Reconstruction strategies for structure solution using precession electron diffraction data from hybrid inorganic-organic framework materials

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Abstract. Precession electron diffraction has received significant recent attention, and has the potential to complement x-ray structure solution methods in situations where the latter are difficult to apply. Certain materials systems may nevertheless present challenges for solution by electron diffraction, and this is particularly true when the unit cell includes light element components. Drawing specifically on our work with hybrid inorganic-organic framework materials, we describe recent approaches to reconstructing their crystal potentials, which have led to significant improvements in the accuracy and quality of the derived potential maps for this type of structure.

1. Introduction
Precession electron diffraction (PED) was proposed by Vincent and Midgley in 1994 [1], and with the development of commercial electron precession systems there has been renewed interest in this technique as a tool for crystal structure determination by electron crystallography. Whilst PED is unlikely to compete with x-ray methods for routine structure determination, it has considerable potential in those cases where the nature of the material is such that x-ray techniques become difficult to apply. This is likely to be the case when samples are available only as very small crystals, when a material can only be synthesised as part of a phase mixture, or when fine scale microstructural features are present (e.g. twinning). In this context we have a particular interest in the application of PED to hybrid inorganic-organic framework materials [2]. Topologically, these compounds are structures in which metal ions act as nodes and linkage is mediated either through inorganic bridges (e.g. metal – oxide – metal) or via organic ligands. Typically, this results in a crystal structure in which a small number of strong scatterers (metal ions) are present on rather widely separated sites, very often at the special positions of the space group. The spaces in between are occupied by groups of much weaker scatterers, and there may be significant voids within the structure.

In order to apply PED successfully to these compounds, both experimental issues and data analysis procedures must be addressed. Rates of electron beam damage are high: complete loss of crystallinity

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within a few seconds is normal and the situation is similar to that encountered in TEM of biological materials. Our goal is therefore to explore the extent to which it might nevertheless be possible to make use of electron crystallographic data, with a particular interest in locating the more weakly scattering elements. Ultimately our aim is to be able to analyse materials where there is little or no prior crystallographic information, and we have therefore sought to develop a procedure which minimises the assumptions which need to made about the structure. For this reason the charge flipping algorithm [3] is particularly attractive, and we have often found it to be more successful with electron diffraction data than established direct methods. It has recently been demonstrated [4] that significant improvements can be made by adding known symmetry information into the charge flipping algorithm, and one might expect this approach to be effective also for the hybrid framework structures.

2. Phasing of structure factors

Figure 1a is a [011] precession electron diffraction pattern from a monoclinic polymorph of copper phosphonoacetate\(^4\) (P2\(_1\)/c, a=0.8263nm, b=0.7645nm, c=0.8971nm, \(\beta =90.52^\circ\)); figure 1b is a structural model viewed along the same direction and figure 1c is a map of the projected potential for scattering by 300kV electrons. Experimental structure factor moduli were derived from the data in figure 1a by using the peak finding and lattice fitting routines from the Semper image processing package to integrate over a small disc surrounding each peak position. Background levels were subtracted by interpolating between those areas of the pattern which lie between these discs, and the resulting experimental structure factors were corrected for geometric effects using the equations derived by Gjønnes [5]. In order to examine the behaviour of the reconstruction algorithm independently of experimental issues, a set of structure factor moduli for equivalent conditions and exact axial incidence on a 50nm thick crystal was also calculated, using a Bloch wave code written by Zuo [6] and adapted by its author for precession conditions.

In order to assign phases to these structure factors, the charge flipping algorithm requires a minimal set of input parameters. In particular, the procedure for handling the charge flipping parameter (\(\delta\)) must be specified, and this determines either the level or the proportion of the reconstructed electron

![Figure 1](image-url)  
*Figure 1* (a) [011] PED pattern obtained at 300kV from copper phosphonoacetate with a precession semiangle of approximately 20mrad; (b) structure model in the same orientation showing the Cu-O groups as polyhedra and the remaining organic elements as individual atoms; (c) projected potential: the strong peaks corresponding to the Cu atoms and the weaker peaks to C, P and O.

\(^4\)Crystallographic data (CCDC 697181) can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
density which is flipped at each iteration. Optimal values for $\delta$ allow for good exploration of the possible phase space for the structure factors and in this case an effective choice proved to be to flip the 75% of pixels with lowest values at each iteration. No assumptions were made about symmetry, except that for the experimental data an average value of the measured structure factor modulus was used for $+g$ and $-g$ reflection pairs in order to maintain the required Friedel's law relationship.

Figure 2 is a montage of six different reconstructions obtained by phasing the calculated data. We note that there are significant differences in the details of the reconstructions: in particular, where we expect to see copper atoms in linear groups of three, the absence of enforced symmetry in the phasing tends to strengthen one of the end positions and weaken the other. We would normally expect this issue to be addressed effectively by enforcing appropriate symmetry elements. However we have found that even when symmetry is included, it remains difficult to obtain charge flipping solutions for these structures which both converge and also deliver reproducible results. If we attempt to constrain the reconstruction to include a centre of symmetry, the origin is frequently wrongly determined (as lying between the two stronger Cu positions), and the resultant phasing identifies two rather than three heavy atom positions. A typical result is shown in figure 3a.

The reason for this appears to be intrinsic to the nature of these structures. As noted above, there are normally a small number of metal ions in each unit cell, often located on special positions. The symmetry associated with these strong scatterers is usually significantly reduced by the presence of the light element ligands, and small deviations from high symmetry are common. Even when the presence of particular symmetry elements is beyond doubt, the symmetry-enforcing stage of the algorithm frequently fails to generate reproducible results, usually because there are insufficient high order symmetry elements to unambiguously determine the origin. This is true whether tested on our own coding of the algorithms [4], or on other implementations [7].

3. Strong scatterer registration

It is both difficult to perform a conventional space group determination for these materials (because of their electron beam sensitivity), and easy to overestimate the symmetry if one relies on lattice parameter measurements and perceived pattern symmetry alone. However, given that at least some of the strong scatterers are normally located on special positions, it is usually straightforward to make a visual determination of an appropriate origin for the unit cell from a single phasing. We might therefore expect to be able to locate light elements by repeating the phase assignment many times, registering each converged solution against an external reference containing only the positions of the strongest scatterers, and summing the registered results to reinforce correct phasings.

We have investigated this approach using the Superflip code [7], which by default includes the required registration and averaging operations. In this case we repeated the charge-flipping procedure

**Figure 2** Phased reconstructions of the [011] projected potential for copper phosphonoacetate obtained from different initial conditions (randomised starting phases) for the charge flipping algorithm. The rectangular boxes identify qualitatively similar features in the potential: in the last two views on the right the box is displaced because the algorithm has located a different origin.
1000 times, of which 134 converged to a stable solution (higher convergence rates can be achieved but at the expense of detail in the reconstruction). It proved to be sufficient to create a reference file containing only the Cu atom situated at the origin: figure 3b is the result of registering each solution against this reference in order to determine the best-fit origin, and summing the set. All three copper atom positions are now correctly located (compare figures 3b, 1b and 1c), and subsidiary features have been generated around the lighter element sites. It is interesting to note that there is little deviation from the expected centrosymmetry even though this was not enforced by the algorithm. Finally therefore (figure 3c), we can examine the experimental data when phased and reconstructed using the same procedure. Unsurprisingly, the quality of the reconstruction is lower, but the metal atoms have again been located, and as before there are clear features around the lighter element positions.

4. Conclusions
The charge flipping algorithm has been shown to be an effective tool for phasing structure factor moduli determined by precession electron diffraction for hybrid inorganic-organic materials. However we note that the symmetry of the metal sublattice is often higher than that of the structure as a whole, and for this reason the most successful approach has proved to be to register a series of reconstructions against a trial structure containing only the strongest scatterers on the highest symmetry positions, followed by averaging the results to reduce the influence of spurious phasings. This allows the metal atom sites to be located, and there are indications from both calculated and experimental data that it might be possible to identify the approximate locations of lighter element groups.

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