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Structural phase and amplitude measurement from distances in convergent-beam electron diffraction patterns

Philip N. H. Nakashima,[a]* Alexander F. Moodie[a] and Joanne Etheridge[a,b]

[a]Department of Materials Engineering, Monash University, Victoria 3800, Australia, and [b]Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia. Correspondence e-mail: philip.nakashima@eng.monash.edu.au

The structure of a periodic object, such as a crystal, may be described by an infinite series of Fourier coefficients and phases. In associating this with scattering theory appropriate to any radiation, a classic problem arises, namely, the determination of phases from the resulting discrete diffraction pattern. The solution to this phase problem is presented in this paper in which the first direct measurement of structural phase by inspection of convergent-beam electron diffraction patterns is described.

1. Introduction

The phase problem refers to the absence of phase information in the intensity deriving from a diffraction experiment within the single-scattering approximation. This is summarized in the following equations (Lipson & Cochran, 1966):

$$\mathrm{I}_{\mathbf{g}} = \mathrm{V}_{\mathbf{g}}\mathrm{V}_{\mathbf{g}}^{*} \quad \text{with} \quad \mathrm{V}_{\mathbf{g}} = |\mathrm{V}_{\mathbf{g}}| \exp(i\phi_{\mathbf{g}}) \tag{1}$$

and

$$\mathrm{P}(\mathbf{u}) = \sum_{\mathbf{g}} \mathrm{I}_{\mathbf{g}} \cos(2\pi\mathbf{g}\cdot\mathbf{u}) = \varphi(\mathbf{r}) * \varphi(-\mathbf{r}), \tag{2}$$

where $\mathrm{I}_{\mathbf{g}}$ is the intensity for the reflection with the reciprocal-lattice vector $\mathbf{g}$, $\mathrm{V}_{\mathbf{g}}$ is the corresponding structure amplitude with a phase $\phi_{\mathbf{g}}$. $\mathrm{P}(\mathbf{u})$ is the Patterson function of the crystal structure expressed as a sum of the scattered intensities for an atomic displacement with vector $\mathbf{u}$, or a self-convolution of the crystal potential, $\varphi(\mathbf{r})$ [nomenclatures for different radiations are compared in Dawson *et al.* (1974)].

A solution is sought for the crystal potential, $\varphi(\mathbf{r})$, however, $\varphi(\mathbf{r})$ is not uniquely defined by the integral equation for $\mathrm{P}(\mathbf{u})$.

For weakly interacting radiation, such as neutrons and X-rays, the single-scattering approximation has useful ranges of validity and hence the phase problem remains. This is conventionally circumvented using Patterson, heavy-atom or direct methods, which all assume the single-scattering approximation holds. In addition, multiple-scattering effects have been employed in X-ray diffraction to determine three-phase invariants, though not amplitudes (for example, Post, 1979; Weckert & Hummer, 1997).

For fast electrons, the interaction constant is approximately 5000 times stronger and the wavelength much shorter, so that the single-scattering approximation no longer holds. This means that phase information is contained in the intensity distribution. However, in general, it is not possible to extract this information because of the complexity of the scattering equations. In other words, an analytical inversion of the equations has not yet been found. However, if the crystal is centrosymmetric [a fact that can be determined unequivocally by convergent-beam electron diffraction (CBED) (Goodman & Lehmpfuhl, 1968; Goodman, 2001)] and, furthermore, if it is oriented such that the electrons are only scattered into three directions, then the equations are much simpler and phase information can be extracted. By exploiting the symmetries of the scattering equations (Moodie *et al.*, 1996) for this three-beam condition, it becomes possible to invert these equations to give

$$|\mathrm{V}_{\mathbf{g}}| = \sqrt{\frac{(\Gamma_3 - \Gamma_2)(\Gamma_1 - \Gamma_2 + \Gamma_3)}{\sigma^2}}, \tag{3}$$

$$|\mathrm{V}_{\mathbf{h}}| = \sqrt{\frac{\Gamma_3(\Gamma_3 - \Gamma_2)}{\sigma^2}}, \tag{4}$$

$$|\mathrm{V}_{\mathbf{g}-\mathbf{h}}| = \sqrt{\frac{\Gamma_3(\Gamma_1 - \Gamma_2 + \Gamma_3)}{\sigma^2}}, \tag{5}$$

and the sign of the three-phase invariant is given by the sign of Γ_3, where

$$\Gamma_3 = \frac{\sigma \mathrm{V}_{\mathbf{h}}\mathrm{V}_{\mathbf{g}-\mathbf{h}}}{\mathrm{V}_{\mathbf{g}}}. \tag{6}$$

Here $\mathrm{V}_{\mathbf{g}}$, $\mathrm{V}_{\mathbf{h}}$ and $\mathrm{V}_{\mathbf{g}-\mathbf{h}}$ are the triplet of structure amplitudes relevant to the scattering geometry and Γ_1, Γ_2 and Γ_3 are distances in the three-beam electron diffraction pattern (σ is the interaction constant for electrons).

These equations are a consequence of invoking the discrete symmetries of the cubic equation and the continuous symmetries of the differential equation describing three-beam scattering.

This inversion depends upon the measurement of distances, Γ_1, Γ_2 and Γ_3, to features in the diffraction pattern, not on absolute intensities. These features are

defined by five loci within the diffraction patterns along which the intensity distribution has the generic form

$$I \propto \frac{\alpha \sin^2 \beta t}{\beta^2}, \qquad (7)$$

often referred to as the two-beam form.

These loci are positioned uniquely in each of the three beams and have specific orientations, which are known *a priori* from the diffraction geometry, as per Fig. 1.

The distances, Γ_1, Γ_2 and Γ_3, required for the inversion [equations (3)–(5)] correspond to the following two features (see Fig. 1)

1. The centre of the centrosymmetric intensity distribution along loci $\mathcal{G}$ and $\mathcal{H}$ gives Γ_3. The centre of the centrosymmetric intensity distribution along locus $\mathcal{C}$ gives $-\Gamma_3$.

2. The intersection of the two loci in either diffracted beam gives (Γ_1, Γ_2), known as the Gjønnes–Høier or G–H point (Moodie *et al.*, 1996; Gjønnes & Høier, 1971).

In particular, the sign of the three-phase invariant is given by the sign of Γ_3, enabling phase to be identified directly from this point.

The three structure amplitudes can be measured twice in a single pattern, once from the loci in the disc g and once from the loci in disc h, and their phase invariant can be measured five times (*i.e.* once from each of the five loci). This enables multiple checks of the measurements from a single pattern.

This is the theoretical result.

2. Experiment

This paper demonstrates, for the first time, the application of this result to experimental data. Furthermore, it shows that it is eminently practical to apply this routinely to the determination of structure amplitudes and their phases directly from the measurement of *distances* as opposed to iterative matching of absolute intensities (Goodman & Lehmpfuhl, 1967). Specifically, it represents a direct experimental inversion of diffracted intensities to obtain the crystal structure, without making any assumptions. This establishes a point of principle, that structural phase can be measured *directly* from experimental intensity distributions. Furthermore, it delivers a new experimental method for the determination of structure amplitudes and phases that makes use of the symmetries in the diffracted intensities and does not require knowledge of their absolute value. In particular, it is found that the sign of the phase can easily be determined, in many cases by inspection, providing an experimental method for the direct measurement of phase from intensity distribution and a solution to the phase problem.

It is emphasized that this approach is distinct from the well known iterative matching of computed and experimental intensity distributions, which was first introduced in CBED by Goodman & Lehmpfuhl (1967) and has been applied extensively by many workers, including the matching of pattern intensities in three-beam orientations [for example, Zuo *et al.* (1989)].

α-Al_2O_3 was chosen to establish both of the above points.

[001] and [100] oriented wedges of 99.999% purity α-Al_2O_3 were tripod polished to achieve wedge angles of 1.5° and

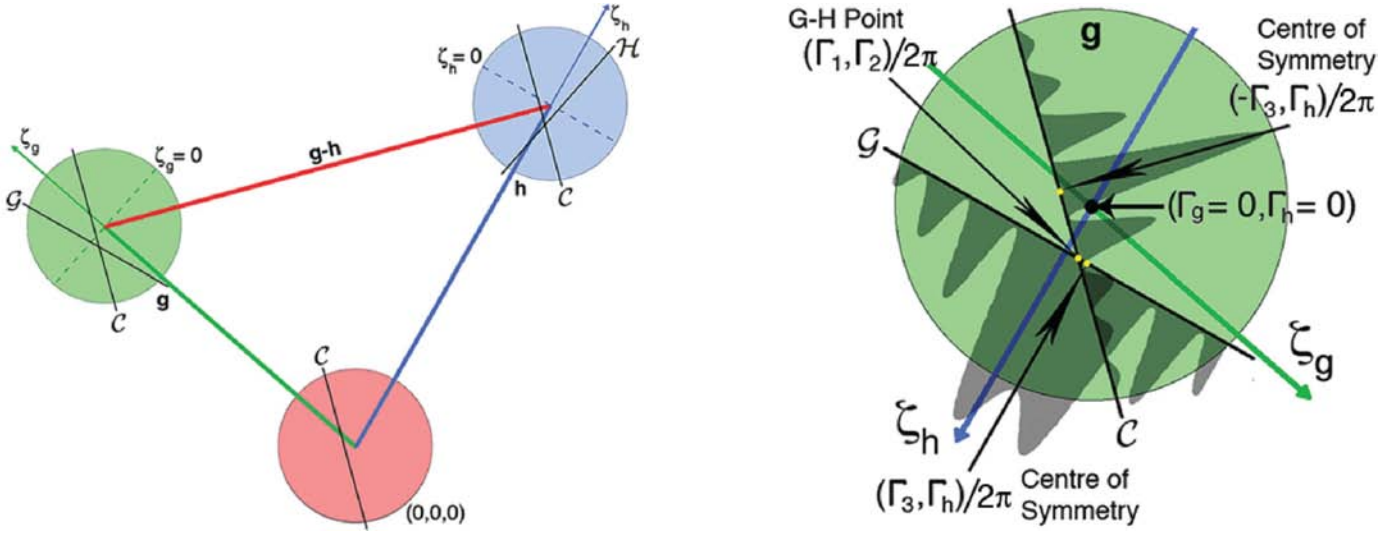
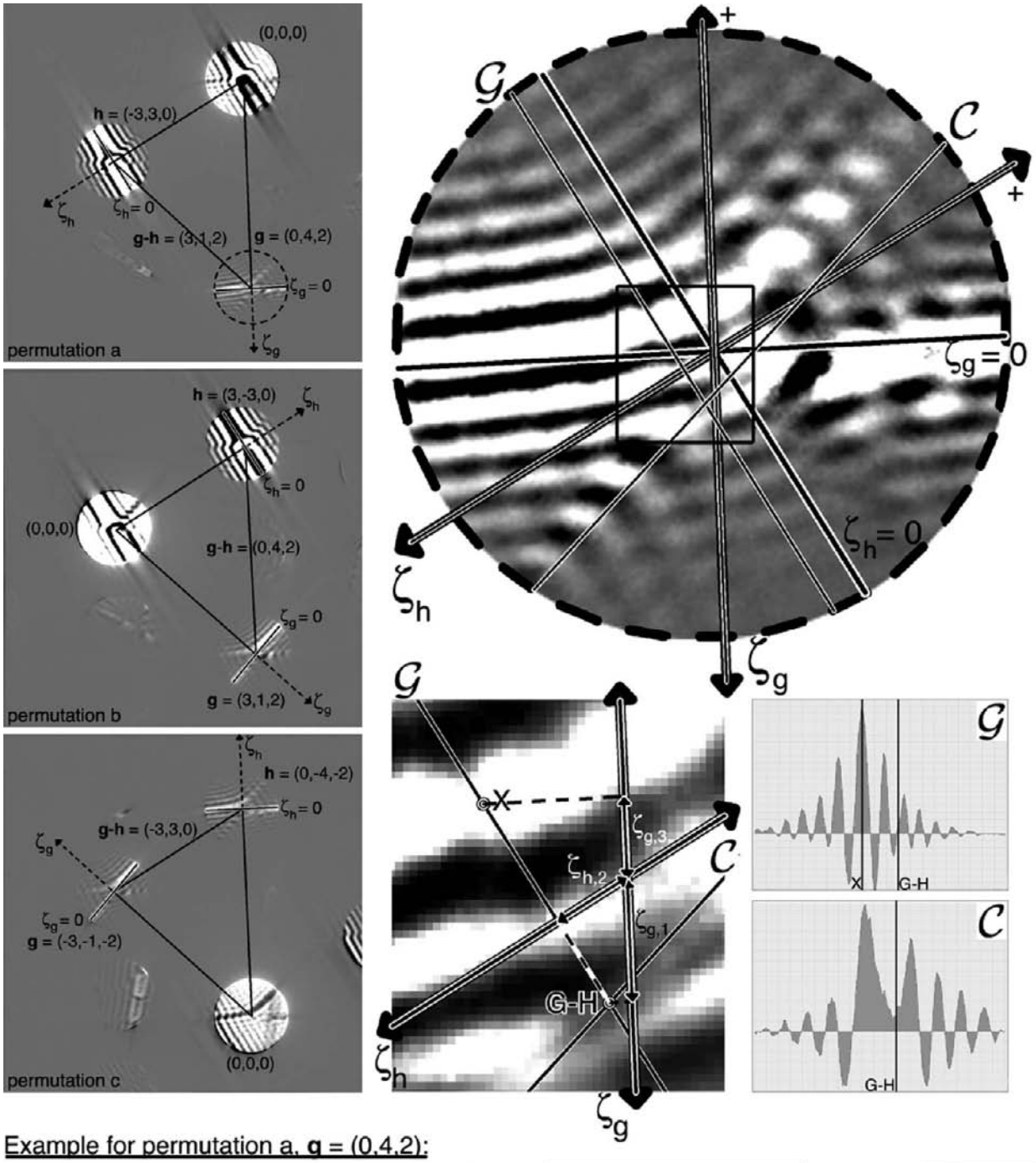


Figure 1
A schematic diagram of a three-beam CBED pattern. There are five loci (marked) that have centrosymmetric intensity distributions. Three of these, marked $\mathcal{C}$, lie perpendicular to the coupling vector $\mathbf{g} - \mathbf{h}$ and have the same position in each disc. The other two loci are marked $\mathcal{G}$ and $\mathcal{H}$. $\mathcal{H}$ lies in disc h and is parallel to the locus of the Bragg condition in disc g. $\mathcal{G}$ lies in disc g and is parallel to the locus of the Bragg condition in disc h. The point of intersection of the two loci in either disc determines the distances Γ_1 and Γ_2. The centre of symmetry of any of the five loci determines the distance Γ_3. These distances are measured in terms of the oblique coordinate axes of the excitation errors, $\zeta_{\mathbf{g}}$ and $\zeta_{\mathbf{h}}$ (see detailed view of disc g). These distances are used in equations (3)–(5) to give the magnitudes of the structure amplitudes $|V_{\mathbf{g}}|$, $|V_{\mathbf{h}}|$ and $|V_{\mathbf{g}-\mathbf{h}}|$. The sign of Γ_3 alone is the sign of the three-phase invariant, $V_{\mathbf{h}}V_{\mathbf{g}-\mathbf{h}}/V_{\mathbf{g}}$ [as in equation (6)]. This process can be repeated in disc h, with the labels g and h interchanged.



Example for permutation a, **g** = (0,4,2):

$\zeta_{g,1} = -6.78\times10^{-4}$Å^{-1}; $\Gamma_1 = 2\pi\zeta_{g,1} = -0.00426$Å^{-1}; $|V_g| = \sqrt{(\Gamma_3-\Gamma_2).(\Gamma_1-\Gamma_2+\Gamma_3)/\sigma^2} = 1.24$V

$\zeta_{h,2} = -3.19\times10^{-4}$Å^{-1}; $\Gamma_2 = 2\pi\zeta_{h,2} = -0.00201$Å^{-1}; $|V_h| = \sqrt{\Gamma_3.(\Gamma_3-\Gamma_2)/\sigma^2} = 4.52$V

$\zeta_{g,3} = +3.88\times10^{-4}$Å^{-1}; $\Gamma_3 = 2\pi\zeta_{g,3} = +0.00244$Å^{-1}; $|V_{g-h}| = \sqrt{\Gamma_3.(\Gamma_1-\Gamma_2+\Gamma_3)/\sigma^2} = 0.92$V

Γ_3 +ve ↓ $\frac{V_h.V_{g-h}}{V_g}$ +ve

Figure 2
An experimental measurement of structural phase and amplitude. Three experimental thickness-difference three-beam CBED patterns from α-Al_2O_3 ($R\bar{3}c$) taken at 200 kV are shown on the left. Patterns *a*, *b* and *c* are generated by permuting the same triplet of structure amplitudes about the [1, 1, −2] zone axis. An expanded view of the disc $\mathbf{g} = (0, 4, 2)$ in permutation *a* is shown top right (with contrast enhanced to show relevant features). The centrosymmetric loci are marked $\mathcal{G}$ (parallel to $\zeta_{\mathbf{h}} = 0$) and $\mathcal{C}$ (perpendicular to $\mathbf{g} - \mathbf{h}$) and their intensity distributions are given at lower right. A magnified view of the boxed region in disc *g* is given at lower centre. The intersection of $\mathcal{G}$ and $\mathcal{C}$ is the Gjønnes–Høier (G–H) point and has the coordinates $(\Gamma_1, \Gamma_2)/2\pi$ whilst the centre of symmetry of the intensity distribution along $\mathcal{G}$ is marked X and has the coordinates $(\Gamma_3, \Gamma_{\mathbf{h}})/2\pi$. From these measured distances, the magnitudes of the structure amplitudes (shown) are determined using no more than a pocket calculator. The phase is determined by inspection. In this case, X lies on the positive side of $\zeta_{\mathbf{g}}$ in disc *g* and hence the sign of the three-phase invariant is positive.

Table 1
Experimental results from the triplet of three-beam patterns in Fig. 2.

Location of measurements†	Structure amplitudes (V) $\lvert V_{0,3,0}\rvert$	$\lvert V_{3,1,2}\rvert$	$\lvert V_{0,4,2}\rvert$	Sign of 3-phase invariant
Permutation *a*, beam *g*	4.52	0.92	1.24	+
Permutation *a*, beam *h*	5.32	1.62	2.07	+
Permutation *b*, beam *g*	5.21	1.61	2.12	+
Permutation *b*, beam *h*	5.56	1.52	1.82	+
Permutation *c*, beam *g*	4.90	1.32	1.92	+
Permutation *c*, beam *h*	5.75	0.79	1.08	+
Known value‡	4.85	0.95	1.19	+

† See Fig. 2 for location of measurements. ‡ Previously measured values from Maslen *et al.* (1993) and Streltsov *et al.* (2003).

examined in a Philips CM20 electron microscope with an LaB_6 filament at 200 and 120 kV. An advantage of CBED is that the crossover of the electron probe can routinely be made very small [<50 Å (LaB_6 source), <10 Å (FEG source) or <2 Å (aberration-corrected FEG)] so that small specimen volumes can be sampled. This ensures that the specimen volume generating the pattern is both perfect and effectively parallel-sided. Three-beam CBED patterns were collected near eight different zone axes and recorded on image plates.

To minimize the contribution to the intensity distribution that has resulted from inelastic scattering, including phonon scattering and Borrmann-like effects (Goodman, 1973), two patterns, taken from regions with slightly different thicknesses, were subtracted to give a thickness difference pattern (Nakashima, 2007). This approach is possible because the inversion depends only on the symmetry of the intensity distribution, not on the absolute intensities.

As an example, Fig. 2 shows three three-beam CBED patterns taken near one of the eight zone axes. Each pattern is a permutation of the same triplet of structure amplitudes ($V_{0,3,0}$, $V_{3,1,2}$ and $V_{0,4,2}$) and corresponds to a slightly different incident-beam orientation that satisfies the Bragg condition for different pairs of the triplet.

3. Results

The unique centrosymmetric intensity profiles were identified in each of the three patterns. The centre of these profiles and their intersection then established Γ_1, Γ_2 and Γ_3. These distances were measured independently in each of the diffracted beams and in each of the three patterns. This resulted in six independent measurements of the magnitude of each of the structure amplitudes ($\lvert V_{0,3,0}\rvert$, $\lvert V_{3,1,2}\rvert$ and $\lvert V_{0,4,2}\rvert$), *i.e.* once each from disc *g* and disc *h*, for each of the three permutations, *a*, *b* and *c* (see Fig. 2). In this way, the influence of the *n*-beam perturbations of the three-beam approximation can be estimated (see Table 1). 15 independent measurements, 5 per pattern, can be made of the three-phase invariant. In particular, with experience, the three-phase invariant can be determined by casual inspection of the pattern, by identifying the direction of the deflection of the intensity oscillations.

The results of these measurements are given in Table 1. It can be seen that the three-phase invariant was always determined correctly. Furthermore, it is noted that, in all cases, it was found that the sign of the three-phase invariant could be determined by inspection. In addition, some individual amplitudes were measured to within 5% of previous measurements (Maslen *et al.*, 1993; Streltsov *et al.*, 2003). This result is typical of those found in the other zone axes, which will be reported elsewhere.

4. Conclusions

This demonstrates, for the first time, that structural phase in any centrosymmetric crystal can indeed be measured directly from an experimental intensity distribution. Furthermore, amplitudes can be measured, at the same time, directly from distances in this intensity distribution with sufficient accuracy as to be suitable for structure determination.

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