

Application notes on the use of softer X-rays for anomalous powder diffraction

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An in-vacuum diffractometer has been modified to collect powder diffraction data from a sample of promazine hydrochloride. Strong anomalous contrast has been observed at, or close to, the sulphur edge. Based on the data collected, a bespoke diffractometer has been designed that, together with minor changes to the geometry of the experiment, will enable the routine collection of powder data at absorption edges below 5.5 keV.

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1. Introduction

There are many occasions in materials science where a detailed understanding of crystal structure can assist and inform the design process. Often this structural knowledge is required on a local scale to determine subtle changes in microstructure or to determine the degree of site occupancy and order. James (1948) first discussed the phenomenon of anomalous scattering and its possible uses for determining local and long-range structure. However, the samples in the materials field are often polycrystalline and multi-phase which greatly complicates this process. Synchrotron radiation from its early days in the late 1970s and during its explosive growth over 25 years (Helliwell, 1998) promised X-ray beams of continuously variable wavelength ideally suited for anomalous scattering studies of local order or structural problems in polycrystalline or otherwise imperfect materials.

Despite the problems that real materials pose, there have been several notable successes in the utilization of anomalous scattering in the materials and engineering sciences. For example, in the area of ceramics Meneghini *et al.* (1999) have shown how diffraction anomalous wide-angle scattering can be combined with absorption spectroscopy to study the formation of glass ceramics in the CaO–SiO₂–ZrO₂ system. Joubert *et al.* (1998) have studied the battery electrode material LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75} by synchrotron anomalous powder diffraction. The anomalous scattering was vital to the refinement of the site occupancies. Powder diffraction with X-rays and neutrons was used to study the cation distribution in NiFe₂(PO₄) (Warner *et al.*, 1995). The real part of the scattering factor for Fe was experimentally determined and used to solve for site occupancies. As a final example, resonant powder diffraction has been used to measure the cation distributions in complex mixed-valence nanocrystalline solids

(Lorimier *et al.*, 2003). In all of these cases the target atom for the anomalous study has its binding energy at 5.5 keV or higher. Lighter atoms ranging from sodium to titanium are just as important from a structural point of view; the main reason why they are not the subject of study by anomalous scattering is problems with absorption. However, there have been structural studies using lighter atoms. For example, Mårdalen *et al.* (1994) studied poly(3-octylthiophene) at the sulfur edge but the data were of poor quality. However, they were able to demonstrate the potential of the method. If the problems associated with handling X-rays in the 1–5 keV range can be routinely solved, anomalous studies using softer X-rays could be applied to a wide range of problems. This would be especially useful in the field of catalysis and microporous materials to evaluate the local structure around Al, P or Ca cations in the channels of zeolites or aluminophosphates. Often in catalysis manufacture a knowledge of the structure surrounding cations in aluminophosphates requires a better structural definition than can be provided by conventional X-ray crystallography.

Other beneficiaries of a softer X-ray anomalous scattering approach could be found in the field of drug design and polymorph identification where structural definition is needed when only light atoms are present. It is therefore interesting to see whether the sulfur atoms present in the material can be used to solve the crystal structure of a number of industrially important pharmaceutical polymorphs. The resolution at an energy of 2.47 keV will be low; however, it would afford a good starting point from which to begin a global optimization structure solution such as that described by Markvardsen *et al.* (2002). Specifically, construction of a difference Patterson map corresponding to diffraction patterns collected on and off edge gives a significant simplification of the Patterson map. For example, when there is only one sulfur atom in the asymmetric

unit of a centrosymmetric triclinic structure the difference Patterson map essentially corresponds to the crystal structure itself.

Taking the difference between on- and off-edge squared structure factors leads to a three-term formula (David, 2004). Considering the exact overlap between \mathbf{h} and $-\mathbf{h}$ reflections reduces the equation to two terms that contain cross terms between symmetry-equivalent sulfur vectors and cross terms between sulfur and the other atoms in the crystal structure. Measuring at 2.35 keV and 2.44 keV ($f' = -3.38$, $f'' = -0.44$; $f' = -7.68$; $f'' = -0.41$) provides sufficient discrimination to give a strong effect for the anomalous signal in the difference map. The success of this approach would have general implications for materials research as an analytical tool (Shankland *et al.*, 2002). Synchrotron radiation is easily able to provide light at the appropriate absorption edges between 2 and 4 keV for these lighter atoms but the use of anomalous dispersion in this energy range brings a number of practical problems. This short paper shows how some of these experimental problems can be overcome.

2. Experimental

Initially, promazine hydrochloride (which is a neuroleptic agent) was chosen as the test sample as it scatters well and its structure ($\text{C}_{17}\text{H}_{21}\text{N}_2\text{S}_1\text{Cl}_1$, $P21/c$, $a = 11.81$, $b = 11.49$, $c = 13.43$ Å, $\beta = 111.72^\circ$, $V = 1692.39$, $Z' = 1$) has previously been solved by David *et al.* (1998).

In order to carry out the experiment we had to modify station 3.4 on the SRS at Daresbury. In order to work close to the sulfur absorption edge at 2.472 keV we used an in-vacuum diffractometer. We used a soft X-ray vacuum diffractometer borrowed from the experimental systems group at Daresbury (Roper *et al.*, 2001). This is a cylindrical vessel, 620 mm in diameter, containing a sample stage and single avalanche photodiode detector. There was limited sample translation and a 2θ axis for mounting the detector. This vacuum vessel had previously been used for testing optical elements, gratings, monochromator elements and for soft X-ray magnetic studies of single crystals and has been used for magnetic studies at the ESRF (Roper *et al.*, 2001) on ID12A, ID12B and ID8. The vessel has been designed for ultra-high-vacuum use which, for our purposes, was a little cumbersome. Ideally, for the purpose of reducing air absorption only a very modest vacuum ($\sim 10^{-1}$ torr) is required. The diffractometer was not optimized for powder samples since there was no way of rotating the sample to improve the powder averaging. This proved to be a problem since at 2.47 keV the softer X-ray penetration depth in the material has a value of 2.5 μm (as shown in Fig. 1). The average grain size of the sample ($5 \mu\text{m} \times 5 \mu\text{m} \times 50 \mu\text{m}$) was measured by optical microscopy; therefore the incident X-ray beam did not penetrate further than one layer of crystallites. The sample was inclined at approximately 7.5° to the incident beam which was 5 mm in width and 0.1 mm in vertical height. This gave a beam footprint of $5 \text{ mm} \times 0.75 \text{ mm}$ incorporating approximately 10000 crystallites or powder grains. According to Warren's powder pattern theorem

(Warren, 1969) the number of crystallites in the diffracting position, dM , is given by $dM = (M/2) \cos\theta \, d\alpha$, where M is the total number of crystallites, θ is the Bragg angle and α is the beam divergence. In this case the 0.1 mm vertical aperture slit was approximately 1.3 m from the nominal focus position. The nominal focus is approximately 0.6–1 mm high, demagnifying the source by approximately 2.5:1. The vertical divergence at the focus was approximately $2.5 \text{ mrad} \times 1 \text{ mrad}$. The figure of 0.6 mrad was the vertical acceptance of the focusing mirror. There is a strong peak cluster at a Bragg angle of 30° which, taken with the other figures, means that there was only an average of ten grains in the diffracting position at any one time. This is clearly insufficient to obtain a proper statistical average so the sample stage was tilted and the data were collected again. The final data set was a sum of 50 small variations in sample angle giving a powder average that was far from adequate but gave a good enough diffraction pattern to observe anomalous differences. This was, however, rather time-consuming and a possible solution is discussed in the conclusions.

3. Results

The direct beam intensity was measured at 7×10^9 photons s^{-1} onto a sample area of $5 \text{ mm} \times 0.7 \text{ mm}$. The diffraction signal was weak but observable. This is shown in Fig. 2 with three traces from promazine hydrochloride, 4 eV, 10 eV and 200 eV below the sulfur edge.

As discussed before, the number of powder grains in the diffracting position is limited. In addition, the method is highly sensitive to those grains lying on the surface of the material. Despite these difficulties we collected many data sets at slightly different ω values and averaged them together. The resulting data fit a LeBail refinement (Fig. 3) with a quadrupled unit cell in the b direction and a distorted triclinic cell compared with the published structure. The peak half-widths are of the order of 0.2° . This is what we expect since the rocking width of the sample is $\sim \lambda^2$. The nature of the peak splitting is still not understood. However, it was noticed that there was a significant amount of sample discoloration around the incident beam position so it is possible that there

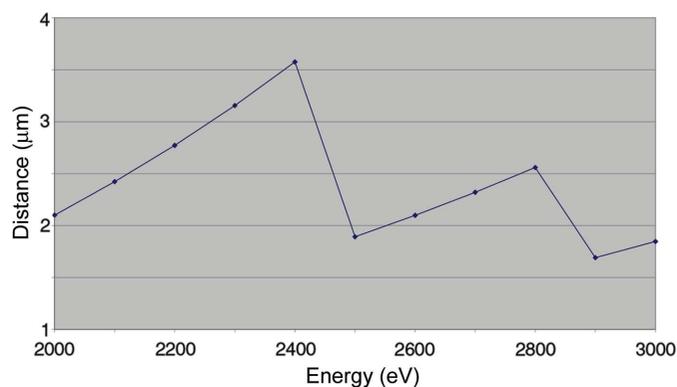


Figure 1
Sample penetration depth variation around the sulfur K -edge.

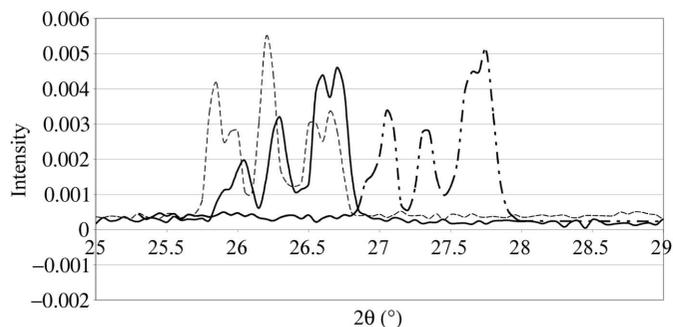


Figure 2
Diffraction pattern of promazine hydrochloride close to the sulfur edge: 4 eV below (dashed line), 10 eV below (solid line) and 200 eV below (dot-dashed line).

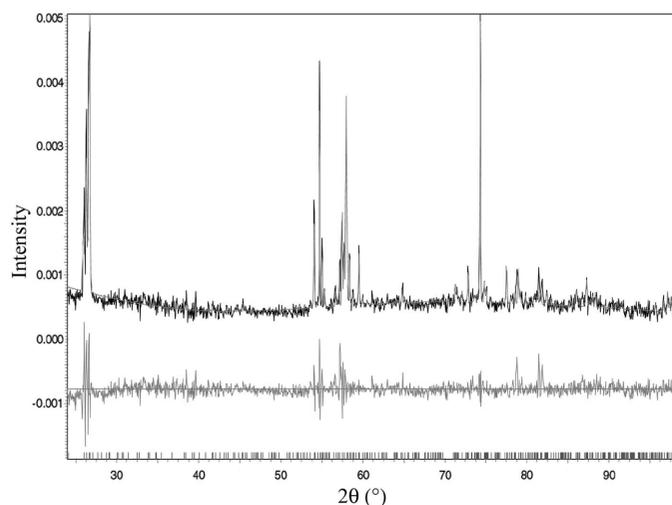


Figure 3
A Le Bail refinement of promazine hydrochloride showing the peak splitting due to decomposition. The Bragg peaks are shown as ticks, the difference curve between the observed and calculated pattern is shown in grey.

has been significant sample deterioration. Whether this occurred during data collection or previously is not known

4. Conclusions

We have demonstrated that we can obtain good anomalous contrast around the sulfur edge in organic materials. The method is time-consuming but many of these difficulties can

be resolved by the construction of a purpose-built in-vacuum diffractometer for softer X-ray work. We have well advanced plans for a simple diffractometer design incorporating an integral direct coupled CCD area detector. In future the beam divergence should be increased by a factor of ten and the sample must be rotated within the diffractometer vacuum. We cannot conclude from our results significant success in structure solution but we are encouraged to believe that this method will be useful in the future for solving structures, for the elucidation of local site information and for indexing structures. To our knowledge this is the first time that such a good anomalous contrast has been observed in polycrystalline materials at these energies.

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