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Towards Routine Structure Solution using Precession Electron Diffraction

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It is generally accepted that the best way to solve crystal structures is to use x-ray or neutron diffraction. In almost all cases, the scattered amplitudes are proportional to the structure factor and the recorded intensities can be used in a variety of different algorithms (direct methods, charge-flipping, genetic algorithms, etc) to solve crystal structures. However because the x-ray and neutron beam size is relatively large, there are groups of important materials for which these techniques are less useful, for example multi-phase samples, polymorphic crystals, disordered crystals and precipitates and inter-phase crystals.

The small beam size available in the TEM enables electron diffraction patterns to be recorded from sub-micron crystals without overlap or ambiguity. However the strong interaction between the electron beam and the underlying crystal potential means that conventional electron diffraction patterns recorded at major zone axes are prone to strong dynamical effects. As such, in general the diffracted intensities in such patterns cannot be used directly to solve crystal structures with conventional direct methods or similar algorithms. Precession electron diffraction [1] in which a focussed beam is rocked in a hollow cone both above and below the specimen allows 'zone axis' patterns to be recorded whose intensities are less prone to dynamical effects; this is because the beam is never exactly at the zone axis and the intensities are integrated through the Bragg condition. In addition, the rocking nature of the precessed beam means that significantly more beams are intercepted by the Ewald sphere than would be true in conventional electron diffraction: being able to record higher order reflections leads to higher resolution crystallographic information in the solution.

In early precession work, it was assumed that for most (inorganic) crystals of interest, the zero order reflections would be too dynamical in nature to be used for structure solution, even when using precession. For some time, the focus was on using reflections in higher order Laue zones as in most circumstances these intensities could be treated as kinematical, to a good approximation. However, it became evident over the years that even the zero layer reflections could be used for relatively low atomic number crystals and thin specimens. Initial attempts to use precessed intensities from zero layer reflections in conventional direct method algorithms recorded from relatively heavy or thick specimens met with rather limited success [2].

We have recently revisited this problem in order to understand when and why electron precession diffracted intensities are successful as input for structure determination algorithms. Figure 1 shows a montage of electron diffraction patterns recorded from the [001] zone axis of $Er_2Ge_2O_7$, comparing a conventional CBED pattern with patterns recorded with precession angles of 20mrad and 45 mrad. The HOLZ reflections can be seen to encroach as the precession angle increases. Figure 2 shows the projected potential (at 300kV) for the [001] zone axis of $Er_2Ge_2O_7$ and structure solutions, one using conventional direct methods [2], one using a charge-flipping algorithm. These results indicate that a faithful solution can be obtained from zero layer electron precession data if a sufficiently high

precession angle is chosen and if a charge flipping algorithm [3] is used that takes into account the phase relationships [4] determined by space group symmetry elements (the 2_1 screw axes in this case).

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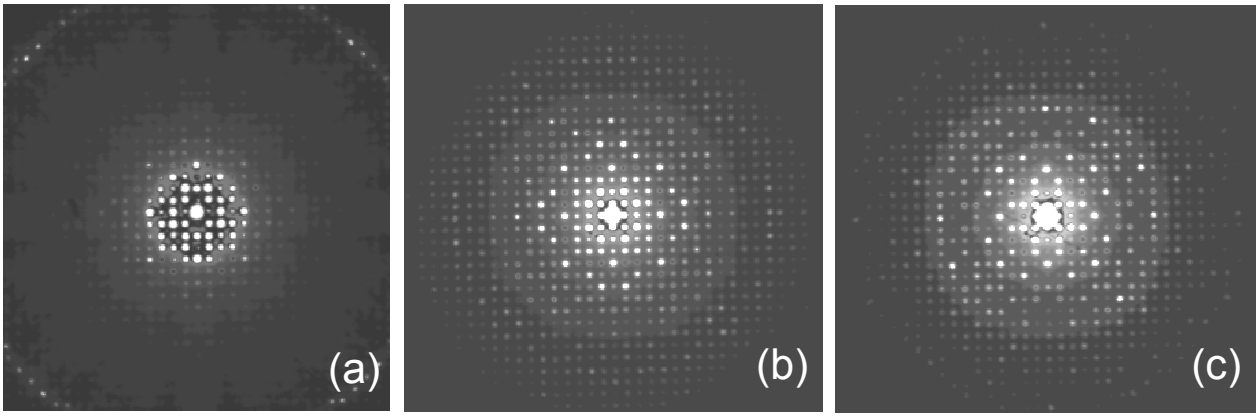

FIG. 1. Precession electron diffraction patterns, recorded on image plates, at the [001] zone axis of $Er_2Ge_2O_7$ with (a) zero, (b) 20mrad and (c) 45mrad precession angle.

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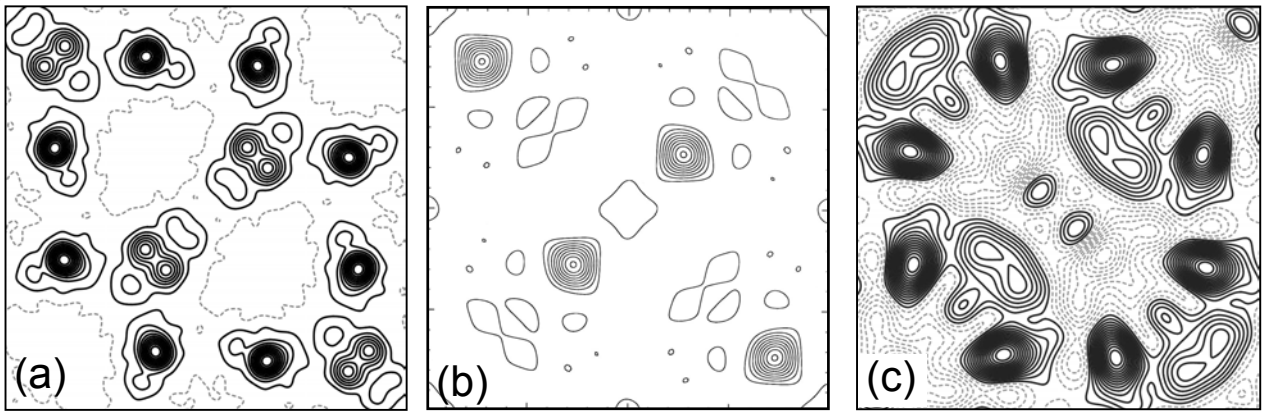

FIG. 2. (a) Ideal projected potential for the [001] zone axis of $Er_2Ge_2O_7$, (b) the structure solution obtained by direct methods [2], (c) a structure solution using a modified charge-flipping algorithm incorporating 'phase symmetry'. Experimental precession data was used for (b) and (c).

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