Diffraction

scattering of radiation by an object observed and described over 300 years ago illustrated with a diffraction grating

Joseph von Fraunhofer
German
1820

Diffraction

exact pattern depends on wavelength (\( \lambda \)) and distance (\( d \)) between slits

Diffraction of Visible Light

works if \( d \approx \lambda \) of radiation
Diffraction of X-rays

In 1910, it was not certain whether x-rays were waves. Based on suggestion, Walther Friedrich and Paul Knipping demonstrated this using a crystal of CuSO$_4$ (off the shelf). Max von Laue suggested that if crystals were periodic, with interatomic distances of ~1 Å, they might act as diffraction gratings towards x-ray waves. German

1912

Laue Diffraction

If polychromatic radiation used

Improved Laue diffraction photo of CuSO$_4$, Friedrich and Knipping. Crystal is stationary.

Laue Equations

For a 3-D crystal, replace $d$ with cell dimensions $a$, $b$, and $c$:

\[
\begin{align*}
    a \cos \delta_a &= h \lambda \\
    b \cos \delta_b &= k \lambda \\
    c \cos \delta_c &= \ell \lambda
\end{align*}
\]

(2 0 0) (1 0 0) (0 0 0) (1 0 0) (2 0 0)

Observe diffraction angle, $\psi$, where diffraction cones intersect.

Note: in 1-D, diffraction from a point. In 2-D, diffraction from a line. In 3-D, diffraction from a (Miller) plane.

Bragg's Law

Also in 1912, William Lawrence Bragg and his father William Henry Bragg. British (1890-1971) and British (1862-1942). Noted similarity of diffraction with reflection from a plane mirror.

Bragg's Law

In phase

2nd wave in-phase after reflection only if:

\[
AC + CB \text{ is an integer multiple of } \lambda.
\]

\[
AC = CB; \quad 2AC = n\lambda
\]

\[
\sin \theta = AC/d; \quad 2AC = 2d \sin \theta
\]

\[
2d \sin \theta = n\lambda
\]
Bragg’s Law

reflection conditions depend on $\lambda$, $\theta$, and $d$

Braggs Law says nothing about absolute intensities, just where maxima are found

$$2d \sin \theta = n\lambda$$

Bragg’s Law

reflected beam deviates from direct beam by $2\theta$

Bragg’s Law

all $e^-$ density is not on the plane

still valid: all $e^-$ density has some contribution to all planes

it is variations in contribution to a reflection that accounts for differing intensities of reflections from various planes; allows for structure determination

X-rays reflect from all Miller planes in the unit cell; crystallographic data often referred to as reflections

since monochromatic radiation is used, the $2\theta$ deviation of a reflection depends on the interplanar spacing, $d$

Bragg’s Law

reflection is from regions of $e^-$ density: atoms

which act as points of Laue diffraction

Bragg’s Law

Reflection from $e^-$ density off the plane is slightly out of phase. Intensity is less.
**Bragg’s Law**

\[ 2d \sin \theta = n \lambda \]

in crystallography, \( n = 1 \) for all reflections

higher order reflections (\( n = 2, 3, \text{etc} \)) are the same as 1st order reflections from parallel planes which are an \( n \) multiple of the original plane

2nd order reflection from (1 0 0) same as 1st order reflection from (2 0 0)

**Example**

- cubic unit cell: \( a = 4.00 \text{ Å} \)
- CuK\(\alpha\) radiation: \( 1.542 \text{ Å} \)

\[ d = 4.00 \text{ Å} \]

1st order from (1 0 0) = 11.1°

\( \theta \) for the 2nd order reflection from (1 0 0)?

\[ 2d \sin \theta = n \lambda; \ \theta = \sin^{-1} \left( \frac{n \lambda}{2d} \right) \]

\[ \theta = \sin^{-1} \left( \frac{(2(1.542 \text{ Å}))}{(2(4.00 \text{ Å}))} \right) = 22.7° \]

45.4°

\( \theta \) for the 1st order reflection from (2 0 0)?

\[ \theta = \sin^{-1} \left( \frac{(1(1.542 \text{ Å}))}{(2(2.00 \text{ Å}))} \right) = 22.7° \]

**Reciprocal Space**

\[ 2d \sin \theta = n \lambda, \]

\[ \sin \theta = \frac{n \lambda}{2d} \]

\( \sin \theta \) inversely proportional to \( d \)

large \( d \) means compressed diffraction and vise versa

to get a direct relationship, instructive to define:

- Reciprocal Space
- Reciprocal Lattice

**Reciprocal Lattice Example**

- monoclinic
  - \( a = 0.75 \text{ Å} \)
  - \( b = 1.00 \text{ Å} \)
  - \( c = 1.00 \text{ Å} \)
  - \( \beta = 105° \)

looking down \( b \) axis

- star notation: \( \frac{1}{x} = x^* \)

- draw a vector from origin \( \perp \) to plane, with a length of \( 1/d \)

- select an arbitrary origin

**Reciprocal Lattice Example**

- (1 0 0) planes
  - \( d^*_{100} \)
  - select an arbitrary origin

- (0 0 1) planes
Reciprocal Lattice Example

\[ \langle 1 \ 0 \ 1 \rangle \text{ planes} \]

\[ d^{*}_{1\ 0\ 1} \]

Reciprocal Lattice Example

\[ \langle 0 \ 0 \ 2 \rangle \text{ planes} \]

\[ d^{*}_{0\ 0\ 2} \]

Reciprocal Lattice Example

\[ \langle 1 \ 0 \ 2 \rangle \text{ planes} \]

\[ d^{*}_{1\ 0\ 2} \]

Reciprocal Lattice Example

\[ \langle 0 \ 0 \ \bar{1} \rangle \text{ planes} \]

\[ d^{*}_{0\ 0\ \bar{1}} \]

Reciprocal Lattice Example

\[ \langle 1 \ 0 \ \bar{1} \rangle \text{ planes} \]

\[ d^{*}_{1\ 0\ \bar{1}} \]

Direct Lattice

\[ (1 \ 0 \ 1) \]

\[ (0 \ 0 \ 1) \]

\[ (1 \ 0 \ 0) \]

\[ (0 \ 0 \ 0) \]

Reciprocal Lattice

\[ (1 \ 0 \ 2) \]

\[ (0 \ 0 \ 2) \]

\[ (1 \ 0 \ \bar{1}) \]

\[ (0 \ 0 \ \bar{1}) \]
Reciprocal Space

\[ a^* = \frac{bc \sin \alpha}{V} \quad b^* = \frac{ac \sin \beta}{V} \quad c^* = \frac{ab \sin \gamma}{V} \]

\[ \cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \]
\[ \cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma} \]
\[ \cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \]

Reciprocal Lattice and Bragg’s Law

a link between the reciprocal lattice and Bragg’s Law that connects x-ray diffraction with unit cell parameters

Sphere of Reflection

Ewald’s Sphere

Paul Peter Ewald
German-American
(1888 - 1985)

Ewald’s Sphere

place a crystal in an x-ray beam at point \( O \)
point \( O \) can also be taken as the reciprocal lattice origin

construct a circle with a radius of \( \frac{1}{\lambda} \), centered on the beam passing through \( O \); \( B \) is where the beam enters the circle

Ewald’s Sphere

place a crystal in an x-ray beam at point \( O \)
point \( O \) can also be taken as the reciprocal lattice origin

construct a circle with a radius of \( \frac{1}{\lambda} \), centered on the beam passing through \( O \); \( B \) is where the beam enters the circle

lattice point \( P \) happens to be on the circle
place a crystal in an x-ray beam at point O
point O can also be taken as the reciprocal lattice origin
construct a circle with a radius of $1/\lambda$ centered on the beam passing through O; B is where the beam enters the circle
lattice point P happens to be on the circle
construct triangle OBP

Ewald’s Sphere

if the crystal is moved to C, $\angle PCO$ is $2\theta$
Ewald's Sphere

\[ \sin \theta = \frac{OP}{OB} = \frac{1}{d} = \frac{\lambda}{2d} \]

\[ 2d \sin \theta = \lambda \]

If the crystal is moved to C, \( \angle PCO \) is \( 2\theta \).

CP is the deviation of the reflected x-ray from the direct beam.

Two of the family of the Miller plane with interplanar spacing \( d \) are shown; CP makes an angle \( \theta \) with the plane; Bragg's Law.

Ewald's Sphere

It is the same geometry if the crystal stays at O.

Ewald's Sphere

It is the same geometry if the crystal stays at O.

by rotating the lattice (the crystal) about the origin, various reciprocal lattice points come into reflecting position; the beam shoots out in the direction that satisfies Bragg's Law.
Ewald’s Sphere

it is the same geometry if the crystal stays at \( O \)
by rotating the lattice (the crystal) about the origin, various reciprocal lattice points come into reflecting position; the beam shoots out in the direction that satisfies Bragg’s Law shorter \( \lambda \) allows more reflections to be coincident with sphere

\[
\text{Number of possible reflections} = \frac{33.6 \ V_{\text{unit cell}}}{\lambda^3}
\]

Ewald’s Sphere

reciprocal lattice visualized on film or detector by rotating crystal in x-ray beam and recording x-rays as they shoot out of sphere of reflection; reciprocal lattice parameters \((a^*, b^*, c^*, \alpha^*, \beta^* \text{ and } \gamma^*)\) measured and direct lattice parameters calculated

axial rotation photograph showing two dimensions of reciprocal lattice