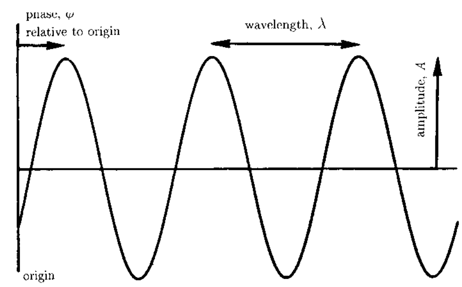
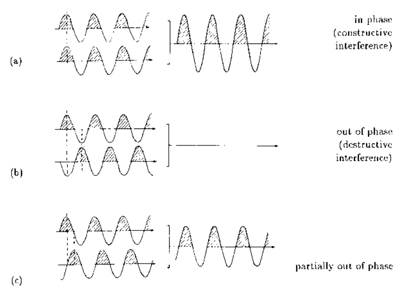
Diffraction

- A basic understanding of diffraction physics is required if crystal structure solution and refinement is to be understood.

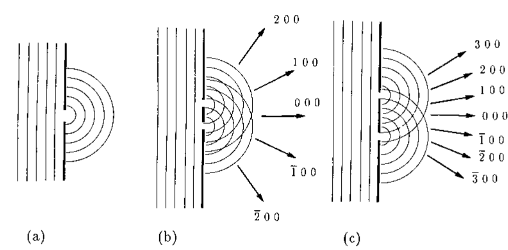
Wave characteristics



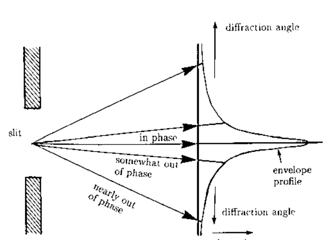
Interference between waves



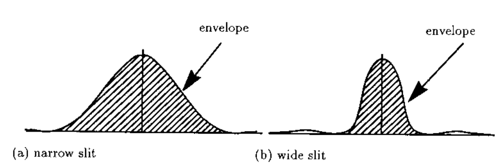
Double slit experiment



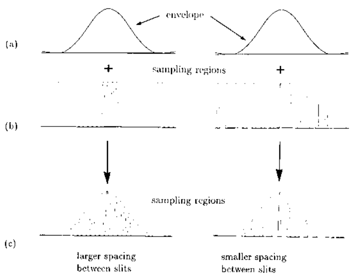
Diffraction at a single slit



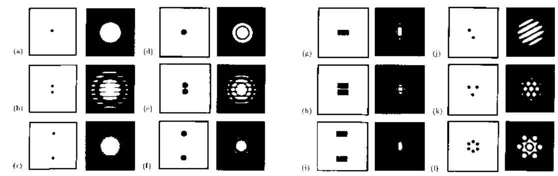
The envelope function



Diffraction and sampling



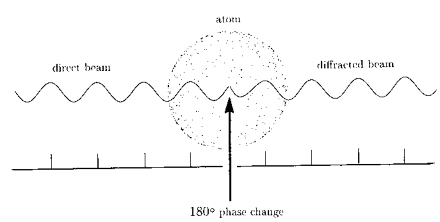
Optical transforms



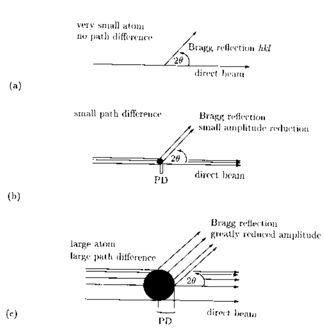
Scattering of X-rays and neutrons by atoms

- X-rays are scattered electrons in atoms
  - the electron cloud is about the same size as the wavelength of the X-rays
- Neutrons are scattered by nuclei
  - nuclei are much smaller than the neutron wavelength
  - for magnetic materials electron spin interacts with neutron spin and gives scattering

Phase change on scattering

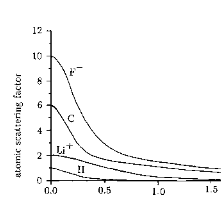


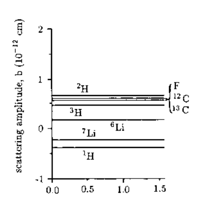
X-ray scattering by atoms



X-ray and neutron form factor

- The form factor is related to the envelope function for an atom





Neutron scattering lengths

TABLE 3.2. Some scattering factors for neutrons and X rays.

Element	*Isotope*	*X rays* $\sin\theta/\lambda = 0$	*X rays* $\sin\theta/\lambda = 0.5/Å$	*Neutrons** $b\,(10^{-12}\ cm)$	*Neutrons*** *(normalized to -1.00 for* ^{1}H*)*
H	^{1}H	1.0	0.07	0.38	– 1.00
	^{2}H (=D)	1.0	0.07	0.65	1.71
Li	^{6}Li	3.0	1.0	0.18+0.025*i*	0.71+0.066*i*
	^{7}Li	3.0	1.0	0.25	– 0.66
C	^{12}C	6.0	1.7	0.66	1.74
	^{13}C	6.0	1.7	0.60	1.58
O	^{16}O	8.0	2.3	0.58	1.53
Fe	^{54}Fe	26.0	11.5	0.42	1.11
	^{56}Fe	26.0	11.5	1.01	2.66
	^{57}Fe	26.0	11.5	0.23	0.61
Co	^{59}Co	27.0	12.2	0.25	0.66
U	^{238}U	92.0	53.0	0.85	2.24

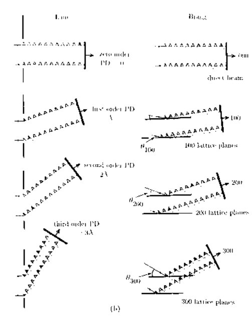
Diffraction from crystals

- A crystal is a three dimensional diffraction grating
- The lattice periodicity of the crystal determines the sampling regions of the diffraction pattern
- The unit cell contents give you the envelope function

Laue equations

- Laue first mathematically described diffraction from crystals
  - consider X-rays scattered from every atom in every unit cell in the crystal and how they interfere with each other
  - to get a diffraction spot you must have constructive interference
  - Laue equations:
    - » $PD_1 = h_1\lambda$, $PD_2 = h_2\lambda$, $PD_3 = h_3\lambda$

Laue and Bragg diffraction

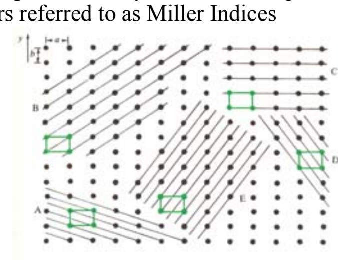


The Bragg equation

- Bragg discovered that you could consider the diffraction to have arisen from reflection from lattice planes
- Reformulated Laue equations
  - $2d_{hkl}\sin\theta_{hkl} = n\lambda$

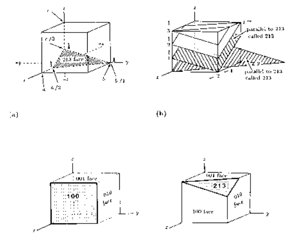
The orientation of lattice planes

- It is possible to describe certain directions and planes with respect to the crystal lattice using a set of three integers referred to as Miller Indices

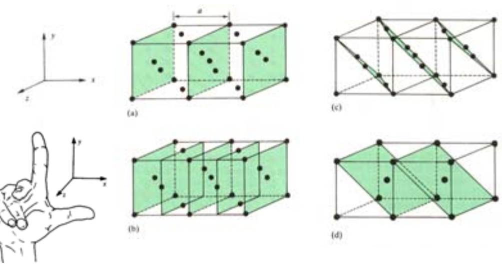


Miller indices (hkl)

- Miller Indices are the reciprocal intercepts of the plane on the unit cell axes
- Identify plane adjacent to origin
  - can not determine for plane passing through origin
- Find intersection of plane on all three axes
- Take reciprocal of intercepts
- If plane runs parallel to axis, intercept is at ∞, so Miller index is 0



Examples of Miller indices

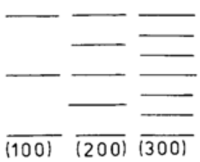


Families of planes

- Miller indices describe the orientation and spacing of a family of planes
  - The spacing between adjacent planes in a family is referred to as the “d-spacing”

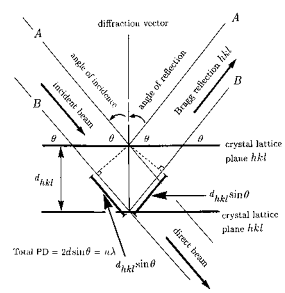
Three different families of planes

d-spacing between (300) planes is one third of the (100) spacing



Note all (100) planes are members of the (300) family

Diffraction Geometry



Unit cells and d_{hkl}

TABLE 3.1. Obtaining unit cell dimensions from d_{hkl} values.

The general equation for the spacings between lattice planes d_{hkl} for a crystal with unit-cell dimensions $a, b, c, \alpha, \beta, \gamma$ is given by:

$$d_{hkl} = X/Y,$$

where X and Y are:

$$X = [1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]^{\frac{1}{2}}$$

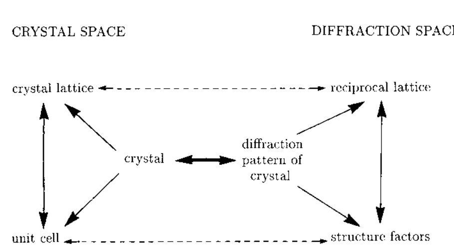
$$Y = \left[\left(\frac{h}{a}\right)^2 \sin^2\alpha + \left(\frac{k}{b}\right)^2 \sin^2\beta + \left(\frac{l}{c}\right)^2 \sin^2\gamma - \frac{2kl}{bc}(\cos\alpha - \cos\beta\cos\gamma) - \frac{2lh}{ca}(\cos\beta - \cos\gamma\cos\alpha) - \frac{2hk}{ab}(\cos\gamma - \cos\alpha\cos\beta)\right]^{1/2}. \quad (3.1.1)$$

In systems of higher symmetry, this equation is greatly simplified. For example, if $\alpha = \beta = \gamma = 90°$:

$$d_{hkl} = 1 \Big/ \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}. \quad (3.1.2)$$

Unit cell dimensions (22.67, 7.67, 9.77 Å) may be determined, with radiation of a known wavelength, $\lambda = 1.5418$ Å, from the values of $2\theta_{hkl}$ for reflections of known hkl indices, as shown below:

Real space and reciprocal space



The reciprocal lattice

- It is convenient when talking about diffraction to use the concept of a reciprocal lattice
- The reciprocal lattice is related to the real space lattice by:

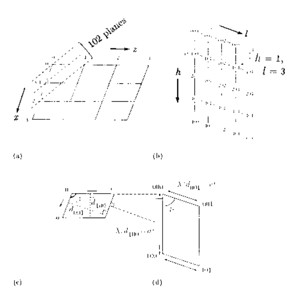
$$b_1 = \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3} \qquad b_2 = \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3} \qquad b_3 = \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}$$

- $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the vectors of the real space lattice (alternatively **a**,**b**,**c**) and $\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$ are the vectors of the reciprocal lattice (alternatively **a***,**b***,**c***).
- Note $a_1.a_2xa_3$ is the unit cell volume

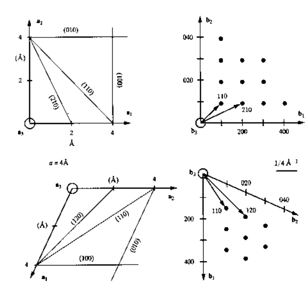
Properties of the reciprocal lattice

- Note $a_i.b_j=\delta_{ij}$
- So $a_1.b_1 = 1$, but $a_1.b_2 = 0$ and $a_1.b_3 = 0$ etc.
  - This is the origin of the term reciprocal lattice.
  - The reciprocal lattice and real space lattice are orthonormal
- Any point on the reciprocal lattice can be specified by a vector $\mathbf{H}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ (hkl are integers)
  - This vector is perpendicular to the plane in real space with Miller indices (hkl)
  - The length of this vector $H_{hkl} = 1/d_{hkl}$ where d_{hkl} is the interplanar spacing in real space
  - We get to represent a whole family of planes in real space by a single point in reciprocal space

The geometrical construction of the reciprocal lattice



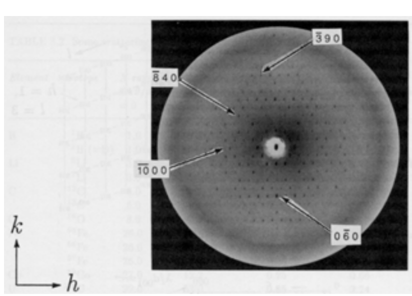
Geometrical relationship between real and reciprocal space



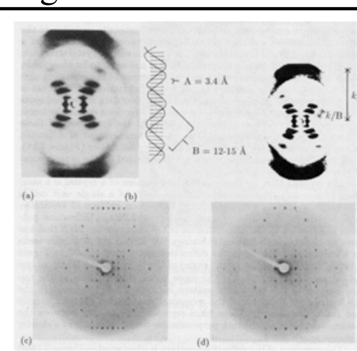
Note reciprocal lattice vector is always perpendicular to the corresponding real space plane

Only in orthogonal axis systems are the real and reciprocal lattice vectors parallel

A precession photograph



Sampling DNA



The Ewald construction

- A crystal at a random orientation in an X-ray beam will not necessarily give a diffraction spot
- Ewald construction allows the prediction of the orientation required for diffraction
  - widely used in diffraction books

Ewald sphere