Precession Electron Diffraction

1 Introduction

The vast majority of inorganic and organic crystal structures are determined by x-ray or neutron diffraction. The interaction of an x-ray or neutron with the underlying crystal potential is strong enough to yield diffraction data with sufficient signal-to-noise but weak enough such that in most situations the scattering can be described as being kinematical in nature. This of course has huge advantages in solving crystal structures because the intensities of reflections in x-ray or neutron diffraction data can be considered as proportional to the square of the structure factor for that reflection. By using phase retrieval algorithms, the structure can then be solved.

The interaction of an electron, a charged particle, with the crystal potential is far stronger. In general, this means the diffracted electron intensities are not kinematical in nature, they are 'dynamical' and dominated by multiple scattering events; using such diffraction data to solve crystal structures is a far greater challenge. Over decades electron microscopists have devised methods to minimize the dynamical effects. These include using ultra-thin crystals, as often prepared for high resolution imaging and/or using high voltage instruments (but beam damage can then often be a limiting factor). In some circumstances the crystal itself may be weakly scattering, as is the case for most organic crystals and some inorganic crystals with low atomic number, see the example of beryl later. However, in general, for most low order reflections, likely to be the strongest in the data set, the effects of this dynamical interaction can dominate.

The advent of convergent beam electron diffraction, with advances especially in the 1970's and 1980's led to a number of groups worldwide attempting to use diffraction data

obtained using CBED in a quantitative fashion. Complex intensity variation is seen in the zero order Laue zone (ZOLZ) reflections at low order zone axes; these can be related directly back to the propagation of the electron wave through the crystal in the form of Bloch waves (Buxton *et al.* 1977).

The relative excitations of the dominant Bloch wave give rise to the variations in the CBED discs. At certain 'critical' beam voltages, Bloch waves of s- and p-type symmetries become degenerate and this leads to characteristic features in the CBED patterns, which persist at any crystal thickness (Sellar *et al.* 1980). Figure 1 shows a series of CBED patterns of Ni recorded at the <110> zone axis, at increasing thickness. Whilst the density of fringes increases in all the discs the centre of the 000 disc remains very bright at all thicknesses; a comparable dark region is seen at the centre of the 200 and 111 discs. By careful calculation, it is possible to use these critical voltages to determine the structure factors of certain low order reflections (Tabbernor *et al.* 1990). However, not all crystals demonstrate such critical voltages at convenient values (microscope operating voltages are typically 100-300kV) and, although structure factors can be refined with this technique to high accuracy, it is in general limited to a few crystal structures.

In the late 1980's and 1990's, with the increasing power of computers, a more brute force approach could be tried, to match as precisely as possible the fine details seen in zone axis CBED patterns (Bird and Saunders 1992) and systematic rows (Zuo and Spence 1991). Such quantitative CBED (QCBED) approaches relied on experimental patterns being recorded with well-calibrated beam voltages and with the patterns filtered of (typically >1eV) inelastic scattering.

Accurate simulations of CBED patterns could be calculated relatively quickly and by refining the structure factors could be made to best fit the experimental patterns. This led to extremely accurate structure factors for relatively simple crystals, accurate enough to allow

the difference between patterns formed from 'neutral' atoms and the experimental patterns to yield information about the bonding charge density. Early work focused on the sphalerite crystal structures, and in Figure 2 we show the charge bonding densities in the {110} plane derived from zone axis CBED patterns recorded at 200kV from silicon, germanium and diamond (Saunders *et al*. 1996). Later work tackled more complex structures included metal oxides (Zuo *et al.* 1999) and intermetallic alloys (Holmestad *et al.* 1999). Recent work by Nakashima has shown how the problems of inelastic scattering that can plague the visibility and interpretation of CBED patterns may be overcome by using a difference technique (Nakashima and Muddle 2010) in which the slowly varying inelastic background is reduced to near-zero. Studies of aluminium showed conclusively the metal-metal bonding was in the tetrahedral interstices and with that was able to predict anisotropic elastic properties (Nakashima *et al*. 2011).

The complex intensity variations in the CBED discs become minimal if ultra-thin crystals are examined where the thickness is very much less than any relevant extinction length. Wu and Spence (2002) investigated how CBED patterns from thin and weakly scattering crystals contained diffraction discs with uniform intensity and thus close to being kinematical in nature. These intensities were used to determine directly the structure of anthracene.

If a coherent source of electrons is used and by allowing the discs to overlap then the overlap region will be a summation of diffracted amplitudes, containing information arising from interference between the two beams. By defocussing the beam slightly this information can be seen in the form of parallel interference fringes (perpendicular to the relevant g-vector). Such fringes can be processed as if a hologram to give the relative phase of the overlapping beams. For zone-axis CBED, this yields multiple phase relationships across the ZOLZ (Midgley *et al*. 1995) and for LACBED (Vincent *et al*. 1993), where two beams alone are allowed to interfere, accurate phase relationships between discs can reveal spatially

varying phase changes across defects etc. This type of phase retrieval first pioneered by Rodenburg as a form of ptychography (McCallum and Rodenburg, 1993), later by the Bristol group (Vine *et al*. 1992) and Tanaka's group in Japan (Terauchi *et al.* 1994), can yield structurally useful phase information but requires very thin crystals and recorded phases suffer from any lens aberrations (Vincent *et al*. 1993).

Other approaches to structure factor phase relationships have been used over the years, including the intersecting Kikuchi line (IKL) technique (Taftø and Gjønnes 1985) and a technique called PARODI in which the beam is defocussed to produce shadow images of the crystal edge in multiple CBED discs (Taftø *et al.* 1998).

Although here we focus on electron diffraction methods, we should not forget the possibilities offered by high resolution imaging to determine crystal structures. The structural information in the image however is prone to many factors that can alter the phase relationships between the scattered beams: (i) if the crystal is not ultra-thin, dynamical effects can dominate, (ii) unless exactly at the zone axis, crystal tilt can be a problem in image interpretation, (iii) lens aberrations can alter dramatically the relative phases of the scattered beams, especially at high resolution. Nevertheless, despite these pitfalls, a great deal of success has resulted from image analysis, retrieving phases from the image and relating these directly to the structure factor phases, starting first with biological molecules (Sperling *et al*. 1974) and later organic and inorganic crystals (Hovmöller *et al*. 2002).

Another approach, pioneered at Bristol in the 1980's was to consider reflections in higher order Laue zones (HOLZ) (Vincent *et al.* 1984). High order reflections have in general much smaller structure factors than low order counterparts. As such the extinction length is longer and the probability for multiple scattering is reduced. However dynamical scattering of course dominates in the ZOLZ and so scattering from ZOLZ to HOLZ can be considered as

scattering from individual excited Bloch states, each of which will give rise to a 'branch' of intensity in the HOLZ reflection (Vincent *et al.* 1984).

For many crystals studied there are typically 2-3 such branches evident in a HOLZ reflection. The intensity of each branch can be related to a partial structure factor, dependent upon the sub-set of atoms in the atomic columns on which the relevant excited Bloch state propagates through the crystal. By knowing the approximate structure of the crystal it is possible to interpret the branch structure and associate the branch intensities with subsets of atoms in the crystal.

Figure 3 shows an example of clear branch structure from the [0001] zone axis of rhombohedral $LaAlO_3$. This illustrates rather beautifully an interesting example of where odd HOLZ reflections have one strong branch and even HOLZ two. This comes about because for $LaAlO_3$ only oxygen atoms contribute to odd HOLZ rings, whereas both the metal atoms and the oxygen contribute to the even HOLZ. For the odd HOLZ, the metal atoms, which come in pairs parallel to the [0001] axis, separated by ½ the repeat distance, are phased out, leaving only the oxygens to contribute (Midgley and Vincent 1991).

In the first pair of papers using this technique the crystal structure of AuGeAs was solved and refined (Vincent *et al.* 1984). Later it was used to refine other crystal structures including modulated structures (Vincent and Pretty 1986) and metastable phases (Midgley *et al.* 1996). However, to use the branch intensity effectively it is necessary to be able to interpret the HOLZ branch structure and that in turn requires some knowledge of the underlying crystal structure. If the crystal structure is completely unknown, a new approach is needed that does not rely on interpretation of the branch structure. By tilting away from zone axes, the dynamical effects are reduced and the electron wave propagates through the crystal in a more plane-wave-like manner. HOLZ reflections then will have just a single near-kinematical intensity, which can be related back to the structure factor for that reflection. To maximize

the number of reflections seen away from a major zone axis, Vincent developed a focused large-angle CBED technique to generate what became known as 'Vincent patterns', an example of which is seen in Figure 4 (Vincent and Exelby 1993).

An alternative method to be able to visualize HOLZ reflections is to tilt the beam relative to the crystal such that the tilt angle coincides with the HOLZ reflection. This can be achieved (i) in a static way, leading to patterns where the ZOLZ reflection appear to resemble the HOLZ, in a geometry sometime referred to as the 'inverse HOLZ' geometry (Rossouw *et al.* 2006), see Figure 5a, or (ii) in a dynamical fashion where a convergent beam is rocked in a hollow cone about the zone axis, see Figure 5b (Tanaka *et al.* 1984).

Although these methods are useful they are not particularly practical or easy to set up, especially for small crystallites, or where the HOLZ reflections are perhaps less visible through small strains, thermal diffuse scattering and so on.

The 'Tanaka method' (Tanaka *et al.* 1980) was introduced to enable LACBED patterns to be recorded using defocused beams, and simultaneously Eades developed a method to record large-angle CBED patterns using a 'double-rocking' method in which a focused convergent is rastered using scan coils to change the orientation of the beam, rather than the beam position on the sample (Eades 1980). The beam is then de-scanned below the specimen to bring the beam back onto the optic axis, see Figure 6a. This was accomplished using a modified STEM rack on a Philips EM 400 with additional electronics to allow the de-scan, and a BF detector used to record the beam intensity variations. An example of an Eades double-rocked pattern is shown in Figure 6b.

Independently, Crewe and Wall had proposed a double-rocking design some 10 years previously to provide an 'angular aperture' to yield phase contrast images in the STEM (Crewe and Wall 1970). A few years after, in 1976, Krakow and Howland produced a design for a hollow cone illumination using the scan coils rather than an annular aperture (Krakow

and Howland 1976). All these elements came together to enable the development of a double conical beam-rocking system that allowed convergent beam patterns to be recorded with intensities integrated over the Bragg condition (Vincent and Midgley 1994). A focused convergent beam was rocked to give hollow cone illumination above the sample and de-rocked below to bring the central beam back on the optic axis. The rocking-derocking action has a net effect equivalent to a focused stationary beam with a crystal precessing about the optic axis, as one would find in x-ray precession experiments. This new technique very quickly became known as 'precession electron diffraction' (PED), the electron analogue of the x-ray precession technique proposed by Buerger (Buerger 1964). Figure 7 shows a schematic diagram of the precession technique together with one of the original precessed patterns recorded from the [001] zone axis of $Er_2Ge_2O_7$.

The circular patch of reflections in the ZOLZ has a radius equal to twice the precession angle, and the width of the annulus of reflections in the HOLZ is equal to the precession angle.

The four key advantages of the technique can be summarized as follows:

1. The precession action of the method leads to many more reflections being visible in both the ZOLZ and HOLZ. The Ewald sphere is rocked backwards and forwards (twice) through the reflection and many more reflections are then intercepted compared to a 'static' Ewald sphere in a conventional pattern.

2. The intensities seen in the diffracted discs are single values and are not dominated by the complex contrast seen in conventional CBED patterns. The precession action leads to intensities integrated through the Bragg condition.

3. With the beam tilted away from the zone axis, the dynamical interactions are minimized but the geometry of the zone axis pattern is preserved; for a qualitative example see Figure 24.

4. A highly focused beam can be retained to enable diffraction data to be collected from small crystallites.

After its introduction in 1994, interest in the precession technique was at first rather limited, being picked up by only a few groups world-wide, particularly that of Marks at Northwestern and Gjønnes in Oslo. However, the commercialization of the method by the NanoMegas Company (Nicolopoulos 2007), and the production of easy-to-use hardware, has led to a rapid growth of interest and applications world-wide, see Figure 8. In addition, with more user-friendly interfaces to modern microscopes, software solutions for precession are now also available (Ishizuka 2001). It is likely that interest in the technique will grow further, especially with PED being combined with other techniques, such as electron tomography to give 'automated diffraction tomography' (ADT) and scanning modes to yield orientation maps – these will be discussed in more detail later in the chapter.

2. Precession Electron Diffraction – Geometry and Diffracted Intensities

2.1 The Geometry of Precession Electron Diffraction

A precession electron diffraction (PED) pattern is formed by the summation of a series of diffraction patterns whose incoming beam is tilted with respect to the optic axis. Tilting the beam in this way excites a Laue circle of reflections that will, if the precession angle is sufficiently large, excite many fewer (strong) reflections than would be the case if the beam were exactly parallel to the zone axis. Accordingly, the number of strong multibeam conditions that are excited by the tilted beam will be reduced compared to the on-axis pattern.

Figure 9 shows a montage of diffraction patterns recorded from a sample of bismuth manganite, in which the rotating illumination describing a hollow cone has been paused at a several different azimuthal angles. A crescent-shaped envelope of reflections is seen forming a Laue circle. During PED, these are superimposed to form the central pattern in the montage, whose geometry is equivalent to a zone-axis pattern. Notice how the reflections in the PED pattern are of uniform intensity across the disc due to the summation around this azimuth.

To consider how the intensity of each reflection in a PED pattern is affected by the precession action, it is very convenient to draw the analogy between the geometry of PED and that of LACBED. Figure 10 shows a ray diagram, adapted from one first presented by Morniroli (Morniroli *et al.* 2008), comparing precession and LACBED. Figure 11 shows a single DF 006 LACBED disc from silicon, together with an two dashed circles describing paths of integration.

In PED, instead of a solid cone of illumination as would be the case for LACBED, the precessed beam forms a hollow cone, which corresponds to an annulus in the LACBED disc whose radius is twice the precession angle. The de-rocking process integrates the intensity

around this LACBED annulus into the recorded PED reflection. In the PED pattern the intensity of that reflection will be an integration around the circle shown, passing through the Bragg condition twice. Of course, for a fixed precession angle, different reflections will have different integration paths, depending on the magnitude of the relevant *g*-vector.

For increasingly higher order reflections the Bragg line seen in the LACBED disc will move further from the centre of the 'integration circle' and thus at the periphery the integration over reciprocal space will be very limited. Likewise for very low order reflections the integration will be limited because of the proximity to the centre of the pattern and the 'fulcrum' of the Ewald sphere rocking.

2.2 Geometric Correction

In order to compare relative precessed intensities it is therefore important to account for the length of the integration path and, in the original paper (Vincent and Midgley 1994), a geometric correction was proposed for ZOLZ reflections to take this into account,

$$I_{\underline{g}}' \propto I_{\underline{g}} \left(1 - \left(\frac{g}{2R_0} \right)^2 \right)^{\frac{1}{2}} \tag{1}$$

where *g* is the magnitude of the reciprocal lattice vector and R_0 is the radius of the Laue circle, equal to $\underline{k}\phi$, where $\underline{k}$ is the electron wave-vector and ϕ is the precession angle. A later, more rigorous, geometric analysis (Gjønnes 1997) showed that the relationship between the integration around the precession cone and through the excitation error (s_g) resulted in:

$$I_{\underline{g}}' = 2\int_{-\infty}^{\infty} I_g(s_{\underline{g}})ds_{\underline{g}} = I_g \frac{R_0 g_{xy}}{\underline{k}} \int_0^{2\pi} \sin(\alpha)d\alpha = I_g \frac{R_0 g}{\underline{k}} \left(1 - \left(\frac{g}{2R_0} \right)^2 \right)^{\frac{1}{2}} \tag{2}$$

where $\underline{g}_{xy}$ is the component of $\underline{g}$ in the plane of the Laue zone. With an additional g in this final correction factor, higher order reflections should be made more significant than lower order reflections, however the presence of finite beam divergence means that instead of all of the Laue circles having a common centre, there is now a disc of Laue circle centres and a corresponding band of Laue circles in each Laue zone. This alters the integration yet again to produce, for ZOLZ reflections:

$$I_{\underline{g}}' \propto I_{\underline{g}} \left(1 - \left(\frac{g}{2R_0} \right)^2 \right) \qquad (3)$$

The increase in intensity by the additional g term in Eq. 2 is compensated by the intensity being spread out in the Laue circle band, whose size also increases with g.

In addition there have been efforts made to go beyond a simple geometric correction and try to introduce a correction for 2-beam dynamical effects. Blackman (1936) showed that in the limit of 2-beam dynamical diffraction, integration across the Bragg condition would lead to diffracted intensities that were proportional to the magnitude of the structure factor. Thus it might be possible to apply Blackman's equation and correct the precessed intensities not just for geometry but also to account for dynamical scattering – at least in a 2-beam approximation. Own (Own 2005) tabulated these possible corrections, see Table 1. In practice however, other factors influence the precessed intensities and for practical purposes an overall empirical correction factor is often applied.

A correctly chosen precession angle will maximise the number of well-integrated reflections and the few reflections with minimal integration will on the whole only slightly reduce the fidelity of the information in the diffraction pattern. If reflections are removed from the data analysis, their structure factors are in effect set to zero and this may have a worse effect on the structure solution than an incorrect non-zero dynamical intensity.

2.3 Practicalities

As verified later in this chapter, the general trend when undertaking PED is for the largest possible precession angle to be used. However there are both microscope and sample parameters that tend to limit that angle. The precession method involves tilting the beam away from the optic axis of the probe-forming lens and thus any spherical aberration of this lens (with coefficient C_s) causes the probe diameter d_{probe} to increase approximately as (Vincent and Midgley 1994):

$$d_{probe} \propto 4C_s\phi^2\alpha \qquad (4)$$

where ϕ is the precession angle and α is the beam convergence.

Experimental evidence has shown that, for many structures, precession angles in excess of 30 mrad are needed to achieve a suitable range of correctly sampled reflections; for a conventional analytical microscope with spherical aberration coefficient, C_s, of say 2.0 mm, a precession angle of 30 mrad and a beam convergence angle of 2 mrad, this leads to a beam size of over 50 nm. In aberration-corrected microscopes the probe size should be considerably smaller (Own *et al.* 2007) and PED may then be applicable to truly nanoscale structures, particles, precipitates and domains.

As the precession angle is increased, the width of the HOLZ annuli also increases and for many lattice types and orientations, a large precession angle, or equally, a large cell parameter parallel to the zone axis will result in HOLZ reflections overlapping directly on top of the ZOLZ reflections, this makes recording unambiguous intensities impossible and as a

result can limit the available resolution of the ZOLZ data. The inner and outer radii of a HOLZ annulus in PED are given by:

$$R_n^{\pm} = (R_n^2 + R_0^2)^{1/2} \pm R_0 \qquad (5)$$

where R_n is the radius of the n-Laue zone ring, hence the maximum radius for the circular patch of ZOLZ reflections is ~70% of the FOLZ radius. This effect is often referred to as HOLZ 'creep'. With care, HOLZ creep can be avoided: an example can be seen in Figures 12a and 12b which compares a CBED and PED pattern from a C-centred orthorhombic crystal of bismuth manganite. The orientation of the crystal and the reflection conditions are such that the HOLZ reflections (marked 'x') creep inwards but appear only in the gaps between the ZOLZ reflections (marked with red dots). This does not lead to ambiguity for any of the reflections. Of course the second HOLZ, if visible, will also creep towards the FOLZ as the precession angle increases and this may limit the maximum usable angle.

A further problem encountered at relatively high precession angles is the issue of systematic row excitation. With a sufficiently large precession angle there will be an annulus of excited reflections (see Figure 13a), and the large radius of curvature of this annulus means that there will be certain conditions met (Figure 13b) where reflections along a systematic row will be simultaneously excited.

This can have a very significant effect on the dynamical transfer of intensity along this row, and can be extremely important if the row contains kinematically forbidden reflections (Morniroli and Ji 2009). An example of this is the hhh systematic row in the silicon $[1\bar{1}0]$ zone axis pattern. Although the reflections of type $h+k+l=4n+2$ (eg 222, 666) in this series are kinematically forbidden (by the special positions of the silicon atoms in the diamond structure) the systematic row excitation means that applying any significant precession angle

will lead always to simultaneous excitation of these reflections with the strong 111 reflection, leading to high intensity in these *hhh* reflections (see Figure 15b), leading to potential misinterpretation of the symmetry and space-group of the material and of course incorrect intensities.

As well as increasing the effects of spherical aberration, large precession angles can push the tilt coil electronics beyond the regime for which they were designed. This can lead to an imperfect probe shape on the sample and may also lead to difficulties in balancing the tilt angle below the specimen with the coils normally used for image shift. Figure 14 illustrates these additional 'aberrations', which can be a problem in PED. Modern commercial precession systems, such as the NanoMegas Digistar, have sophisticated electronics which allow many of the residual microscope beam 'aberrations' to be compensated through the application of additional signals to the tilt coils (Avilov *et al.* 2007).

As with all other electron diffraction techniques there are practical considerations that must be taken into account when using PED. While PED can have a significant reduction on the effects of coherent multi-beam dynamical scattering on the diffracted intensities, there are many other processes that can scatter the electron wave and so alter the recorded intensities.

The effects of inelastic scattering must also be taken into consideration. For energy losses greater than 1eV, zero-loss energy filtering will give PED patterns of much higher contrast, although to date no systematic study has been made to determine the advantages of energy filtering as far as the authors are aware. Lattice vibrations will lead to diffuse scattering throughout the diffraction pattern, whether 'thermal diffuse scattering' or more defined scattering due to correlated motion (phonons), the rocking action of the precessed beam integrates through the diffuse scattering leading to a 'background' signal in PED that may be greater than that seen in conventional patterns. To minimize this it may be possible in some circumstances to cool the specimen using liquid nitrogen or helium to reduce the effects of

lattice vibrations

Other practical considerations for PED experiment include whether to use a focused or parallel beam illumination. This will be determined to a large extent by the nature of the sample e.g. the region of interest may be small and require a focused convergent beam or the need to record very weak reflections which may be aided by parallel illumination or a focused beam with a very small convergence angle. Finally the choice of recording medium will also affect the sensitivity of any experiments. The development of imaging plate technology allows high dynamic range recording of diffraction patterns, which is essential to achieve the subtlety in intensity measurements desired for any diffraction experiment. There have been improvements in the size, speed, sensitivity and dynamic range of CCD cameras allowing them to be used for PED experiments, though the cost may be a limiting factor. Direct electron detection methods, based on Faraday cages are also being developed to provide extremely accurate intensity measurements (Avilov *et al*. 2007, Nicolopoulos 2007).

2.4 How Kinematical are PED Intensities?

In order to use justify the use of PED intensities for structure solution it is important to understand the mechanisms by which dynamical effects are reduced across the whole diffraction pattern, or conversely, to understand how kinematical the PED intensities really are. Central to this goal are several studies that have compared experimental and simulated PED intensities (calculated using multislice and Blochwave calculations).

One way to monitor the effects of dynamical scattering is to track the intensity of kinematically-forbidden reflections, which of course ideally should give zero intensity in the PED pattern. Ciston *et al.* (2008) mapped the intensity of reflections in PED patterns of andalusite (a polymorph of Al_2SiO_5, space-group *Pnnm*) forbidden by glide planes. They

were able to fit a simple exponential decrease in the intensity with increasing precession angle; see Figure 15a.

This trend can be explained using the simulations seen in Figure 15b (Eggeman *et al*. 2010) and by referring back to the LACBED analogy shown in Figures 10 and 11. As the precession angle increases the Laue circle will intercept the Bragg line, leading typically to a maximum in PED intensity and then moving away from the strong multi-beam dominated centre of the Bragg reflection, leading to the decrease in PED intensity. This behaviour is most easily seen in the behaviour of the 226 reflection. The 002 Bragg angle is small and so the initial increase in intensity is missed. The 222 reflection has an initial rise but the decay is not seen for reasons explained in the previous section and the influence of multiple scattering along the *hhh* systematic row. In the andalusite experiments the low order reflections investigated have maxima coincident with a small precession angle so the upward portion of the curve is difficult to distinguish.

The excitation of a single Laue circle at any given moment in the precession motion confers the effect of reducing the number of possible multi-beam conditions that are simultaneously excited. Furthermore with a sufficiently large precession angle the individual g-vectors through which the intensity is scattered will be longer, resulting in a further reduction in the likelihood of transfer of intensity into a specific reflection. In order to study this mechanism further a simple but elegant test case was proposed first by Wharton Sinkler – the effect of PED on the relative scattering intensity between homometric structures. A homometric pair of structures has identical kinematical diffraction patterns (i.e. structure factor magnitudes) but different structure factor phases (i.e. the arrangement of the real-space potential). Thus, if dynamical diffraction dominates, the recorded diffraction intensity will be different for the individual homometric structures, if the scattering is kinematical, the two will be the same. In other words, if the precession pattern intensities I_g behave in a

kinematical fashion, then I_g depends only on F_g and no other structure factors. White *et al.* (2010a) calculated <110> PED patterns for silicon and for a (simulated) homometric structure (identical structure factor moduli but with phases randomised). Intensities of reflections were calculated, using a modified multislice code (Kirkland 1998), as a function of sample thickness and precession angle.

With the exception of a few reflections that exhibit strong systematic row excitation, the related pairs of reflections from the two structures show similar trends. Figure 15 shows a comparison of the 004 intensity as a function of sample thickness for the two homometric structures a) with no precession and b) with 50 mrad precession angle. With no precession, as seen in Figure 16a, the 'randomised structure' intensity (indicated by the dotted line) and 'real' intensity (solid line) begin to diverge after only about 10nm, indicating the two different potential distributions have resulted in different dynamical scattering. When a large precession angle is applied however, as seen in Figure 16b, the two intensities remain largely the same across a wide range of crystal thickness. Since the dynamical mechanisms in the two structures are different this suggests that precession does indeed lead to behaviour that is 'more kinematical'.

However, although the convergence of the two intensity plots indicates some measure of kinematical behaviour, the intensity cannot be considered as truly kinematical as the intensity does not continue to rise with increasing thickness but starts to fall at about 150nm thickness, indicative of some kind of extinction.

To compare all the reflections in the pattern a correspondence plot of the intensity of reflections from the 'randomised' structure on the ordinate against silicon intensity on the abscissa was produced for a range of thickness and precession angles, as shown in Figure 17. The behaviour of the 004 reflection is typical of the general trend seen in the correspondence plot. At small precession angles, the diffraction intensities of the two samples diverge even

for relatively small crystal thickness, shown in the spread of scatter away from a straight line (which would indicate exact correlation of intensities and perfect kinematical behaviour). At larger precession angles the differences between the reflection pairs in the two samples becomes much less pronounced, even at relatively large thicknesses. As a result the correspondence plots show an increasing linearity at higher precession angles.

That precession intensities were not kinematical was recognised previously by Sinkler and Marks (1999), who developed a modified Bloch wave approach based on simplified channelling theory (van Dyck and Op de Beek 1995) and multislice methods (Own *et al.* 2006b) to investigate this behaviour. This research has continued with a recent study (Sinkler and Marks 2010) discussing how PED intensities should be interpreted, trying to determine the relationship between the underlying structure factors and the final PED intensities. Whilst investigating this relationship, through extensive study of multislice and Blochwave simulations of PED (using the test material $(Ga,In)_2SnO_4$ – GITO), it was shown how the variation of intensity with thickness becomes less 'chaotic' under precession conditions than with conventional electron diffraction, in agreement with the behaviour seen in Figure 16b.

To investigate this further, PED simulations were performed for an increasing number of steps around a precession circle of fixed tilt angle, but for a structure with randomly assigned phases. The result of this simulation is shown in Figure 18, with the average standard deviation of the reflection intensities calculated for 50 different sets of random phases shown. This complements the results in Figure 17, as it shows a much more general case for how PED produces intensities that are less sensitive to other structure factor phases, (i.e. less dynamical) compared to conventional electron diffraction.

While this still leaves the unanswered question of exactly how one can directly relate PED intensities to the underlying structure factors, it is clear that this phase insensitivity is a major reason why PED intensities are less sensitive to thickness changes than conventional electron

diffraction intensities, and hence why PED data is in general more reliable for crystal structure solution.

3. Structure solution using precession electron diffraction

As highlighted throughout this article, electron diffraction data, and even precession electron diffraction data, are always prone to the effects of dynamical interactions. As such, any attempt at structure solution using electron intensities can be fraught with difficulties and solutions may be derived from direct methods or other solution algorithms, which are wrong. The development of new algorithms to solve structures, coupled with the increased speed of hardware, has been of great importance to those wising to solve structures using PED.

3.1. Patterson transforms

It is often worthwhile as an intermediate step before applying direct methods or other solution algorithms, to use Patterson transforms to yield maps of inter-atomic vectors. The 3D Patterson transform $P(\underline{r})$ can be written as:

$$P(\underline{r}) = \sum_{\underline{g}} I_{\underline{g}} e^{2\pi i \underline{g} \cdot \underline{r}} \tag{6}$$

where the summation is over all the reflections $\underline{g}$ with intensities $I_{\underline{g}}$.

Often in electron diffraction, patterns are recorded at low order zone axes and information from successive Laue zones, ZOLZ, FOLZ etc can be used. As such it is useful to be able to write the Patterson transform as 'conditional' on the nth Laue zone. The conditional Patterson transform can be written as:

$$P^{(n)}(\underline{R}) = \int_0^1 P(\underline{r})e^{-2\pi inz}\,dz \qquad\qquad (7)$$

where z is the direction parallel to the zone axis and $\underline{R} = (\underline{r}, z)$. For the nth Laue zone, the nth conditional Patterson can be found from:

$$P^{(n)}(\underline{R}) = \sum_{\underline{G}^{(n)}} I_{\underline{G}^{(n)}}\,e^{-2\pi i\underline{G}^{(n)}.\underline{R}} \qquad\qquad (8)$$

where $\underline{G}^{(n)}$ refers to a vector in the nth Laue zone of the zone axis.

To avoid a large self-correlation peak at the origin, rather than plot the Patterson map using $I_{\underline{g}}$ an E^2-1 formalism can be used where $E=I/\langle I\rangle$ which, by definition, will set the origin peak in the Patterson map to zero. It is also worth noting that the conditional Patterson transform is complex (Midgley and Vincent 1991) and the phase of the peaks can be used to determine the z-component of the inter-atomic vectors; a recent illustration of this was in the determination of a new tin oxide phase (White *et al*. 2010b).

In some cases, for example for the familiar test case of $Er_2Ge_2O_7$ (EGO), by knowing the plane group symmetry, the unit cell and the likely number of atoms in the cell, the Patterson map alone can be used to determine atomic positions directly and not just inter-atomic vectors.

Concerns in the early days of PED led researchers to concentrate on HOLZ data in the knowledge that these reflections would be less prone to dynamical effects than the low order reflections in the ZOLZ. Whilst this later turned out to be unnecessarily pessimistic (if due care is applied in the structure solution algorithm), it is worth considering the progress that was made using only HOLZ reflections. FOLZ data sets similar to those in Figure 7 were used to solve the structure of EGO. Following the analysis above, conditional Patterson transforms were made using the [001] zone axis FOLZ intensity data, an example of which is

shown in Figure 19. The background 'ripple' seen in such maps comes about because of the very limited data set used for the transform: only an annulus of FOLZ reflections is available and the characteristic ripple wavelength seen reflects the width of that annulus. Nevertheless, two clear symmetry-independent peaks emerge. Knowing the space group of the crystal ($P4_12_12$), and thus the plane group for this orientation (*p4gm*), the peaks refer to interatomic vectors linking atoms in the 8(b) positions, in this case Er atoms. It is easy to show that A = ½-2y → y = 0.35 and B = ½-2x → x = 0.87.

Given the positions of the Er atoms it is possible to form difference Fourier maps (Giacovazzo 1998). The phases of structure factors of a crystal composed of just Er atoms are used as best estimates of the true structure factor phase and the contribution of the Er is subtracted from the overall experimental structure factor magnitude, namely:

$$\Delta\rho(\underline{R}) = \sum_{\underline{g}} \left(\left| F_{obs} \right| - \left| F_{calc} \right| \right) e^{2\pi i \phi_{calc}} e^{-2\pi i \underline{g} . \underline{R}} \tag{9}$$

where in this case F_{calc} and ϕ_{calc} refer to the calculated Er-only crystal.

Such a map should show approximately the positions of the remaining atoms in the cell. In this case, Ge atoms are revealed (Sleight 1997), and a second difference map yielded approximately half of the oxygen atoms – and, remarkably, all from one HOLZ data set!

3.2. Direct Methods

The term 'direct methods' encompasses those approaches which try to directly assign structure factor phases using the intensities of the reflections. Such approaches are rigorous mathematical solutions of the crystallographic phase problem. Early work in the area (albeit for X-ray diffraction) used Schwartz's inequality to relate the phase of a specific reflection *g*

to that of the reflection 2g (Harker and Kasper 1948), with further relationships being formed with the inclusion that the recovered electron density must be positive (Karle and Hauptmann 1950). However it was through the work of Sayre that a comprehensive means of relating the phases of arbitrary structure factors to one another was found (Sayre 1952). The important development in Sayre's work was the assumption of a sparse density, i.e. one that includes only a small number of strong peaks (corresponding to the atoms) and the remainder of the density being essentially flat. This means that the square of the density is closely related to the original density, and can be described mathematically by:

$$F_{squared}\left(\underline{g}\right) = S\left(\underline{g}\right)F\left(\underline{g}\right) \tag{10}$$

where $S\left(\underline{g}\right)$ is a shape function accommodating the change in line shape of the two atomic form factors. Since squaring a function is the same as a self convolution, Equation 10 can be rewritten as:

$$\Omega S\left(\underline{g}\right)F\left(\underline{g}\right) = \int_{\underline{p}} F\left(\underline{p}\right)F\left(\underline{g}-\underline{p}\right) = \sum_{\underline{p}} F\left(\underline{p}\right)F\left(\underline{g}-\underline{p}\right) \tag{11}$$

with Ω being a constant associated with the convolution and $\underline{p}$ being a reciprocal space vector. If we assume that a single term in the summation is large enough to dominate its value then the phase of $F\left(\underline{g}\right)$ must be very similar to the phase of the strong term $F\left(\underline{p}\right)F\left(\underline{g}-\underline{p}\right)$; for a centrosymmetric structure (where phases must be 0 or π) there must exist the following phase relationship

$$\varphi_{\underline{g}} = \varphi_{\underline{p}} + \varphi_{\underline{g}-\underline{p}} \text{ or } \varphi_{-\underline{g}} + \varphi_{\underline{p}} + \varphi_{\underline{g}-\underline{p}} = 2\pi n \tag{12}$$

The Sayre equation (Equation 11) therefore allows triplet invariants, where the phases of three reflections, whose indices add up to zero, will equal zero. This is not a definitive solution to the phase problem because the step between Equations 11 and 12 requires certain assumptions about the suitability of the triplet. To determine the probability of Equation 11 being applicable Cochran devised the expression

$$P(\Phi) = \frac{1}{2\pi J_0(G)} \exp(G\cos(\Phi)), \tag{13}$$

where J_0 is a modified Bessel function of order zero and importantly, $G \propto \left| E_{\underline{g}} E_{\underline{p}} E_{\underline{g}-\underline{p}} \right|$ is the concentration parameter and $\Phi = \varphi_{\underline{g}} - \varphi_{\underline{p}} - \varphi_{\underline{g}-\underline{p}}$ (Cochran 1955). Typically a small subset containing the strongest reflections would be selected initially and then the triplets within this set that have the largest concentration parameters would be used to establish an initial set of phase relationships. This set could then be expanded by allowing more reflections, and hence new sets of triplets, to be included until a solution is determined for the structure.

A common application of direct methods is through the 'tangent formula' (Giacovazzo 1998) where a probable phase value (β_h) for a reflection h can be determined from the invariant triplets (with different reflections g_j) in which it is included:

$$\tan(\beta_h) = \frac{\sum_j G_{h,g_j} \sin(\varphi_{g_j} + \varphi_{h-g_j})}{\sum_j G_{h,g_j} \cos(\varphi_{g_j} + \varphi_{h-g_j})}. \tag{14}$$

This approach has become widely accessible to crystallographers through such packages as SIR (now part of the Il Millione package) (Burla *et al.* 2007) and has led to a large number of successful structure solutions from both X-ray and electron diffraction data (see section 4.1).

The relative success of the Patterson techniques for structure solution from HOLZ reflections was attributed to those intensities being less prone to dynamical effects. In line with this approach, some of the first work using direct methods to solve structures from PED of ZOLZ reflections was in the study of crystals composed of light elements which are more weakly scattering. For this purpose the mineral beryl ($Be_3Al_2Si_6O_{18}$, space group P6/mmc) was investigated (Sleight 1997). Figure 20a shows a [0001] precession diffraction pattern recorded at 300kV using a convergent beam that just avoids disc overlap. The structure of beryl is shown in Figure 20b.

Figure 20c shows the structure solution map (using the tangent formula) and Figure 20d shows the ideal map. The agreement is remarkably good; in the experimental map there is artefact amplitude seen in the channel (at the corner of the cell), and the Be atoms are missing but otherwise the map is quite consistent.

Over time direct methods have been employed to solve structures from PED data for a wide range of materials including materials that contain several heavy atoms, rather than the only the light elements seen in beryl. An example includes the work done by the Marks group at Northwestern University on the transparent oxide $(Ga,In)_2SnO_4$ (GITO), which has a monoclinic cell with space-group *P2/m* and cell parameters *a* = 11.69 Å , *b* = 3.17 Å , *c* = 10.73 Å, and γ = 99° (Sinkler *et al.* 1998). The geometry of the unit cell enabled the metal atoms to be well-separated in projection parallel to the [010] zone axis and by application of precession electron diffraction, coupled with the use of a direct methods package EDM (Kilaas *et al.* 2005) the structure of GITO was solved and refined. Solutions for the precessed and unprecessed diffraction intensities of this material (Own *et al*. 2006a) are shown in Figure 21a and 21b respectively.

While both solutions seem to recover the heavy atom positions for this structure there is a significant improvement in the ability to recover lighter atom peaks in the structure recovered from PED intensities.

However, for some time, direct methods solutions of ZOLZ PED data from other structures (e.g. EGO) remained unsatisfactory. It was felt that dynamical effects were too strong and the direct methods algorithms were not returning correct structure solutions.

3.3 Charge-flipping algorithms

While direct methods are a rigorous mathematical way to solve the phase problem in crystallography there are a number of alternative methods that allow the structure factor phases to be estimated. One of the most widely accepted approaches in recent years has been the charge-flipping algorithm (Oszlányi and Sütő 2004, 2005, 2008). Like many other iterative algorithms (Gerchberg and Saxton 1972) this is based on a Fourier cycle, where the normalized structure factors have random phases assigned to them initially and an inverse Fourier transform is applied to create a real space density. This density is then modified by the algorithm and the forward Fourier transform is applied to return a new set of structure factor phases. Importantly these phases are then combined with the original input structure factor moduli before the process is repeated.

In the general charge-flipping approach the only criterion put on the eventual solution is that the real space density (either electron density or potential) must be positive, this is enforced by inverting the sign of any pixel with a value lower than a user-determined threshold, δ (hence flipping the 'charge' of that pixel), this Fourier cycle is shown schematically in Figure 22a.

The success of this algorithm is based partly on the relative simplicity of the active part of the process, making it easy to write software to perform the calculation. Another advantage is that the iterative nature of the algorithm means that it is possible to monitor the solution as it progresses, via an internal residual calculation of the differences between structure factors in successive iterations, which in turn allows the user to see when a stable solution has been reached (this can also be incorporated into a feedback system to improve the speed of the algorithm (Zhou and Harris 2008)). These advantages have made charge-flipping popular with X-ray crystallographers (e.g. Wu *et al.* 2004) although this is by no means the limit of its applicability.

The development of a solution during the progression of the charge-flipping algorithm can be visualized in terms of allowable sets. Figure 22b shows a cartoon of a virtual space containing every possible density, within this there will be a set of densities that satisfy the measured structure factor moduli (S_1) and another set that satisfy the positivity requirement (S_2); for a unique structure and perfect kinematical data we would expect a single point of contact between the two sets.

Each cycle of the algorithm acts to minimize the distance between the two sets (Marks *et al.* 1999) until a stable minimum is reached. The threshold value, δ, allows the 'positive' set boundary to be over- or under-relaxed and thus allows a wider range of possible solutions to be navigated before the stable solution is reached. This increases the chances of reaching a genuine global minimum and not just a local minimum.

There has been significant interest in developing charge-flipping as a general crystallographic tool. Examples include the *Superflip* program (Palatinus and Chapuis 2007) which is a widely used method for getting statistically significant solutions from a large number of repeated applications of the algorithm. Coehlo (2007) has incorporated some

aspects of the tangent formula into the algorithm to prevent the 'uranium solution' where all of the intensity is 'phased' into a single large peak.

An example of how solution algorithm development is integral to the development of crystallography in general, and PED in particular, is the incorporation of further constraints to the allowed solutions in the charge-flipping algorithm, namely the projection symmetry of the diffraction pattern.

For this purpose the EGO structure (Smolin 1970) was re-visited as a test case to pursue further whether or not ZOLZ reflections could be used for structure solution (Eggeman *et al.* 2009). EGO is an excellent model structure (space group $P4_12_12$), composed as it is of heavy, medium and light atoms, and with a relatively complex structure that leads to a striking patterning of intensities in the PED patterns. Figure 23 shows a [001] CBED pattern where Gjønnes-Moodie lines are evident in reflections of type $0k0$ with k odd. These indicate glide planes and together with the overall 4mm pattern symmetry leads to a crystallographic plane-group symmetry of *p4gm*. The glide plane mirrors reflections of equal magnitude but with either equal or opposite phase such that there is a set of reflections, for which $h+k=2n$, which have 4mm symmetry and a set, for which $h+k=2n+1$, which have 4'm'm symmetry where the prime indicates an anti-mirror or anti-rotation, inverting the phase of the symmetry-related reflections. Simulations of the contributions from the two heavy atom sub-lattices show that the erbium sub-lattice dominates certain strong reflections (e.g. the 400, 440 and 110 reflections) while the germanium sub-lattice contributes significantly to many lower-order reflections in the patterns; importantly this includes reflections such as 210 and 320.

Initial attempts to use ZOLZ data, even with relatively large precession angles, using conventional direct methods (tangent formula) or charge flipping algorithms met with failure, much the same as earlier efforts from the 1990s. Peaks in the solution map from the tangent formula appeared to correspond to Ge positions only with no evidence of the Er; solutions

from charge flipping gave too many peaks although there was some hint that Er positions were being retrieved.

It is known that the success of charge flipping relies considerably on choosing an appropriate threshold parameter and allowing the algorithm to explore unrestrained solution space using projection plane group symmetry of $p1$. However electron diffraction data is recorded often as zone axis patterns and the plane group symmetry at that axis is known. It was shown (Eggeman *et al.* 2009) that applying the known symmetry to the charge flipping algorithm (schematic in Figure 24a), after a certain number of cycles allowed the solution to reach a more 'global minimum' and produce a better solution (see Figure 26c). The inclusion of known symmetry reduces the number of allowed solutions in the 'positive' set (see Figure 24b) and has been suggested to produce a non-convex set of solutions. It is therefore possible to see that if the plane group symmetry was imposed from the outset, the same initial starting point as in Figure 24b (shown by the grey arrows) for the reduced set could lead to a rapid stagnation of the solution in a local minimum.

Instead by allowing the algorithm to find an intermediate solution before symmetry is enforced, there is a greater chance of finding a suitable solution, as indicated by the additional black arrows in Figure 24b. There are other (empirical) ways to 'kick' the algorithm out of the intermediate local minimum solution but applying known symmetry simply adds *a priori* information into the iterative process.

3.4 Solving precession electron diffraction data

The development of new structure solution algorithms allows previously 'unsolvable' structures to be recovered using 2D PED data. This also offers the opportunity to study more quantitatively the optimum precession angle needed to solve such structures.

Figures 25a-25c shows experimental diffraction patterns recorded at increasing precession angles, compared to the kinematical pattern simulated from structure factors (Figure 25d). Figure 26a-26c shows the corresponding structure solutions recovered using the 'symmetry-modified' charge flipping algorithm (Eggeman *et al*. 2010). The data recorded at small precession angles returns strong peaks apparently only at the Ge atomic column positions whereas the pattern recorded at high precession angles returns a solution that contains information about all heavy atoms, c.f. the ideal structure formed at the same allowed resolution in Figure 26d. While this structure is not exact there is sufficient information to allow subsequent refinement of the atom positions.

What was clear from these results was that there appeared to be a precession angle above which the algorithm returned a good solution and below which it did not. To investigate this further, the phase residual was calculated, in which a normalized phase difference is found between the known structure and the structure solution. The phase residual is defined as:

$$R_p = \frac{\sum_h \left| F_h^{kin} \right| \left(e^{-i\phi_h^{kin}} - e^{-i\phi_h^{calc}} \right)}{\sum_h \left| F_h^{kin} \right|} \tag{15}$$

where F_h^{kin} and ϕ_h^{kin} are the amplitude and phase of the correct structure factors of the h-reflection and ϕ_h^{calc} is the recovered phase from the structure solution. Since the projected structure is centrosymmetric in this case, the phase residual essentially becomes a simple weighted count of the correctly phased reflections.

From Figure 27a it is clear that an abrupt reduction in the phase residual appears in this case at about 35 mrad precession angle indicating that many more of the recovered phases from the structure solution are correct above that 'threshold' angle. Whilst this calculation can be performed knowing the true structure, for an unknown structure it is not obvious *ab initio* which angle to choose. To help with this decision, an intensity residual can be

calculated which offers a possible practical method for determining the optimum precession angle. In this case the residual is calculated with respect to the most highly precessed diffraction intensities (rather than the kinematical ideal as would normally be the case) such that any change in the residual will be some measure of a transfer of intensity between reflections and thus some practical measure of 'residual' dynamical scattering. The intensity residual (R_2) can be defined as:

$$R_2 = \frac{\sum_h \left| I_h^{obs} - KI_h^{ref} \right|}{\sum_h I_h^{obs}} \qquad (16)$$

$$K = \frac{\sum_h I_h^{obs}}{\sum_h I_h^{ref}}$$

where I_h^{obs} and I_h^{ref} are the measured and reference intensities of the h-reflection, respectively.

The abrupt change in the phase residual coincides with the flattening of the intensity residual curve (in Figure 27b) where the residual remains approximately constant for precession angles above about 35 mrad. This suggests that there is sufficient precession angle to avoid the multi-beam pathways that involve the strongest reflections in the pattern, since these reflections carry the largest weight in the residual calculation.

The practical upshot of this is that with sufficiently high precession angles the intensities of the strongest and (most probably) the medium strength reflections remain reasonably in-step with respect to one another. This is exactly the situation that is needed for successful application of direct methods as the concentration parameters being calculated for any particular triplet will be approximately correct. This in turn will mean that the correct basis

set of reflections are used to generate the partial structure and this will extend to a greater chance of correct phases for the remainder of the system.

The condition that the strongest reflections be correct also applies to a charge-flipping solution equally well. Although there is no simple mathematical description for this to be the case it is clear that for a 'peaky' solution the high intensity peaks are far more likely to be associated with a small number of strong reflections rather than many weak reflections. The phase relationships that result in these high-intensity pixels are less likely to be altered by the charge flipping process (after an initial few cycles) and so will go on to form the basis of the solution.

This reliance on the correct phasing of the strongest sub-set of reflections is further supported by work from Barnard *et al*. (2009) and Klein and David (2010) who showed that deliberate degradation of PED intensities still yielded successful structure solution of the materials presented in these studies. PED clearly reduces the dynamical effects that transfer intensity out of strong reflections, meaning that strong reflections remain strong and the basis-set of reflections used to create the solutions is therefore correct.

It appears that the fidelity of the structure solution remains high if the intensities of reflections are incorrect but the relative order of the intensities (from say strong to weak) remains correct. The order or rank of the reflection indicates the relative position of a reflection in terms of its intensity relative to other reflections within the pattern.

In the work of Barnard *et al*. (2009), it was found that by keeping the order constant, but significantly altering the intensities, the symmetry-modified charge flipping algorithm was still able to solve the structure. Only when the low and medium order reflections had their intensities enhanced to be comparable with the strong reflections did the solution return a false structure. This indicated strongly that in most cases so long as the order of the reflections was not too far from the kinematical ordering, the absolute intensities could vary

considerably. This was explored further using multislice simulations varying precession angle and thickness and monitoring the order of the reflections. Figure 28 shows the resulting trend, plotting only the first five reflections with the highest kinematical intensity for clarity.

The wide variation of rank in Figure 28a illustrates how, with zero precession, the rank of the reflection changes rapidly with sample thickness (1 slice = 1.23 nm). Even at relatively small thickness the variation is rapid; meaning that there is significant transfer of intensity between the strong reflections shown here and the remaining reflections in the system. At an arbitrary sample thickness, any structure solved from these intensities could be misleading or entirely incorrect.

Figure 28b shows how the rank for the strongest reflections remains approximately constant across the thickness range examined when a sufficiently high precession angle (40 mrad) is used. Clearly here there is minimal dynamical transfer of intensity outside the subset of strongest reflections; this is sufficiently low that quite large sample thicknesses (in excess of 100nm) would be needed to change the reflections that comprise this subset. Structure solutions from patterns recorded at these precession angles should therefore have a common basis set, and one that is essentially correct compared to the kinematical case, leading to a more reliable complete solution.

4: Applications and New Developments of PED

4.1. Solving crystal structures

We have seen how the intensities recorded in PED experiments can offer a greater likelihood of successful structure solution compared to conventional electron diffraction. Central to this advantage is the two-fold benefit of a greater number of reflections and the improved fidelity of many of the reflection intensities within the pattern compared with the kinematical ideal. With the introduction of commercial precession hardware which can be fitted to almost any microscope, there has been a rapid increase in the interest and application of precession electron diffraction (see Figure 8), for structure solution and refinement but also for uses beyond those originally imagined. These advantages, along with the development of new and more powerful structure solution algorithms have offered electron crystallographers the opportunity to study increasingly complex materials with PED.

In this section we review some of the work that has been published to date to illustrate how PED has been used to investigate the crystallography of many different materials systems.

4.1.1 Inorganic materials

Early in the development of PED two groups saw the potential of the method, namely the groups of Marks at Northwestern University and Gjønnes in Oslo. As well as tackling some of the fundamental issues concerning the quantification of PED intensities (Own *et al.* 2006), the Marks group focused also on solving the structure of complex oxides, including $(Ga,In)_2SnO_4$ (GITO, see section 3.2). In solving the structure they explored ways to improve

the use of PED intensities, proposing a 2-beam Blackman-like formula to help quantify the intensities and gain a better understanding of the parameters used in PED, such as the precession angle (Ciston *et al.* 2008). Coming out of that group, the work of Own (Own 2005) highlighted how PED could be applied to a number of oxide systems including $La_4Cu_3MoO_{12}$, Al_2SiO_5 (andalusite), cordierite and mordenite, all of which were solved using 2-D PED data.

The group in Olso concentrated on solving the structures of precipitates and second phases found in Al alloys, such as in the Al-Fe system (Gjønnes *et al.* 1998) and Al-Zn-Mg alloys (Kverneland *et al.* 2006). In an early example of structure solution using PED, precipitates in the Al-Fe system were investigated (see Figure 29), and by combining PED patterns recorded at different zone axes, a 3D set of diffraction intensities were used first to form a 3D Patterson map to yield 3D inter-atomic vectors. The diffracted intensities were then used with direct methods (tangent formula) and maximum entropy algorithms, together with insights about the symmetry and values of low order structure factors from conventional CBED patterns, to determine the structure of a complex Al-Fe intermetallic (Berg *et al.* 1998). The tetragonal Al_mFe structure found (a = 8.84 Å, c = 21.6 Å , space group $I\bar{4}2m$) had 90 Al and 20 Fe atoms and can be described by ten-coordinated Fe positions or by a distorted CsCl type network with vacancies.

The study of the Al-Zn-Mg system revealed nanoscale coherent η' precipitates within the Al-rich matrix that were far too small at the time to study by PED as individual crystallites. Instead the Oslo group took the decision to record patterns with a beam of sufficient diameter to incorporate a large number of precipitates. Although the diffracted intensity would be dominated by reflections from the Al matrix, the large unit cell precipitates provided weaker reflections at positions in reciprocal space between the Al reflections. Figure 30 shows examples of PED patterns recorded from the alloy.

The complexity of the diffraction patterns comes about partly because of the large unit cell of the precipitates but also because the precipitates adopt different orientations with respect to the matrix as indicated in the table of Figure 30.

Remarkably, despite each precipitate being only 2-3 unit cells thick and, from high resolution lattice imaging could be seen to be faulted, a possible structure model was proposed related to the equilibrium η-$MgZn_2$ structure (space group *P6₃/mmc*). The η' precipitate has a composition $AlMg_2(Al,Zn)_6$, space group *P6₃/mmc* with unit cell parameters $a = 4.96$Å, $c = 14.05$Å.

Gemmi has developed further the idea of 3D data sets recorded by PED to solve mineral structures (uvarovite and åkaermanite, both silicates) and Ti_2P, the last case combining PED with high resolution imaging to confirm the structure (Gemmi *et al* 2002). For Ti_2P, electron diffraction confirmed a hexagonal unit cell with $a = 19.969$ Å, $c = 3.4589$ Å (values refined by x-ray diffraction). PED patterns, see Figure 31, were used to solve the structure within space group $P\bar{6}2m$ leading to a unit cell with 54 Ti and 21 P atoms, indicating a number of P vacancies in the cell. In some regions, lattice images showed a reduction of symmetry locally to $P\bar{6}$ which could be linked to the presence of P vacancies.

There have been a number of other studies investigating metal oxide structures including the lithium ion battery electrolyte Li_2CoPO_4F (Haderman *et al*. 2011), also the complex perovskite structures $Pb_{13}Mn_9O_{25}$ (Haderman *et al*. 2010), $LaBaCuCoO_{5.2}$ and $Ba_6Mn_5O_{15}$ (Boulahya *et al.* 2007). With such heavy metal oxides in the last two examples, dynamical effects are likely to be quite prevalent unless precession angles are large or the sample is thin. To try to counter dynamical effects, for these studies the precession intensities were made proportional to the structure factor, as would be the case for the 2-beam Blackman correction. All cation positions were solved in this study. Similarly, Weirich (Weirich *et al.* 2006) solved

the structure of the complex oxide $Cs_xNb_{2.54}W_{2.46}O_{14}$ (*Pbam, a* = 27.145Å, *b* = 21.603Å, *c* = 3.9463Å) using a combination of PED and x-ray powder diffraction.

Recently White *et al.* (2010b) studied a long-standing problem associated with tin oxide. It is well known that in a reducing atmosphere tin oxide can transform from SnO_2 to SnO but can do so through an intermediate form of tin oxide. Early X-ray diffraction studies (Lawson 1967) concluded the cell was triclinic and a distorted supercell of the rutile SnO_2 structure. Samples investigated were cylindrical in nature and sufficiently thin areas difficult to find. As seen in Figure 32a the cylindrical intermediate phase is attached to a hemispherical Sn crystal and with a diameter ~1μm. Figure 31b shows a typical PED pattern recorded from the [001] zone axis of the intermediate monoclinic structure (*P2₁/c, a* = 8.0 Å, *b*= 5.5 Å, *c*= 4.8 Å, *β* = 95.9°). Using direct methods (tangent formula) the positions of the Sn atoms were solved and refined. The oxygen atom positions were not found but a structure model was proposed to make the intermediate cell Sn_3O_4, consistent with a structure proposed in a theoretical study by Seko *et al.* (2008). As part of the solution, the FOLZ data from the [001] axis, seen clearly is Figure 32b was used and the signs of the peaks seen in the conditional Patterson transform were used to determine the heights of the Sn atoms parallel to the zone axis.

4.1.2 Zeolites

One class of inorganic crystals whose structures have often proven difficult to solve by X-ray diffraction are zeolites. These are aluminosilicates whose structure contains a large regular pore (caused by the orientation of corner sharing silicate or aluminate rigid units). Interest in these materials as molecular sieves, for petrochemical industries and nuclear waste management, means that complete structural information relating to the pore dimension is critical. McCusker (1991) contains an excellent overview of zeolite chemistry, applications

and methods for solving their structures. However production of large single crystals of zeolite for X-ray diffraction can be difficult. The large size of the unit cell (cell parameters of 20 Å or more are not uncommon) often leads to near-degeneracy of the Bragg angle for symmetry-independent reflections and so interpretation of powder X-ray diffraction patterns can be difficult. Dorset began his work on PED of zeolites by combining electron diffraction data with powder data to improve the fidelity of the recovered structures (Dorset *et al.* 2006). For the ZSM-10 zeolite, powder X-ray diffraction was unable to differentiate between two different structures, PED intensities were compared with simulated electron diffraction patterns for the different structures and hence the ZSM-10A structure was identified as the correct form. Direct phasing of these reflections was also possible using a maximum entropy algorithm, MICE (Gilmore *et al.* 1990), which returned the correct locations of the Al/Si positions (although with some distortion of the oxygen positions). This raised the possibility of using PED as a stand-alone method for zeolite analysis. Extensive studies of a range of zeolites (Dorset *et al.* 2007, Gilmore *et al.* 2007) showed that this was indeed the case, with successful identification of the Al/Si atoms in a number of ITQ-n, as well as the ZSM-10, zeolite structures directly from PED data (although there was an anomalous structure ZSM-5 whose solution could not be improved upon using PED data). In all successful cases, the improvements in both the resolution of the PED data and the intensities (especially for the special case of kinematically forbidden reflections) were identified as advantages of PED over conventional selected-area diffraction. Included in this set is the zeolite MCM-68. This crystallizes in the tetragonal space group *P4₂/mmm*. The diffraction pattern (Figure 33a) recorded parallel to the tetragonal axis clearly shows the *p4gm* plane group symmetry (systematic absences for $0k0$ when k is odd). Figure 33b shows the projected structure solved using MICE in good agreement with the Al/Si atomic positions identified from X-ray diffraction experiments.

Interestingly, to solve the MCM68 structure, Dorset (Dorset *et al.* 2007) found that a better solution was achieved if the Lorentz correction factor (Equation 1) was not applied. Although geometrically correct, it appears that in many cases other factors, such as dynamical effects or temperature factors may play a role in negating this correction (White 2009).

More recently McCusker and Baerlocher in Zurich have combined PED with powder X-ray diffraction and high resolution imaging to solve zeolite structures (Xie *et al.* 2008). In this case, the authors were unable to solve the zeolite structures directly from the PED intensities (using charge-flipping algorithms), but the PED intensities were invaluable when used to improve the deconvolution of the overlapping reflections in the powder X-ray data. Despite the differences in the electron and X-ray scattering factors of the different atoms it should hold that weak reflections will be weak in either data set. As a result weak reflections could be identified from the PED data and removed from X-ray diffraction data, making deconvolution of the powder pattern much easier. This resulted in improved reliability of the medium and strong reflections and hence increased fidelity of structure solutions.

4.1.3 Organic Crystals.

A major difficulty in the electron microscopy of organic materials is that they can be extremely beam-sensitive. If a sample is tilted fractionally away from a zone-axis a sufficiently large precession angle can accommodate this mis-tilt and lead to a diffraction pattern with improved symmetry. This works because the precessing Ewald sphere sweeps through the recorded intensities, from one side of the Bragg condition to the other. As long as the majority of the intensity in the rel-rod is contained near the Bragg position, the resultant PED pattern will appear more symmetric than a conventional pattern. This has been of

particular importance for low-dose diffraction experiments on beam-sensitive samples, where it is often difficult, or impossible, to spend extended periods aligning the sample.

While the application of PED to organic materials is still in its infancy there have been some examples of the benefits it can offer (Wu *et al*. 2011). Metal-organic frameworks (MOFs) and hybrid inorganic-organic (HIO) materials are a new class of materials that have been developed in recent years. These have a combination of rigid sections containing metallic elements with torsionally flexible organic bridging ligands which, in the case of MOFs, results in structural pores with a very similar form to those of zeolites, though with the potential for greater control over the pore size.

Bithell *et al.* (2010) developed a 'strong-scatterer registration' technique for identifying the metal-ion positions in HIOs. This involves assigning the strong peaks in a solution to specific strong scattering centres and to specific sites within the cell; then by summing over a large number of solutions the strong scatterer relationships can be identified. Figure 34a shows a PED pattern recorded parallel to the [011] zone axis of a copper phosphonoacetate crystal. Figure 34b shows a potential map recovered from the experimental PED data using strong scatterer registration and Figure 34c shows an ideal map of the projected potential. It is clear from the PED map that the metal atoms in the structure have been identified and there is some evidence for the positions of the lighter atoms.

The potential to improve the quality of diffraction data can be seen from PED patterns from pharmaceutical crystals such as aspirin and sildenafil citrate (Figures 35a and 35b respectively). There has been speculation that such improvements in diffraction data could allow structural polymorphs to be identified which would be of great interest for pharmaceutical research and development.

4.2. Other crystal information

The general improvement in the intensities of PED versus conventional electron diffraction techniques enables other structural features to be investigated. One of the most important stages in the crystallographic characterization of a material is the determination of the point group and space group. Work by Morniroli showed how, compared to SAD, PED increases the sensitivity of electron diffraction data to the symmetry present within the structure (Morniroli and Redjaima 2007, Morniroli *et al*. 2007). This was further reinforced using the case of non-centrosymmetric GaAs (Morniroli *et al*. 2009), in which the symmetry breaking between the (002) and $(00\bar{2})$ can be identified clearly both theoretically and experimentally in PED patterns. The improvement in sensitivity to subtle symmetry differences allows issues such as twinning to be investigated in a very rigorous way using PED. Notable examples of this are studies on quartz (Jacob and Cordier 2010), the mineral coesite (Jacob *et al.* 2009) and $LaGaO_3$ (Ji *et al.* 2009), as shown in Figure 36. In this material the fine structure recovered in PED patterns allows the clear differentiation between actual mirror planes and pseudo-mirror planes within the structure, the arrangement of which allows the different twin domains to be identified.

PED diffraction data has also been used investigate the bonding present in inorganic materials. Avilov *et al.* (2007) investigated a simple ionic compound CaF_2 and reported a clear electron density surrounding the different ions within the structure, a strong polarization of the electron density surrounding the anions towards the neighbouring cations was noted. To achieve this level of detail the diffraction intensities were measured using a specially designed Faraday cage detector, which returns precise intensities; however this can be a time-consuming approach which might not suit every PED experiment.

Lastly, an early application of precession was in the study of Debye-Waller factors. Midgley *et al.* (1998) used precession intensities in HOLZ reflections to determine the

Debye-Waller factor of simple structures through the use of Wilson plots (Wilson 1942) and subsequent refinement.

4.3. Technical applications

4.3.1. Automated diffraction tomography.

The practice of constructing 3-D datasets from discrete zone-axis diffraction patterns has already been discussed in section 4.1.1. However, only a small fraction of reciprocal space is sampled and is concentrated at a few low-index zone-axes. Whilst zone-axis data is convenient for indexing and for intercepting many reflections at once we would also expect dynamical effects to be maximised, potentially reducing the reliability of the recorded data.

To overcome this problem automated diffraction tomography (ADT) has been developed (Kolb *et al.* 2008, White 2009). In this technique, electron diffraction patterns are recorded at discrete tilt-steps (with inter-step angle θ) about a single tilt axis, so as to build up reciprocal space slice-by-slice. This arrangement not only offers the possibility of completely sampling all reflections (within the wedge of reciprocal space allowed by the goniometer geometry), but also does not rely on the sample ever being exactly aligned with a low-order zone-axis parallel to the optic axis.

One of the inherent difficulties in the reconstruction of reciprocal space is the fact that the Ewald sphere can intersect a reflection away from its exact Bragg condition. The majority of TEM specimens studied are in the form of thin films and the finite thickness of the film leads to the Bragg spot being elongated into a rod (a reciprocal lattice rod or 'rel-rod') whose length kinematically is inversely proportional to the film thickness. As the sample is tilted, the extent of the rel-rod and its intensity depend on the crystal orientation and any dynamical

effects at that orientation. A reflection can appear in several different diffraction patterns within a tilt-series. This is especially true for low-order reflections that are often integral to correctly defining the reciprocal lattice basis vectors and the initial positioning of the heaviest atoms in the cell. A cluster search approach can find the centre of the resulting 'cluster' of reciprocal lattice spots leading to an 'average' peak intensity (Kolb *et al.* 2008).

Precession electron diffraction can be applied in this situation to each diffraction pattern in the tilt-series. By integrating through a precession angle of say half the tilt-step (i.e. from $-\theta/2$ to $+\theta/2$) it is possible to integrate through the wedge of reciprocal space under investigation. By including the entire rel-rod in the PED integration the accuracy of the cluster centring is improved. The net effect of precession is to not only improve the resolution of each pattern within the tilt series, and to make the intensities within these patterns more reliable, but also to improve the ease with which reciprocal space can be reconstructed from the tilt-series.

The incorporation of precession into the ADT system does have potential drawbacks, from a practical standpoint the electron microscope is normally run in microprobe STEM mode, with a HAADF image used to track the movement of the object being analyzed during tilting. Precessing the beam whilst scanning degrades the STEM image meaning that fully automated tracking is not always possible and operator interaction is required.

The Mainz group have been extremely active in developing the ADT technique and have successfully incorporated PED into its operation. Through the combination of ADT and PED they have reported structure solutions of inorganic materials (Mugnaioli *et al.* 2009, Birkel *et al*. 2010), as shown in Figure 37, and even MOFs (Denysenko *et al.* 2010) with extremely high accuracy in the atomic coordinates of even light atoms.

4.3.2. Rotation method and digital sampling

An alternative to ADT, but based on similar principles is the rotation method (Zhang *et al*. 2010a). Much like ADT, in this technique the goniometer control is used to make relatively coarse (ca 1°) steps and the beam tilts are used to sample the space between these steps. The difference here is that instead of using precession to integrate the intensity from $-\theta/2$ to $+\theta/2$, the beam tilt is used to record a far larger number of discrete tilt steps within that range.

Through control of the beam-tilt step size it is possible to retain information about the rocking-curve of each reflection; as a result the dynamical effects present within each reflection can be studied, and perhaps compensated. This approach has been extended to all reflections in a PED pattern by recording the patterns at intermediate steps about the precession circle and recombining these into a small reciprocal space volume (Zhang *et al*. 2010b). The intensities of the different reflections can therefore be interpreted either as the integrated intensity under the individual rocking curve or as the intensity at the exact Bragg condition of the reflection. While this can be more time consuming there is built into this method the means to avoid misrepresentation of reflection intensity as a result of incomplete integration.

An example of this can be seen in Figure 38. Here an individual tilted pattern is shown (Figure 38a) but along with this are effective rocking curves for two different reflection (6 6 0) and (19 19 0) in Figures 38b and 38c respectively. Despite the wide range of excitation errors that each are sampled over, it is possible (for a fine enough sampling angle) to determine the intensity of all reflections within a reasonable range at their exact Bragg condition, offering additional quantitative information beyond that of conventional PED.

4.3.3 Orientation Mapping

Orientation mapping is another method, like ADT, that has benefitted greatly from the development of PED. For this technique an electron beam is scanned across a sample with diffraction patterns recorded at each point. Each diffraction pattern can then be analyzed automatically, allowing the orientation of the crystal at each point to be determined, for example by comparison with a pre-calculated library of diffraction data (Rauch *et al*. 2008). In practice, the quality of diffraction data recorded from such an automated system can be poor leading to ambiguities in identifying the exact orientation of each diffraction pattern. Precession of the electron beam increases the reliability of indexing a diffraction pattern when compared to a kinematical simulation. The way in which precession accommodates small mis-tilts also helps to overcome the effects of local buckling that regularly occur in thin films

The speed of identifying each diffraction pattern is affected greatly by the symmetry of the material being investigated: high symmetry cubic crystals have a smaller number of independent zone-axes compared to materials with lower symmetry. Each scanned diffraction pattern is then compared with a data-base to determine the most likely orientation. In order to make this process as accurate as possible it is desirable to compare reflections to as high a resolution as possible, again making PED, with its increased sampling of reciprocal space, a suitable way of improving the process (Moeck *et al*. 2011).

An example of the improvement that PED can offer is seen in a study of polycrystalline aluminium. Figure 39 shows a comparison between orientation maps for the unprecessed and precessed cases. It is clear that the use of PED results in a higher quality orientation map of the grain structure. Without precession the increased difficulty in indexing the diffraction patterns (Figure 39b cf. Figure 39d) has led to the shape of the grains being less well defined, and in some cases it is possible to identify a completely different grain structure to that which

is actually present. This approach has been successfully applied to a number of metallic and inorganic systems for grain orientation, for example iron oxide nanocrystals (Moeck *et al.* 2009), copper and δ-*trip* steels (Rauch *et al.* 2010) and to identify crystals of different phases in more complex systems, for example tungsten carbide in polycrystalline cobalt alloys (Rauch *et al.* 2010) and MnAs in GaAs (Moeck *et al.* 2011).

There are still problems with the technique, for example the inability to differentiate between grains oriented at <112> and <013> axes in aluminium (given the similarity of the basis vectors) (Moeck *et al.* 2011). There is also the possibility of HOLZ creep leading to ambiguous indexing of individual reflections, which would lead to quite dramatic errors in the orientation mapping. Nevertheless, this combination of PED and orientation mapping should prove extremely powerful and complementary to the more conventional EBSD-based orientation maps in the SEM.

5. Conclusions

Precession electron diffraction is now seen as a key technique available to electron microscopists to elucidate the structure of inorganic crystals. Although originally envisaged as a method to produce integrated intensities that could be used for structure solution and refinement, the method has shown itself to be much more versatile, enabling symmetry determination, texture analysis and even measurements of bonding charge densities.

Recent developments in both hardware, with the introduction of commercial precession systems, and in software, with the availability of different solution algorithms, including novel charge flipping and maximum entropy methods, has led to a growing interest in PED world-wide. Indeed, many x-ray crystallographers are now exploring the advantages of precession electron diffraction for solving crystal structures that are not amenable to conventional x-ray methods.

For structure solution, the PED intensities are not strictly kinematical in nature but can in many cases be treated like kinematical intensities and be used to solve structures. Structure solution is still not yet routine, but rapid progress is being made to understand and optimize the precession and specimen parameters. Charge flipping offers a powerful method to use PED intensities and may be of particular benefit for electron intensities. It appears that although PED intensities are not kinematical the precession method minimizes the changes in the intensity order of reflections: strong and weak reflections maintain their relative positions allowing structure solution algorithms to work effectively.

Looking to the future, it seems that PED will continue to gain in popularity. The implementation of PED on a microscope is relatively straightforward and more robust software enables less experienced crystallographers to try solving structures. The ability to form PED patterns on aberration-corrected instruments opens up the possibility of large

precession angles but maintaining ultra-small convergent probes. This would enable fine-scale precipitates, interfacial phases and domain structures to be studied by PED.