Modern Crystallography II

Topics:

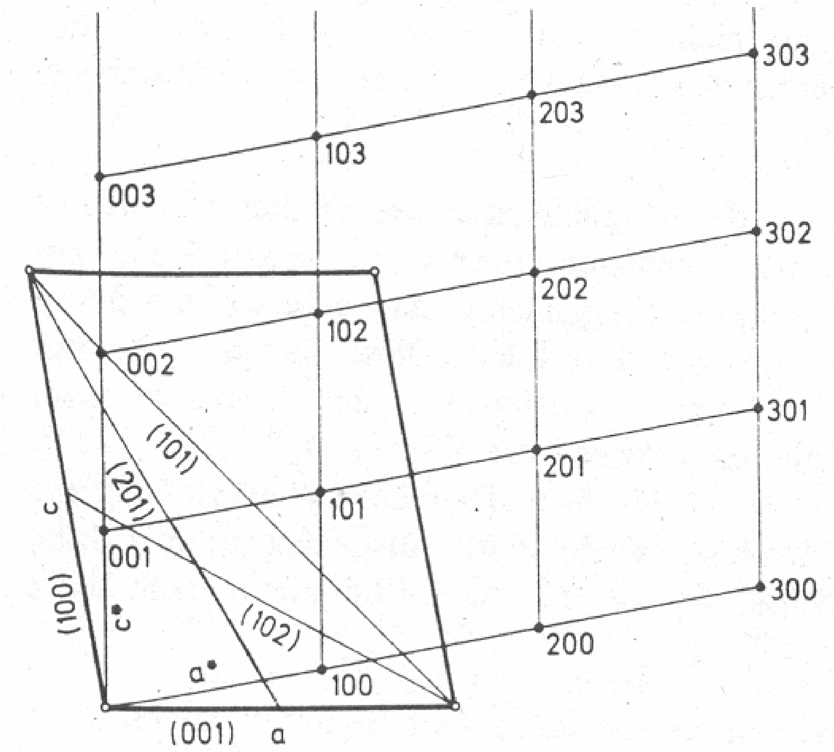
20.11. **Crystalline state**
definition, interaction types in crystalline materials
lattice types, symmetry operations, reciprocal lattice

27.11. **X-ray diffraction (kinematic theory)**
Bragg equation, Laue equations, Ewald sphere, atomic form factor, structure factor, absorption

4.12 **experimental X-ray structure determination**
experimental methods, phase problem, phase retrieval methods, structure refinement

11.12 **modern applications of crystallography**
protein crystallography, powder diffraction,
time-resolved crystallography (pump and probe)

Repetition: reciprocal lattice & Laue equations



diffraction maxima for
(h,k,l = integer):

$$\vec{a}\cdot\vec{s}=h$$
$$\vec{b}\cdot\vec{s}=k$$
$$\vec{c}\cdot\vec{s}=l$$

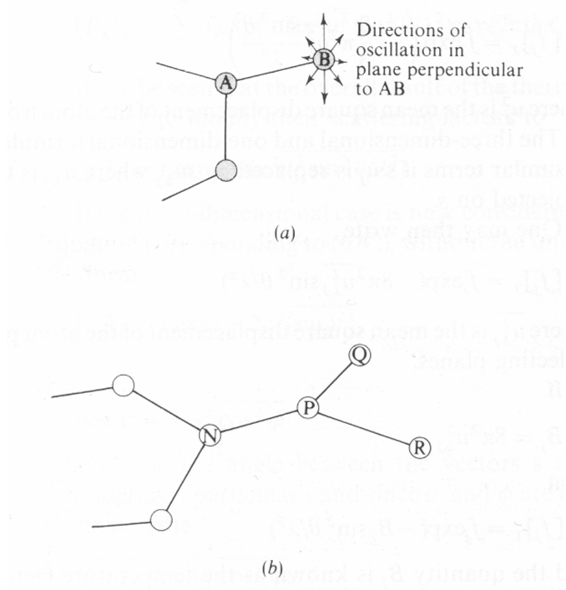
reciprocal lattice vector:

$$\vec{d}^*_{hkl}=h\cdot\vec{a}^*+k\cdot\vec{b}^*+l\cdot\vec{c}^*$$

combination of (1) and (2):

$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{a}=h$$
$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{b}=k$$
$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{c}=l$$

temperature factor



assuming a one dimensional unit-cell:

$$F_h = \sum_{j=1}^{N} f_j \exp\left(2\pi i h\left(\frac{u_j}{a} + x_j\right)\right) = \sum_{j=1}^{N} f_j \exp\left(2\pi i h\frac{u_j}{a}\right)\exp\left(2\pi i h x_j\right)$$

at temperature T:

$$\left[F_h\right]^T = \sum_{j=1}^{N} f_j \overline{\exp\left(2\pi i h\frac{u_j}{a}\right)}\exp\left(2\pi i h x_j\right)$$

$$\overline{\exp\left(2\pi i h\frac{u_j}{a}\right)} \approx 1 + 2\pi i h\frac{u_j}{a} - 2\pi^2 h^2 \frac{u_j^{\,2}}{a^2}$$

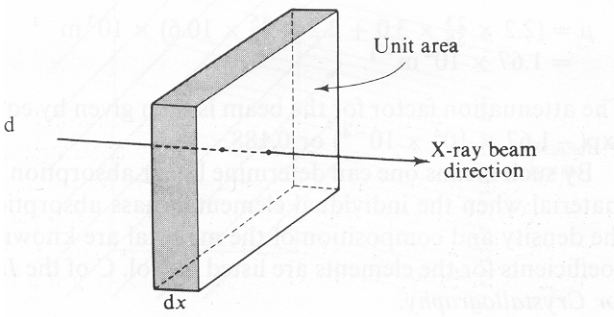
Assuming a harmonic potential: $\overline{u_j} = 0$ and using: $h/a = \sin\theta/\lambda$

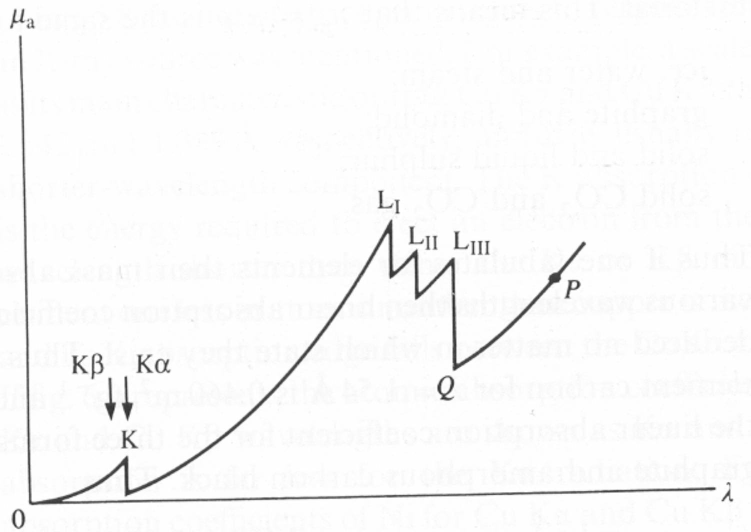
$$\left[f_j\right]^T = f_j \exp(-8\pi^2 \overline{u_j^{\,2} \sin^2\theta/\lambda^2})$$

three dimensional case:

$$\left[f_j\right]^T = f_j \exp\left(-\frac{8}{3}\pi^2 \overline{u_j^{\,2}} \sin^2\theta/\lambda\right) \qquad B_j = 8\pi^2 \overline{u_{\perp j}^{\,2}}$$

Absorption of X-rays





Lambert-Beer equation:

$$I = I_0 \exp(-\mu d)$$

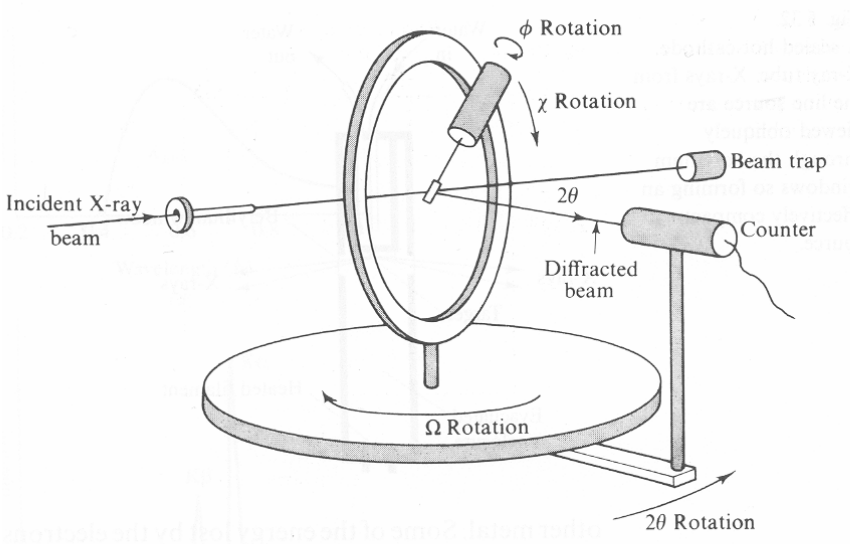
Transmission:

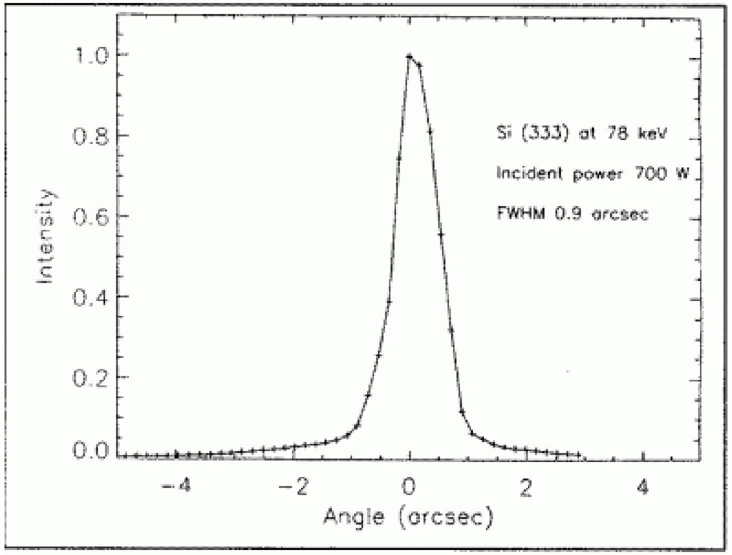
$$T = \frac{I}{I_o} = \exp(-\mu d)$$

Mass absorption coefficents
for 15 keV X-rays:

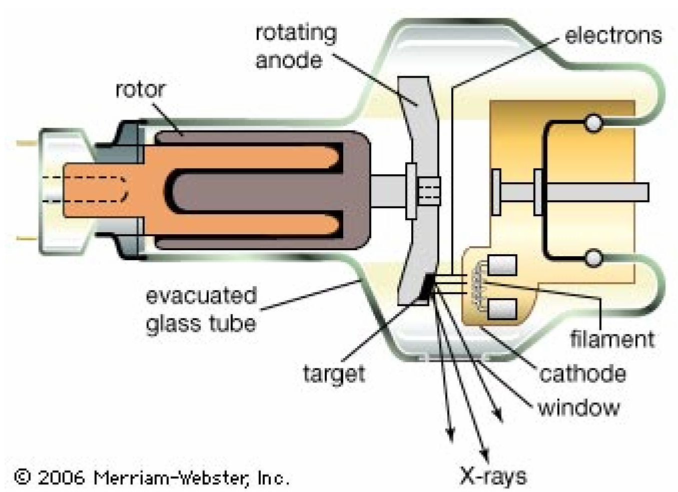
Element	μ [mm^{-1}]	T [d=1mm]
Be	0.0568	0.945
Si	2.4085	0.090
Pb	127.20	5×10^{-56}

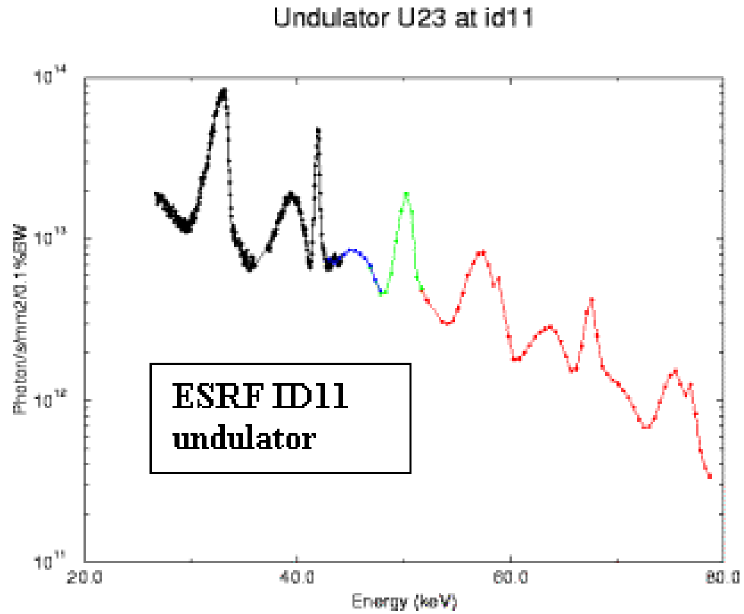
4-circle diffractometers

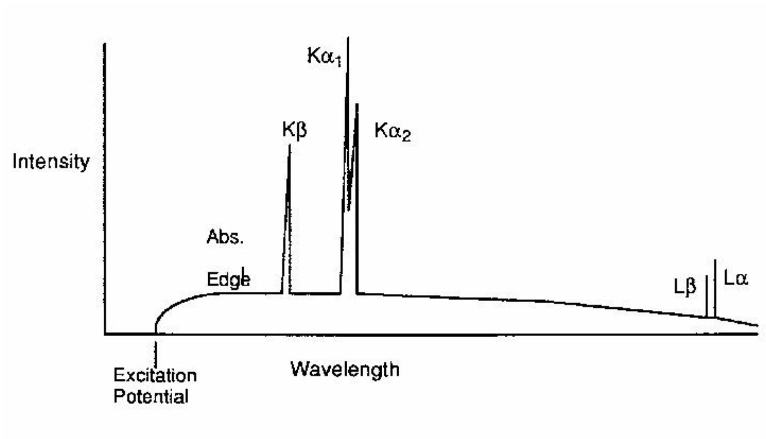




X-ray tube vs. synchrotron

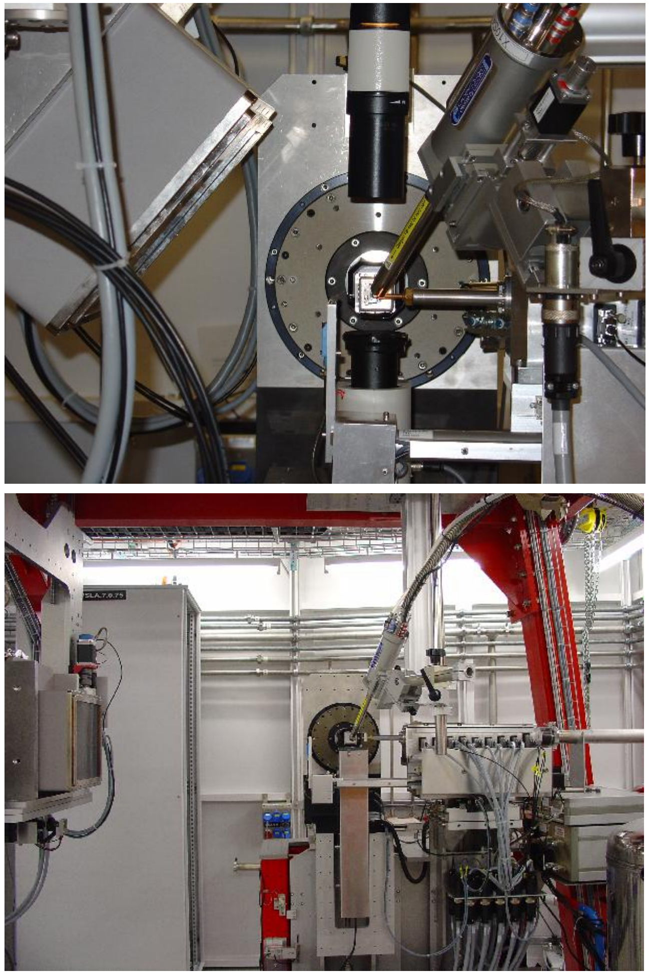






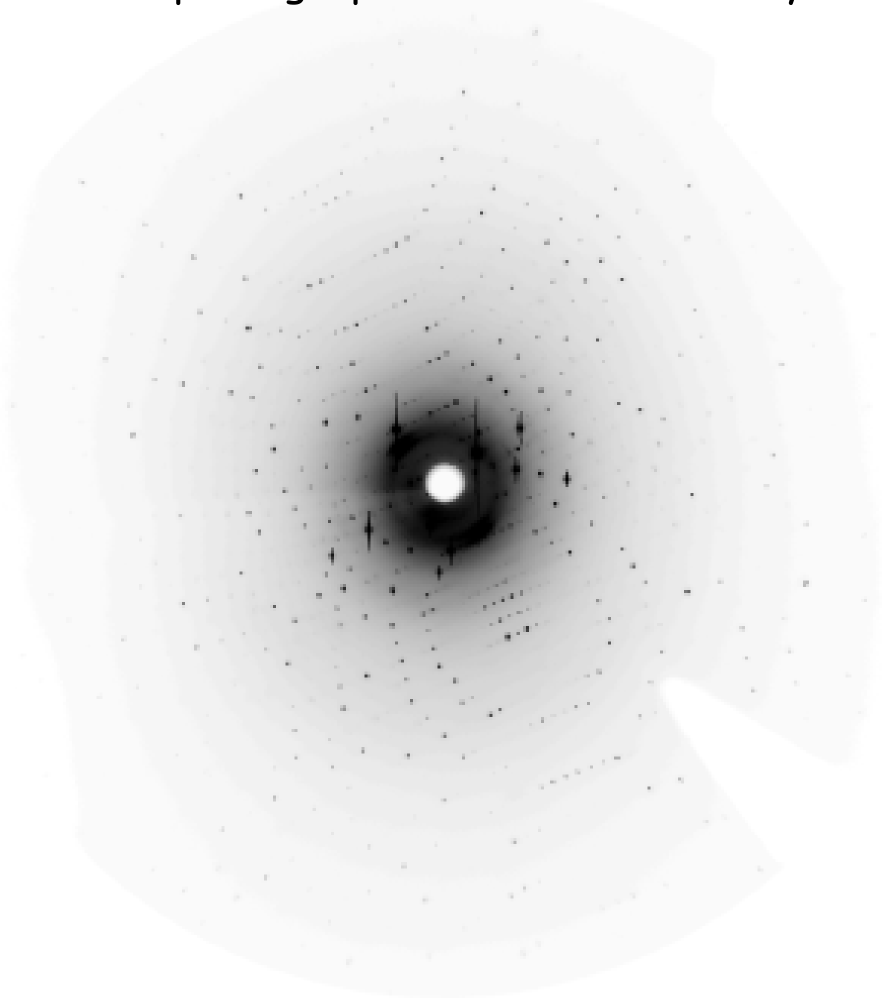
source	Monochromatic photon flux in 300 x 300 μm	Monochromatic photon flux in 5 x 5 μm
X-ray tube	10^7 - 10^8 ph/sec	10^7 ph/sec
2nd gener. bending magnet	10^8 ph/sec	10^6 ph/sec
3rd generation undulator	10^{12}-10^{13} ph/s	10^{12}-10^{13} ph/s

Modern crystallographic data collection

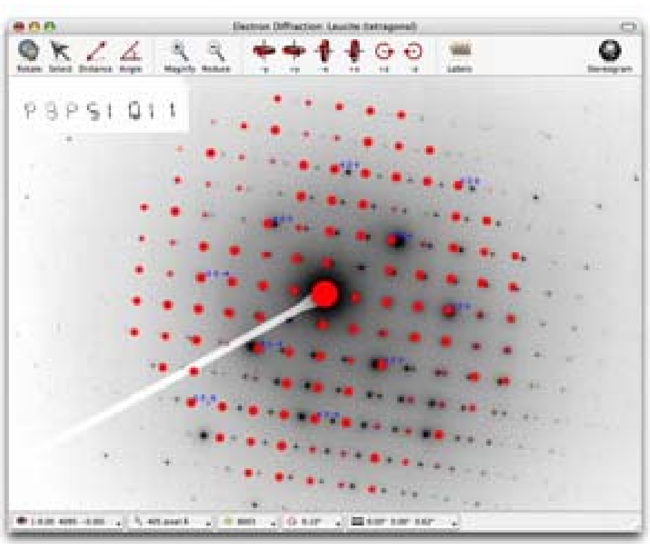


Beamline X10SA at the Swiss Light Source

rotation photograph of a vitamin B12 crystal



Information from a diffraction pattern



Geometrical arrangement of spots:

information about unit cell size and symmetry

Intensity of spots:

Information about the motive (molecule) in the assymetric unit

Problem: missing phases!

Course of a crystallographic structure determinations:

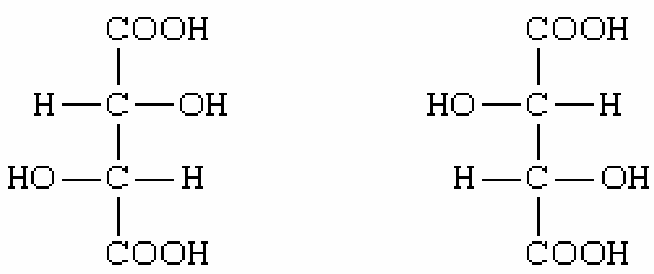
1. collection of many (all) different reflections (diffraction experiment)
2. Indexing of reflections (determination of unit cell)
3. Extraction of intensities and their sigma's from diffraction spots
4. Application of absorption, polarization and geometrical corrections
5. Structure solution and refinement (phase retrieval and refinement)

Friedels law

"The Diffraction experiment generates a center of symmetry"

$$\left|F_{hkl}\right| = \left|F_{\bar{h}\bar{k}\bar{l}}\right|$$

$$\left|F_h\right| = \sum_{j=1}^{N} f_j \exp\left(2\pi i \vec{h} \cdot \vec{r}_j\right) \qquad \left|F_{-h}\right| = \sum_{j=1}^{N} f_j \exp\left(2\pi i (-\vec{h}) \cdot \vec{r}_j\right)$$



d-tartaric acid *l*-tartaric acid

-> enantiomorphs are indistinguishable in an diffraction experiment

Symmetry of diffraction patterns

diad axis along b: (x,y,z) -> (-x,y,-z)

$$F_h = \sum_{j=1}^{N} f_j \exp\left\{2\pi i\left(hx_j + ky_j + lz_j\right)\right\}$$

$$F_h = \sum_{j=1}^{N/2} f_j \exp\left\{2\pi i\left(hx_j + ky_j + lz_j\right)\right\} + \left\{2\pi i\left(-hx_j + ky_j - lz_j\right)\right\}$$

$$F_h = \sum_{j=1}^{N/2} f_j \exp\left\{2\pi i\left(ky_j\right)\right\} + \left\{2\pi i\left(hx_j + lz_j\right)\right\}$$

result for structure amplitudes:

$$\left|F_{hkl}\right| = \left|F_{h\bar{k}l}\right| = \left|F_{\bar{h}k\bar{l}}\right| = \left|F_{\bar{h}\bar{k}\bar{l}}\right|$$

Systematic absent reflections (I)

some reflection classes are forbidden by symmetry:

- Centered unit cell: integral extinctions, affects all (hkl)
- Mirror glide planes: serial extinctions, affects reflection planes:
  (hk0), (h0l),(0kl)
- Srew axes: axial extinction, affects axes reflection:
  (h00), (0k0),(00l)

Example C-face centering: (x,y,z) -> (x+1/2, y+1/2, z)

$$F_h = \sum_{j=1}^{N/2} f_j \left[\exp\left\{2\pi i\left(hx_j + ky_j + lz_j\right)\right\} + \exp\left\{2\pi i\left(hx_j + ky_j + lz_j\right) + \pi i(h+k\right\}\right]$$

$$\exp(i\varphi) = \exp(i(\varphi + 2\pi n)) \qquad \exp(i\varphi) = -\exp(i(\varphi + (2n+1)\pi))$$

$$F_h = \sum_{j=1}^{N/2} f_j \left[\exp\left\{i\left(\varphi\right)\right\} + \exp\left\{i\left(\varphi\right) + \pi i(h+k\right\}\right]$$

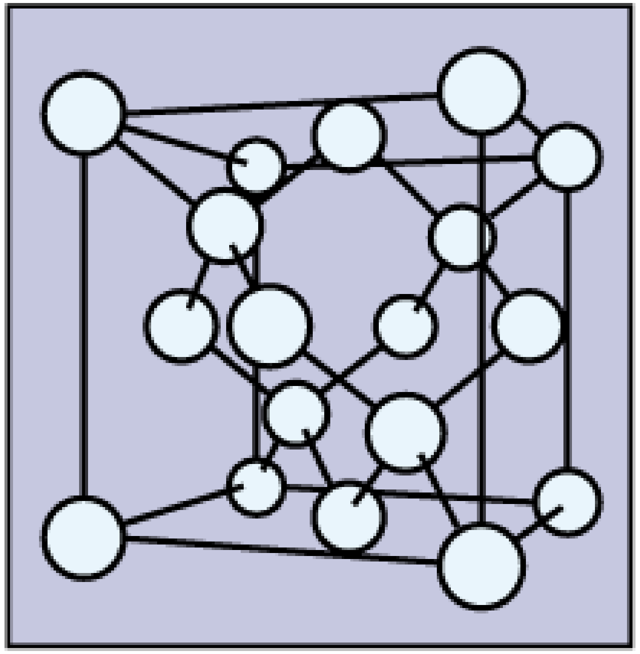
-> F_h=0 for h+k = 2n+1

Systematic absent reflections (II)

Lattice	Absences	Symmetry element	Absences
P	None	$\bar{1}, \bar{3}, \bar{4}, \bar{6}, m$	None
A	$k + l = 2n + 1$	$2, 3, 4, 6$	
B	$h + l = 2n + 1$	$a \perp$ to b axis	$h0l$ for $h = 2n + 1$
C	$h + k = 2n + 1$	$a \perp$ to c axis	$hk0$ for $h = 2n + 1$
F	h, k, l not all odd or all even	$b \perp$ to a axis	$0kl$ for $k = 2n + 1$
		$b \perp$ to c axis	$hk0$ for $k = 2n + 1$
I	$h + k + l = 2n + 1$	$c \perp$ to a axis	$0kl$ for $l = 2n + 1$
		$c \perp$ to b axis	$h0l$ for $l = 2n + 1$
Symmetry element		$n \perp$ to a axis	$0kl$ for $k + l = 2n + 1$
		$n \perp$ to b axis	$h0l$ for $h + l = 2n + 1$
$2_1 \parallel$ to a axis	$h00$ for $h = 2n + 1$	$n \perp$ to c axis	$hk0$ for $h + k = 2n + 1$
$2_1 \parallel$ to b axis	$0k0$ for $k = 2n + 1$		
$2_1 \parallel$ to c axis	$00l$ for $l = 2n + 1$		

Example: systematic absent reflections for silicon

space group: Fd-3m = F 4/d -3 2/m



$$hkl\ :\ h = 2n+1$$
$$\text{or}\ \ h,k,l = 4n+2$$
$$\text{or}\ \ h,k,l = 4n$$