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A new approach to structure amplitude determination from 3-beam convergent beam electron diffraction patterns

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ABSTRACT

The intensity distribution in three-beam CBED patterns from centrosymmetric crystals can be inverted analytically to enable the direct measurement of crystal structure amplitudes and three-phase invariants. The accuracy of the measurements depends upon the accuracy and precision with which specific loci within the discs can be identified. The present work exploits the equivalence in form of the intensity distribution along these loci to provide an algorithm for their automated location, enabling the rapid and unequivocal identification of their position. Moreover, it demonstrates how the loci can be used to determine directly the relative magnitudes of structure amplitudes with superior accuracy and without recourse to complex pattern-matching calculations.

1. Introduction

The direct determination of structural phases and magnitudes from the analytical inversion of 3-beam convergent beam electron diffraction (CBED) patterns has been demonstrated on several occasions for centrosymmetric crystals [1–3]. This experimental method, which is based on the measurement of distances in 3-beam CBED patterns and was developed from the theory established by Moodie et al. [4–6], has proven an extremely powerful approach to structure solution. In recent work [7], it was shown that the structure of α-Al_2O_3, with 30 atoms in its unit cell, could be determined to 0.1 Å precision by starting from the direct measurement of 3-phase-invariants and then adding measurements of 4 independent structure amplitudes, which were made using the 3-beam CBED techniques of [2,3].

Whilst such inversion of 3-beam CBED patterns has proved a quick and reliable way to determine three-phase invariants (often by inspection), the accuracy of the measurement of magnitudes of structure amplitudes can be limited, in part because of the potential for ambiguity in identifying the position of specific loci, which mark the distances to be measured. These loci have a known orientation and a known form of the intensity distribution but their lateral position within the CBED disc must be identified and this can sometimes be ambiguous, particularly in the presence of significant n-beam perturbations. In the present work, we present a new approach for locating one of the two loci, locus *C*, which enables it to be more rapidly, precisely and objectively located (locus *C* is the locus oriented perpendicular to the coupling vector between the two diffracted discs, g and h). This results in more accurate measurements of the 3 distances required to determine the absolute magnitudes of the structure amplitudes, namely, the distances to the Gjønnes–Høier (GH) point and the distance to the centre of symmetry in the intensity along locus *C*, as per the approach of [2,3]. More significantly, we show that this locus can be used to determine directly and rapidly the relative magnitudes of structure amplitudes from the relative intensities in the diffracted discs along locus *C*, providing an additional and more accurate means for acquiring this information from the 3-beam CBED pattern.

Professor Spence [8] has fostered much research in the related area of structure amplitude refinement through iterative pattern-matching of CBED patterns, including 3-beam patterns [9]. We have enjoyed enthusiastic and fruitful engagement with Professor Spence in this and many other areas of electron diffraction and we present this work in honour of him on the occasion of his birthday.

2. 3-Beam CBED revisited

At this point, it is worth re-examining the main features of 3-beam CBED patterns from centrosymmetric crystals relevant to the present work. It has already been demonstrated [2,3] that the distances to particular features in 3-beam CBED patterns are

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sufficient to determine the phase and magnitude of the relevant structure amplitudes without recourse to any pattern-matching refinement. As already described in [2,3], the sign of a three-phase invariant can be obtained by inspection of the corresponding 3-beam CBED pattern, from the direction of deflection of the rocking curve near the 3-beam Bragg condition. This corresponds to the displacement of the centres of symmetry of the two centrosymmetric loci in each diffraction disc. The magnitudes can be determined from the distances of the GH point and centres of symmetry of the centrosymmetric loci from the origin as in [2,3]. Alternatively, we show here that their relative magnitude can be determined from the locus *C* in the discs g and h alone and that the position of the locus *C* can be determined with considerable accuracy. This locus is found in every disc and is oriented perpendicular to the coupling vector, **g–h**, as shown schematically in Fig. 1.

This new approach derives from one of the apparent redundancies in the three-beam derivations. In particular, as illustrated in Fig. 1 (see also Fig. 2), a two-beam distribution is generated in all three discs along the locus *C* whereas the locus has only to be detected in one to complete the inversion. Since the accuracy to which this locus can be defined is an important factor in establishing the accuracy to which the structure can be determined, it becomes relevant to compare the calculated intensity distributions along locus *C* in both the discs g and h. This can be done very simply using the reduction of the three-beam equations to two-beam form, with the pseudopotential

$$V_C = V_{\mathbf{g}} + iV_{\mathbf{h}} \tag{1}$$

and the effective excitation error

$$\zeta_C = 2\pi\zeta_{\mathbf{g}} + \frac{\sigma V_{\mathbf{h}} V_{\mathbf{h}-\mathbf{g}}}{V_{\mathbf{g}}} \tag{2}$$

as per [5] and using the same notation therein. Thus,

$$\begin{pmatrix} U(0) \\ U(1) \end{pmatrix} = e^{i\pi\zeta_C z} \exp\left\{ i \begin{pmatrix} -\pi\zeta_C & \sigma V_C^* \\ \sigma V_C & \pi\zeta_C \end{pmatrix} z \right\} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3}$$

with the solution,

$$U(1) = e^{i\pi\zeta_C} i\sigma V_C \frac{\sin\left(\sqrt{(\pi\zeta_C)^2 + \sigma^2 V_C V_C^*}\right) z}{\sqrt{(\pi\zeta_C)^2 + \sigma^2 V_C V_C^*}} \tag{4}$$

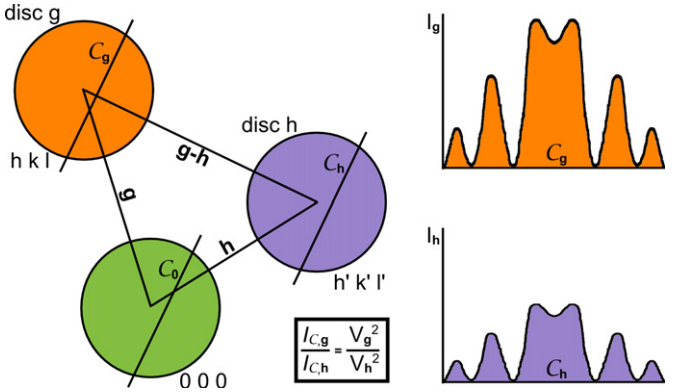

Fig. 1. A schematic illustration of a general ($|\mathbf{g}| \neq |\mathbf{h}| \neq |\mathbf{g}-\mathbf{h}|$) 3-beam pattern. The locus *C*, is perpendicular to the vector **g–h**, has a centrosymmetric intensity distribution and is located at the same position in each disc as described in [1–6]. The form of the intensity distribution is identical in the discs g and h as shown by the two graphs of intensity along $C_{\mathbf{g}}$ and $C_{\mathbf{h}}$. The relative intensities along $C_{\mathbf{g}}$ and $C_{\mathbf{h}}$ are determined by the relative magnitudes of the structure amplitudes, as shown in the boxed equation.

Equating real and imaginary parts, the central result for this communication is obtained in the form,

$$\frac{I_{C,g}}{I_{C,h}} = \frac{V_{\mathbf{g}}^2}{V_{\mathbf{h}}^2}. \tag{5}$$

Here the symbols for the intensities are italicised in order to emphasise that the ratio holds only along the locus *C*. It is important to note that this result derives from a dynamical calculation, which is exact within the three-beam approximation. In particular it is not related to the single scattering or kinematical approximation and so the concept of extinction cannot apply.

To emphasise this important point, it is briefly elaborated upon. The kinematical or single scattering approximation is properly written as

$$I_{\mathbf{g}} \propto |V_{\mathbf{g}}|^2 \tag{6}$$

As is widely known, this has wide currency when the interaction is weak, for instance in X-ray and neutron scattering (though even here a number of restrictions and corrections are usually invoked). Extinction in X-ray diffraction is the effect of applying the kinematic scattering approximation to the analysis of the total integrated intensity within each reflection via Eq. (6). The lack of a treatment of all dynamic scattering effects gives rise to the concept of extinction and departures from the relativity of structure amplitudes that is suggested by Eq. (6). The fact that Eq. (5) applies to the intensity distribution along a unique locus (locus *C*), located at equivalent positions in the discs g and h in a 3-beam CBED pattern, and is a consequence of dynamic scattering, removes the concept of extinction all together.

Given that Eq. (5) holds for the locus *C*, which traverses both discs g and h, a simple algorithm can be developed that not only locates the locus *C* very accurately within all discs, but also results in a more accurate approach to determining $V_{\mathbf{g}}/V_{\mathbf{h}}$ compared with the measurement of amplitudes from distances described previously in [2,3]. A description of the algorithm follows in the next section, making use of a synthetic 3-beam CBED pattern calculated with $V_{\mathbf{h}}=1.0$ V, $V_{\mathbf{g}}=2.0$ V and $V_{\mathbf{g}-\mathbf{h}}=3.0$ and shown in Fig. 2. The location of locus *C* is shown in the discs g and h and the corresponding intensity profiles are shown to have the same 2-beam intensity distributions. The amplitudes of these distributions differ by a factor of 4, resulting from $V_{\mathbf{g}}/V_{\mathbf{h}}=2$ and evident from Eq. (5). As a consequence, the subtraction of disc h multiplied by 4 from disc g reveals a sharp line of zeroes along locus *C* across which, the sign of the difference map flips.

3. The algorithm

Fig. 3 explains the algorithm using the synthetically calculated 3-beam CBED pattern of Fig. 2 as an example (a). The physics of 3-beam-scattering ensures that the locus *C* is always oriented perpendicular to the coupling vector, **g–h**, so the starting point is to rotate the pattern in order to make this vector horizontal (the locus *C* is then oriented vertically in the image) as has already been done in Fig. 2. The angle of rotation is found simply by drawing the tangent common to both discs g and h as shown in Fig. 3a. The discs g and h are then extracted from the pattern (b and c, respectively) with particular care taken in making sure that the sub-images containing each disc are correctly registered with respect to one another (i.e. each point in each of the sub-images b and c are exactly related to one another by the coupling vector **g–h**).

Eq. (5) is the foundation of the algorithm and can be rewritten as:

$$I_{\mathbf{g}} = \frac{V_{\mathbf{g}}^2}{V_{\mathbf{h}}^2} I_{\mathbf{h}} = m I_{\mathbf{h}}, \quad m = \frac{V_{\mathbf{g}}^2}{V_{\mathbf{h}}^2} \tag{7}$$