Enhanced X-Ray Phase Determination by Three-Beam Diffraction

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For decades, solving the phase problem of x-ray scattering has been a goal that, in principle, could be achieved by means of n-beam diffraction (n-BD). However, the phases extracted by the actual n-BD phasing techniques are not very precise, mainly due to systematic errors that are difficult to estimate. We present an innovative theoretical approach and experimental procedure that, combined, eliminate two major sources of error. It is a high precision phasing technique that provides the triplet-phase angle with an error of about 2°.

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It is well known that the n-beam diffraction (n-BD) phenomenon contains structural phase information and can provide a physical solution to the fundamental *phase problem* in x-ray crystallography [1–8]. Several phasing techniques based on n-BD have been proposed during the last few decades [9–13]. For practical applications, these techniques are time-consuming and limited to a few n-BDs that present good phase sensitivity. Very recently, several authors have demonstrated that the linear polarization of synchrotron radiation can be used to change the relative strength of multiple diffracted waves [14,15] and/or improve phase sensitivity in some cases [16]. Polarization resolved n-BD has also been considered for enhancing phase sensitivity [17]. However, phase determination is more complex than just carrying out measurements at optimized phase sensitive conditions. In fact, there are unpredictable systematic errors, such as the loss of phase coherence of the diffracted waves due to crystal defects, that are difficult to estimate, causing the reliability on the measured phases to be highly questionable.

This Letter introduces very simple modifications in a standard theoretical approach for n-BD that completely eliminates the most common systematic errors in phase determination. In this modified approach, which is capable of dealing with interfering wave fields partially coherent, the errors of the measured phases are extremely small, about 2°. A scattering angle of $\pi/2$ is used for increasing phase sensitivity and resolution, as well as for collecting a polarization-dependent set of data that provides a sense of the reliability of the results. Moreover, this is a n-BD phasing technique that can be carried out fully automated on samples with unknown structure.

The physical principle of the n-BD phase sensitivity relies on the fact that two or more excited wave fields, from different sequences of reflections inside a crystal, interfere as they travel along the same propagation direction. For example, the $\mathbf{D}_\mathrm{p}$ and $\mathbf{D}_\mathrm{d}$ wave fields of the three-BD are shown in Fig. 1, both with wave vector $\boldsymbol{k}_\mathrm{A}$. $\mathbf{D}_\mathrm{p}$ is produced by a single Bragg reflection, represented by plane A, while $\mathbf{D}_\mathrm{d}$ comes from a double-bounce reflection in the planes B and C. By keeping one wave excited and changing the angular condition for the other, characteristic interference profiles are obtained. These profiles carry information on the phase difference between the waves. For the three-BD, the simplest n-BD case, it is known as the triplet phase (Ψ_T), which is the sum of the structure factor phases of the B and C reflections minus the phase of the A reflection, i.e., $\Psi_\mathrm{T} = \delta_\mathrm{B} + \delta_\mathrm{C} - \delta_\mathrm{A}$.

Azimuthal scans (ϕ scans) generate three-BD interference profiles as the secondary wave field, $\mathbf{D}_\mathrm{d}$, is excited by the rotation of the crystal around the diffraction vector of the primary reflection (A reflection in Fig. 1) whose wave field, $\mathbf{D}_\mathrm{p}$, is kept excited during the ϕ scans. At their maximums, these wave fields are given by $\mathbf{D}_\mathrm{p} = \mathrm{D}_\mathrm{A}\boldsymbol{v}_\mathrm{p}\mathrm{e}^{i\delta_\mathrm{A}}$ and $\mathbf{D}_\mathrm{d} = \mathrm{D}_\mathrm{BC}\boldsymbol{v}_\mathrm{d}\mathrm{e}^{i(\delta_\mathrm{B}+\delta_\mathrm{C})}$, where D_A and D_BC are

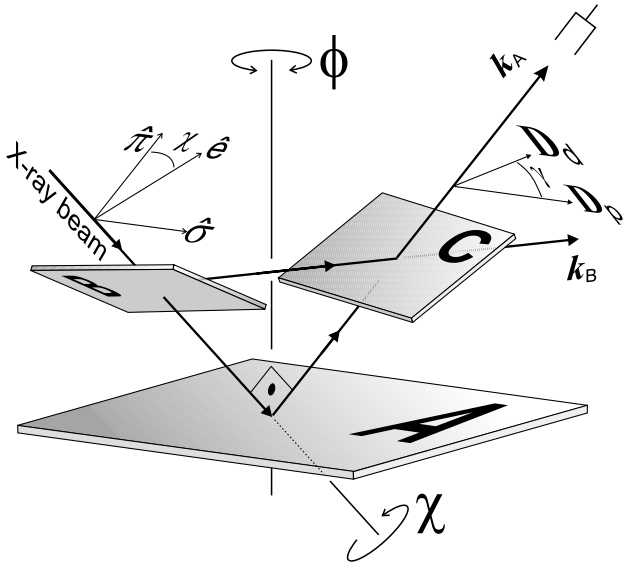

FIG. 1. Three-beam diffraction in a single crystal. The primary, $\mathbf{D}_\mathrm{p}$, and secondary, $\mathbf{D}_\mathrm{d}$, wave fields are generated by the A reflection (represented by the plane A) and by the sequence of B and C reflections, respectively. The reflection indexes of B + C are equal to A. γ is the angle between these wave fields, $\boldsymbol{k}_\mathrm{A,B}$ are the wave vectors of the diffracted beams, and $\hat{e}$ is the polarization direction of the incident synchrotron radiation. The χ axis rotates the crystal around the incident beam. In terms of χ, $\hat{e} = \sin\chi\,\hat{\sigma} + \cos\chi\,\hat{\pi}$.

proportional to the magnitude of the incident wave field and to the Fourier components of the crystal polarizability for the respective reflections. The vectors $\boldsymbol{v}_p = \hat{k}_A \times \hat{k}_A \times \hat{e}$ and $\boldsymbol{v}_d = \hat{k}_A \times \hat{k}_A \times (\hat{k}_B \times \hat{k}_B \times \hat{e})$ represent the dependence of the waves on the linear polarization direction, $\hat{e}$, of the incident synchrotron radiation—the cross products are done from right to left. The intensity due to the superposition of these waves along the primary beam direction, $\hat{k}_A$, as a function of ϕ is

$$I(\phi) = D_A^2 v_p^2 + |f(\phi)|^2 D_{BC}^2 v_d^2 + 2|f(\phi)|D_{BC} v_d D_A v_p \cos\gamma \cos(\Psi_T + \Omega). \quad (1)$$

The function $f(\phi)$ is the resonance term [11,13,17] describing the excitation of the secondary wave, $\mathbf{D}_d$, during the ϕ rotation. In practice, simple functions can be used as the resonance term for fitting the azimuthal scans and extracting the triplet phases. Here, the function

$$f(\phi) = \frac{\pm w}{2(\phi - \phi_0) - iw}, \quad (2)$$

serves this purpose. Its phase angle, $\Omega(\phi) = \pm \tan^{-1}[w/2(\phi - \phi_0)]$, properly takes into account the 180° phase shift across the maximum of the scattering condition at ϕ_0. The FWHM of the Lorentzian function, $|f(\phi)|^2$, is w. The + (in/out) and − (out/in) signals stand for two distinct geometries in which the $\mathbf{D}_d$ wave is excited in a full rotation of the ϕ axis. The third term of Eq. (1) is the interference term, the term that has the phase information and is responsible for the asymmetry in the three-BD profile. The optimal phase sensitive condition occurs when the wave fields are parallel, $\cos\gamma = \pm 1$ [18], and have nearly the same amplitude, $|\mathbf{D}_p| \approx |\mathbf{D}_d|$ [11,17].

The approach for the three-BD given by Eq. (1) is within the framework of the 2nd-order Born approximation [13,19,20]. Although it allows a good description of the diffraction process when the primary wave is weaker than the secondary wave, i.e., $|\mathbf{D}_p| < |\mathbf{D}_d|$, it has two major deficiencies: (i) it assumes that the diffracted wave fields are completly coherent and (ii) it fails in describing the reduction in the magnitude of a strong primary reflection due to the amount of energy taken by the $\boldsymbol{k}_B$ beam, the so-called *Aufhellung* effect [21]. The n-beam dynamical theory [2,11] exactly describes the energy balance among the diffracted beams but can only be applied for perfect crystals. Crystalline imperfections generate diffracted waves without phase coherence, known as kinematical diffraction, which are unable to participate in the interference predicted by the third term of Eq. (1). In order to effectively include these two effects (loss of coherence and *Aufhellung*), we introduce two new parameters into Eq. (1), which becomes

$$I(\phi) = D_A^2 v_p^2 [1 - b|f(\phi)|^2] + |f(\phi)|^2 D_{BC}^2 v_d^2 + 2\sqrt{1-a}\,|f(\phi)|D_{BC} v_d D_A v_p \times \cos\gamma \cos(\Psi_T + \Omega). \quad (3)$$

The $\sqrt{1-a}$ takes into account the attenuation of the contribution of the interference term to the intensity profile. This attenuation is due to the loss of coherence of the kinematically diffracted waves—hereinafter called the kinematical effect. The introduction of the attenuation parameter a, ranging from 0 to 1, is justified by the extreme physical limits of Eq. (3) that these values represent; for $a = 0$ the waves are completely coherent, while for $a = 1$ they have no phase coherence, then, no interference is observed, and the ϕ profile has a symmetric shape given only by $|f(\phi)|^2$. The b parameter stands for the reduction in the intensity of the base line, $|\mathbf{D}_p|^2$, as the secondary wave is exited. Under the present approach, Eq. (3) can be split up in two terms, $I(\phi) = I_\sim(\phi) + I_\wedge(\phi)$, where

$$I_\sim(\phi) = D_A^2 v_p^2 + (1-a)\,|f(\phi)|^2 D_{BC}^2 v_d^2 + 2\sqrt{1-a}\,|f(\phi)|D_{BC} v_d \times D_A v_p \cos\gamma \cos(\Psi_T + \Omega) \quad (4)$$

and $I_\wedge(\phi) = (aD_{BC}^2 v_d^2 - bD_A^2 v_p^2)\,|f(\phi)|^2$. $I_\sim(\phi)$ is the asymmetric term of the profile, containing the phase information, and $I_\wedge(\phi)$ is the symmetric term due to kinematical and *Aufhellung* effects. Although the a and b parameters provide only symmetric contributions to the profile of the ϕ scan, assignment of any value, different from zero, to these parameters does distort the asymmetry of the profile. Consequently, by fitting a profile (even one measured in the optimized phase sensitivity condition) with diffraction theories that neglect one or both effects, the amount of distortion cannot be estimated. This generates systematic errors preventing an accurate value of Ψ_T to be extracted, unless both effects happen to cancel each other, i.e., $aD_{BC}^2 v_d^2 \approx bD_A^2 v_p^2$. It is also very important to emphasize that the profiles of these effects, summarized in $I_\wedge(\phi)$, have been assumed here to be the same as that of the resonance term. It is certainly valid for crystals with low levels of defects or with surface damages, or even for an incident beam with short longitudinal coherence length. Otherwise, more appropriated functions in $I_\wedge(\phi)$ must be used for describing the presence of defects in the materials. Independently of the types of defects, the resonant term in $I_\sim(\phi)$ stays unchanged, as given by Eq. (2). It is defined by the dynamical diffraction that takes place at large perfect regions of the crystal.

In order to experimentally demonstrate the systematic errors due to the kinematical and *Aufhellung* effects as well as to prove that Eq. (3) correctly takes them into account, a polarization-dependent set of ϕ scans had to been collected. According to $I_\wedge(\phi)$, these effects can be discriminated when investigated as a function of the incident beam polarization direction since they have different weight, given by v_d^2 and v_p^2. The b parameter also depends on the polarization direction. The simplest way to take this into account is by replacing b with $b'(r_B v_B^2 + r_C v_C^2)$, where $\boldsymbol{v}_B = \hat{k}_B \times \hat{k}_B \times \hat{e}$, $\boldsymbol{v}_C = \hat{k}_B \times \hat{k}_B \times (\hat{k}_A \times \hat{k}_A \times \hat{e})$, and $r_{B,C}$ are proportional to the square of the structure factor of the B and C reflections.

To maximize the sensitivity with the polarization, the primary reflection and x-ray energy are chosen to produce a $\pi/2$ scattering angle. Besides the most obvious reason for using such scattering geometry, which is the possibility of tuning the strength of the primary wave from zero to its maximum value (D_A) [15], it also allows a direct measurement of the intensity ratio, $R = D_{BC}^2/D_A^2$, and an adjustment of the γ angle (Fig. 1). After selecting a nonforbidden primary reflection with Bragg angle of $\pi/4$ and measuring reference values for D_{BC} and D_A at $\chi = 0$ ($\upsilon_p = 0$) and $\chi = 90°$ ($\upsilon_p = 1$), respectively, the amplitude of the waves, $|\mathbf{D}_p|$ and $|\mathbf{D}_d|$, can be plotted as a function of χ. In general, with χ in the range from $-90°$ to $+90°$ (see Fig. 1), these plots show two polarizations where $|\mathbf{D}_p| \approx |\mathbf{D}_d|$. The value of $\cos\gamma$ defines which one of these two polarizations has a better phase sensitivity.

The experiments were carried out in a three-axis goniometer mounted on top of an inclination table (χ table) at the x-ray diffraction beam line of the National Synchrotron Light Source, Brazil. The χ-table rotation axis is lined up with the incident beam, and the inclination of the table allows the adjustment of the χ angle in the required range of $-90°$ to $+90°$ (see Ref. [15] for more details). A GaSb (001) crystal was chosen as a sample, the $\bar{2}26$ reflection as the primary reflection (A reflection in Fig. 1), and the [110] direction was taken as the reference for the ϕ rotation ($\phi = 0$). For the wavelength of 1.2992 Å, selected by a double-bounce Si 111 monochromator, the Bragg angle of the $\bar{2}26$ reflection is very close to $\pi/4$. The divergences were limited by slits and estimated as $14''$ (vertical) and $27''$ (horizontal).

Two three-BDs were analyzed, one that has a strong secondary wave ($R = 1.334$) produced by the $\bar{3}\bar{1}3 + 113$ reflections (B and C reflections in Fig. 1) and another with a much weaker secondary wave ($R = 0.332$) from the $226 + \bar{4}00$ reflections. The latter is a very extreme case since at $\chi = 50.8°$ the 226 reflection is a polarization forbidden reflection ($\upsilon_d = 0$) [15]. Only the *Aufhellung* effect will be observed at this polarization. For both three-BDs, the ϕ scans as a function of χ, the simulated curves obtained by Eq. (3), and the respective values of Ψ_T and a are shown in Fig. 2. The observed smooth variation of a with χ reflects the instrumental dependence of R with the χ rotation of the incident x-ray optics.

In Fig. 3 there is a comparison between the triplet phases extracted from the ϕ scans in Fig. 2 by two different theoretical approaches: (i) one that assumes diffracted waves fully coherent as in the standard 2nd-order Born approximation, Eq. (1), and (ii) the modified approach introduced above, Eq. (3), that allows one to simulate the kinematical and *Aufhellung* effects onto the profiles of ϕ scans. In the case of the $\bar{3}\bar{1}3 + 113$ three-BD, a polarization-independent triplet-phase value (Ψ_T^{exp}), of $66.5(\pm 1.5°)$, is obtained by eliminating only the systematic errors due to kinematical diffraction. As can clearly be seen, the errors are so significant that make the standard approach useless for phase determination. When the distortion of the profile due to the positive symmetrical contribution of $I_\wedge(\phi)$ is ignored in Eq. (1), the values of Ψ_T are shifted in order to compensate for the distortion. In the other case, the $226 + \bar{4}00$ three-BD, it was also necessary to consider the *Aufhellung* correction ($b' \neq 0$) in order to obtain a near constant value of the triplet phase, $\Psi_T^{exp} = 4.5(\pm 3.5)°$. It is interesting to note that in scan No. 4, shown in Fig. 2(b) with $\chi = 28°$, the distortion of the profile due to both effects cancel each other, i.e., $I_\wedge(\phi) = 0$, and then, both the standard and the modified approaches provide the same Ψ_T value.

The results presented above clearly demonstrate that it is possible to obtain very accurate phase values from the

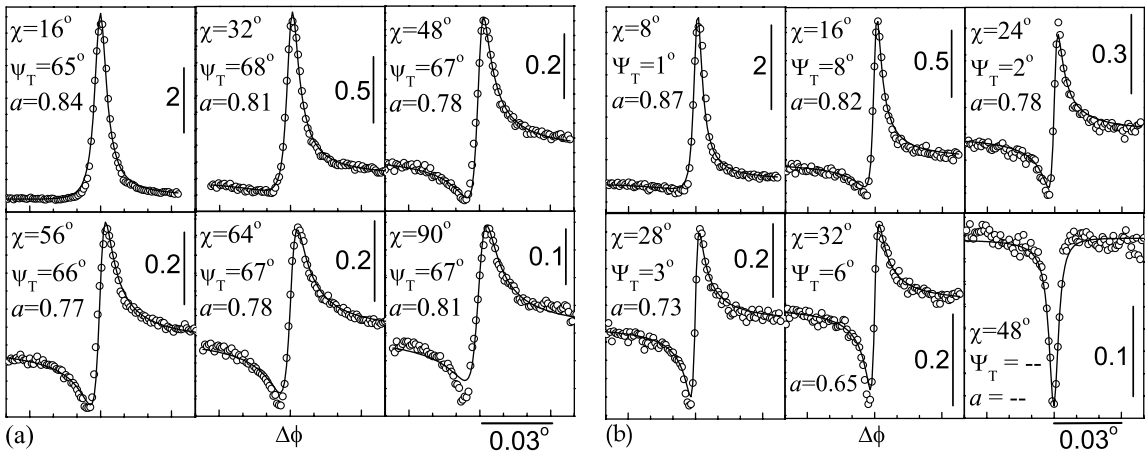

FIG. 2. Experimental (open circles) and simulated (solid lines) ϕ scans of the $\bar{3}\bar{1}3 + 113$ (a) and $226 + \bar{4}00$ (b) three-BDs as a function of the polarization angle (χ). Simulated curves were generated by Eq. (3). The improvement of the fitting is driven by the mean-absolute deviation of the data. The best-fit values of Ψ_T and a are shown at the left-hand side of each scan, while the vertical scale is at the right. The base line is normalized to the unit. $b = 0$ in (a) and $b' = 0.7$ in (b) with $r_B = 0.039$ and $r_C = 0.961$. The center of the curves as well as their widths (w) were optimized for each scan. Other relevant values: experimental intensity ratios, $R = 1.334$ (a) and $R = 0.332$ (b); expected polarizations for optimizing phase sensitivity, $\chi = 60°$ (a) and $\chi = 12.5°$ (b); azimuthal positions, $\phi_0 = 80.807°$ (out/in) (a) and $\phi_0 = 29.452°$ (in/out) (b); theoretical triplet phases, $\Psi_T^{theo} = 62°$ (a) and $\Psi_T^{theo} = 0°$ (b).

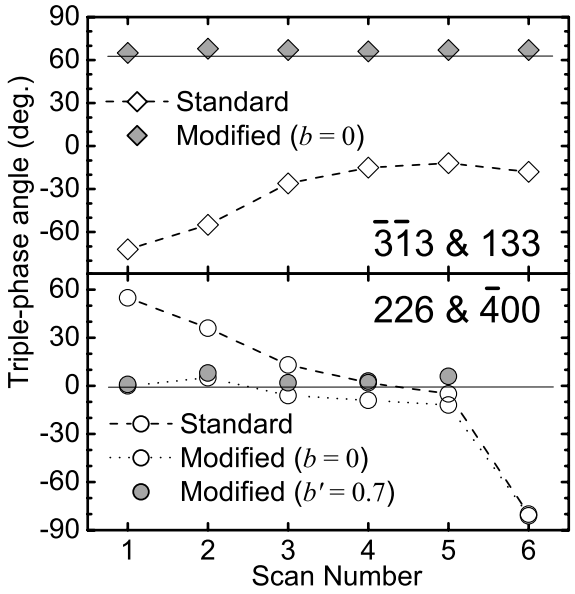

FIG. 3. Comparison of the triplet-phase angles obtained from fitting the ϕ scans in Fig. 2 by the *standard* 2nd-order Born approximation, Eq. (1), and its *modified* form, Eq. (3). The horizontal solid lines show the expected values, Ψ_T^{theo}. The scan number refers to the different polarizations where the ϕ scans were measured, as ordered in Fig. 2. In Eq. (3), $b = 0$ corrects systematic errors due to kinematical diffraction only, while $b' \neq 0$ allows some corrections for the *Aufhellung* effect. Data fitting with Eq. (1) is carried out by adjusting Ψ_T and the intensity ratio (R), or equivalently, Ψ_T and a in Eq. (4). The fit quality is exactly the same as those obtained by Eq. (3). When $b' \neq 0$, no phase value can be assigned to scan number 6 (226 + $\bar{4}00$) because it contains no phase information. It is a pure *Aufhellung*.

three-BD interference profiles. The modified approach for kinematical corrections is essential to the accuracy of these results. The attenuation of the interference term for simulating the loss of coherence, mainly due to kinematical diffractions, is a general concept and must be considered for most crystals. What may change from one crystal to another is the line profile functions describing the contribution of the a and b parameters in $I_\Lambda(\phi)$. *Aufhellung* corrections are also necessary in some cases, although its systematic errors are minimized when the scattering plane is close to the horizontal, i.e., $\chi \approx 0$.

Enhanced triplet-phase determination, with the accuracy reported here, leads to new methods for structural study of crystalline materials, where fine features of the structures are probed by selecting a few suitable reflections. For instance, even the small discrepancy between the theoretical, 62°, and experimental, 66.5(±1.5)°, triplet-phase angles of the $\bar{3}\bar{1}3$ + 113 three-BD is significant for an error bar of ±1.5°. In this case, it indicates that the cloud of charge due to shared electrons in the covalent bounds increases (decreases) the average x-ray scattering around the Ga (Sb) atoms. Since the Ga donates three and the Sb donates five electrons to the cloud, and the contribution of the cloud to the scattering at either atomic site is even, the net charge (core + cloud/2) around each site is better represented by Sb^{+1} and Ga^{-1}. By transferring one scattering charge unit from the Sb to the Ga atoms, the theoretical triplet-phase value raises to 66°.

In the content of this Letter there are three very important points that we now highlight: (i) the inclusion of an attenuation parameter for the interference term in the 2nd-order Born approximation of the three-BD; (ii) the use of the $\pi/2$ scattering geometry for a direct measurement of the intensity ratio R. No previous knowledge of the structure factor is therefore required. For other scattering angles different from $\pi/2$, R can be obtained by simultaneously fitting a polarization-dependent set of ϕ scans; (iii) the phasing technique proposed here seems to have the highest precision ever presented for direct measuring reflection phases. The precision can still be improved by using a better-conditioned incident beam and by elaborating more flexible equations for data simulation and sophisticated algorithms for fitting the dataset.

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