Trigonal (rhombohedral axes)	3	[111]	None
	32	[111], $[1\bar{1}0]$, $[01\bar{1}]$, $[\bar{1}01]$	None
	$3m$	None	$[uuw]$, $[uvv]$, $[uvu]$, $[1\bar{1}0]$, $[01\bar{1}]$, $[\bar{1}01]$
Hexagonal	6	[001]	None
	$\bar{6}$	None	[001], $[uv0]$
	622	[001], [100], [010], $[\bar{1}\bar{1}0]$, [210], [120], $[\bar{1}10]$	None
	$6mm$	None	$[2uuw]$, $[u2uw]$, $[u\bar{u}w]$, $[u0w]$, $[0vw]$, $[uuw]$
	$\bar{6}m2$	None	$[2uuw]$, $[u2uw]$, $[u\bar{u}w]$
	$\bar{6}2m$	None	$[u0w]$, $[0vw]$ $[\bar{u}\bar{u}w]$
Cubic	23	⟨111⟩, ⟨100⟩	None
	$\bar{4}3m$	None	$[uuw]$, $[\bar{u}uw]$, $[uvu]$, $[\bar{u}vu]$, $[uvv]$, $[u\bar{v}v]$
	432	⟨111⟩, ⟨100⟩, ⟨110⟩	None

Note that in classes $4mm$, $3m$, $\bar{6}$, $6mm$, $\bar{6}2m$ and $\bar{4}3m$ all second-rank axial tensors [at least the symmetric parts; see Agranovitch & Ginzburg, (1965)] are zero, whereas higher-order (4 and 6) symmetric axial tensor components do occur (Molchanov, 1966). This extension to higher-order tensor components is just like the extension from 1st- to 3rd-rank polar tensors implied in Table 10.5.2 of *International Tables for Crystallography* (1987).

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Bragg's Law with Refraction

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Abstract

Expressions for Bragg's law have been derived for the general case of Bragg diffraction in which an incident beam strikes a crystal surface at an angle α, is then diffracted by planes inclined to the surface by φ and leaves the same surface at an angle β. The crystal is assumed to have a refractive index $n = 1 - \delta$ and λ is the X-ray wavelength in air or vacuum. Under these conditions Bragg's law can be written as

$$\lambda = 2d(1-\delta)[\cos\varphi \sin(\alpha - \delta/\tan\alpha) + \sin\varphi \cos(\alpha - \delta/\tan\alpha)\cos\sigma]$$

and

$$\lambda = 2d(1-\delta)[\cos\varphi \sin(\beta - \delta/\tan\beta) + \sin\varphi \cos(\beta - \delta/\tan\beta)\cos\tau].$$

σ and τ are dihedral angles defined in terms of N, the normal to the crystal surface; d^*, the normal to the diffracting planes; $-s_0$, a ray in air antiparallel to the incident beam and s, the diffracted ray in the air. σ is the angle between $(-s_0, N)$ and (d^*, N) and τ the angle between (s, N) and (d^*, N). When the plane of diffraction contains N, σ and τ are either 0 or 180° and Bragg's law takes the form

$$\lambda = 2d(1-\delta)\sin(\alpha - \delta/\tan\alpha \pm \varphi) \quad +\varphi \text{ for } \sigma = 0°, \quad -\varphi \text{ for } \sigma = 180°$$

$$\lambda = 2d(1-\delta)\sin(\beta - \delta/\tan\beta \pm \varphi) \quad +\varphi \text{ for } \tau = 0°, \quad -\varphi \text{ for } \tau = 180°.$$

The magnitude of the refraction effect varies primarily with X-ray wavelength, electron density, and beam-to-crystal angle. Because of refraction the beam-to-crystal-surface angle required to satisfy Bragg's law can change by 10^{-4} to 10^{-1} degrees.

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Introduction

To measure accurately the spacing between planes of atoms in a single crystal by X-ray diffraction one must account for the refraction that an X-ray beam experiences when it passes from a medium of one electron density to another (Bond, 1960). A recent study has shown that for the case of X-ray powder diffraction, little or no correction for refraction is generally needed (Hart, Parrish, Belloto & Lim, 1988). Refraction generally causes a beam to change both its direction and wavelength and therefore the quantities λ' and θ' in Bragg's law, $\lambda' = 2d \sin\theta'$, should be interpreted as the wavelength and diffraction angle inside the crystal rather than in the air or vacuum that surrounds it. A well known form of Bragg's law (Compton & Allison, 1947; Guinier, 1963) that makes use of the more accessible quantities θ and λ is

$$\lambda = 2d \sin\theta(1 - \delta/\sin^2\theta) \quad (1)$$

where 2θ is the angle between the incident and diffracted beams in the air and λ is the tabulated wavelength associated with transmission in a vacuum. Differences between transmission in air and vacuum are small enough to be neglected here. Equation (1), however, applies only to the special case of Bragg diffraction from planes which are parallel to the surface of a crystal. It assumes a refractive index of $n = 1$ outside the crystal and $n = 1 - \delta$ inside the crystal.

The derivation of this equation makes use of the facts that upon entering the crystal the X-ray wavelength changes from $\lambda/1$ to λ/n and that the beam changes propagation direction as described by Snell's law.

Snell's law is illustrated in Fig. 1 and can be written

$$\sin\varphi/\sin\varphi' = n'/n = \cos\alpha/\cos\alpha'. \quad (2)$$

If one substitutes into (2) $n = 1$, $n' = 1 - \delta$ and $\alpha' = \alpha - d\alpha$ and then expands $\cos(\alpha - d\alpha)$, one obtains $d\alpha = \delta/\tan\alpha$. To obtain (1) one substitutes into the expression $\lambda' = 2d \sin\theta'$ the quantities $\lambda' = \lambda/n$ and $\theta' = \theta - d\theta$, sets $n = 1 - \delta$, expands $\sin(\theta - d\theta)$, sets $d\theta = \delta/\tan\theta$ and drops second-order terms in δ.

In (1) δ is given by

$$\delta = \lambda^2(e^2/mc^2)(1/2\pi)F(0)N \quad (3)$$

where $F(0)$ is the structure factor evaluated at $\theta = 0°$ and N is the number of unit cells per unit volume of material. When anomalous dispersion can be neglected $F(0)N = \rho_e$ where ρ_e is the number of electrons per unit volume in the material.

Fig. 2 illustrates the effects described above. Ray AO makes an angle $\theta(n_c = 1)$ with both the crystal surface and diffracting planes, PP. $\theta(n_c)$ is the angle that a ray in air makes with the crystal surface such that it will be diffracted by planes PP in a crystal of refractive index n_c. Because n_c is actually less than one, the wavelength of the incident beam inside the crystal is slightly larger than λ and the angle required to satisfy Bragg's law is increased by $\delta \tan\theta$. Ray BDO satisfies this condition. Because of Snell's law the ray that travels in the direction DO inside the crystal must strike the crystal surface at a steeper angle. This steeper ray, CD, strikes the crystal at $\theta(n_c < 1)$ and changes direction by $\delta/\tan\theta$ upon entering the crystal. Thus when n_c changes from 1 to $1 - \delta$ the incident beam changes direction by $\Delta\theta$ to satisfy Bragg's law, where*

$$\Delta\theta = \delta(\tan\theta + 1/\tan\theta) = 2\delta/\sin 2\theta. \quad (4)$$

To define $\Delta\theta$ very accurately one must know the shape of the rocking curve or diffraction peak in detail. For the ideal case of a plane wave scattered by a perfect non-absorbing crystal this shape is well known and

* As written $\Delta\theta$ is given in radians.

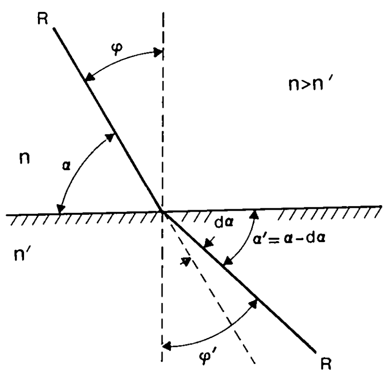

Fig. 1. Construction illustrating Snell's law. Ray RR undergoes refraction when passing through the surface separating regions of refractive index n and n'.

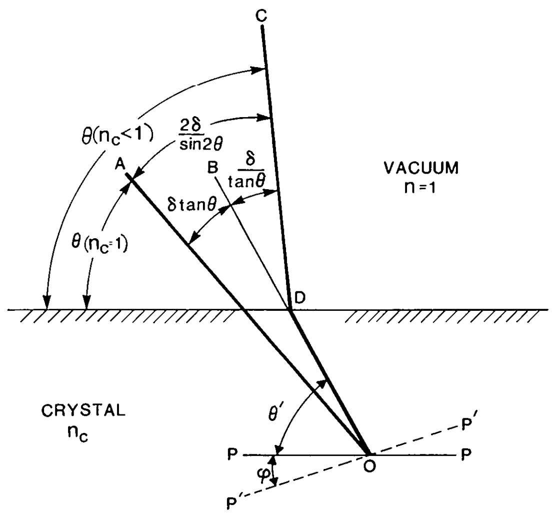

Fig. 2. For a crystal of refractive index $n_c = 1$, ray AO satisfies Bragg's law for diffraction from planes PP which are parallel to the crystal surface. When $n_c < 1$ a ray of the same vacuum wavelength follows path CDO in order to satisfy Bragg's law.

the centroid of the rocking curve can be used to define $\Delta\theta$ (James, 1965). For real crystals the shape of the rocking curve is affected by absorption and the occurrence of simultaneous reflections as well as beam polarization, collimation, monochromaticity and dispersion (Ewald, 1986).

The general case of Bragg diffraction

The general case of Bragg diffraction can be represented by Fig. 3. In this stereogram N represents the outward facing normal to the crystal surface and d^* the normal to a set of diffracting planes. The angle between d^* and N is φ. In the region outside the crystal it is assumed that $n = 1$ and that ray $-s_0$, which is anti-parallel to the incident beam, makes an angle of $(90-\alpha)°$ with N. When s_0 enters the crystal it is refracted away from N, changing direction by $d\alpha = \delta/\tan\alpha$, and becomes s'_0. The dihedral angle between plane (N, d^*) and plane $(N, -s_0, -s'_0)$ is σ. Within the crystal diffracted ray s' makes an angle of $(90-\theta')°$ with d^*. When s' leaves the crystal it is refracted towards N, changing direction by $d\beta = \delta/\tan\beta$. It becomes ray s which makes an angle of $(90-\beta)°$ with N. The dihedral angle between planes (N, d^*) and (N, s, s') is τ.

To obtain the desired form of Bragg's law one first expresses $\sin\theta'$ in terms of experimentally measurable quantities by using the trigonometric relationship $\cos a = \cos b \cos c + \sin b \sin c \cos A$. This relates the three sides of spherical triangle a, b, c to angle A opposite side a (Donnay, 1945). In our case consider the two triangles $-s'_0, d^*, N$ and s', d^*, N. For the first we have

$$\cos(90-\theta') = \cos\varphi\cos(90-\alpha+d\alpha) + \sin\varphi\sin(90-\alpha+d\alpha)\cos\sigma,$$

which can be substituted into Bragg's law, $\lambda = 2d(1-\delta)\sin\theta'$, to obtain

$$\lambda = 2d(1-\delta)[\cos\varphi\sin(\alpha-d\alpha) + \sin\varphi\cos(\alpha-d\alpha)\cos\sigma]. \quad (5a)$$

For the second triangle we have

$$\cos(90-\theta') = \cos\varphi\cos(90-\beta+d\beta) + \sin\varphi\sin(90-\beta+d\beta)\cos\tau,$$

which yields

$$\lambda = 2d(1-\delta)[\cos\varphi\sin(\beta-d\beta) + \sin\varphi\cos(\beta-d\beta)\cos\tau]. \quad (5b)$$

Equations (5a) and (5b) are the desired expressions. Depending upon the knowns these equations can be used individually or simultaneously.

When measuring rocking curves or d spacings by the Bond method the plane of diffraction contains the normal to the crystal surface. In this special case $N, d^*, -s_0, -s'_0, s$ and s' all lie in one plane, σ and τ are either 0 or 180°, and (5a) and (5b) simplify to (6a) and (6b) respectively. If the angles between the incident beam, surface normal and d^* have been established then α and φ are known and (6a) can be used.

$$\lambda = 2d(1-\delta)\sin(\alpha-d\alpha\pm\varphi) \quad \begin{matrix} +\varphi \text{ for } \sigma = 0° \\ -\varphi \text{ for } \sigma = 180° \end{matrix} \quad (6a)$$

or

$$\lambda = 2d(1-\delta)\sin(\beta-d\beta\pm\varphi) \quad \begin{matrix} +\varphi \text{ for } \tau = 0° \\ -\varphi \text{ for } \tau = 180°. \end{matrix} \quad (6b)$$

Fig. 3 can be used to determine the sign of φ in the above equations. Assume that N lies on great circle QR that runs through $-s'_0$, d^* and s'. If N lies between Q and $-s'_0$ or between s' and R then $\sigma = \tau = 0$; if N lies between $-s'_0$ and d^* then $\sigma = 180°$ and $\tau = 0°$; and if N lies between d^* and s' then $\sigma = 0°$ and $\tau = 180°$.

The expression for $\Delta\theta$ is given by (7) if $-s_0$, d^*, N and s all lie in one plane and if d^* is not parallel to N. This corresponds to equation (2-113) of James (1965). This case is illustrated by planes $P'P'$ in Fig. 2.

$$\Delta\theta = \delta\left[\tan\theta + \frac{1}{\tan(\theta\pm\varphi)}\right] \quad \begin{matrix} \theta-\varphi \text{ for } \sigma = 0° \\ \theta+\varphi \text{ for } \sigma = 180°. \end{matrix} \quad (7)$$

The effect of neglecting φ in calculating $\Delta\theta$ can be quite significant. For the 224 reflection from a 001-cut GaAs wafer studied with Cu $K\alpha$ radiation $\Delta\theta = 29{\cdot}5''$ using (7) but only $6{\cdot}2''$ if φ is neglected. Values of

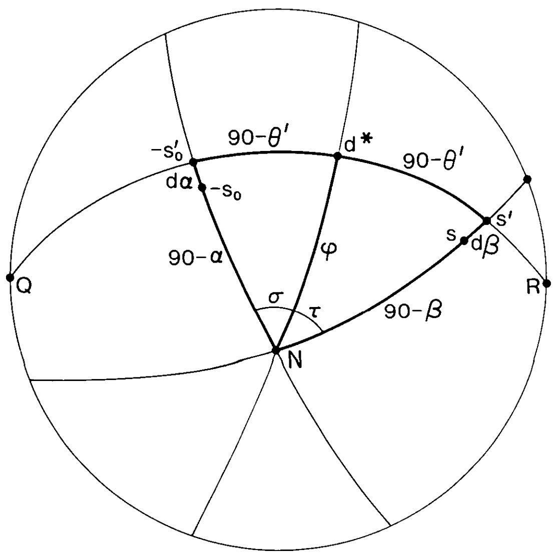

Fig. 3. Stereogram used to describe the general case of Bragg diffraction. N represents the normal to the crystal surface; d^*, the normal to the diffracting planes; $-s_0$, the direction antiparallel to the incident beam in the air; $-s'_0$, the direction antiparallel to the incident beam inside the crystal; s', the diffracted ray in the crystal; and s, the diffracted ray in the air.

$\Delta\theta$ can easily vary by three orders of magnitude from 10^{-4} degrees to 10^{-1} degrees as electron density, wavelength and angles vary. For example, δ differs by a factor of 70 when comparing silicon irradiated with Mo $K\alpha$ radiation ($\delta = 0{\cdot}158 \times 10^{-5}$) to tungsten irradiated with Cr $K\alpha(\delta = 11{\cdot}0 \times 10^{-5})$. When $\varphi = 0$, $1/\sin 2\theta$ varies from 5·75 to 1 as 2θ changes from 10 to 90° and when φ is slightly less than θ (*i.e.* grazing incidence) the trigonometric term in the expression for $\Delta\theta$ can be large. For example when $\theta - \varphi = 1{\cdot}0°$, $1/\tan(\theta - \varphi) = 57{\cdot}3$.

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On Integrated Intensities in Kato's Statistical Diffraction Theory

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Abstract

A new approach to Kato's [*Acta Cryst.* (1980), A**36**, 763-769, 770-778] calculations in the Laue case is presented, giving a clearer and simpler derivation of the mixed terms of the integrated intensities (Bragg- and forward-diffracted beams). The results are in agreement with calculations by Al Haddad & Becker [*Acta Cryst.* (1988), A**44**, 262-270] showing the necessity of correcting two errors in the original treatment of Kato.

I. Introduction

The statistical theory of Kato (1980*a*, *b*) is an outstanding contribution to diffraction theory because it spans in principle the whole range of crystal perfection, from perfect to ideally imperfect (extinction-free) crystals. The 'lattice phase factor' $\exp[i\mathbf{g}\,.\,\mathbf{u}(x, y, z)]$ which characterizes the crystal distortion in the wave-optical Taupin–Takagi equations (Kato, 1976) [$\mathbf{g}$ is the diffraction vector and $\mathbf{u}(x, y, z)$ is the displacement field] is considered as a random function characterized by a static Debye–Waller factor E and a correlation length τ. In the present state of the theory the condition $\tau \ll \Lambda$, Λ being the extinction length, is assumed.

$E = 0$ is the case of secondary extinction, for which diffraction from the incident direction (O beam) to the Bragg direction and conversely is entirely described by intensity-coupling equations (incoherent multiple scattering). $E = 1$ is the case of perfect crystals, for which the O and G beams are coherent. For other values of $E (0 < E < 1)$, the coherent waves are attenuated, even if the crystal is not absorbing, because anywhere in the crystal a diffraction event may transfer them into incoherent beams named the 'mixed' components of the O and G beams. There are also the purely incoherent components, the only ones present if $E = 0$, which are built by diffraction of the incident undiffracted wave into the incoherent G beam directly and then distributed between the O and G beams.

In Kato (1980*b*), the coherent (I_0^c and I_g^c), the purely incoherent (I_0^i and I_g^i) and the mixed (I_0^m and I_g^m) intensity distributions are calculated as functions of the (s_0, s_g) coordinates of Fig. 1, for an incident beam limited by an infinitely narrow slit on the front face of a parallel-sided crystal in the Laue case. Integration of these distributions on the back face of the crystal of thickness t gives the following terms of the forward and Bragg integrated intensities expressed as

$$R_0(t) = R_0^c(t) + R_0^i(t) + R_0^m(t)$$
$$R_g(t) = R_g^c(t) + R_g^i(t) + R_g^m(t).$$

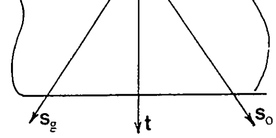

Fig. 1. Illustration of the (s_0, s_g) and (x, t) coordinates. $x = (s_0 - s_g)\sin\theta_B$; $t = (s_0 + s_g)\cos\theta_B$.

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