadening processes affecting peak profiles (Chantler et al., 2007). This work follows on from the developments by our group in the analysis of diffraction peaks (Rae et al., 2006).

Using SRM LaB_6 (660a) with a well known lattice parameter, we have collected and analysed powder diffraction patterns, which have consequently been used to correct for a systematic shift in the monochromator energy reading. This permits accurate calibration of the beam energy over a broad range of energies. The importance of accurate beam calibration has been demonstrated and a range of applications is discussed.

2. Experimental details

The powder diffraction patterns were recorded on X-ray image plates, mounted on the perimeter of the powder diffractometer BigDiff (Barnea et al., 1992), employing a Debye–Scherrer camera setup. BigDiff's large radius (573 mm) corresponds to 1 cm per degree and permits high resolution profiles to be obtained. Radioactive fiducial markers located at precise locations around the perimeter of BigDiff allow angular positions on the image plates to be calibrated. Full powder patterns are obtained in a relatively short time, permitting simultaneous analysis of multiple systematic errors (Rae et al., 2006).

The LaB_6 powder sample was placed in a capillary with an outer diameter (OD) of 300 μm, which was then attached to one of the eight goniometer heads located in the centre of BigDiff (Creagh et al., 1998). The powder sample was spun at a rate of 60–100 rpm to ensure that all random crystal orientations were averaged over to obtain a full, accurate powder pattern. The diffractometer is evacuated to reduce scattering in the chamber.

Fig. 1 shows 17 powder patterns recorded on a single image plate. Bright black spots at the bottom of the image plate indicate radioactive fiducial markers. Diffraction peaks were collected for five separate experimental runs at regular energy intervals. Four X-ray imaging plates were used for each run, corresponding to an approximate angular region of $-135^\circ < 2\theta < 45^\circ$ for the majority of the data. Fig. 2 illustrates the Bragg peaks and amplitudes across this angular region. The spectrum has minimal background noise permitting accurate peak position determination via a robust fitting procedure.

The capillary holding the powder sample is manually aligned to the beam, so the sample will likely be offset from the diffractometer axis. This eccentricity of the powder sample is described by the parameters δ_y and δ_z, the vertical and horizontal eccentricity, respectively. A similar system comes from the uncertainty in the image plate angular locations, such that each image plate is considered to have a constant angular offset of $\delta\theta_{p_i}$ for the *i*th image plate. These offsets and how they affect the powder pattern are shown in Fig. 3.

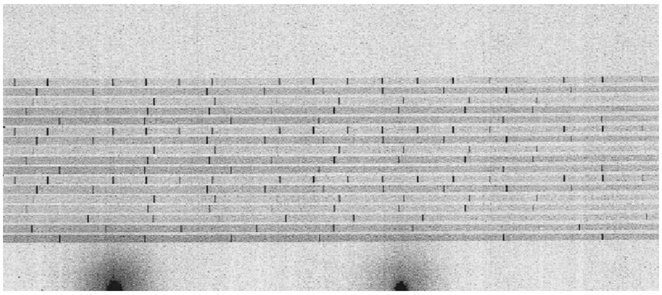

Fig. 1. Powder diffraction patterns recorded on a single image plate, covering an angular region of approximately 40°. The two dark spots at the bottom of the image are the radioactive fiducial markers.

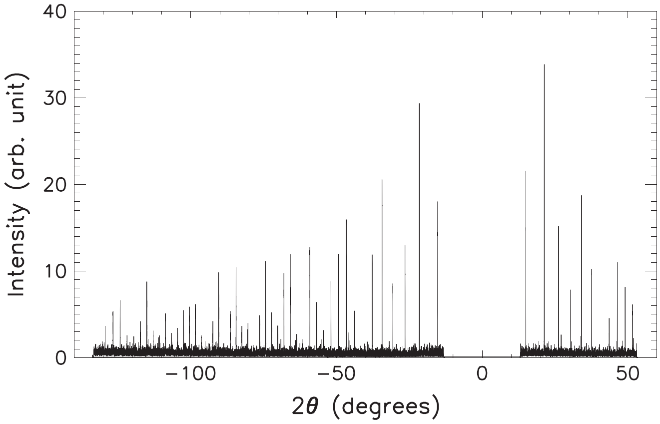

Fig. 2. A typical LaB_6 powder pattern recorded across four image plates, at a nominal energy of 11.3 keV.

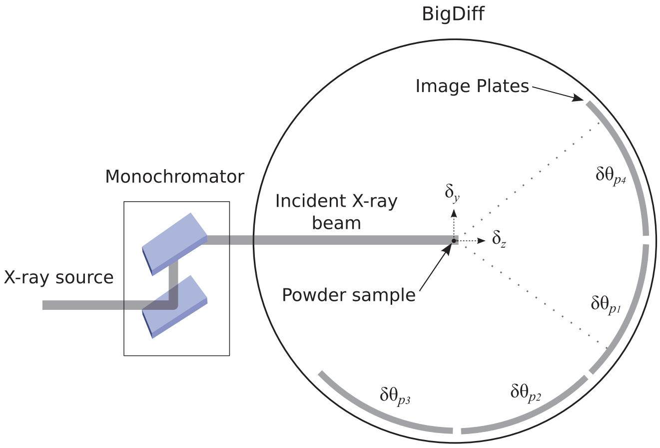

Fig. 3. Schematic of BigDiff, showing the image plate locations and the effect of different offsets such as each individual plate offsets $\delta\theta_{p_i}$ and the sample eccentricity δ_y and δ_z.

The Debye–Scherrer camera setup, illustrated in Fig. 1, allows for multiple powder patterns to be recorded on a single image plate and ensures that powder diffraction pattern measurements are not time consuming. In the energy range considered, exposures of the LaB_6 powder sample in a 300 μm OD capillary typically took 5–10 min depending on the specific energy.

After an experimental run was finished, the image plates were digitised using the Fujifilm BAS2500 image plate reader. Once digitised, the images were then read by the PPDA program, which determines the intensity along a particular diffraction pattern as a function of the diffraction angle 2θ. The angular positions are calibrated by fitting a Gaussian to the recorded fiducial markers.

3. Fitting procedure

A robust peak finding algorithm was applied to detect and locate numerous Bragg peaks. This was subject to two possible problems: cases where Bragg peaks were not detected by the algorithm and cases where spurious peaks were mistakenly detected. Spurious peaks caused incorrect *hkl* indices to be assigned. A filtering process, based on the shape and quality of the peak, was implemented to recognise and discard weak local peaks which were not Bragg reflections. As the powder sample may be approximated as a slit source, each diffraction peak profile