



Phase Determination Using X-ray Multi-beam Diffraction

To determine a crystal structure, the information about the magnitudes and the phases of the structure factors is required. Ordinary 2-beam X-ray diffraction could only give us the magnitudes. The missing information of phase in the ordinary diffraction process prevents us from reconstructing the structure factors. In contrast, the coherent dynamical interaction of X-rays in a crystal involved in multiple diffraction, provides a direct means to extract the phase information from multiply diffracted intensity measurements. This multi-beam diffraction method for phase determination can be utilized to analyze the crystal structure of complicated systems, such as thin films and macromolecules.

The three-dimensionality of a single-crystal makes possible the occurrence of X-ray multiple diffraction in crystals. That is, two or more sets of atomic planes can be brought simultaneously into position to diffract an incident beam. In reciprocal space, more than two reciprocal lattice (r.l.) points are rotated onto the surface of an Ewald sphere at the same time. Usually, the rotation involves the Bragg angle, θ (or ω), of a given reflection and the azimuth angle, ψ , around the reciprocal lattice vector of the same reflection. In analogy with optical holography, each diffracted beam of multiple diffraction can be treated as a reference beam for the others and the interference among the diffracted beams gives rise to intensity variation of each diffracted beam, which provides phase information for the structure-factors involved. Various diffraction geometries, accompanied with different detector systems, for generating multiple diffraction have been developed, including Renninger (azimuthal) scan, Kossel diagram,

reference-beam, stereoscopic imaging/detection, and others. Since the geometry for multiple diffraction depends on both the crystal lattice and the wavelength used, a large variety of experiments and investigations could be carried out with synchrotron radiation. In this article we report on the development of multi-beam diffraction techniques for phase determination of X-ray in-plane reflection from single-crystal and thin films and then extended to wide-angle reflection from macromolecular crystals.

The geometry of multiple diffraction is shown in Fig.1. The crystal is first aligned for a given (primary) reflection G and is then rotated around the r.l. vector \vec{g} ($=OG$) of the G -reflection to bring additional r.l. point, say L , of a secondary reflection L onto the surface of the Ewald sphere (Fig. 1), where O stands for the direct reflection. This crystal rotation along \vec{g} is the Renninger scan or ψ -scan. During the scan, the diffracted intensity I_G of the primary reflection G is monitored by a scintillation counter, a point detector. The interaction of the direct incident wave O , the primary reflected G and the secondary reflected L gives rise to intensity variation ΔI_G on I_G . The resultant intensity I_G versus the azimuth angle ψ around \vec{g} is usually called the multiple diffraction (MD) pattern. The interaction causing ΔI_G involves the interference of the primary reflected G -beam and the detoured consecutive reflection, first L -reflection then the G - L coupling reflection. Therefore, ΔI_G depends on the structure-factor triplet, $F(L)F(G-L)/F(G)$, which is a function of the structure factors F 's of all three involved reflections. In other words, ΔI_G provides information about the triplet phase $\delta_3 =$

$\delta(L) \delta + (G-L) - \delta(G)$, where δ 's are the phases of the individual structure factors F 's.

Three-beam diffraction involving in-plane reflection, similar to diffraction in a 2-D crystal lattice, cannot be generated by crystal-rotation as for bulk crystals (shown in Fig.1), mainly because grazing incidence geometry needs to be maintained for carrying out 2-D diffraction. Under this geometrical condition tuning the wavelength across a specific λ_c , or the energy E_M , at grazing incidence is equivalent to the crystal-rotation for a bulk and the involved r. l. points must lie on the equatorial circle of the Ewald sphere.

The experiments are carried out at the SRRC using the 1.8 tesla, 22-pole wiggler beamline, BL-17B1. The storage ring is operating at 1.5 GeV and 200 mA. The incident beam is focussed by a mirror and then monochromatized by a silicon sagittal double-crystal monochromator (SDCM). The beam divergences are 0.02° vertical and 0.04° horizontal. The crystal sample is placed at the center of an 8-circle Ψ Huber diffractometer.

The sample studied is a 90 \AA thick $\text{Ge}_{0.9}\text{Si}_{0.1}$ thin film grown on the $(\bar{1}11)$ surface of a 500 \AA thick Ge substrate. Fig. 2a shows the experimental setup. The $[\bar{1}11]$ of GeSi/Ge is nearly perpendicular to the plane of incidence. The σ -polarized radiation of the energy E near $E_M=7.1571 \text{ keV}$ is incident on the sample at the angle close to the critical angle 0.30° of total external reflection. The surface specularly diffracted (440) and (404) waves are monitored by two scintillation counters placed near/at $2\theta=120^\circ$ and -

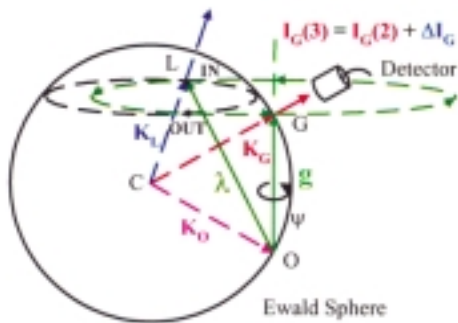


Fig. 1: Geometry of multiple diffraction. C denotes the center of the Ewald sphere; O is the origin of reciprocal lattice space. K_0 , K_G and K_L stand for incident, primary diffracted and secondary diffracted wavevectors, respectively. When both G and L are located on the surface of the Ewald sphere, a three-beam diffraction condition is satisfied.

120° and the scattering angle $\alpha = \beta = 0.3^\circ$. The ω -scan, the rotation of the sample around the $[\bar{1}11]$, is employed to measure the reflections from both GeSi and Ge. Fig. 2b displays the pair of the ω -scans of (440) and (404) reflections for $E=7.1527 \text{ keV}$. The broad profiles are the diffraction intensity distributions of (440) and (404) reflections from the film, while the sharp peaks, A and C, on top of the broad profiles are the corresponding (404) and (440) of the Ge substrate, respectively. The small kinks, B and D, are due to the four-beam interactions involving $(404)_F$, $(404)_S$, $(440)_F$, and $(440)_S$ reflections, where S and F stand for substrate and thin film, respectively. Since the reflections from the substrate act only as intermediate to enhance the multi-beam interaction in the thin film, these four-beam diffractions can be treated as three-beam cases, i.e., (A) $(404)_F/(440)_F$; (B) $(440)_F/(440)_F$;

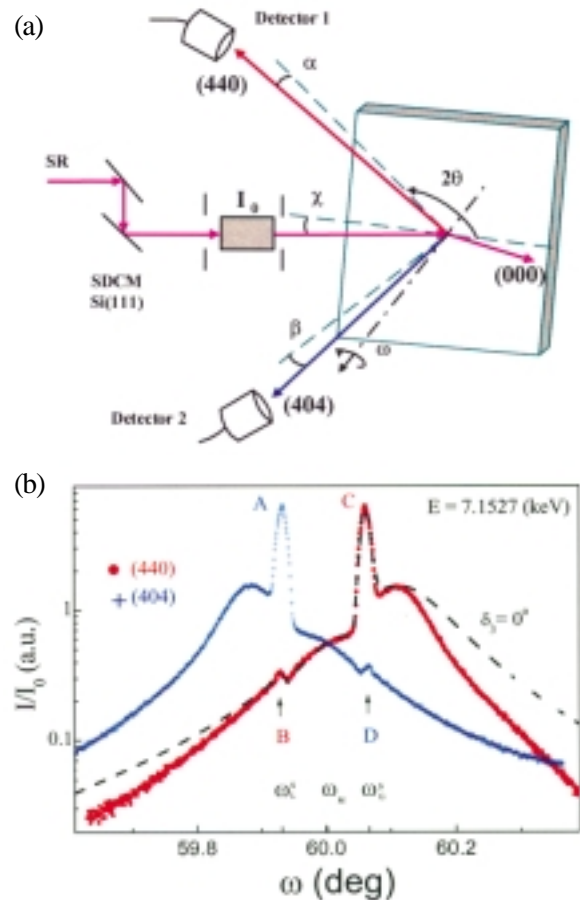


Fig. 2: (a) Experimental setup for three-beam GIXD. The incident angle α is fixed at 0.3° ; both (440) and (404) diffracted beams are monitored simultaneously. (b) The intensity variation of GeSi/Ge (440) and (404) diffracted beams during ω -scans.



(C) (440)F/(404)F; and (D) (404)F/(440)F. The intensity variations ΔI_G are, as stated in Sec.1, related to the triplet phase δ_3 . For centrosymmetric crystals like Ge and GeSi/Ge, δ_3 is either 0° or 180° . With the asymmetry of the profile shown in Fig. 2b, the triplet phase is determined as $\delta_3 = \delta(\bar{4}\bar{4}0F) + \delta(404F) + \delta(04\bar{4}F) = 0^\circ$. Based on the known sample symmetry, we obtained individual phase factor $\delta_3(\bar{4}\bar{4}0F) = \delta(404F) = \delta(04\bar{4}F) = 0$.

The intensity profiles of multiple diffraction, shown in Fig. 2b are obtained one at a time using a point detector. It is very time consuming. The detection of a large collection of diffraction profiles, which is necessary for crystal-structure analysis, is almost impossible because macromolecular crystals deteriorate quickly under X-ray exposure. The use of ω -scan to obtain multiple diffraction profile for in-plane reflection inspired us to apply it in generating a large number of multiple diffraction in macromolecular crystals. By considering the enantiomorph involved in macromolecules, we proposed a stereoscopic oscillation-crystal imaging technique at multiple diffraction geometry. Consider two inversion-symmetry related (ISR) three-beam diffractions, (O, G, L) and $(O, -G, -L)$, in 3-D lattices. For each

of the three-beam cases, say (O, G, L) , the intensity of the secondary L reflection (or the primary G reflection) is considered as a reference background for revealing the interference between the primary G and the secondary L reflection. Therefore, the crystal needs to be brought first to the vicinity of the Bragg angle, θ_G , of the G -reflection and is then rotated around an axis perpendicular to the plane of incidence of the G -reflection by the Bragg angle scan, the ω -scan, across the exact Bragg diffraction position for the primary G reflection. For each ω angle in the ω -scan, the crystal needs to be rotated around the r. l. vector \vec{g} of the G reflection, the azimuthal Ψ -scan, to bring the reciprocal point of the L reflection to cross the surface of the Ewald sphere, thus generating multiple diffraction. The recorded intensity variation on the reference background of the L reflection versus ω (or the angular deviation $\Delta\theta$ from the Bragg angle θ_G of the G -reflection) is a multiple diffraction profile.

Tetragonal hen-egg white lysozyme crystals are mounted on an eight-circle Huber diffractometer. The diffracted beams of the L -reflections are recorded in an image plate IP set about 10 cm from the crystal and parallel to OG . The same procedure is taken also for the oscillations around the $-OG$. The speed of oscillation is $0.125^\circ/\text{sec.}$, the oscillation range is 2° , and the total exposure time for each image is 102 seconds. Fig. 3 shows typical four-beam multiple diffraction patterns, $I_{Ll}(\Delta\theta)$ and $I_{Ll}(\Delta\theta)$, for two ISR cases $(000; 200; 12, 2, \bar{1}; \bar{1}0, 2, \bar{1})$ and $(000; \bar{2}00; \bar{1}\bar{2}, \bar{2}, 1; 10, \bar{2}, 1)$ of lysozyme at $\lambda = 1.24 \text{ \AA}$.

For the non-centrosymmetric crystals, such as lysozyme, δ_3 can be determined quantitatively. The phase δ_{est} estimated from the experimental results and the values $\delta_{3(\pm Ll)}$ calculated from the known structure are indicated in Fig. 3. They are in good agreement with each other.

We have successfully demonstrated that multi-beam diffraction can be applied to determine the phases of X-ray reflections from thin films and macromolecular crystals. The coherent interference among multiply diffracted beams in the crystal is the key for the success in the direct measure of phase.

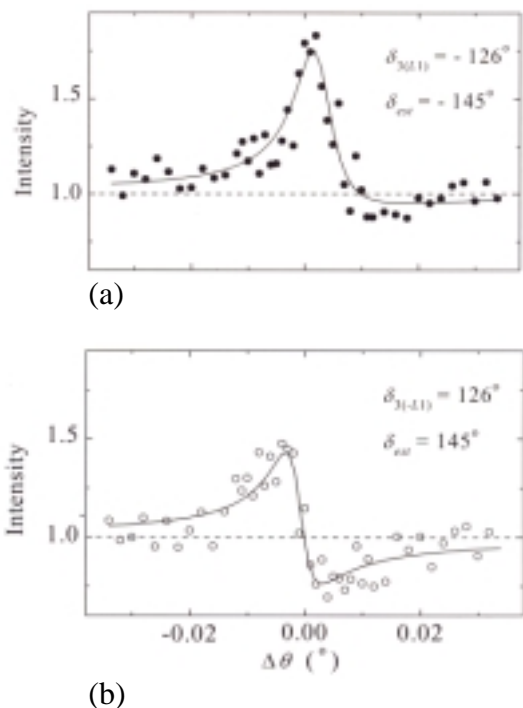


Fig. 3: Four-beam diffraction profiles of two ISR cases for hexagonal lysozyme.

Beamlines:

15B1 Tender X-ray beamline

17B1 Wiggler beamline

SPring-8 BL12B2 beamline

Experimental Stations:

Soft X-ray diffractometer

8-circle diffractometer

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Publications:

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