3.014 Materials Laboratory
Fall 2006

Background for Laboratory 2: Modules γ_1, γ_2

<u>Diffraction from Materials</u>
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Diffraction describes the perturbation of the propagation of wave motion when the wave encounters an object with different properties from the medium in which the wave is normally propagating. It is a subset of the more general phenomenon of scattering, for example the scattering of accelerated subatomic particles by nuclei that is explored by nuclear physicists or the scattering of visible light photons from surfaces of objects in a field of view into the retina of our eyes that gives us a visual impression of our surroundings. The utility of diffraction—or scattering— phenomena in general is that it is by the interaction of electromagnetic waves (like light or X-rays) or particles (like electrons or neutrons or He nuclei) that we learn about the constituents of matter and its internal organization. This is of crucial importance to a materials scientist who wishes to understand the fundamental atomic-scale origins of useful physical properties of solids (like strength, deformation and fracture, electrical conduction, magnetic response) that underlie both traditional historical uses and more modern applications in ubiquitous 21st-century devices. To the extent that moving particles can be considered as having wave-like properties (the "wave-particle duality" in modern physics), the two phenomena of diffraction and scattering are in essence the same and can be treated with the same formalism and with the same result.

These 3.014 experimental modules are designed to acquaint you with the diffraction phenomenon and its potential for elucidating structure in solid materials. This introduction provides background information common to each. More detailed treatments can be found in the set of laboratory notes on waves and diffraction by Professor Hobbs or his book *Diffraction Principles and Materials Applications* (Case Western Reserve University, 1981), copies of which resides on the shelf above the diffractometer.

A diffraction experiment consists of a source of waves, an object, and a wave detector. A wave is a disturbance in a medium that propagates in space and time. The most interesting and useful waves are disturbances that repeat regularly in space and time—that is, that are periodic. The spatial period is known as the wavelength λ, while the *inverse* of the time period is called the frequency ν. The inverse of the spatial period is also a useful representation, known as the *wave vector* **k**, that can be used to describe at the same time both the wavelength and the direction of wave propagation

$$\mathbf{k} = (1/\lambda)\, \hat{\mathbf{k}}, \qquad\qquad (1)$$

where $\hat{\mathbf{k}}$ is a unit vector along the direction of wave propagation. The "momentum" of a propagating wave (first described in 1923 by the French physicist Prince Louis-Victor de Broglie) is

$$\mathbf{p} = h\mathbf{k}, \tag{2}$$

where h $= 6.6 \times 10^{-34}$ J s is Planck's constant (after the German physicist Max Planck, inventor of quantum mechanics in 1900), so that $\mathbf{k}$ is really a momentum vector. Notice that $\mathbf{k}$ is measured in units of inverse length and is therefore best represented in a space, called *reciprocal space*, which has dimensions of inverse length.

In diffraction, a wave (as represented by its wave vector) incident on an object (Fig. 1) is scattered by the object through some angle Θ, called the diffraction angle, into a wave propagating into direction $\hat{\mathbf{k}}'$, where it is registered by a detector. The vector difference between incident and diffracted waves is called the diffraction vector $\mathbf{\kappa}$, which—provided that the wavelength is not altered in the scattering process—is given geometrically by

$$\mathbf{\kappa} = \mathbf{k}' - \mathbf{k} = (1/\lambda)(\hat{\mathbf{k}}' - \hat{\mathbf{k}}) = 2\sin(\Theta/2)/\lambda. \tag{3}$$

How small a component in an object from which we can infer information by diffraction (say, the smallest dimension along the *x* axis) is governed by a quantum-mechanical limit of knowability, known as the *Heisenberg Uncertainty Principle* (after German physicist Werner Heisenberg's 1927 revelation). The Uncertainty Principle states that we can simultaneously know information about the momentum p_x in a given direction and position *x* along that direction—in this case of our investigating wave—only to the precision
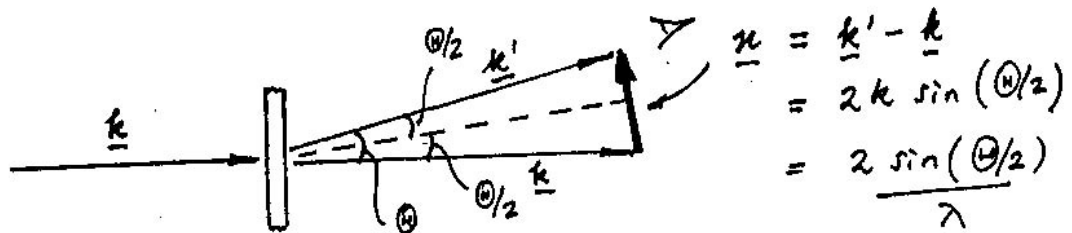
$$\delta p_x \bullet \delta x > h. \tag{4}$$

Substituting (2) and (3) into (4) yields

$$h\,\delta k_x \bullet \delta x = h\,(\pm\kappa_x)\cos(\Theta/2) \bullet \delta x = (h[\pm 2\sin(\Theta/2)\,/\,\lambda]\cos(\Theta/2) \bullet \delta x$$
$$= h\,(1/\lambda)\,4\sin(\Theta/2)\cos(\Theta/2) \bullet \delta x = h\,2\sin\Theta/\lambda \bullet \delta x > h \tag{5}$$

or

$$\delta x > \lambda/2\sin\Theta. \tag{6}$$

Since the maximum value of $\sin\Theta$ is 1, the *minimum* object component size that can be investigated has dimensions $\sim\lambda/2$, or half the investigating wave's wavelength. This is a fundamental limitation. It explains why light microscopes ($\lambda \sim 0.5$ μm) are not generally configured for magnifications beyond 1000×, and why electron microscopes using fast electrons ($\lambda \sim 2\text{-}4$ pm) are required to obtain images at the atomic scale ($x \sim 100$ pm).

The diagram shows an incident wave vector $\underline{k}$ passing through a plate, producing a diffracted wave vector $\underline{k}'$ at angle $\Theta/2$, with the diffraction angle Θ and the diffraction vector $\varkappa$.

$$\underline{\varkappa} = \underline{k}' - \underline{k}$$
$$= 2k \sin\left(\Theta/2\right)$$
$$= \frac{2 \sin\left(\Theta/2\right)}{\lambda}$$

Fig. 1 Definition of diffraction vector κ and diffraction angle Θ

The amplitude of the scattered wave is determined by the nature of the interaction between the internal components of the object and the incident wave. The strength of the interaction at some point r_j in the object can be characterized by the *scattering factor* $f_j(\Theta)$, which measures the amplitude of the scattered wave (relative to an incident wave of unit amplitude) emanating from that point. The strength of interaction with matter may be large (as for electrons or light) or small (as for X-rays or thermal neutrons). The interaction strength operationally governs from how small a volume information may be extracted (from as small as a single large atom to a tens of atoms for electron waves, millions of atoms for X-rays, tens of millions of atoms for thermal neutrons) because of the necessity to accumulate a statistically significant detector signal.

The information appearing on the exit-face surface of an object illuminated by a wave source is known as the *transmission function of the object* $\Phi(x,y)$, which recounts point-by-point the changes in phase and amplitude of the incident wave effected by its interactions with constituents of the object as it traverses the object along the z direction. These changes could, in principle, be detected with spatial resolution given by the Uncertainty Principle using a suitably microscopic incident probe or similarly microscopic exit-face detector system (such as a magnifying imaging system focusing on the exit face, as is done in electron microscopes at atomic resolution and in light microscopes at micrometer resolution). A *distant* observer or detector, however, records a very different picture. This is because waves emanating from different points on the object exit face interfere with each other as they continue to propagate (Fig. 2).

For a wave source located far from the object (this ensures that the wave is a *plane* wave) and a similarly distant detector, what appears at the detector is an intensity pattern known as the *Fraunhofer diffraction pattern* that corresponds to a *Fourier transformation* of $\Phi(x,y)$. Fourier transformation (named after its late 18th c. originator, French mathematician J. B. J. Fourier) is a mathematical operation that takes information in real space—such as constituent identities and positions—over into reciprocal space. A distant observer can reference the emitting object only by the *angular* relationship between the direction of the incident wave ψ (that would be detected in the absence of the object), as represented by its wave vector $\mathbf{k}$, and the direction of the diffracted wave ψ', which starts out as $\psi' = \psi \, \Phi(x,y)$ at the exit face of the distant object and propagates to the observer along a direction represented by $\mathbf{k'}$. Hence, the observer's *position* is defined by the angular relationship $\mathbf{\kappa} = \mathbf{k'} - \mathbf{k}$ in (3), which means that the observer's position is defined in reciprocal space $\mathbf{\kappa}$. The diffracted intensity observed is

$$I'(\mathbf{\kappa}) \;=\; |\, \mathscr{F}\{\psi \, \Phi(x,y)\}\,|^2 \qquad\qquad (7)$$

where $\mathscr{F}$ indicates the Fourier transform operation and $|\;|^2$ indicates the intensity of the transform. The Fourier transform $\mathscr{F}\{\Phi(x,y,z)\}$ of the real-space details of the object—as deduced by the investigating wave ψ—is thus what is in principle retrievable. Because the *intensity* of the diffracted wave, and not its separate amplitude and phase, is what is generally measured, $\mathscr{F}\{\Phi(x,y,z)\}$ cannot in general be inverse-transformed to retrieve

Fig. 2   One dimensional derivation of the Fraunhofer diffraction result
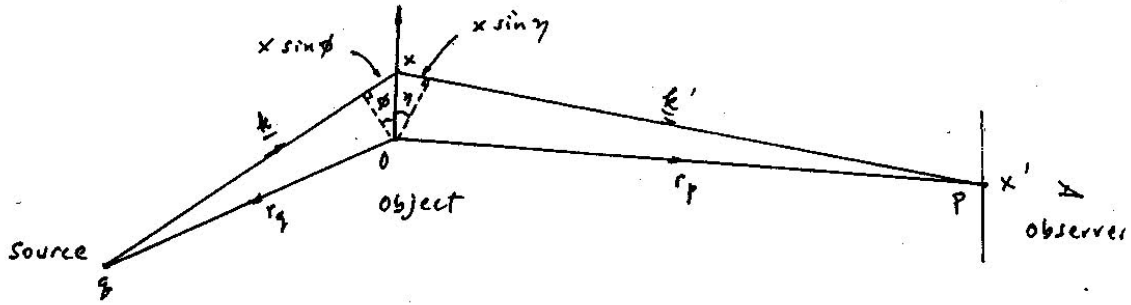
$$r_q(x) = r_q + x \sin\phi \qquad \text{for } r_q \text{ large, } r_q \to \infty$$
$$r_p(x) = r_p + x \sin\eta \qquad \text{for } r_p \text{ large, } r_p \to \infty$$

$$k\, r_q(x) = kx \sin\phi = \mathbf{k} \cdot \mathbf{x}$$
$$k\, r_p(x) = kx \sin\eta = -\mathbf{k'} \cdot \mathbf{x}$$

$$\Psi' = \int \Phi(x)\, \Psi\, (1/r_p)\, \exp(2\pi i\, k r_p')\, dx$$

$$= \int \Phi(x)\, (A_q/r_q)\, \exp[2\pi i\, k r_q(x)]\, (1/r_p)\, \exp[2\pi i\, k r_p(x)]\, dx$$

$$= (A_q/r_q)\,(1/r_p) \int \Phi(x)\, \exp(2\pi i\, \mathbf{k} \cdot \mathbf{x})\, \exp(-2\pi i\, \mathbf{k'} \cdot \mathbf{x})$$

$$= (A_q/r_q)\,(1/r_p) \int \Phi(x)\, \exp[-2\pi i\, (\mathbf{k'} - \mathbf{k}) \cdot \mathbf{x}]\, dx$$

$$= (A_q/r_q)\,(1/r_p) \int \Phi(x)\, \exp(-2\pi i\, \boldsymbol{\kappa} \cdot \mathbf{x})\, dx \; .$$

Thus,

$$\Psi'(\kappa_x) = (A_q/r_q)\,(1/r_p)\, \tilde{\Phi}\,(\kappa_x)$$

the object transmission function $\Phi(x,y,z)$. This difficulty is known as the *phase* problem, and the attempt to inverse transform the diffracted intensity

$$\mathscr{F}^{-1}\{I'(\mathbf{\kappa})\} = \int \Phi(x-x',y-y',z-z')\,\Phi(x',y',z')\,dx\,dy\,dz = \Phi(x,y,z) * \Phi(-x,-y,-z) \quad (8)$$

yields what is known as a Patterson function involving a convolution (the "*" operation in (8), discussed below) of the transmission function with itself inverted through the origin, which represents the object as viewed through itself and not $\Phi(x,y,z)$ as viewed directly by a proximate observer.

Some properties of the Fourier transform operation can be easily demonstrated optically, using the laser diffractometer (*see* Fig. 11) set-up that uses macroscopically accessible diffraction phenomena to provide hands-on experience with the Fourier transform operation. What is most important to note, and most easily demonstrable, is the inverse relationship of the two spaces: large distances or dimensions in real space transform to small distances or dimensions in reciprocal space. If a large but almost infinitely distant luminous object (like a star) is viewed, the distant observer sees a(n infinitesimally small) point of light. The two spaces, real and reciprocal, also act as if they were rigidly fixed to each other: rotating one space similarly rotates the other space. A third notable property is that the diffraction process, in which an intensity is observed, introduces a *center of inversion symmetry* to the diffraction pattern where none may be present in the original object.

Constituents of an object that are repeated in space, such as identical atoms in a monatomic solid, contain both positional and transmission-function information, $\phi(x,y,z)$. These are separable in diffraction space. If $D(\mathbf{r}) = \Sigma_n\ \delta(\mathbf{r}-\mathbf{r}_n)$ represents the *positions* of identical atoms at $\mathbf{r}_n$, where the δ function

$$\delta(\mathbf{r}-\mathbf{r}_n) = \begin{cases} \infty & \text{when } \mathbf{r} = \mathbf{r}_n \\ \\ 0 & \text{when } \mathbf{r} \neq \mathbf{r}_n \end{cases} \qquad (9)$$

identifies (emphatically!) an atom position at $\mathbf{r} = \mathbf{r}_n$, and $\phi(\mathbf{r})$ represents their (identical) *atom transmission functions*, then the transmission function of the whole solid

$$\Phi(\mathbf{r}) = D(\mathbf{r}) * \phi(\mathbf{r}) \qquad (10)$$

is given by another mathematical operation called convolution, which reproduces $\phi(\mathbf{r})$ at every position $\mathbf{r}_n$. The convolution representation is useful because the Fourier transform

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[1]Actually, such a distant source effectively functions as a point source, emitting light in all directions, but an astronomer can collect its emitted light only over a small solid angle—defined for example by the diameter $2r$ of the telescope lens used for observation, over which small distance the light wave resembles a plane wave. Aperturing the optics in this way converts what should be a point-like image of the star at the image plane (magnified M times) into a larger disk of intensity, of width (at half maximum intensity) of about $M(1/2r)$, accompanied by a weaker set of concentric rings around the central disk. This function, called the Airy function after the 19th c. English astronomer-Royal Sir George Airy, is the Fourier transform of the effective lens aperture.

of a convolution of two functions is the product of their individual transforms:

$$\mathscr{F}\{\Phi(\mathbf{r})\} = \mathscr{F}\{D(\mathbf{r})\} \cdot \mathscr{F}\{\phi(\mathbf{r})\}. \tag{11}$$

That is, the diffraction pattern from the array of points in space (*i.e.* a set of δ functions) representing atom *positions* and the diffraction pattern from an *individual atom* transmission function are *superimposed* on each other, with the same origin at $\boldsymbol{\kappa} = 0$ in reciprocal space.

The Fourier transforms of a δ function $\delta(\mathbf{r}-\mathbf{r}_n)$ at $\mathbf{r} = \mathbf{r}_n$ and of a set of such position functions $\{\Sigma_n\ \delta(\mathbf{r}-\mathbf{r}_n)$ are respectively

$$\mathscr{F}\{\delta(\mathbf{r}-\mathbf{r}_n)\} = \exp(-2\pi i\ \boldsymbol{\kappa}\cdot\mathbf{r}_n)$$

$$\mathscr{F}\{\Sigma_n\ \delta(\mathbf{r}-\mathbf{r}_n)\} = \Sigma_n \exp(-2\pi i\ \boldsymbol{\kappa}\cdot\mathbf{r}_n). \tag{12}$$

The Fourier transform of the transmission function of a single atom, which corresponds to the Fraunhofer amplitude of a unit wave diffracted from a single atom *j*

$$\psi_j{}'(\boldsymbol{\kappa}) = \mathscr{F}\{\phi_j(\mathbf{r})\} \equiv f_j(\boldsymbol{\kappa}), \tag{13}$$

is the *scattering factor* f_j for that atom and clearly depends on the nature of the interaction between the incident wave (which could be X-rays or electron or thermal neutron particle waves) and the atom, as represented by the atom transmission function ϕ_j. Since $\boldsymbol{\kappa} = 2 \sin(\Theta/2)/\lambda$ from (3), f can also be represented as a function of diffraction angle, $f(\Theta)$, and represents the angular distribution of scattered amplitude from an atom. The Fraunhofer diffraction wave amplitude from a collection of (possibly different) atoms,

$$\psi'(\boldsymbol{\kappa}) = \mathscr{F}\{\Sigma_j\ [\phi_j(\mathbf{r}) * \delta(\mathbf{r}-\mathbf{r}_j)]\} = \Sigma_j f_j(\boldsymbol{\kappa}) \exp(-2\pi i\ \boldsymbol{\kappa}\cdot\mathbf{r}_j) \equiv F(\boldsymbol{\kappa}), \tag{14}$$

is called the *structure factor* if the summation in (14) is carried out over the atoms of the unit cell of a crystal with $\mathbf{r}_j$ the positions of atoms within the unit cell.

A crystal, which is a collection of N unit cells stacked upon each other (Fig. 3), can be represented by a set of δ functions representing the positions of the unit cells

$$D_n(\mathbf{r}) = \Sigma^N{}_{n=1}\ d(\mathbf{r}-\mathbf{r}_n) \tag{15}$$

which represent a lattice of points in space known as the *real lattice*. The Fourier transform of real lattice of unit cells
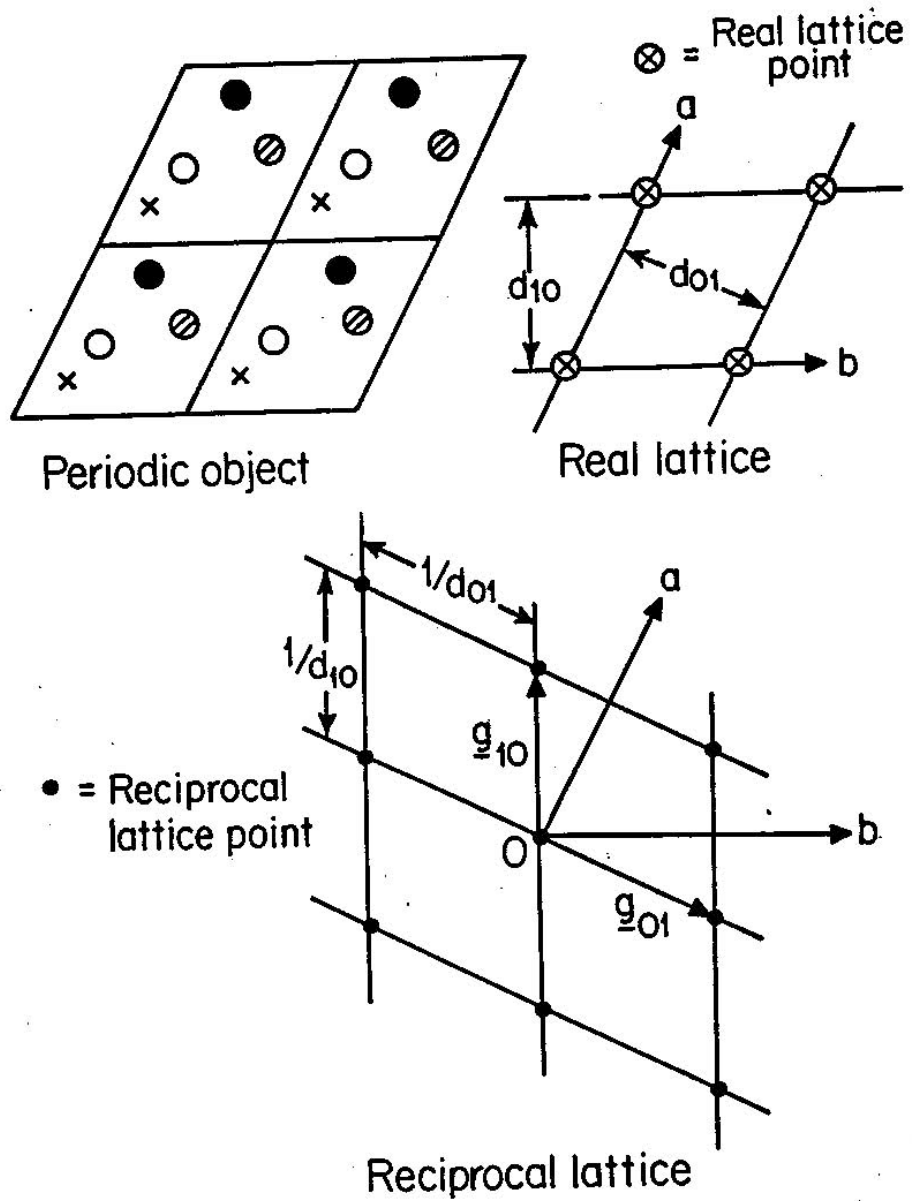
Fig. 3 Real and reciprocal lattices associated with a periodic object (crystal).

$$\mathscr{D}(\boldsymbol{\kappa}) \;=\; \mathscr{F}\{\Sigma^{N}_{n=1} \; d(\mathbf{r}-\mathbf{r}_{n}) \} \;\; =\Sigma^{N}_{n=1} \; \exp\,(-2\pi i \; \boldsymbol{\kappa}\bullet\mathbf{r}_{n}) \qquad (16)$$

converges to another periodic set of δ functions at positions $\boldsymbol{\kappa}_{n}$ in reciprocal space, called the *reciprocal lattice*

$$\mathscr{D}_{\infty}(\boldsymbol{\kappa}) = \Sigma_{n} \; \delta(\boldsymbol{\kappa}-\boldsymbol{\kappa}_{n}) \;, \qquad (17)$$

for $N \rightarrow \infty$ (a very large crystal). The reciprocal lattice is thus the Fourier transform of the real lattice and is a property of a given Bravais lattice type (face-centered cubic, body-centered tetragonal, *etc.*). Because the real and reciprocal lattices act as if rigidly fixed together, there is a convenient geometric way to relate the two (suggested in 1850 by the 19th-century French mining engineer, Auguste Bravais, who also classified the 14 possible crystal lattice types that bear his name). A periodic array of points in 3-space defines set of parallel *planes* (Fig. 4) that contain varying densities of those points and are defined by the *inverses* of their intersections $u^{-1}a$, $v^{-1}b$, $w^{-1}c$ with the principal axes $\mathbf{a,b,c}$ of the unit cell chosen. A planar set is represented by the set of integers (*hkl*) obtained when all fractions are removed by multiplying each reciprocal intersection value by the lowest common multiple in *uvw*; (*hkl*) are called the Miller indices (after William Hallowes Miller (1801-1880), a British mineralogist and crystallographer). That they are represented by *inverse* distances already transforms their representation into one of reciprocal space! The spacing d_{hkl} of a given set of planes depends on the values of (*hkl*) and the crystal structure. For example, for a cubic crystal with lattice parameter a,

$$d_{hkl} \;=\; a \; (h^{2} + k^{2} + l^{2})^{-1/2} \;. \qquad (18)$$

Because the planar spacing d_{hkl} is measured normal to the (*hkl*) planes, one way to construct the reciprocal lattice from the real lattice is to (starting from a common origin $\boldsymbol{\kappa}$ = 0) measure out multiples of d_{hkl}^{-1} along these planar normals and erect a reciprocal lattice point $\mathbf{g}$ at each multiple. In this way, each real lattice set of planes (*hkl*) corresponds to a reciprocal lattice point

$$\mathbf{g}_{hkl} = h\mathbf{a}^{*} + k\mathbf{b}^{*} + l\mathbf{c}^{*} \qquad (19)$$

where $\mathbf{a}^{*}$, $\mathbf{b}^{*}$ and $\mathbf{c}^{*}$ are unit vectors along the principal axes of the reciprocal lattice. The length of this reciprocal lattice vector is

$$|\mathbf{g}_{hkl}| \;= d_{hkl}^{-1} \qquad (20)$$

For example, the (246) set of planes, which are parallel to but have *half* the spacing of the (123) planes, corresponds to the reciprocal lattice vector

$$\mathbf{g}_{246} \;=\; 2\mathbf{a}^{*} + 4\mathbf{b}^{*} + 6\mathbf{c}^{*} \;=\; 2(\mathbf{a}^{*} + 2\mathbf{b}^{*} + 3\mathbf{c}^{*}) \;=\; 2\mathbf{g}_{123}$$

at *twice* the distance from the reciprocal space origin along the same direction. A simple analysis shows that a simple cubic real lattice with lattice parameter a transforms to a
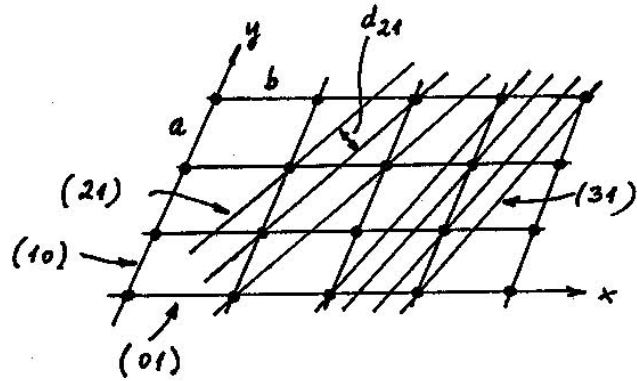
Fig. 4 Some planes in a two-dimensional lattice. The (21) plane divides a unit length of the x-axis into two parts and a unit length of the y-axis into one. The spacing d of planes in a set of planes in directly related to its indices and the characteristic unit lengths a,b along each axis. The latter are called lattice parameters.

simple cubic reciprocal lattice with lattice parameter a^{-1}; a body-centered cubic real lattice becomes a face-centered cubic reciprocal lattice and *vice versa*. Some sets of planes (*hkl*) are crystallographically equivalent to other sets of planes (*h'k'l'*), for example (100), (010) and (001) in a cubic crystal for which a cubic unit cell is chosen with orthogonal principal axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of equal length *a*. This can easily be seen in reciprocal space, where the equivalent reciprocal lattice points are related by the symmetry elements of the lattice (in this example, by the 4-fold rotation axes coincident with the orthogonal principal axes **a*,b*,c***). Such families of equivalent planar sets are designated {*hkl*} (but only in the cubic system can they be readily obtained by simply transposing the indices, as in the above example!).

The Fraunhofer intensity diffracted from a very large crystal is, using (7), (14) and (20),

$$I'(\boldsymbol{\kappa}) = |\psi'(\boldsymbol{\kappa})|^2 = |\mathscr{F}\{D_\infty(\mathbf{r}) * \psi\Phi_{\text{unit cell}}(\mathbf{r})\}|^2 = |\psi|^2 |\mathscr{D}(\boldsymbol{\kappa}) \bullet F(\boldsymbol{\kappa})|^2 \quad (21)$$

which is just the pattern of the reciprocal lattice modulated by the structure factor. The intensity at each reciprocal lattice point therefore depends on the details of structure factor $F(\boldsymbol{\kappa})$, which depends on where and what kind of atoms are located in the unit cell. Note in particular that whenever the structure factor $F(\boldsymbol{\kappa}) = 0$ there will be no intensity, and that for an infinite perfect crystal there will be no intensity appearing between the reciprocal lattice points. How, then, is this reciprocal-space intensity distribution sampled by the observer (or detector)? The answer was first provided by the German physicists Max von Laue and his student P. P. Ewald in 1915. Since diffracted intensity appears only at the reciprocal lattice points, the observer must clearly reside at the positions

$$\boldsymbol{\kappa} = \mathbf{g} \quad\quad\quad\quad\quad\quad (22)$$

where **g** is a reciprocal lattice vector. The condition (22) is known as the Laue condition. Ewald deduced from simple geometry, and using $\boldsymbol{\kappa} = \mathbf{k}' - \mathbf{k}$ from (3), that if one draws the incident wave vector **k** in the proper orientation (Fig. 5), terminating at the origin of reciprocal space (*i.e.* at the reciprocal lattice point $\boldsymbol{\kappa} = 0$), and constructs a sphere of radius $|\mathbf{k}| = \lambda^{-1}$ centered on the beginning of the **k** vector, then that sphere (called the Ewald sphere, which must necessarily pass through $\boldsymbol{\kappa} = 0$) will also intersect another reciprocal lattice point **g** whenever the Laue condition $\boldsymbol{\kappa} = \mathbf{k}' - \mathbf{k} = \mathbf{g}$ is satisfied. The wave then traveling along direction **k'** represents a strongly diffracted "beam" at the discrete angle Θ defined between **k** and **k'**. These strongly diffracting discrete orientations physically represent a condition where all the unit cells are scattering exactly in phase.

The Ewald construction shows that the reciprocal space is sampled by the detector *along the surface of the Ewald sphere*. As the angle the incident wave makes with the object is varied (either by rotating the object or by changing the source position), the Ewald sphere rolls on the point $\boldsymbol{\kappa} = 0$, sampling other parts of reciprocal space along its surface. For a crystal with its largest planar spacings d_{hkl} of the same order as the
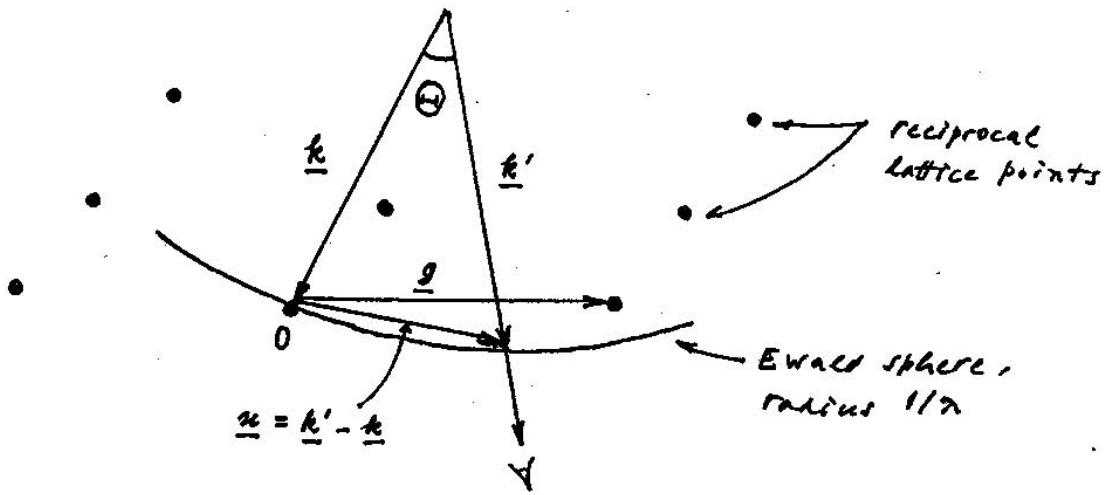
(a)
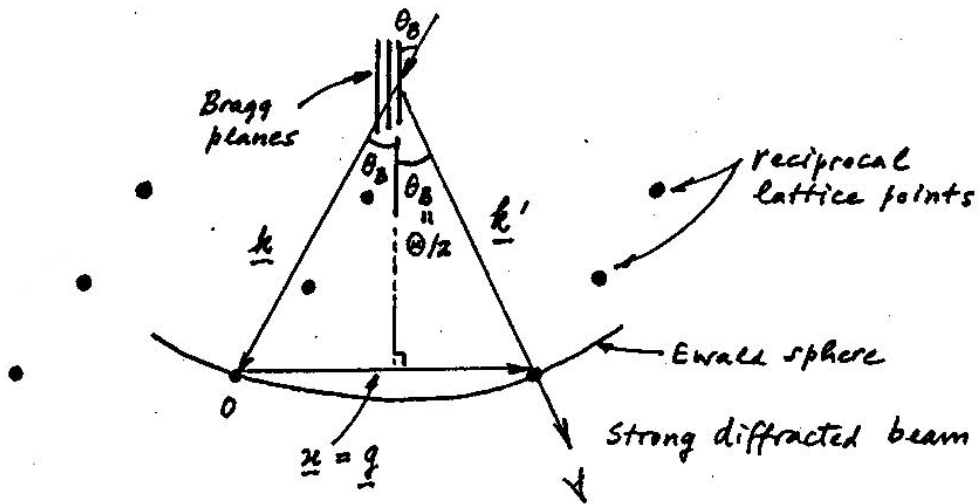
(b)

Fig. 5 Ewald construction a) removed from the Laue condition, and b) at the Laue condition.

wavelength λ of the interrogating wave, the distances between reciprocal lattice points and the radius ($= \lambda^{-1}$) of the Ewald sphere are comparable, and the sphere must be rotated through large angles (~tens of degrees) in order to guarantee an intersection with a reciprocal lattice point and generation of a strongly diffracted "beam" along $\mathbf{k'}$ (Fig. 6a). A mechanical device for accomplishing this rotation is a *diffractometer*, an example of which is the X-ray diffractometer ($\lambda = 154$ pm) utilized in experiment 2, modules β_1, β_2 and γ_1, for which $\lambda \sim d$. For the case that $\lambda << d$, which occurs in the diffraction of He-Ne laser light ($\lambda = 632.8$ nm) from macroscopic objects with $d \sim$ a few mm (and also in the diffraction of energetic electrons from crystals, for which $\lambda \sim 2$ pm and $d \sim 100$ pm), the Ewald sphere radius is large compared to reciprocal lattice point spacings, and therefore the Ewald sphere appears nearly planar. In this case, a whole plane of the reciprocal lattice can be sampled at once, with small (~1°) diffraction angles Θ and many beams collectible simultaneously on a fixed flat-plate detector.

The relationships (3) and (20) may be combined to reformulate the Laue reciprocal-space condition (22) into a real-space diffraction criterion, first put forward in 1913 by the father-son pair of English physicists, Sir William H. and Sir W. Lawrence Bragg, as follows:

$$|\mathbf{k'} - \mathbf{k}| = (1/\lambda)\,|\hat{\mathbf{k}}' - \hat{\mathbf{k}}| = 2\sin(\Theta/2)/\lambda = g_{hkl} = d_{hkl}^{-1} \qquad (23)$$

whereupon rearranging (23)

$$\lambda = 2\,d_{hkl}\sin(\Theta'/2) = 2\,d_{hkl}\sin(\theta_B) \qquad (24)$$
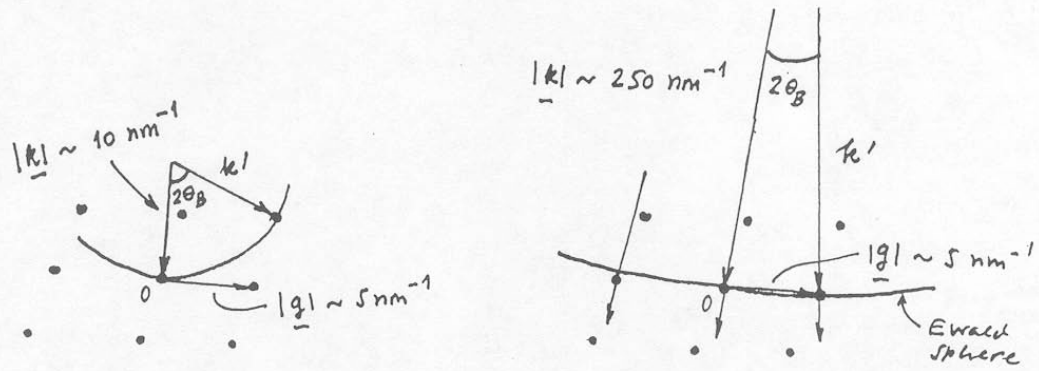
where θ_B is known as the Bragg angle and (24) is known as Bragg's Law. This criterion suggests that an incident wave can be envisaged as "reflecting" off a given set of parallel planes, as from a mirror with equal incident and reflection angles θ (Fig. 7), but only when incident upon those planes at the discrete Bragg angle

$$\theta_B = \sin^{-1}(\lambda/2d_{hkl}). \qquad (25)$$

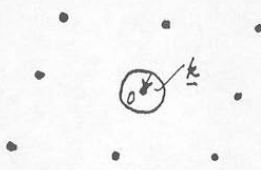The corresponding total diffraction angle for strong scattering is then

$$\Theta' = \theta_B + \theta_B = 2\theta_B. \qquad (26)$$

Note that, in a conventional diffractometer, (26) implies that the crystal sample must be rotated through angles θ, while the detector must be simultaneously rotated through angle $\Theta = 2\theta$. Because θ_B must necessarily be $\leq \pi/2$, spacings $d_{hkl} < \lambda/2$ are therefore not detectable and are said to be beyond the Bragg limit (the Ewald sphere is too small to intersect *any* reciprocal lattice points $\mathbf{g} > 0$, Fig. 6c). Regrettably, the "mirror" analogy has been assumed by many students (and too many of their mentors!) as proof of the condition (26) in a real-space derivation of the Bragg law. In fact, it takes more than a page of vector algebra to *prove* that the incident and "reflected" angles are equal in the most general case. This fact falls right out of the reciprocal-space Laue construction, however, because $\mathbf{g}$ lies along the normal to the diffracting planes, and the "Bragg"

$|\underline{k}| \sim 10 \; nm^{-1}$

$\underline{k}'$

$2\theta_B$

0

$|\underline{g}| \sim 5 \, nm^{-1}$

(a)

$|\underline{k}| \sim 250 \; nm^{-1}$

$2\theta_B$

$\underline{k}'$

0

$|\underline{g}| \sim 5 \, nm^{-1}$

Ewald sphere

(b)

$\underline{k}$

0

(c)

Fig. 6   Scale of the Ewald sphere for a) X-rays, b) fast electrons, c) light.
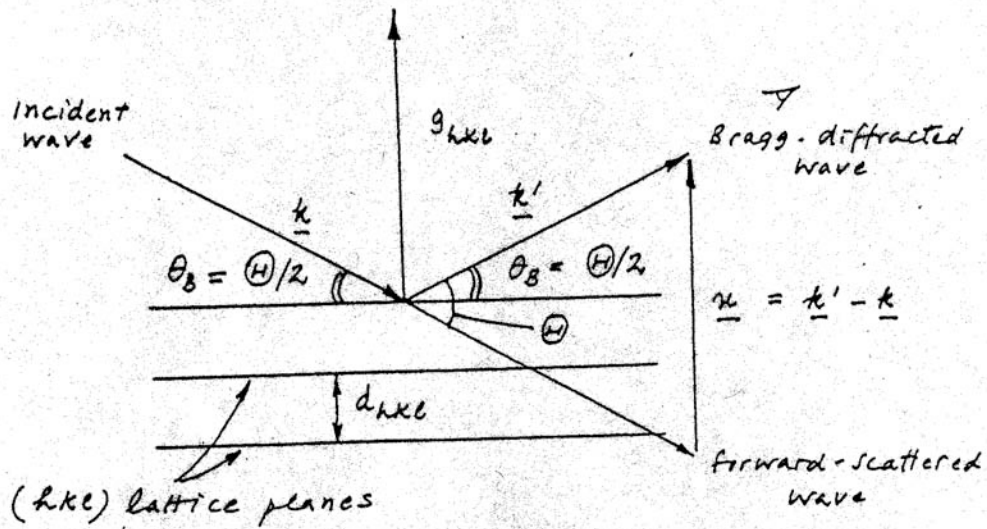
Fig. 7 Bragg diffraction from real-space lattice planes. The incident wave appears to be reflected from a set of planes (hkl) at the Bragg angle $\theta_B = \Theta/2$.
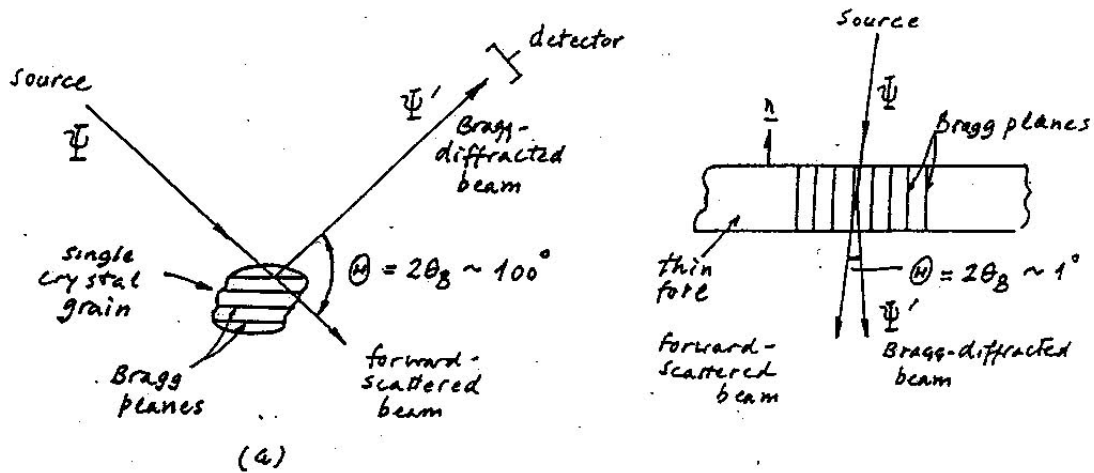

Fig. 8 Electron diffraction geometry for a) X-ray and b) fast electrons. The Bragg "reflecting planes" are nearly parallel to the electron beam.

planes therefore bisect Θ at the Laue condition, yielding the Bragg condition (25). Note, too, that even though atoms may not *physically* exist on identifiable higher-order planes (for example, on (200) "planes" of a simple monatomic cubic crystal which recur with half the (100) unit-cell spacing), nevertheless the higher-order Bragg peaks (for this example, (200), (300), (400) *etc.* multiples) still occur, because the reciprocal lattice extends forever.

The derivation of the distribution of diffraction intensity $I'(\mathbf{\kappa})$ in (21) assumes an infinite crystal, which is a clearly always an unrealized assumption. We can nonetheless retain the simplicity of (21) for finite crystals, by defining a "*shape" function*

$$S(\mathbf{r}) = \begin{cases} 1 & \text{when } \mathbf{r} \le \mathbf{R} \\ \\ 0 & \text{when } \mathbf{r} > \mathbf{R} \end{cases} \tag{27}$$

where $\mathbf{R}(x,y,z)$ represents the spatial extent of the finite crystal (*e.g.* a grain in a polycrystalline solids in an X-ray diffraction experiment, Fig. 8a; or the film thickness for thin transmission electron microscopy specimens, Fig. 8b). The finite real lattice of the crystal may then be represented as the product of the infinite real lattice and the shape function

$$D(\mathbf{r}) = D_\infty(\mathbf{r}) \bullet S(\mathbf{r}) \tag{28}$$

whose Fourier transform is the convolution of the individual transforms

$$\mathscr{D}(\mathbf{\kappa}) = \mathscr{F}\{D_\infty(\mathbf{r}) \bullet S(\mathbf{r})\} = \mathscr{D}_\infty(\mathbf{\kappa}) * \mathscr{F}\{S(\mathbf{r})\} \tag{29}$$

Hence, the shape transform $\mathscr{F}\{S(\mathbf{r})\} = \mathscr{S}(\mathbf{\kappa})$—the Fourier transform of the shape of the crystal—appears at *every* reciprocal lattice point, extending every reciprocal lattice point (Fig. 9) and consequently broadening the angular width $\Delta\Theta' = \Delta2\theta_B$ of each Bragg "peak" in a plot of $I'(\Theta)$ against Θ. For a parallelopiped crystal with dimensions A,B,C, for example, the shape transform is the damped sine function (in fact, the Airy function, Fig. 9a)

$$\begin{aligned} \mathscr{S}(s_x) &= A^{-1} \sin(2\pi s_x x)/2\pi s_x x \\ \mathscr{S}(s_y) &= B^{-1} \sin(2\pi s_y y)/2\pi s_y y \\ \mathscr{S}(s_z) &= C^{-1} \sin(2\pi s_z z)/2\pi s_z z \end{aligned} \tag{30}$$

with width at half amplitude given by A^{-1}, B^{-1} and C^{-1} along the x, y and z axes passing through a reciprocal lattice point that misses intersecting the Ewald sphere by an amount $\mathbf{s}$ (called the deviation parameter) whose components are s_x, s_y and s_z. Crystallite dimensions can therefore be estimated by systematically measuring the size and shape of any broadened reciprocal lattice point, for example in a diffractometer by keeping the detector fixed at $\Theta' = 2\theta_B$ and varying θ by rotating the crystal alone (a "rocking curve"); or keeping the crystal fixed at $\theta = \theta_B$ and scanning the detector angle Θ (Fig. 10). These
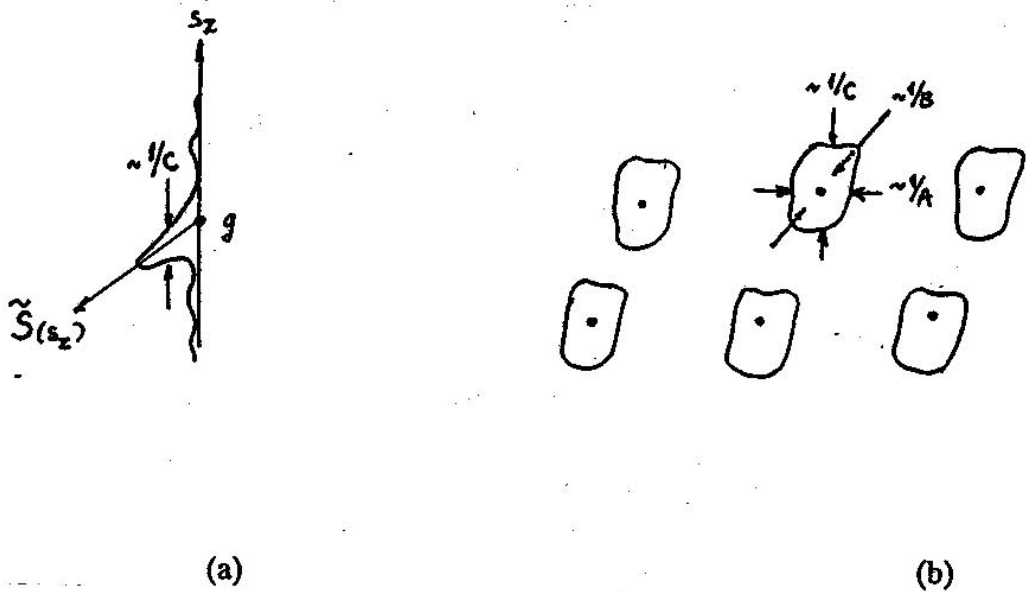
Fig. 9   a) Form of $\tilde{S}(s_z)\,\tilde{S}(s_z)$ and b) the consequent extension of all reciprocal lattice points by the shape transform.
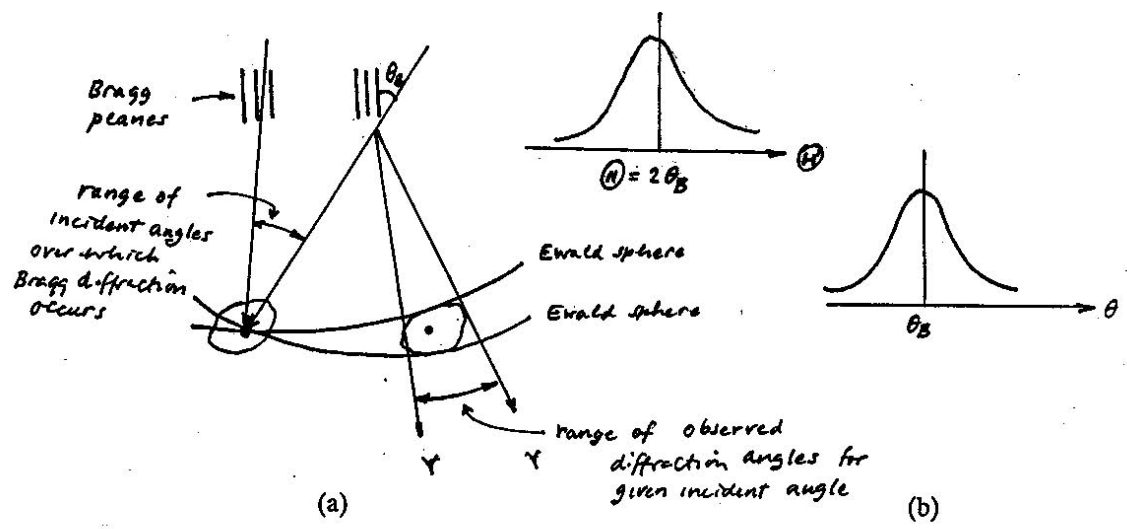

Fig. 10   a) Range of incident angles and diffraction angles over which Bragg diffraction is observed for a finite crystal, and b) the observed intensity variations.

sweeps provide different cuts through the extended reciprocal lattice point. The corresponding intensity profiles enable the shape of the diffracting crystal to be deduced.

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