Is the X-ray diffraction theory we use correct? By Dr Paul Fewster – Webinar Q+A

Q……The calculation of the scattering from a stack of planes has several large peaks as well as the Bragg peak, what are these?

These correspond to the direct beam hkl = 000 that has a path length difference of 0λ, with the Bragg peak for hkl with a path length of 1λ, and also shown is the harmonic for *d* with a path length of 2λ. This is analogous to Young's slits with peaks for path lengths of =0λ, 1λ, 2λ, 3λ, 4λ,…..etc., i.e. a single spacing will create all these peaks.

Suppose we add in more layers then they have the same repeat *d*, then their intensity pattern will be the same as the original, but modified by the scattering strength and their peaks will be in exactly the same position as the original. However, when their amplitudes are combined with a phase term relating them to the original set of planes, their combination will give the intensity variations observed, including systematic absences.

This will all be covered in my next article.

Q……What do you mean by the 222 reflection from diamond appearing, without asymmetry in the bonding?

This can be understood by the sum of amplitudes from all the contributions in the repeat unit, i.e. from all contributions separated by the distance *d*. In this case the repeat is ~ 0.31 nm, and there will be another set of repeating planes displaced by 0.75*d* from the original, which will give the characteristic 111, 333 and 444 peaks expected. However, when the finite size of the planes is included by adding further planes of weak scattering to represent a symmetrical spread in the electron density, the 222 peak appears. Again, this will all be covered in my next article.

Q…..Does this new theory modify the structure factors?

The first point is that if the intensity is dispersed, so measuring just the peak may not be representative of the full intensity associated with the planes. This is especially important when capturing intensity over different intensity truncation levels through background removal, e.g. a weak diffraction peak might result in an underestimated intensity level.

XFEL data can capture this distribution (this, I believe is the variability observed in snapshots) and should lead to a good estimate of the total intensity from a plane. But, a sufficient number of snapshots is required to achieve this. In powder diffraction, the dispersed intensity is captured, but the nature of the experiment (capturing intensity out of the plane) will lead to oversampling and this needs to be corrected. When all these contributions are included it does not follow the familiar 1/sin(Theta) form, and the difference is most marked at small angles, below ~12 degs.

Q….How does your theory change the interpretation of texture measurements?

This is an interesting question, it could mean that the degree of texture is underestimated, by capturing intensity from planes remote from the Bragg condition. I have not looked into this in any detail, but I am sure it will have an impact.

Q….Does this change the interpretation of Laue patterns?

I have not explored this, but it almost certainly will, since it suggests that monochromatic radiation can form a full pattern (this can be seen in the data from XFELs), so I would see this as a combination of the enhancement contribution and the wavelength spread in the source. It certainly doesn't make the interpretation easier.

Q….What is the effect of X-ray sharing between points on different planes in large perfect crystals

If I understand your question correctly, I presume you are referring to the re-scattering of X-rays that return to the incident beam direction and reduce the strength of the beam entering the crystal. If that is the case then this is the essence of dynamical theory, where the wave is scattered strongly towards the Bragg peak position and incident beam direction. These waves are continuously re-scattered through the crystal, resulting in a complex wave-field. This results in a limited beam penetration, when the diffraction peak is strongest and as the incident angle is changed the beam penetrates further. This mechanism should be present whenever the Bragg condition is satisfied, but in general the intensities measured do not show this unless the crystal is large and perfect. This leads to the mosaic model to break the crystal into small blocks so that the wave-field re-scattering is weak, or as I propose, small curvatures of the planes (going around defects, etc.) limits the crystal planes to small regions at any one orientation where the Bragg condition can be satisfied, and therefore this dynamical scattering only contributes a small part to the measured scattering in imperfect crystals. The non-Bragg scattering though puts this intensity at the Bragg angle, rather than requiring the mosaic block orientation to satisfy the Bragg condition before it can contribute intensity to the Bragg angle.

Q….How does the theory this effect/be incorporated to understand peak profile analysis? Particularly deformed metals.

My thoughts are that there is much more information in the background and intensity distribution than is presently used. This obviously requires the correct theory! My most recent work considers the scattering from perfect and imperfect crystals, the latter is represented by some prior distribution of crystal regions and orientations that could also be associated with strain. By randomly selecting from the prior distributions for the likely microstructure it is possible to build an intensity distribution at a given 2Theta setting (this intensity distribution would appear around the Debye-Scherrer ring in polycrystalline materials). This would require good resolution so that there is not too much intensity averaging, but that distribution should then be possible to model. This approach would also work for single crystals, although it would require many rotations to capture the information. The addition of strain is also possible to include, but would add considerably to the calculation time, unless the strain and micro-structure description were considered uncorrelated. This would require a considerable quantity of data, but is perhaps not too demanding with present day area detectors, so I think it is feasible. The direct profile fit from a Theta-2theta scan will include an enormous amount of averaging and instrumental broadening effects. This theory does give a measure of the intrinsic width and when all the aberrations are included seems to give a good fit (2014 paper assuming the Si crystals are perfect) but the aberrations really dominate (wavelength, slits, etc.). But if a very high-resolution instrument is used it is possible to study the Debye-Scherrer rings in detail, in Al for example we found multiple rings suggesting that the sample had distributed macro-strain (crystal to crystal) rather than micro-strain (within a crystal), Fewster & Andrew (1997) *Defect Microstructure Analysis by Diffraction* Chapter 18, pp346-364. Ed: Snyder, Fiala, Bunge, IUCr Monographs on Crystallography No.10.