Solving the Phase Problem Using Reference-Beam X-Ray Diffraction

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A new method of obtaining Bragg reflection phases in an x-ray diffraction experiment is presented. It combines the phase-sensitive principles of multiple-beam diffraction and x-ray standing waves, and allows direct phase measurements of many multiple reflections simultaneously using a Bragg-inclined oscillating-crystal geometry. A modified-two-beam intensity function is devised to extract the phase information in a way similar to the standing wave analyses. [S0031-9007(98)05790-1]

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X-ray diffraction and scattering techniques are used widely in structural studies of crystalline materials. These techniques provide real-space charge density information by probing its Fourier components, or structure factors, in reciprocal space. In a typical diffraction experiment, what one measures is the intensity of a scattered or diffracted beam, which is related only to the structure factor *amplitude* and not to its *phase*. This loss of phase information is the classic *phase problem* in diffraction physics and crystallography, and its solution remains the most difficult part of a crystal structure determination [1].

To date, all practical methods leading to solutions of the phase problem in crystallography can be grouped into two categories. In the first category are various mathematical techniques, such as the direct methods [2,3]. These methods rely largely on the overdetermination in the intensity measurements of a great number of Bragg reflections and use a probability distribution of possible phases to solve a crystal structure. While very powerful for small molecule structures, application of these statistics-based mathematical methods to larger crystal structures remains to be difficult and is still an active area of research. In the second category of crystallographic methods are various chemical methods involving heavy-atom derivatives and replacements [4], using x-ray dispersion corrections in the heavy-atom scattering factor in either single- or multiple-wavelength anomalous diffraction [5]. With these chemical methods, a crystal structure is solved by the additional phase information provided by the heavy-atom substructure. In general, the chemistry-based techniques often require complex and time-consuming chemical treatments to bond heavy atoms in proteins and other biological systems.

In recent years, there have been considerable efforts to find a *physical* solution to the phase problem, namely, to obtain the phases of the Fourier components directly from diffraction experiments. One promising physical solution is the multiple-beam Bragg diffraction [6–9], which is based on the interference among simultaneously excited Bragg reflections. The effect has been shown visible both for small molecule compounds [10,11] and for complex crystals such as quasicrystals [12] and proteins [13,14]. The conventional technique for performing such an experiment involves exciting one Bragg reflection **H** and then rotating the crystal around the scattering vector **H** to bring another reflection **G** into its diffraction condition [15]. Reflection **H** is called the main reflection and **G** the detour reflection (*umweganregung*). This one-reflection-at-a-time measurement method limits seriously the practical implications of the multiple-beam diffraction technique and makes it almost impossible to measure a large number of phases that are required to solve a complex crystal structure.

In this Letter, we present a reference-beam x-ray diffraction method for obtaining both the phases and the magnitudes of a large number of Bragg reflections. The method is based on the same multiple-beam diffraction principle but with the important distinction that a single *umweganregung* serves as the reference beam and is common to all recorded multiple Bragg reflections. This is achieved by incorporating features in x-ray standing wave experiments as well as in common crystallographic data collection techniques. The combined result allows straightforward phase-sensitive diffraction measurements of a large number of reflections with a well-controlled phase variation of the reference Bragg beam.

To introduce the reference-beam diffraction technique, it is helpful to review how a normal crystallographic x-ray diffraction experiment is performed. By far, the most popular way of collecting crystallographic data is the rotating or oscillating crystal method [1]. In this method, a crystal is rotated around an axis perpendicular to the incident beam and the Bragg reflection diffraction data are collected on a two-dimensional detector such as a photographic film, an image plate (IP), or a charge-coupled device (CCD), as shown in Fig. 1(a). In reciprocal space, the sphere of reflection (Ewald sphere) sweeps through a volume of a toroid during a full 360° rotation and every reciprocal lattice point in this volume is set to diffract at a certain rotation angle.

The new reference-beam diffraction technique uses almost the same geometry as the standard oscillation method, *except* that the rotation axis is aligned along a reference Bragg reflection **G**, which is brought to its

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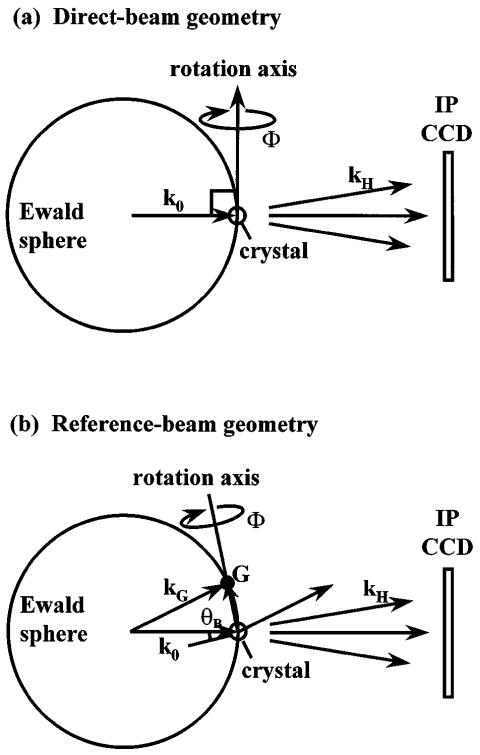

FIG. 1. (a) Conventional crystallographic x-ray diffraction technique using direct-beam rotating crystal method with an IP or a CCD detector. (b) New reference-beam diffraction technique allows simultaneous measurements of both the intensities and the relative phases of all Bragg reflections recorded on the same two-dimensional detector.

diffraction condition, as shown in Fig. 1(b). We will call this the Bragg-inclined geometry. Since the crystal rotation axis coincides with **G**, the reference reflection is always excited during the rotation or oscillation, therefore *all* of the reflections recorded on the two-dimensional detector are, in fact, multiple-beam excitations and their intensities are affected by the interference with the reference beam, much like in a hologram. The reciprocal space volume that the sphere of reflection sweeps through is very similar to that in the standard rotation case, and, therefore, a similar large number of reflections can be measured.

The basic concepts shown in Fig. 1 can be easily visualized using the standard scattering theories in quantum mechanics and electrodynamics [16,17]. A scattered x-ray wave field $\mathbf{D}(\mathbf{r})$ from a crystal can be represented by a Born approximation series, with its zeroth-order solution $\mathbf{D}^{(0)} = \mathbf{D}_0 \exp(-i\mathbf{k}_0 \cdot \mathbf{r})$ being the incident wave, the first-order solution $\mathbf{D}^{(1)}$ being a singly scattered wave in the usual kinematic or two-beam approximation, and the second-order solution $\mathbf{D}^{(2)}$ representing a doubly scattered detoured wave with three-beam interactions, and so on [18]:

$$\mathbf{D}(\mathbf{r}) = \mathbf{D}^{(0)} + \mathbf{D}^{(1)} + \mathbf{D}^{(2)} + \cdots . \tag{1}$$

It can be seen immediately that the direct-beam rotating crystal geometry in Fig. 1(a) is based on observing the two-beam reflections $\mathbf{D}^{(1)}$ with the rotation axis lined up on the incident beam $\mathbf{D}^{(0)}$, while the Bragg-inclined geometry in Fig. 1(b) is set up automatically to observe the three-beam interactions $\mathbf{D}^{(2)}$ with the rotation axis chosen to diffract a reference beam $\mathbf{D}^{(1)}$.

In general, if $\mathbf{D}^{(1)}$ is the diffracted wave for **H** reflection and $\mathbf{D}^{(2)}$ is the detour-diffracted wave through **G** and **H**-**G** reflections, it can be shown [18] that, apart from a scale factor, the diffracted wave $\mathbf{D}_\mathrm{H}$ up to the second order can be expressed as

$$\mathbf{D}_\mathrm{H} = \hat{\mathbf{k}}_\mathrm{H} \times \left[\hat{\mathbf{k}}_\mathrm{H} \times F_\mathrm{H} \left(\mathbf{D}_0 - \Gamma \frac{F_\mathrm{H\text{-}G} F_\mathrm{G}}{F_\mathrm{H}} \frac{\mathbf{k}_\mathrm{G} \times (\mathbf{k}_\mathrm{G} \times \mathbf{D}_0)}{k_0^2 - k_\mathrm{G}^2} \right) \right], \tag{2}$$

where $\Gamma = r_e \lambda^2 / \pi V_c$; $r_e = 2.818 \times 10^{-5}$ Å is the classical radius of an electron; λ is the x-ray wavelength; V_c is the unit cell volume; F_H, F_G, and $F_\mathrm{H\text{-}G}$ are the structure factors; and $\mathbf{k}_\mathrm{G} = \mathbf{k}_0 + \mathbf{G}$, $\mathbf{k}_\mathrm{H} \equiv k_0 \hat{\mathbf{k}}_\mathrm{H} = \mathbf{k}_0 + \mathbf{H}$ are the wave vectors of the reflections involved. The two terms in Eq. (2) correspond to $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$, respectively. Equation (2) demonstrates that the three-beam interference between $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$ depends on the relative phase difference $\delta_\mathrm{HG} = \alpha_\mathrm{G} + \alpha_\mathrm{H\text{-}G} - \alpha_\mathrm{H}$, where α_H's are simply the phases of the corresponding structure factors. This phase difference δ_HG is called the *invariant triplet phase* in crystallography since it is independent of the choice of origin in the unit cell.

In the Bragg-inclined reference-beam diffraction geometry, a complete interference profile of each recorded Bragg reflection is obtained by varying the relative phase of the **G**-diffracted beam. This is accomplished by rocking the crystal through the Darwin width of the **G** reflection, causing a phase change of π, in a way analogous to that used in the x-ray standing wave technique [19]. It should be noted that the role of the **G** reflection in the new reference-beam diffraction technique is switched from that in the conventional multiple-beam azimuthal scanning method. Here, the reference **G** reflection is the detour reflection, and each reflection measured on the two-dimensional detector is actually the main reflection **H**. All of these main reflections have the **G** reflection as the common *umweganregung*. It illustrates one of the main advantages of the reference-beam diffraction technique: A single reference **G** reflection provides a common perturbation and a common dynamical phase shift of π, determined by $k_0^2 - k_\mathrm{G}^2$, on all main reflections. Therefore, any differences in their interference profiles are due purely to the values of the triplet phases δ_HG.

We have performed a synchrotron x-ray diffraction experiment on a GaAs single crystal to demonstrate

the reference-beam diffraction principle. The experiment was done at the C1 station of the Cornell High Energy Synchrotron Source (CHESS), using unfocused bending-magnet monochromatic radiation of 13.5 keV with an incident beam size of 0.25×1 mm^2. The crystal was a 5-mm-thick rectangular-shaped plate and was mounted at the center of a standard four-circle diffractometer. The reference reflection **G** was chosen to be the symmetric (004) and it was aligned parallel to the ϕ axis of the diffractometer, which served as the oscillation axis in the vertical diffraction plane. The rocking curve of the (004) was controlled by the θ-rotation axis of the diffractometer.

A Fuji image plate was mounted on the 2θ detector arm to collect the oscillating-crystal diffraction patterns. A series of oscillation exposures with the same rotation range of $\Delta\phi = 20°$ were taken at 16 different θ settings across the (004) rocking curve. The rocking range of $\Delta\theta = 0.045°$ was about seven times the measured full width at half maximum of the (004) rocking curve [shown in Fig. 2(d)]. To minimize the possible systematic readout errors in image plates, all 16 exposures were recorded on a single image plate by slightly translating the image plate after each θ movement, similar to a streak camera. Each 20° oscillation took about 40 s. During the exposure, the incident beam intensity was monitored by an ionization chamber to ensure that the incident beam variations were taken into account. A portion of the diffraction image recorded on image plates is shown in Fig. 2(a) which covers a 2θ range from 5° to 103°.

A magnified view of the recorded (317) Bragg reflection is shown in the inset of Fig. 2(a). Each rectangular spot in the image corresponds to a given θ step in the **G**-reflection rocking curve. The reference-beam interference profile is essentially the intensity distribution along the strip as a function of θ, and can be seen clearly in the raw data without any processing. Such peak-and-valley interference profiles exist on *all* recorded reflections. To further quantify the interference profile, we integrate the intensities around each spot and plot the integrated intensities as a function of the θ steps, as shown in Fig. 2(b). For comparison, a rocking curve of the reference (004) reflection is shown in Fig. 2(d) on the same θ scale.

The reference-beam interference profile in Fig. 2(b) can be understood by using the perturbation theory of Eq. (2). In our experiment, the incident x-ray beam is linearly polarized with $\mathbf{D}_0$ perpendicular to the scattering plane defined by $\mathbf{k}_0$ and **G**. In this case, Eq. (2) reduces to the following simple form:

$$\mathbf{D}_{\mathrm{H}} = F_{\mathrm{H}}\mathbf{D}_{0\perp}\left(1 + \left|\frac{F_{\mathrm{H\text{-}G}}F_{\mathrm{G}}}{F_{\mathrm{H}}}\right|\frac{\Gamma e^{i\delta_{\mathrm{HG}}}}{2\sin 2\theta_{\mathrm{G}}\Delta\theta}\right), \quad (3)$$

where $\mathbf{D}_{0\perp}$ is the projection of $\mathbf{D}_0$ onto a plane perpendicular to $\mathbf{k}_{\mathrm{H}}$, and we have used Bragg's law for **G** reflection and have written explicitly the δ_{HG} dependence. Equation (3) indicates that when the grazing angle θ changes from less to greater than the Bragg angle, $\Delta\theta$ changes from negative to positive, and, thus, a destructive (constructive) interference always occurs at the low (high) angle side, *unless* δ_{HG} provides an additional phase shift to compensate it. Therefore, by examining the experimental data in Fig. 2(b), we conclude that δ_{HG} for the (317)/(004) three-beam reflection has to be around zero. This conclusion is confirmed both by the perturbation calculation using Eq. (3), shown as the dashed curve in Fig. 2(b), and by a full three-beam dynamical calculation using NBEAM approach [6], shown as the solid curve.

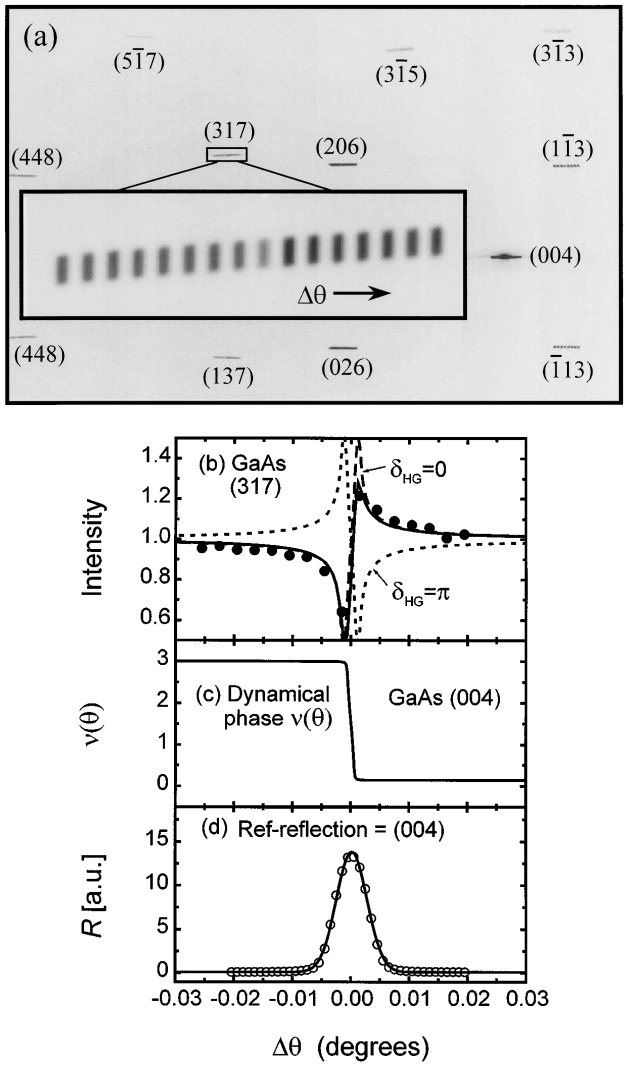

FIG. 2. (a) Recorded image-plate oscillation-diffraction data of the GaAs crystal at 16 θ positions across the (004) rocking curve. The inset shows a magnified view of the (317) reflection. (b) Integrated intensities (filled circles) of the 16 spots for the (317), as a function of θ. The solid curve is a three-beam dynamical calculation with $\delta_{\mathrm{HG}} = 0°$, and the dashed and the dotted curves are calculated using Eq. (3). (c) Dynamical phase shift $\nu(\theta)$ of the (004), calculated using the standard two-beam dynamical theory. (d) Measured (004) rocking curve plotted on the same θ scale and fitted with a Gaussian profile.

The multiple-beam diffraction analyses in the new reference-beam geometry can be made entirely analogous to that in the x-ray standing wave method. To remove the singularity at $\Delta\theta = 0$ in Eq. (3), we use the finite reflectivity $R(\theta)$ and the phase shift $\nu(\theta)$ of D_G/D_0 in the usual two-beam dynamical theory [19] for **G** and substitute $1/\Delta\theta$ with $\sqrt{R(\theta)}\, e^{i\nu(\theta)}/w$, where w is the Darwin width of the **G** reflection. Squaring the modulus of Eq. (3) and keeping only the linear term in Γ, we obtain a normalized three-beam interference intensity as

$$I_H = 1 + \left| \frac{F_{H\text{-}G}}{F_H} \right| \sqrt{R(\theta)} \cos[\delta_{HG} + \nu(\theta)]. \quad (4)$$

A plot of $\nu(\theta)$ for the GaAs (004) as calculated in the standard two-beam dynamical theory is shown in Fig. 2(c). Apparently, Eq. (4) is the x-ray standing wave effect of the **G** reflection on another Bragg reflection **H**. Because three-beam diffraction is a coherent process, the effect is somewhat different from the standing wave intensities that govern the incoherent fluorescence yield. Equation (4) is used in Fig. 2(b) to produce the perturbation calculations for two different triplet phase values: $\delta_{HG} = 0$ and π. The calculation with $\delta_{HG} = 0$ agrees very well both with the experimental data and with the more rigorous NBEAM calculation.

In addition to the simplified multibeam analysis and the ability to measure the phases of many Bragg reflections in a simple manner, the new reference-beam diffraction method also reduces the need for the high angular incident-beam collimation perpendicular to the vertical scattering plane. The reason for this is that the reference reflection **G** can always be set to diffract in the vertical plane where the natural collimation of the synchrotron radiation is best. Complications on the three-beam interference due to polarization mixing [20,21] are also eliminated as shown by Eq. (3). Furthermore, the phase of the reference beam can be varied by changing the incident x-ray energy instead of rocking the crystal. In this way, the data collection for reference-beam diffraction can be made as routine as other crystallographic techniques such as the multiwavelength anomalous diffraction [5], without the need for heavy atoms.

In summary, we have presented a simple reference-beam x-ray diffraction technique to measure many Bragg reflection phases directly from an oscillating-crystal diffraction experiment. A single detour reflection common to all measured Bragg reflections is used as the reference beam, and its phase is varied by either rocking the crystal or changing the incident beam energy. This allows a straightforward analysis similar to that used in the x-ray standing wave method. Additional experiments are under way to employ this new technique on more complex crystal systems. With further research and development, we believe that the new method can become a powerful and ultimate technique for solving the phase problem in crystallography and diffraction physics.

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