AP6180/AP8180:
Modern Scattering Methods in Materials Science

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Application of the Kinematical Scattering to Solve Problems in Materials Science

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City University of Hong Kong

in more detail:

Little crystallography
Bragg’s law of scattering,
Kinematical versus dynamical scattering,
Physical meaning of extinction length,
Scattering by a small crystal,
Incorporating the unit cell and translational symmetry,
Structure factor,
Ewald construction in reciprocal space,
Fundamental equipment for
    X-ray diffraction experiments,
Diffractometers and detectors

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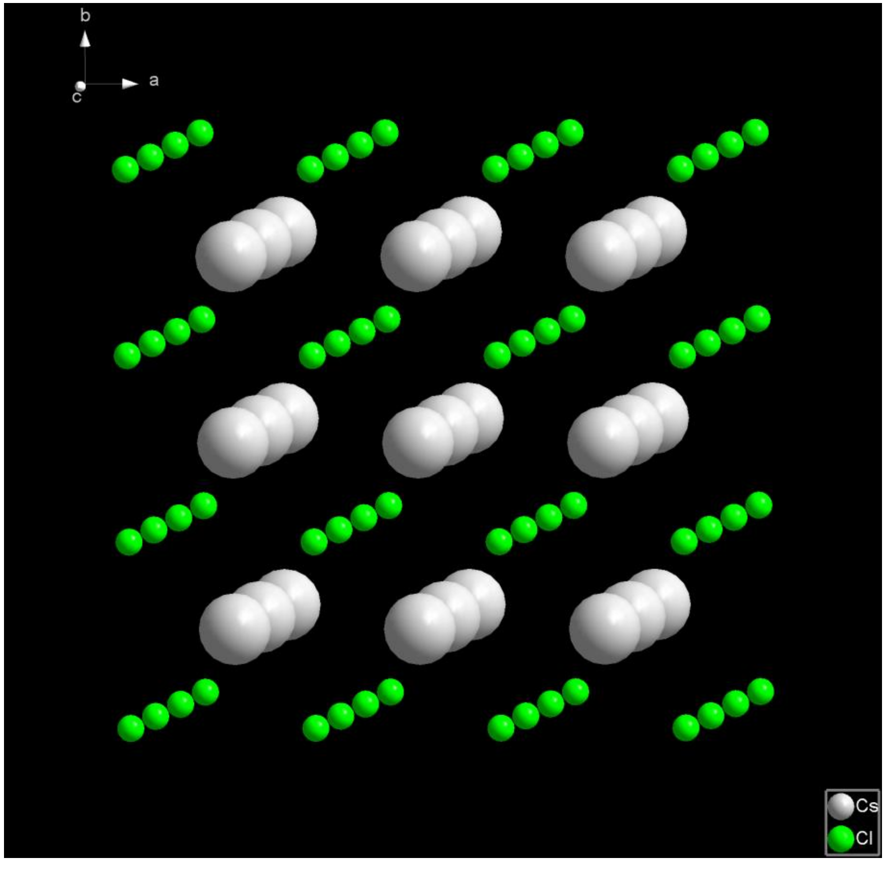
Atoms (molecules) pack together in a regular pattern to form a crystal.
There are two aspects to this pattern:

Periodicity

Symmetry

First, consider the periodicity…

A Primitive Cubic Lattice (CsCl)



Little crystallography

a ***unit cell*** of a lattice (or crystal) is a volume which can describe the lattice using only translations.

in 3 dimensions (for crystallographers), this volume is a parallelepiped.

such a volume can be defined by six numbers

- the lengths of the three sides,

  or three basis vectors

- and the angles between them

Little crystallography: lattice vectors and angles

Figure 2-2 (a) Illustration of lattice vector and interaxial angle designations.

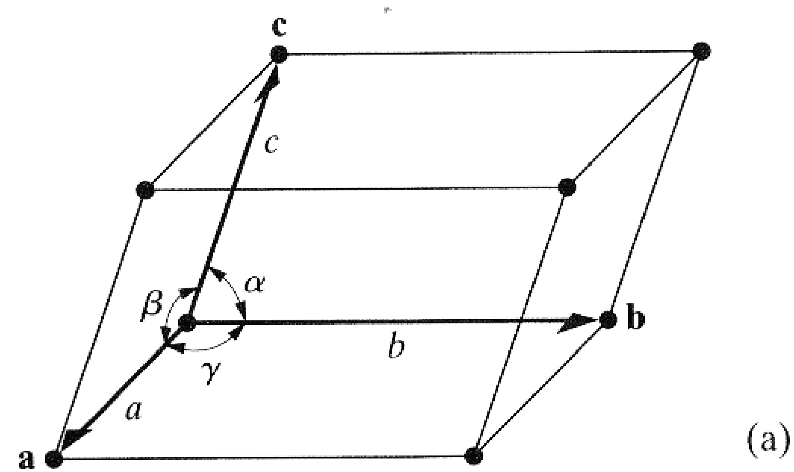


TABLE 2.1 DETERMINING WHICH INTER-AXIAL ANGLE IS BETWEEN WHICH PAIR OF AXES. THE ANGLE BETWEEN ANY TWO TRANSLATION VECTORS IS GIVEN BETWEEN THOSE VECTORS ON THE LINE BELOW.

Axis	**a**		**b**		**c**		**a**
Inter-axial Angle		γ		α		β	

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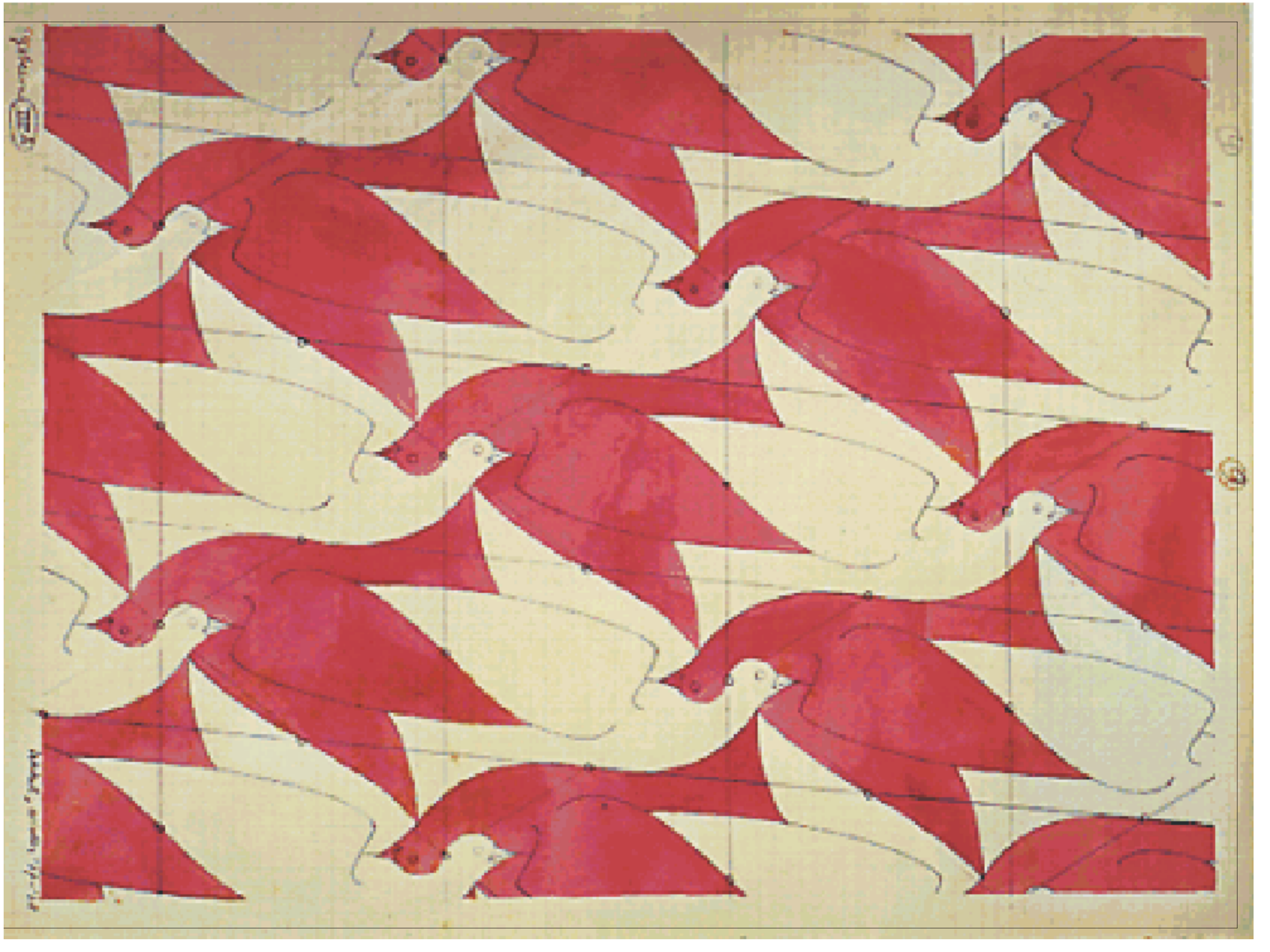
the unit cell is not unique

(c:\MyFiles\Clinic\index2.wrl)

Little crystallography



Little crystallography

Little crystallography

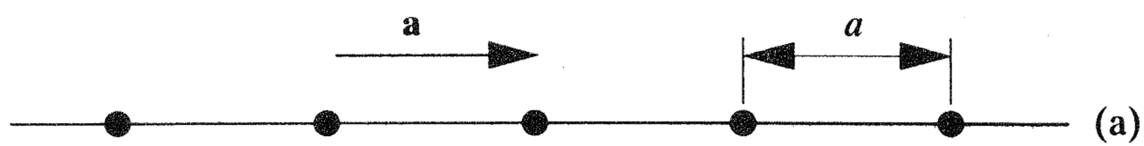
how to pick the unit cell?

- axis must be right-handed
- angles should be close to 90°
- periodicity **plus** symmetry

has to be fulfilled at the same time

Little crystallography: lattices

Figure 2-1 (a) One-dimensional lattice with parameter *a*.



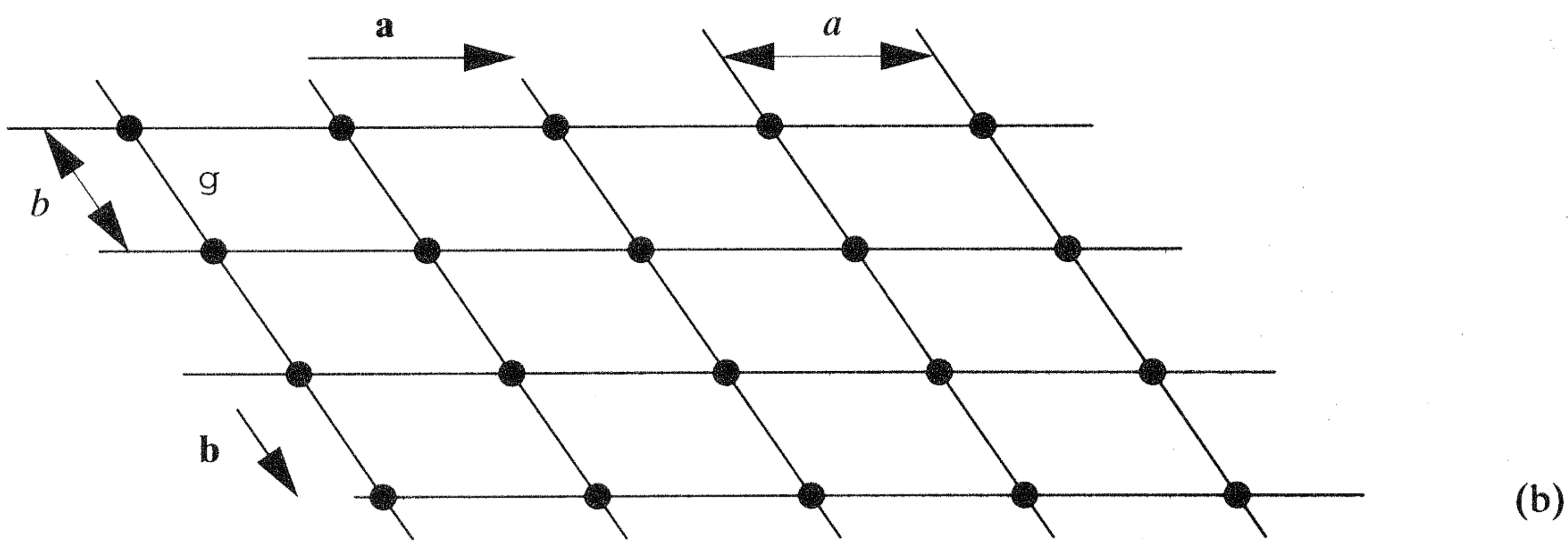


Figure 2-1 (b) Two-dimensional lattice with lattice translation vectors **a** and **b** and interaxial angle γ.

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Little crystallography: lattices

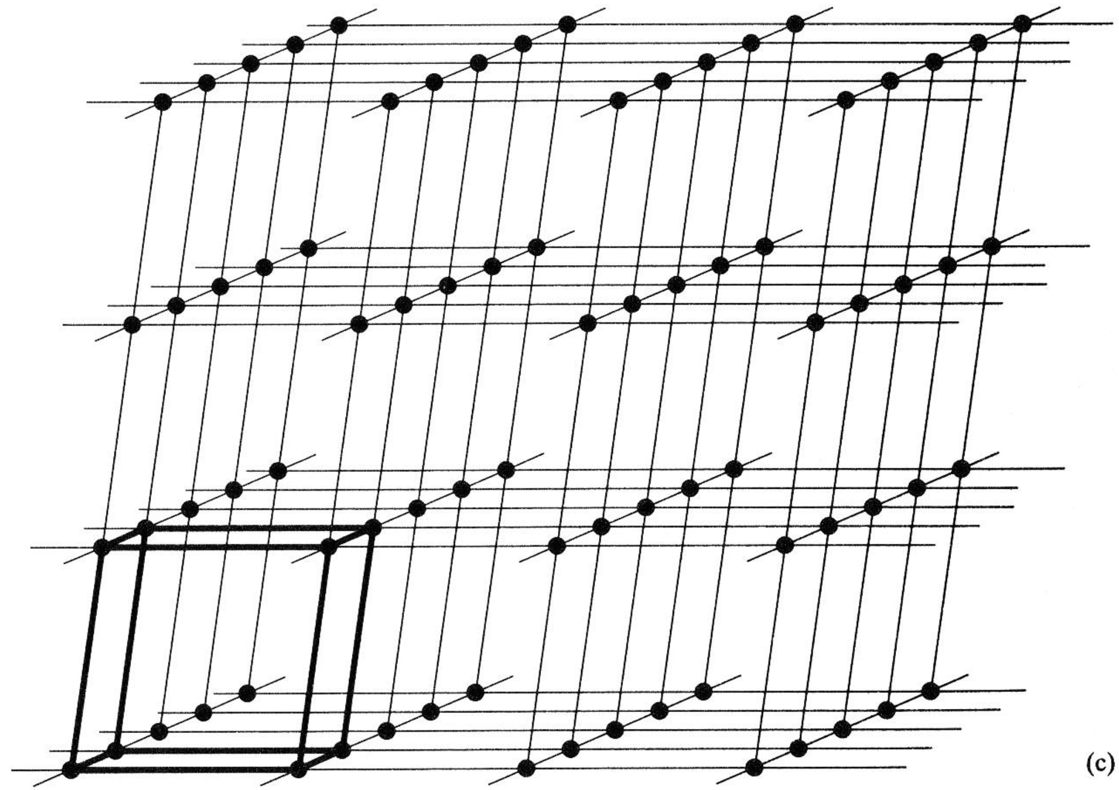

Figure 2-1 (c) Three-dimensional lattice with a primitive unit cell highlighted in bold. Lattice points are represented by the solid circles/spheres.

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Little crystallography: the unit-cell

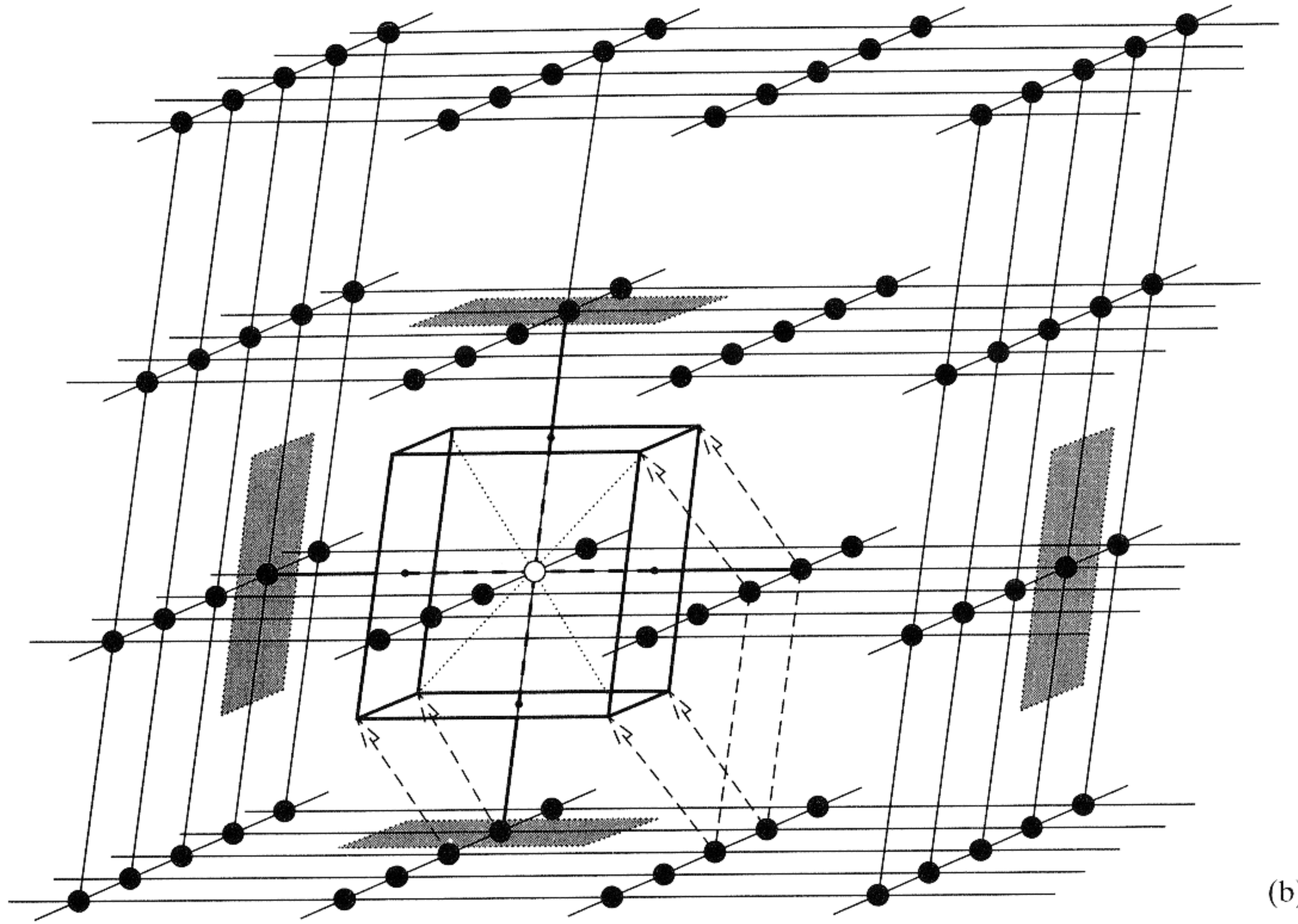
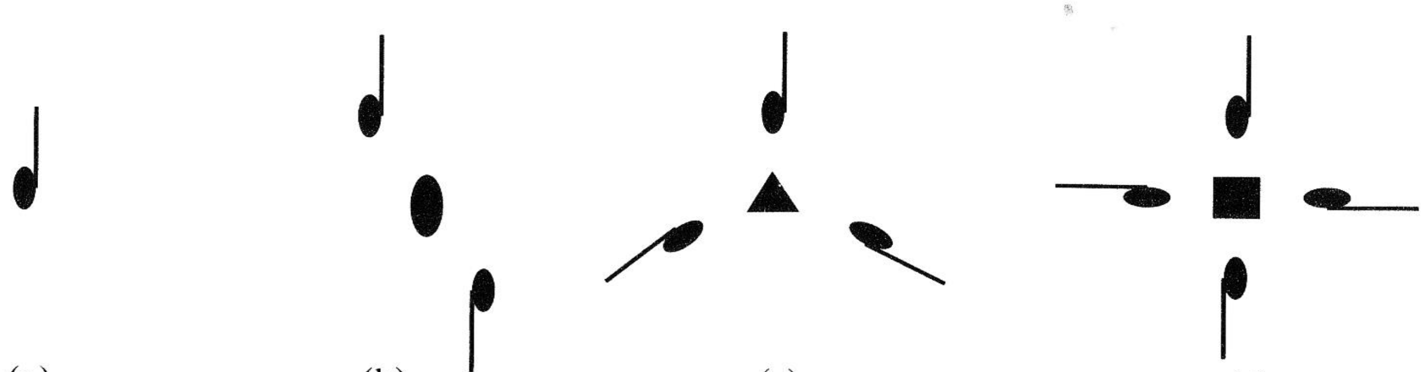


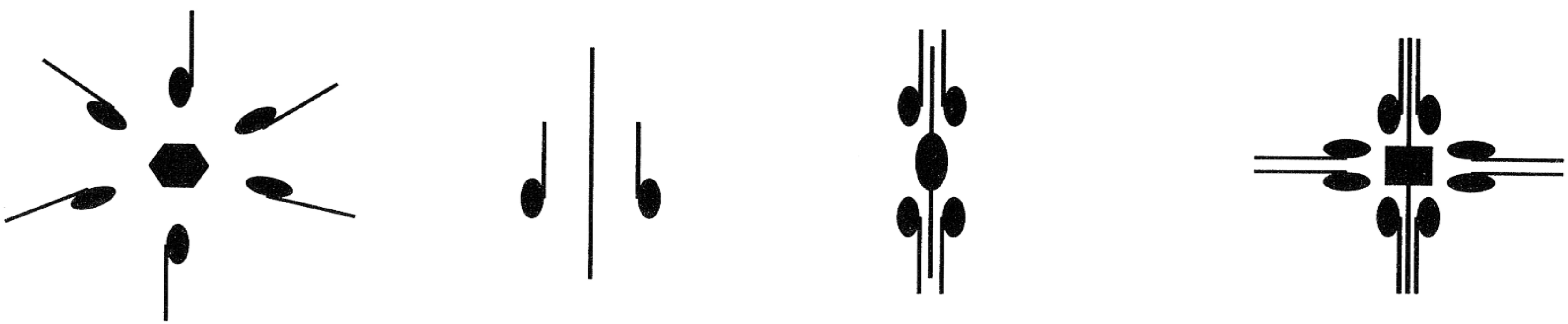
Figure 2-2 (b) Unit cells with the lattice points located at the cell corners and an alternative unit cell centered on one lattice point.

Little crystallography: symmetry operators



(a) (b) (c) (d)

one-fold "1"   two-fold "2"   three-fold "3"   four-fold "4" axis



(e) (f) (g) (h)

six-fould "6" axis   mirror-plane "m"   mirror plus two-fold axis   mirror plus four-fold axis

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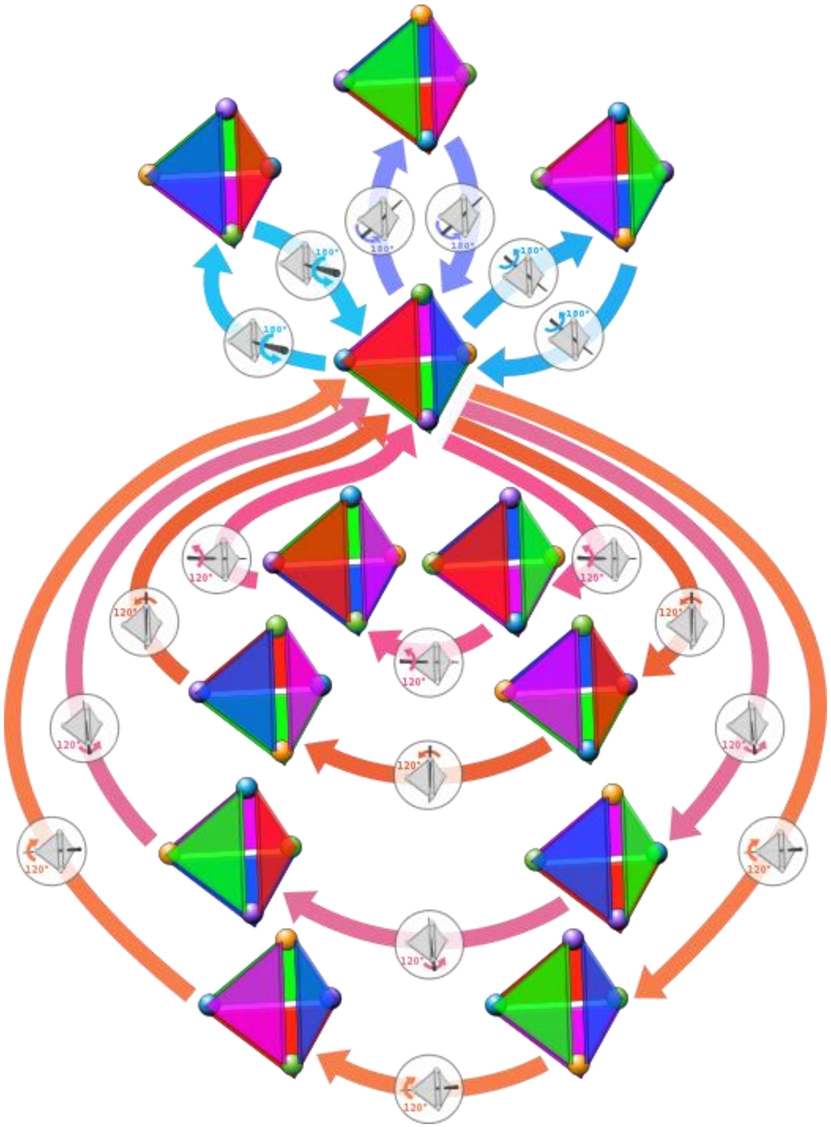
symmetry group: group of symmetry operations

a tetrahedron can be placed in
12 distinct positions by
rotation alone

the 12 rotations form the rotation group
group of symmetry operations
of the tetrahedron



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Point Group

a crystallographic point group is

a set of symmetry operations, like rotations or reflections,

that leave a central point fixed while moving

other directions and faces of the crystal

to the positions of features of the same kind

point groups must comply with translational symmetry

there exist 32 point-groups

Schoenflies notation

C_n (c:cyclic): n-fold rotation axis

S_{2n} (s:piegel=mirror) 2n-fold rotation-reflection axis

Dn (d:dihedral=two-sided) n-fold rotation axis

plus n twofold axes perpendicular to that axis

T (tetrahedron) symmetry of a tetrahedron

O (octahedron) symmetry of an octahedron or cube

Space Group

crystallographic space groups are

the crystallographic or Fedorov groups,

of consecutive symmetry operations

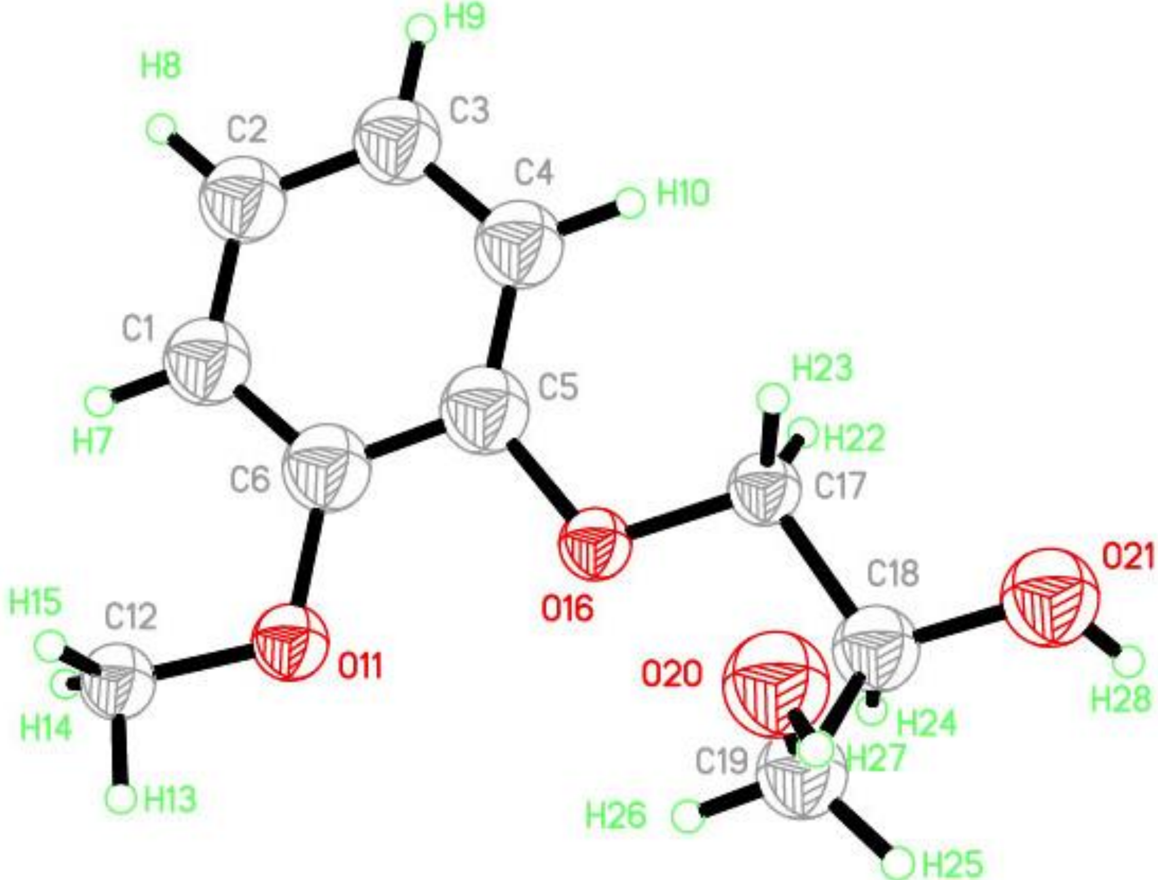
describing the symmetry of a crystal

there are 230 space-groups

Symmetry information is tabulated in *International Tables for Crystallography, Volume A* edited by Theo Hahn Fifth Edition 2002

Little crystallography: "spacegroup" notation

Guaifenesin, $P2_12_12_1$ (#19)

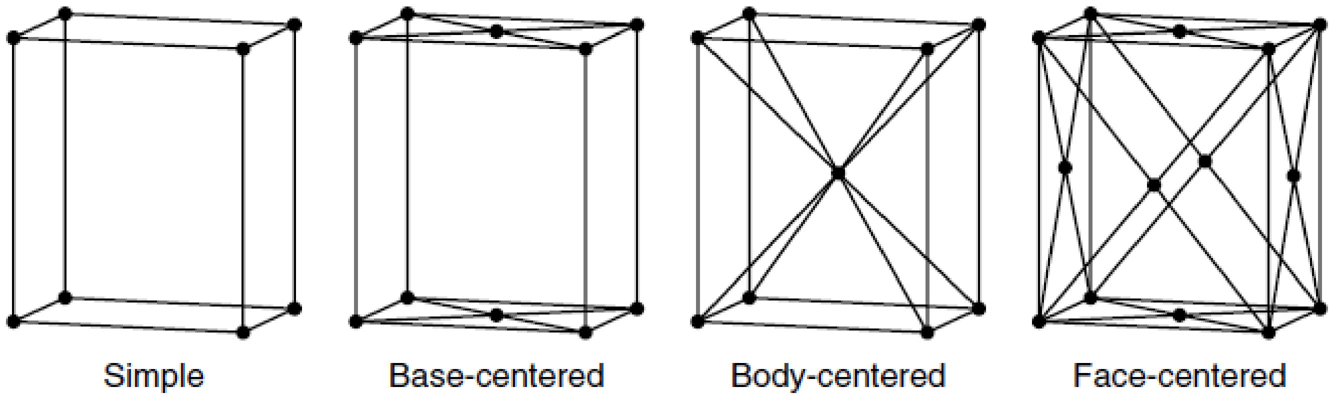


Little crystallography: "spacegroup" notation

$P2_12_12_1$ (#19)

P: simple

2_1: two-fold screw-axis



orthorhombic Bravais lattices

2_1 is a 180°, twofold rotation followed by a translation of ½ of the lattice vector,
3_1 is a 120°, threefold rotation followed by a translation of ⅓ of the lattice vector.

Guaifenesin:

also glyceryl guaiacolate,
an expectorant drug sold over the counter
usually taken orally to assist the bringing up (expectoration) of phlegm from the airways in acute respiratory tract infections

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Little crystallography: Bravais lattices

- space-groups can be sorted into 14 symmetry groups
- these form 7 crystal systems
- the spatial forms of the 14 symmetry groups

  are the Bravais lattices
- the Bravais lattices are the conceivable unit-cells

  which comply with:

  translational symmetry ***and*** crystal symmetry

  at the same time

Little crystallography: Bravais lattices

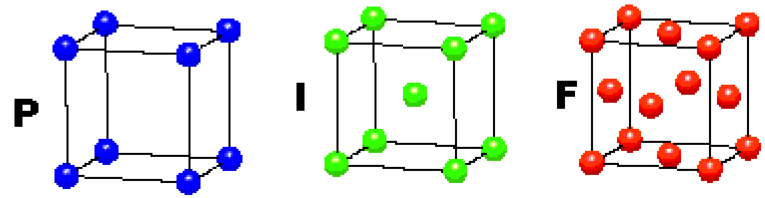
space groups (#)

195-230

CUBIC

a = b = c

$\alpha = \beta = \gamma = 90°$

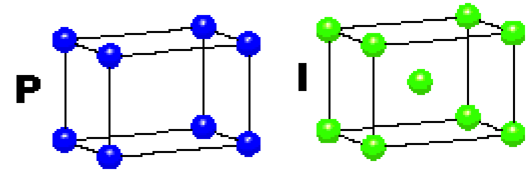


75-142

TETRAGONAL

a = b ≠ c

$\alpha = \beta = \gamma = 90°$

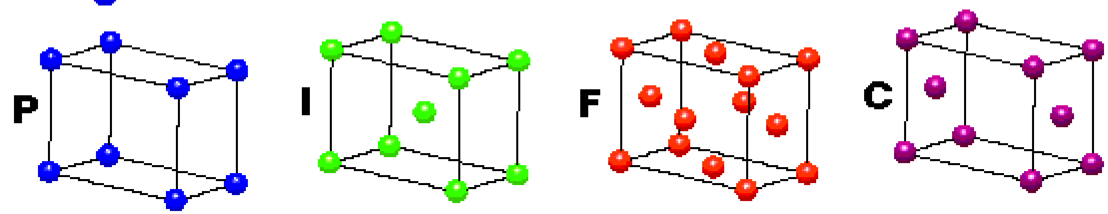


16-74

ORTHORHOMBIC

a ≠ b ≠ c

$\alpha = \beta = \gamma = 90°$



168-194

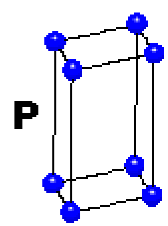
143167

HEXAGONAL

a = b ≠ c

$\alpha = \beta = 90°$

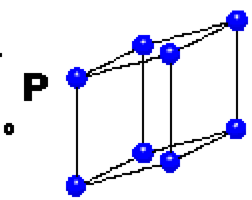
$\gamma = 120°$



TRIGONAL

a = b = c

$\alpha = \beta = \gamma \neq 90°$



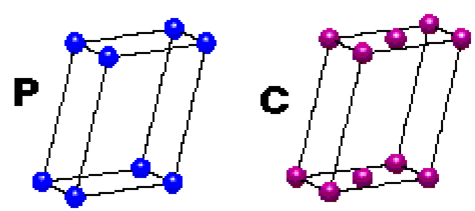
3-15

MONOCLINIC

a ≠ b ≠ c

$\alpha = \gamma = 90°$

$\beta \neq 120°$

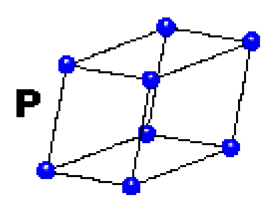


1-2

TRICLINIC

a ≠ b ≠ c

$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

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Little crystallography: Bravais lattices

TABLE 2.2 CRYSTAL SYSTEMS AND BRAVAIS LATTICES

(The symbol $\neq$ means that equity is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 2-7.)

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral* (trigonal)	Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90° \quad (\gamma = 120°)$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad (\alpha \neq \beta \neq \gamma \neq 90°)$	Simple	P

* Also called trigonal.

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Little crystallography: Bravais lattices

once again

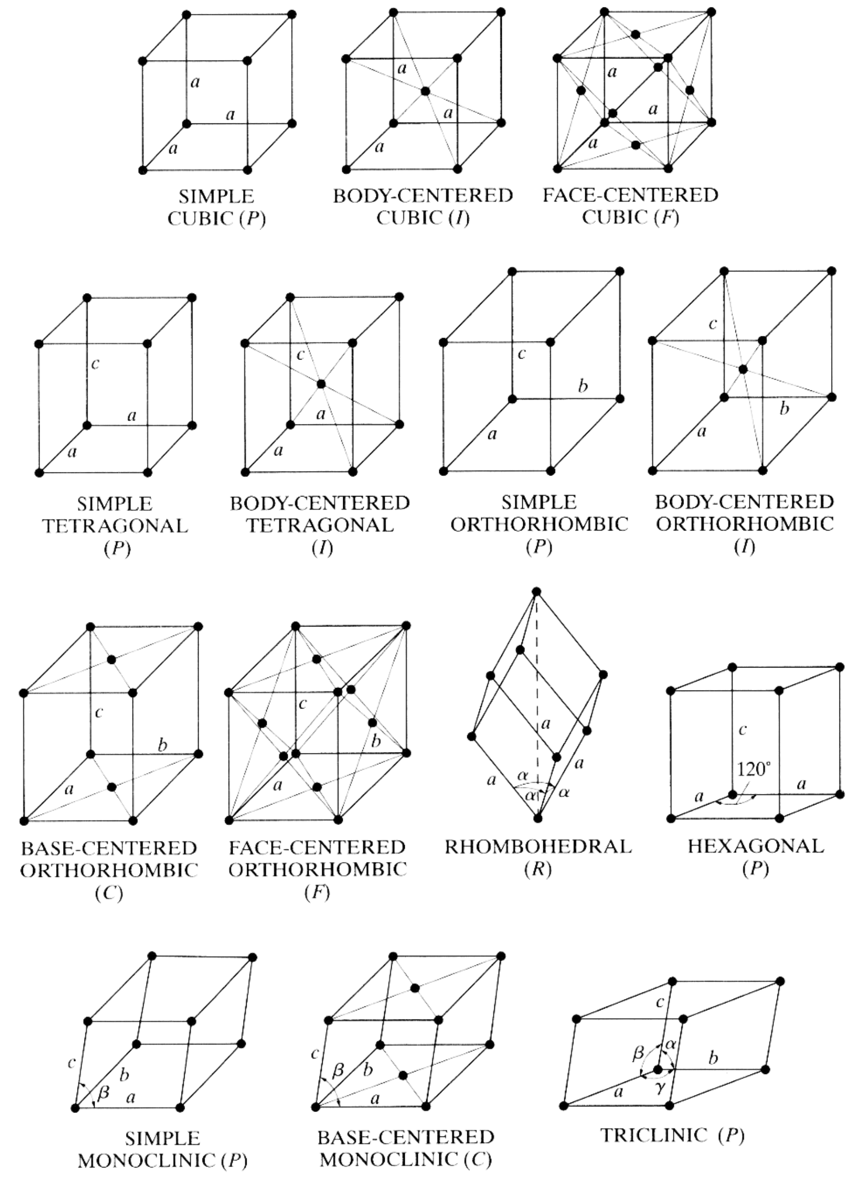

Figure 2-10 The fourteen Bravais lattices.

Little crystallography

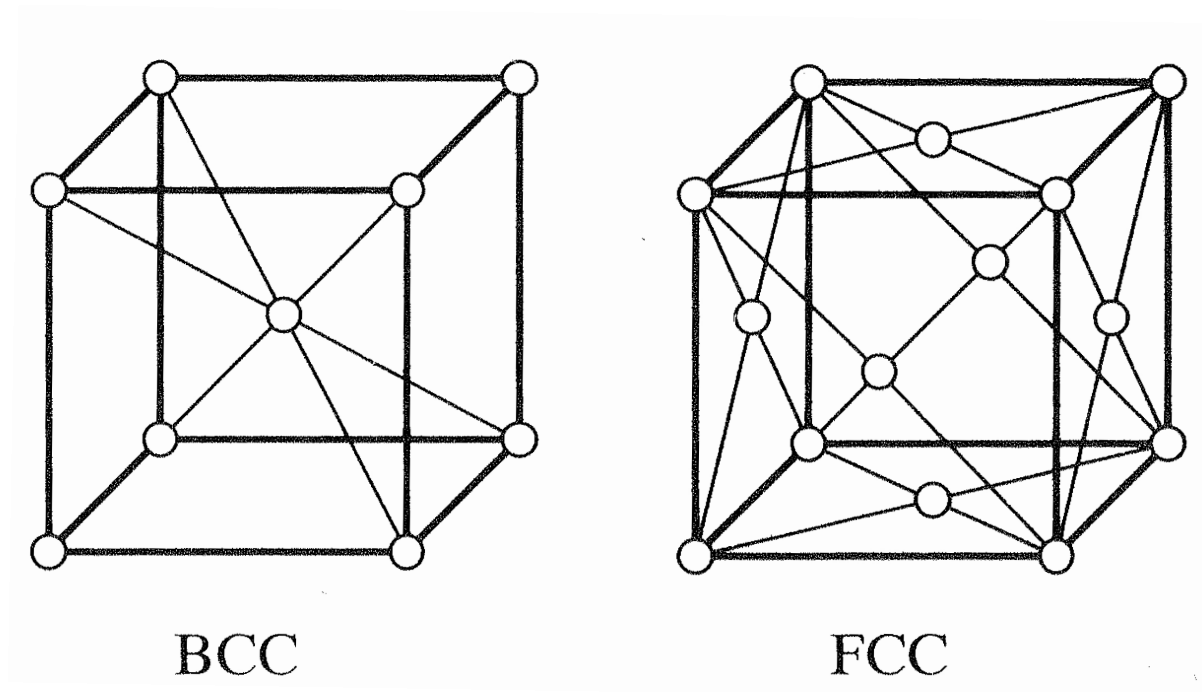

Figure 2-17 Structures of some common metals. Body-centered cubic: α-Fe, Cr, Mo, V, etc.: face-centered cubic: γ-Fe, Cu, Pb, Ni, etc.

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Little crystallography

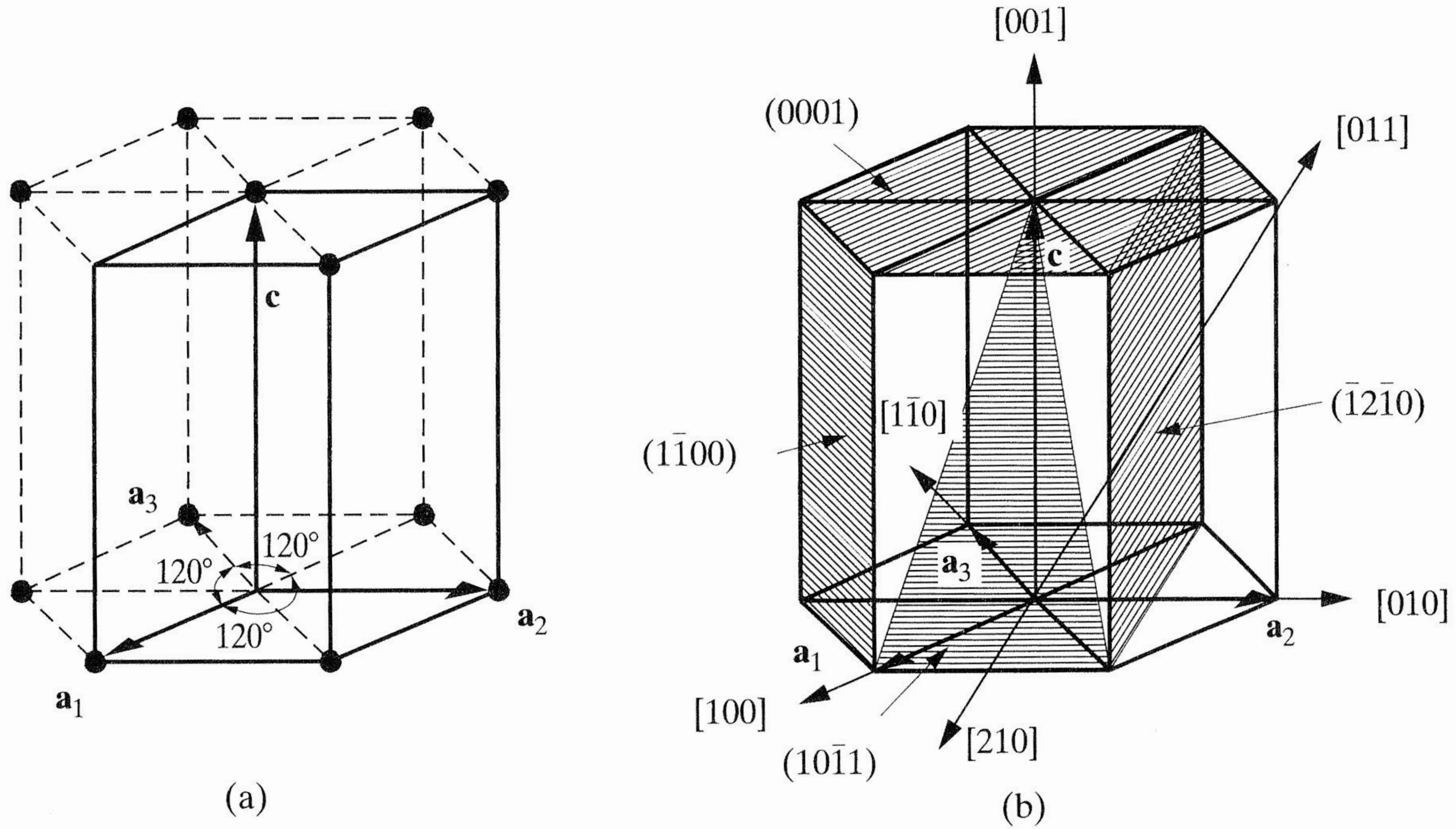

Figure 2-15 (a) The hexagonal unit cell (heavy lines) and (b) indices of planes and directions.

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Little crystallography

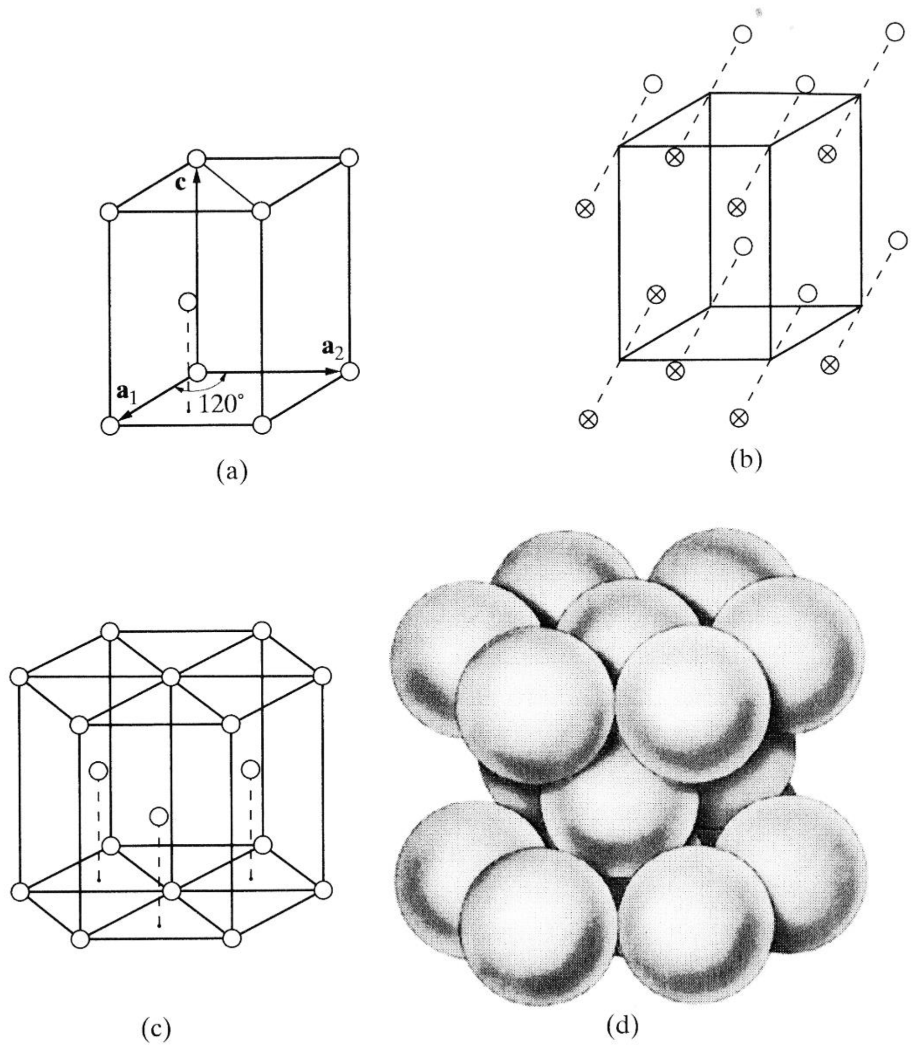

Figure 2-18 The hexagonal close-packed structure, shared by Zn, Mg, Be, αTi, etc.

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Little crystallography: lattice-planes in two dimensions

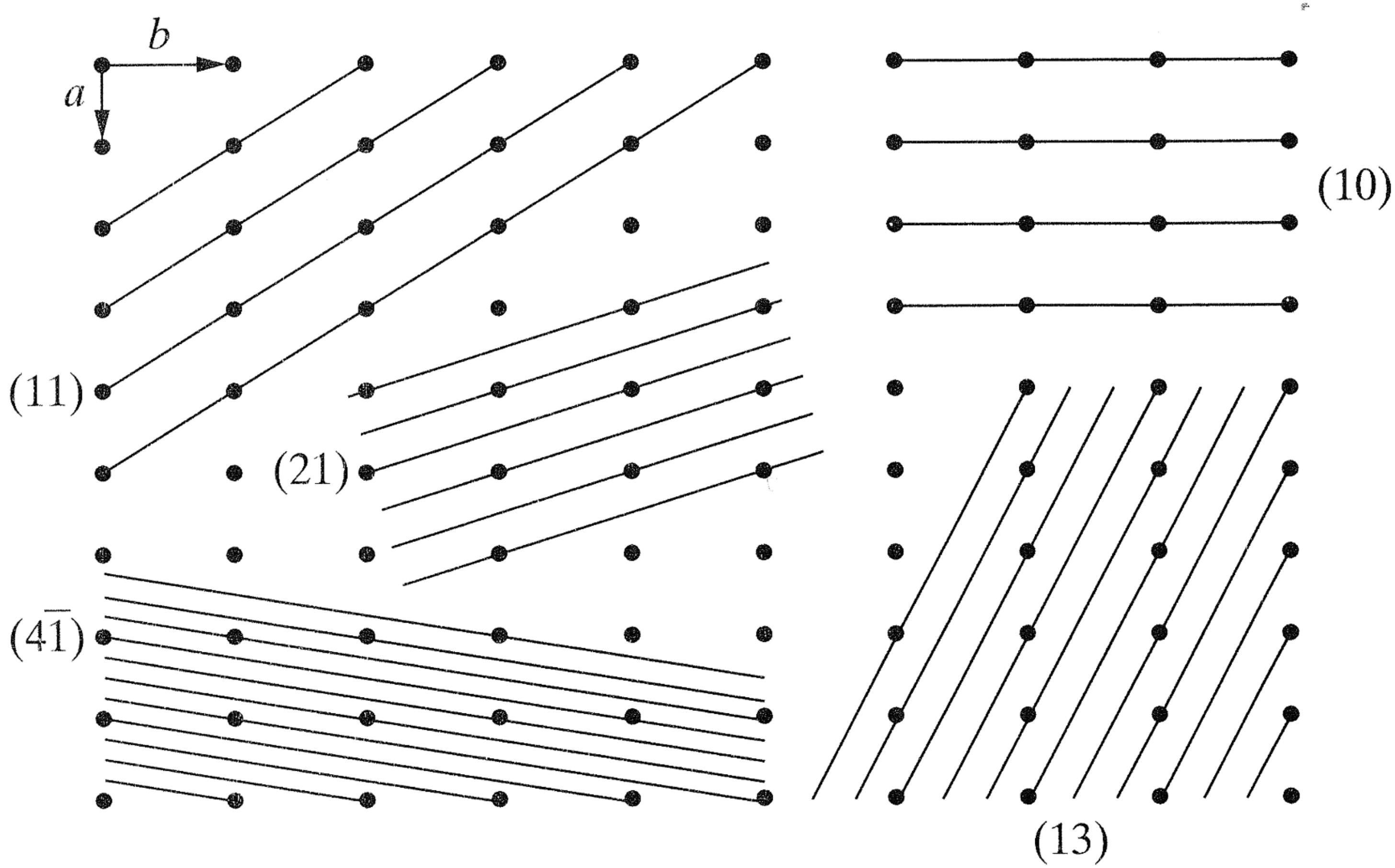

Figure 2-6 Two-dimensional lattice, showing that lines of lowest indices have the greatest spacing and the greatest density of lattice points.

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Miller indices

intercepts of the lattice plane:

a, b/2, 3c: 1, ½, 3

reciprocals of the intercepts:

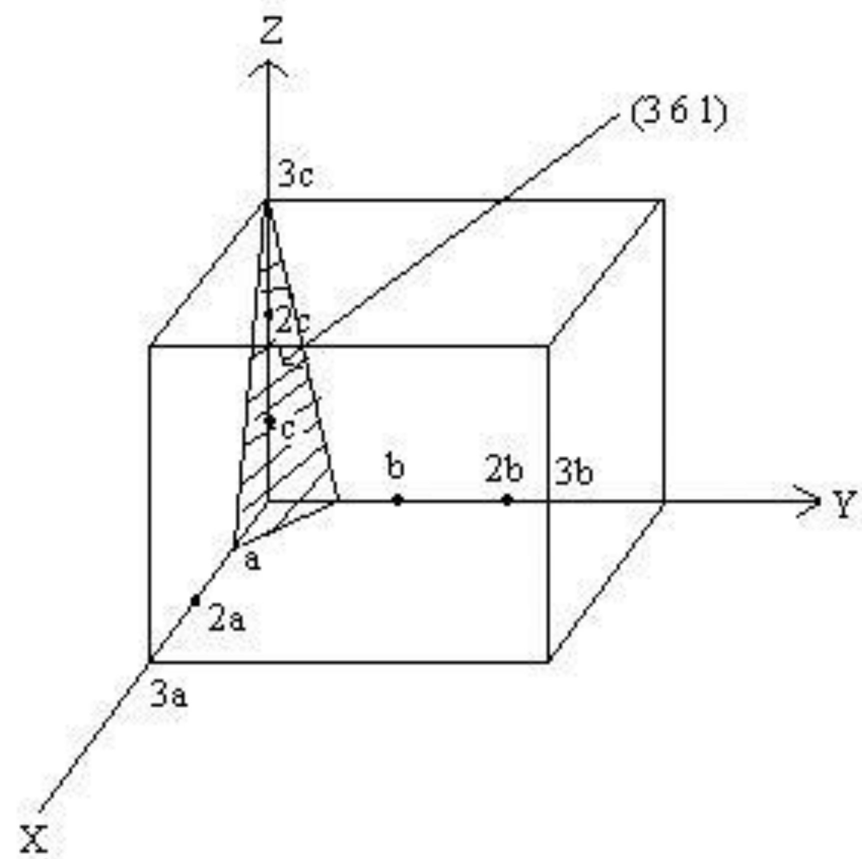
1, 2, 1/3

the smallest integers of the same ratio:

1:2:1/3 = 3:6:1

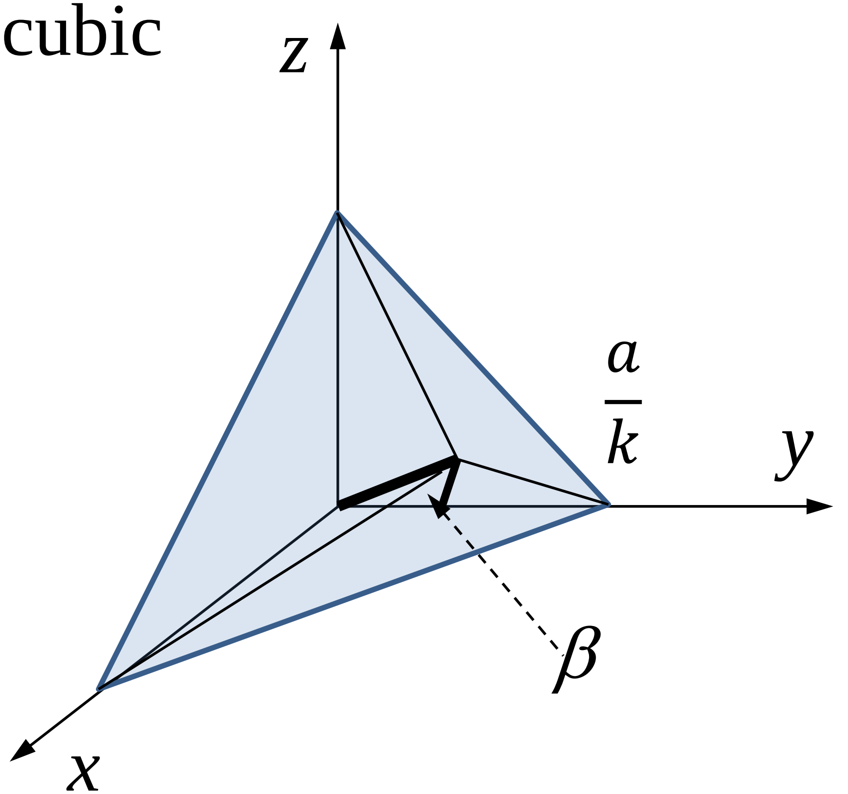
3,6,1: are the Miller indices of the plane

general denotation: *h,k,l*



properties of the Miller indices

cubic



$$\cos\alpha = \frac{hd}{a}$$

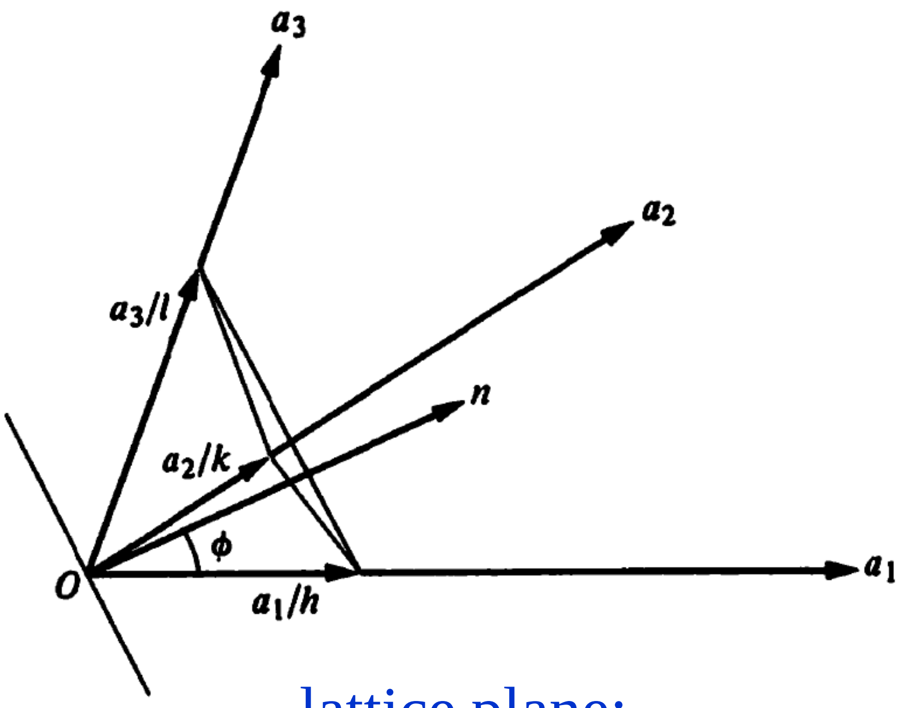
$$\cos\beta = \frac{d}{a/k} = \frac{kd}{a}$$

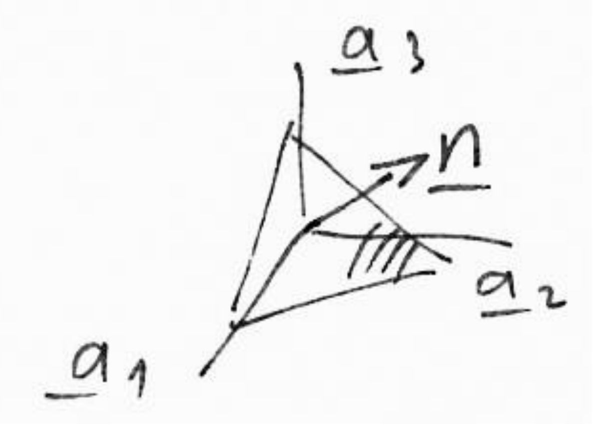
$$\cos\gamma = \frac{ld}{a}$$

$$\sum cos^2 = 1 = \frac{d^2}{a^2}(h^2 + k^2 + l^2)$$

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

properties of the Miller indices





lattice plane:

goes through the lattice points

n: normal vector of the lattice plane

$\mathbf{n} = h\mathrm{a}_1 + k\mathrm{a}_2 + l\mathrm{a}_3$

The integers *hkl* are usually called the Miller indices.

distance formulas for different lattices

Rhombohedral, $a = b = c$, $\alpha = \beta = \gamma$:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + lh)(\cos^2\alpha - \cos\alpha)}{a^2(1 + 2\cos^3\alpha - 3\cos^2\alpha)}$$

Hexagonal, $a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}.$$

Monoclinic, $\alpha = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right).$$

Orthorhombic, $\alpha = \beta = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.$$

Tetragonal, $a = b$, $\alpha = \beta = \gamma = 90°$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.$$

Cubic, $a = b = c$, $\alpha = \beta = \gamma = 90°$:

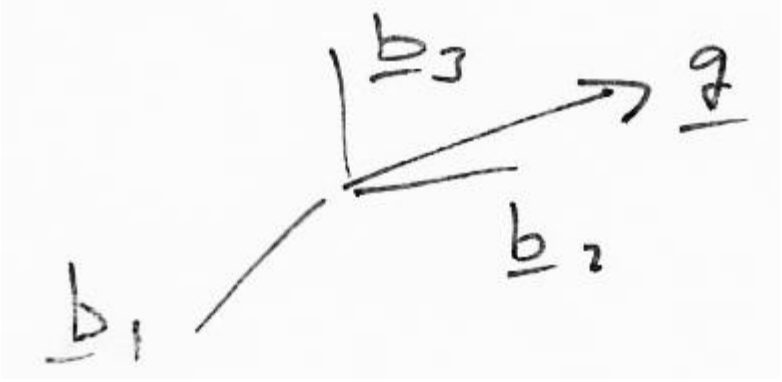
$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}.$$

reciprocal lattice

reciprocal space:

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \qquad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \qquad \mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

reciprocal-space vector: $\boldsymbol{g}$



$$\mathbf{a}_i \cdot \mathbf{b}_j = \begin{cases} 1, & i = j, \\ 0, & i \neq j. \end{cases}$$

$$\boldsymbol{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

$$\boldsymbol{ng} = h^2 + k^2 + l^2$$

Little crystallography

crystal lattice

reciprocal lattice

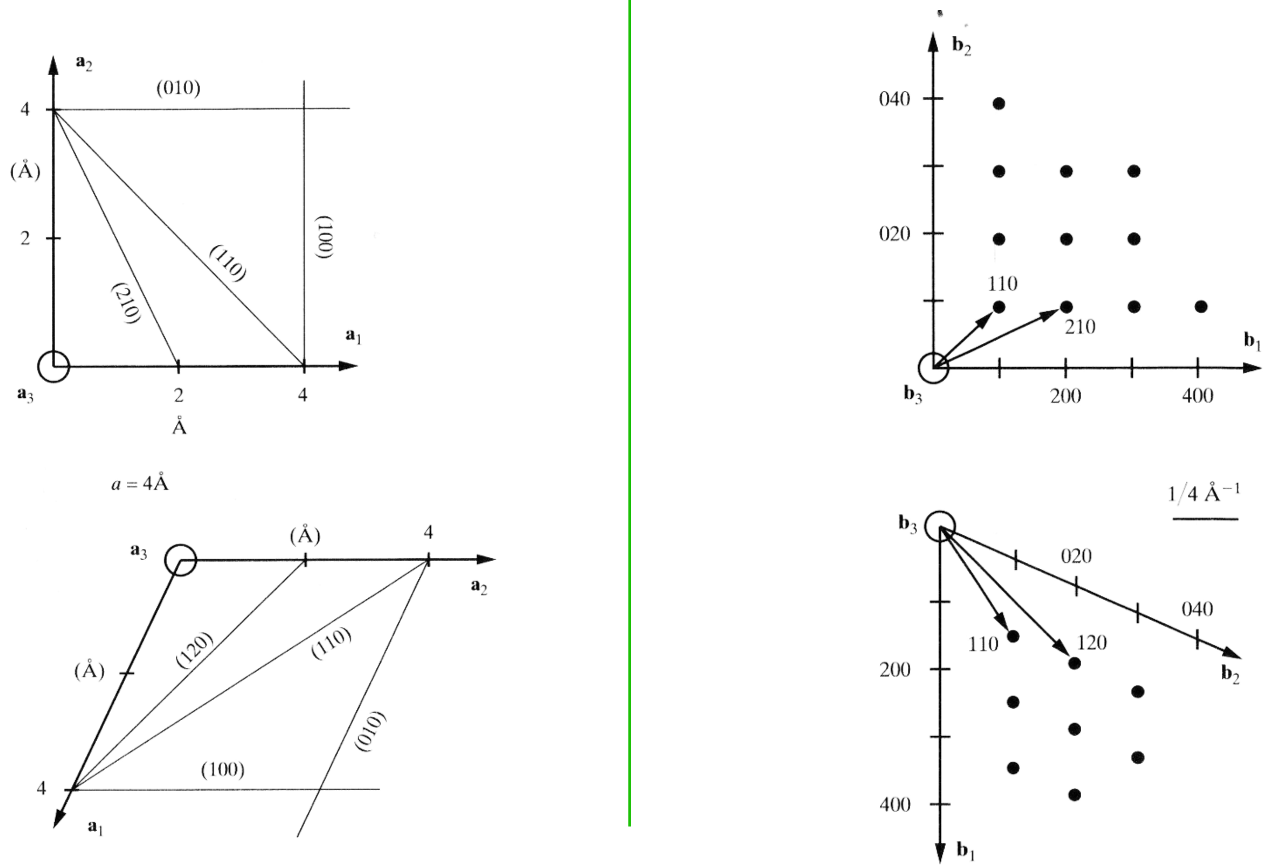
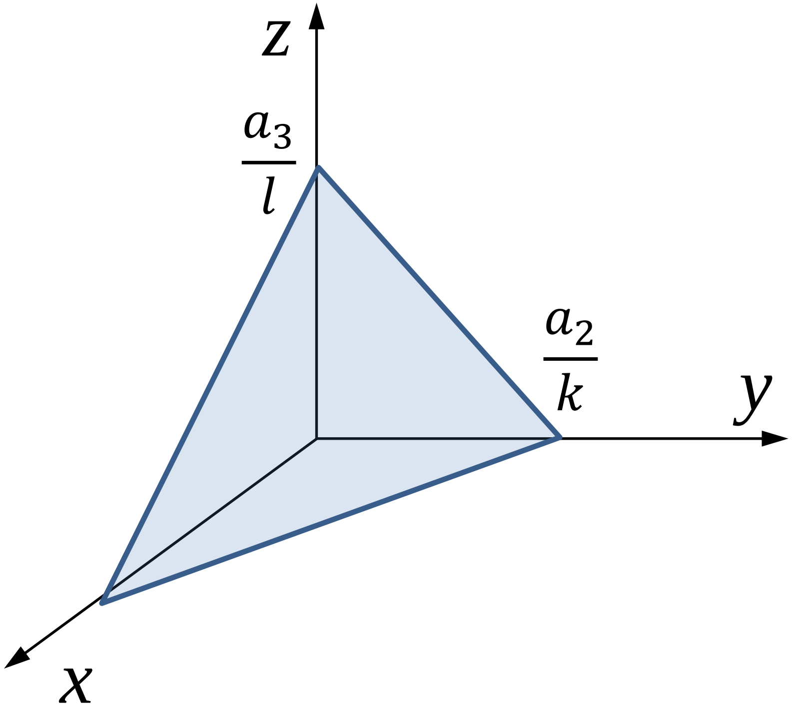


Figure 2-7 Illustration of crystal lattices (left side) and corresponding reciprocal lattices (right side) fo a cubic system (top) and an hexagonal system (bottom).

theorem #1:

$$\boldsymbol{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

$\boldsymbol{g}$ is perpendicular to the hkl crystal-plane



$\left(\frac{\boldsymbol{a}_3}{l} - \frac{\boldsymbol{a}_2}{k}\right)$ is a vector in the plane

$$\boldsymbol{g}\times\left(\frac{\boldsymbol{a}_3}{l} - \frac{\boldsymbol{a}_2}{k}\right) = 0$$

theorem #2:

$$|\boldsymbol{g}|_{hkl} = \frac{1}{d_{hkl}}$$

for cubic crystals:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$|\boldsymbol{g}| = \mathrm{b}\sqrt{h^2+k^2+l^2}$$

$$|\boldsymbol{g}| = \mathrm{b}\frac{a}{d} = \frac{ba}{d} = \frac{1}{d}$$

in more detail:

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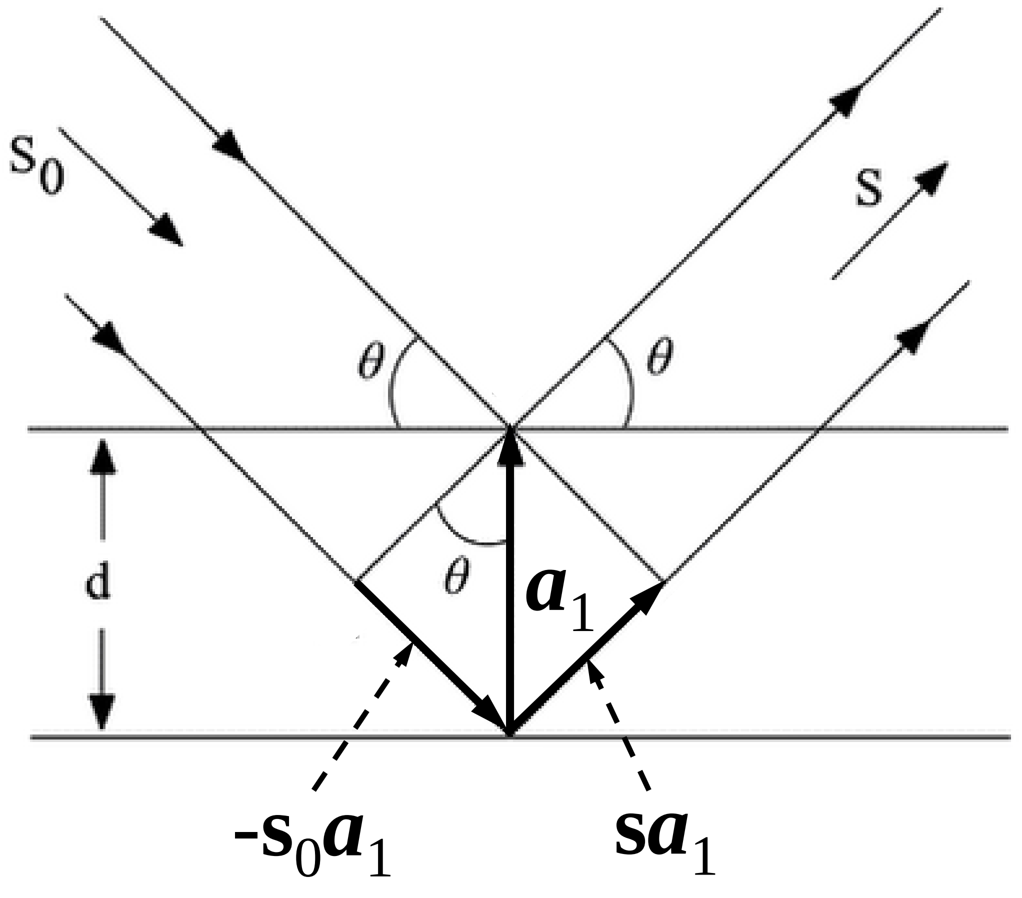
equations of Laue



difference of path for intensity maxima:

$$\boldsymbol{a}_1\mathbf{s} - \boldsymbol{a}_1\mathbf{s}_0 = n_1\lambda$$

$$\boldsymbol{a}_1(\mathbf{s} - \mathbf{s}_0) = n_1\lambda$$

$$\boldsymbol{a}_2(\mathbf{s} - \mathbf{s}_0) = n_2\lambda$$

$$\boldsymbol{a}_3(\mathbf{s} - \mathbf{s}_0) = n_3\lambda$$

the equations of Laue

equations of Laue

$$\frac{1}{\lambda}\mathbf{s} = \mathbf{k}$$

$$\boldsymbol{a}_1(\mathbf{k} - \mathbf{k}_0) = n_1$$

$$\boldsymbol{a}_2(\mathbf{k} - \mathbf{k}_0) = n_2$$

$$\boldsymbol{a}_3(\mathbf{k} - \mathbf{k}_0) = n_3$$

theorem #3:

n_i are integers

this can only be satisfied if and only if:

$\mathbf{k} - \mathbf{k}_0$ is a reciprocal-space vector:

$$\mathbf{k} - \mathbf{k}_0 = \boldsymbol{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$$

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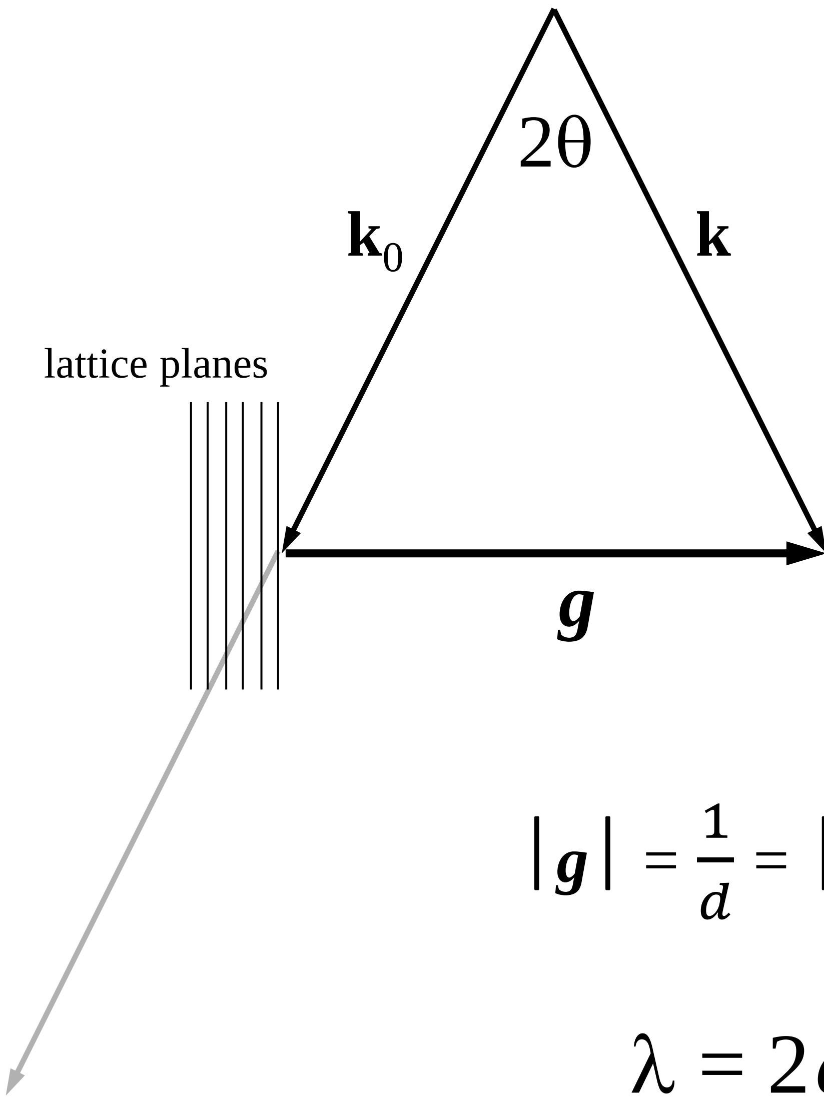
Bragg's law of scattering



$$|\boldsymbol{g}| = \frac{1}{d} = |\mathbf{k}-\mathbf{k}_0| = \frac{2sin\theta}{\lambda}$$

$$\lambda = 2dsin\theta$$

in more detail:

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Debye's equation of diffraction,

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Structure factor,

Patterson function,

Ewald construction in reciprocal space,

Fundamental equipment for

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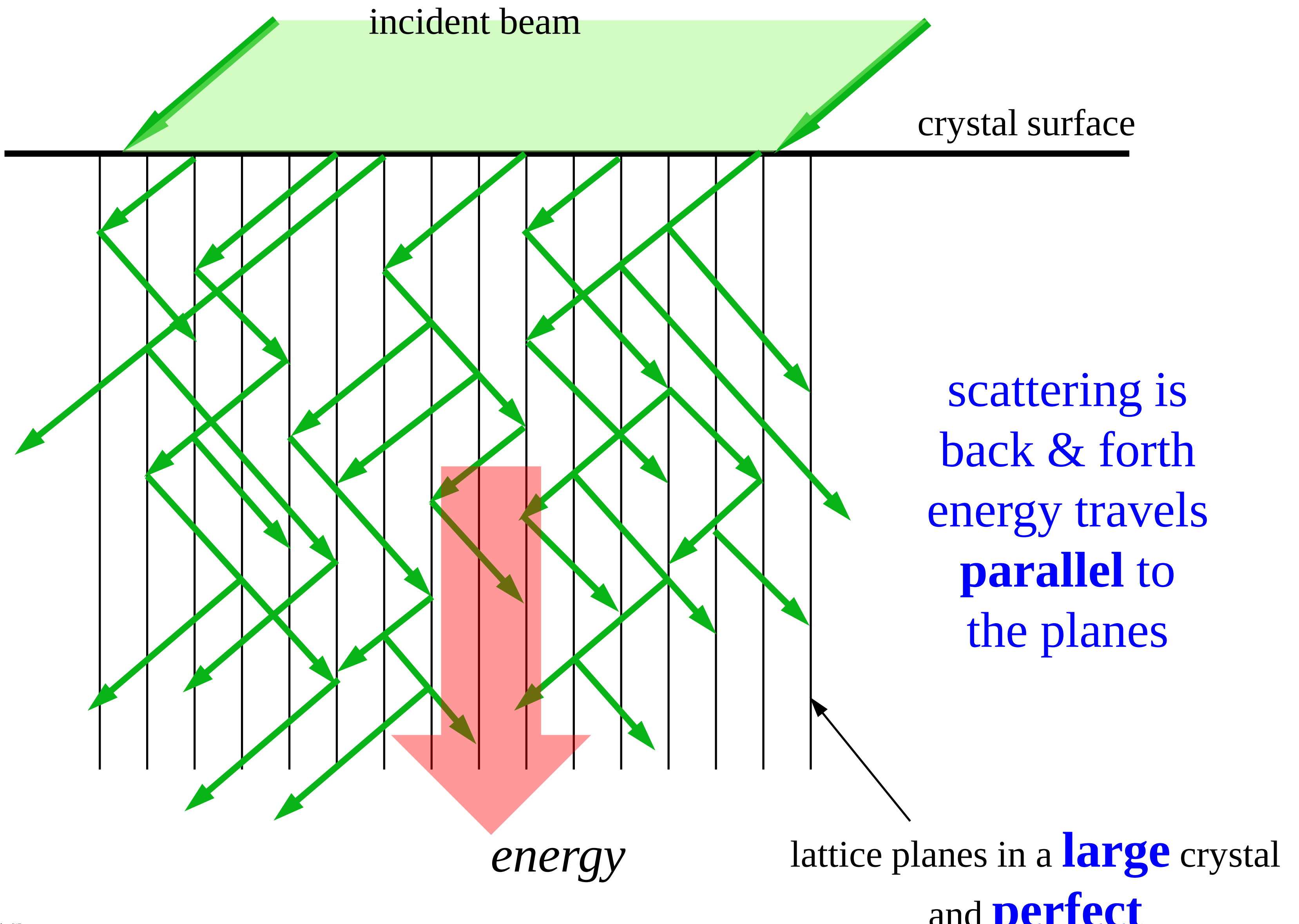
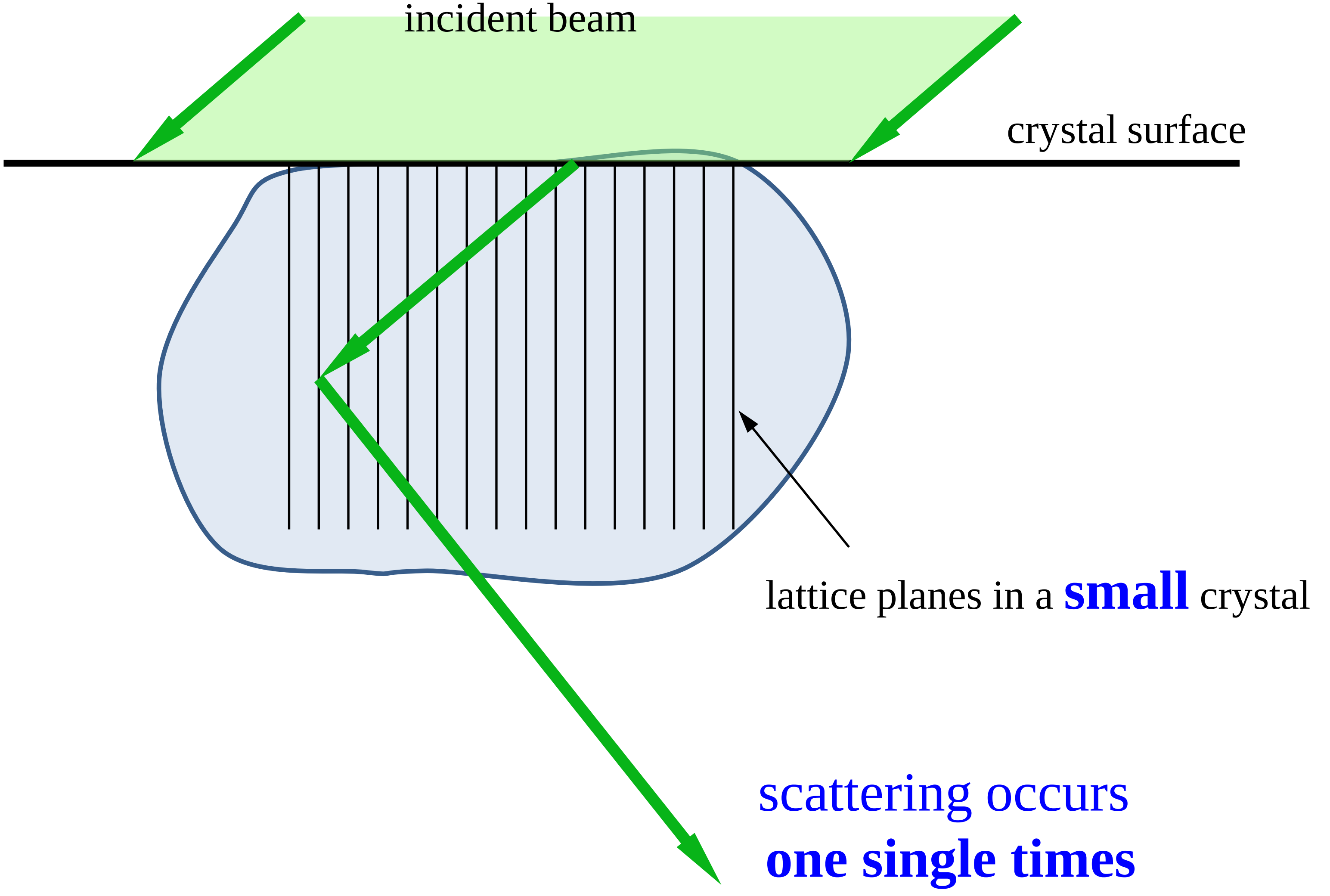
Diffractometers and detectors

kinematical *vs.* dynamical scattering



scattering is back & forth energy travels **parallel** to the planes

kinematical *vs.* dynamical scattering



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kinematical *vs.* dynamical scattering

we want to deal with **small crystals**

where **scattering occurs one single times**:

this is: **kinematical scattering**

in more detail:

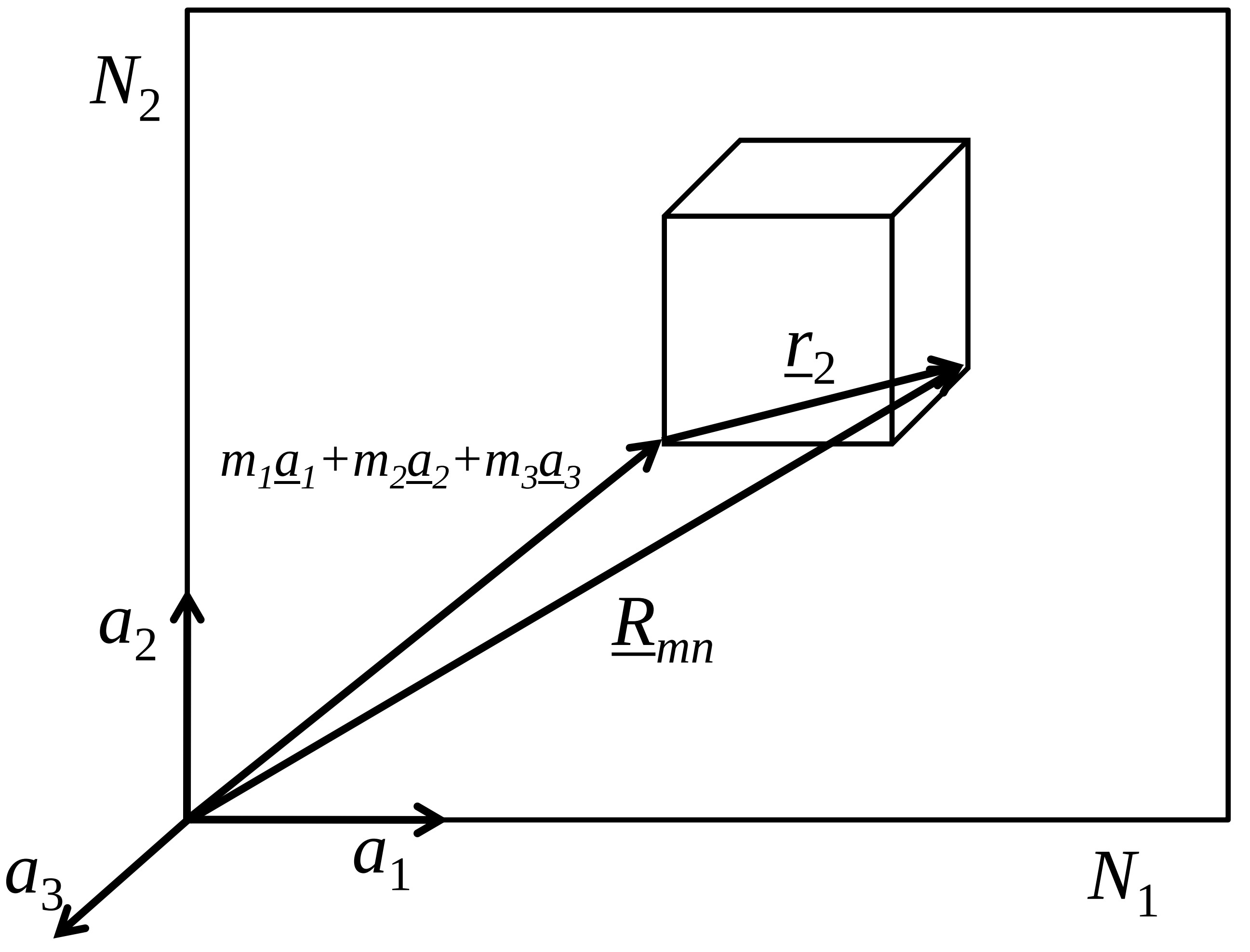
Little crystallography
Bragg’s law of scattering,
Kinematical versus dynamical scattering,
Physical meaning of extinction length,

Scattering by a small crystal,

Incorporating the unit cell and translational symmetry,

Structure factor,
Patterson function,
Ewald construction in reciprocal space,
Fundamental equipment for
X-ray diffraction experiments,
Diffractometers and detectors

scattering by a small crystal



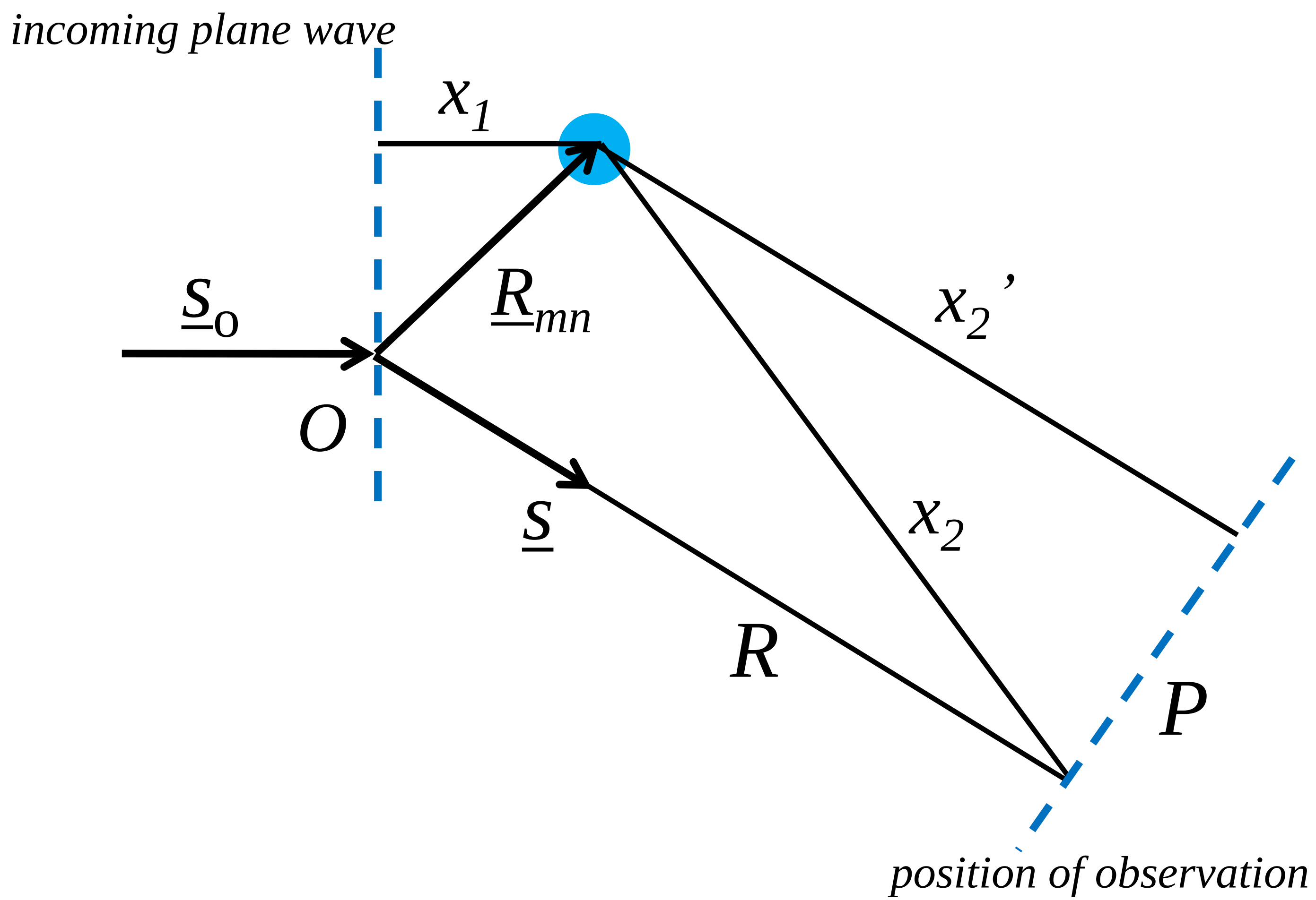
$$\underline{R}_{mn} = m_1\underline{a}_1+m_2\underline{a}_2+m_3\underline{a}_3+\underline{r}_n$$

By introducing the elementary-cell:

translational symmetry is taken care of

scattering by a small crystal

The X-ray beam is: **a plane wave** (Fraunhofer conditions)



Warren, X-ray Diffraction

Electromagnetic field at P

$$\mathcal{E}_{\mathrm{P}} = \frac{E_o e^2}{mc^2 R} f_n \, e^{2\pi i[\nu t - \frac{x_1 + x_2}{\lambda}]}$$

$$x_1 = \underline{s}_{\mathrm{o}} \underline{R}_{\mathrm{mn}}$$

$$x_2 = R - \underline{s}\, \underline{R}_{\mathrm{mn}} \qquad x_2 \cong x_2'$$

$$x_1 + x_2 = R - (\underline{s} - \underline{s}_{\mathrm{o}})\underline{R}_{\mathrm{mn}}$$

$$\mathcal{E}_{\mathrm{P}} = \frac{E_o e^2}{mc^2 R} f_n \, e^{i\{2\pi\nu t - \frac{2\pi}{\lambda}[R - (\boldsymbol{s} - \boldsymbol{s}_o)\boldsymbol{R}_{mn}]\}}$$

scattering by a small crystal

$$\mathcal{E}_{\mathrm{P}} = \frac{E_o e^2}{mc^2 R} \; f_n \, e^{i\{2\pi\nu t - \frac{2\pi}{\lambda}[R - (\boldsymbol{s}-\boldsymbol{s}_o)\boldsymbol{R}_{mn}]\}}$$

This has to be summed up for all atoms
within the
1) molecules
2) the “basis”
consisting of molecules
3) the “nodes” of the space group
consisting of basis and molecules

i.e. for all n and m indices

scattering by a small crystal

four summation terms: n, m_1, m_2, m_3,

$$\epsilon_p = \frac{E_0 e^2}{mc^2 R} e^{2\pi i[\nu t - (R/\lambda)]} \times$$

$$\sum_n f_n e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot \mathbf{r}_n} \times$$

$$\sum_{m_1=0}^{N_1-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_1\mathbf{a}_1} \times$$

$$\sum_{m_2=0}^{N_2-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_2\mathbf{a}_2} \times$$

$$\sum_{m_3=0}^{N_3-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_3\mathbf{a}_3}$$

scattering by a small crystal

the first term:

$$\epsilon_p = \frac{E_0 e^2}{mc^2 R} e^{2\pi i[\nu t - (R/\lambda)]}$$

is NOT affected by the structure

scattering by a small crystal

the three terms with: m_1, m_2, m_3: are equivalent with the

Laue equations:

$$\sum_{m_1=0}^{N_1-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_1\mathbf{a}_1}$$

$$\sum_{m_2=0}^{N_2-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_2\mathbf{a}_2}$$

$$\sum_{m_3=0}^{N_3-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_3\mathbf{a}_3}$$

Warren, X-ray Diffraction

scattering by a small crystal

the three terms with: m_1, m_2, m_3 have the form of a geometric series:

$$S = a + ar + ar^2 + \cdots + l = \frac{rl - a}{r - 1}$$

using this relation:

$$\sum_{m_1=0}^{N_1-1} e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot m_1\mathbf{a}_1} = \frac{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot N_1\mathbf{a}_1} - 1}{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{a}_1} - 1}$$

for all three sums over m_i:

$$\frac{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot N_1\mathbf{a}_1} - 1}{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{a}_1} - 1} \frac{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot N_2\mathbf{a}_2} - 1}{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{a}_2} - 1} \frac{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot N_3\mathbf{a}_3} - 1}{e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{a}_3} - 1}$$

the intensity is the squared absolute value of the amplitude: $\epsilon_p \epsilon_p^*$

this will have the form:

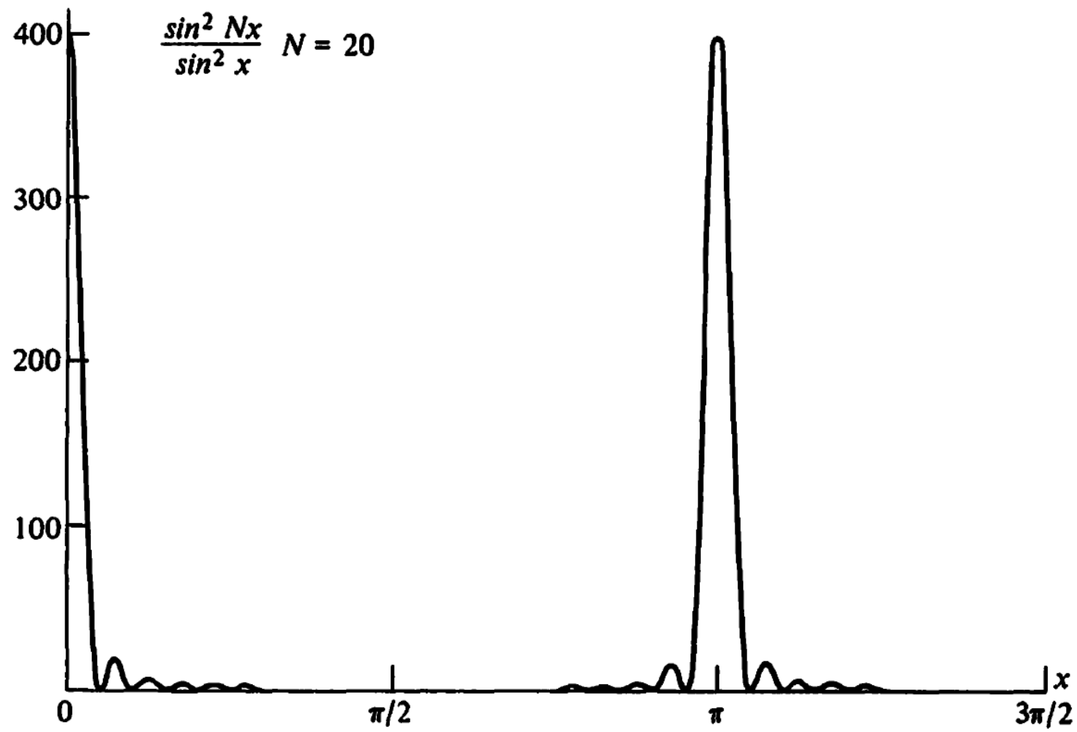
$$\left(\frac{e^{iNx} - 1}{e^{ix} - 1}\right)\left(\frac{e^{-iNx} - 1}{e^{-ix} - 1}\right) = \frac{2 - 2\cos Nx}{2 - 2\cos x} = \frac{\sin^2 Nx/2}{\sin^2 x/2}$$

Warren, X-ray Diffraction

scattering by a small crystal

the function $\frac{\sin^2 Nx/2}{\sin^2 x/2}$ has

the form for N=20:



it can be shown that:

$$\lim_{N\to\infty} \frac{\sin^2 Nx/2}{\sin^2 x/2} = \delta(x)$$

the maxima are at: $\boldsymbol{r}(\boldsymbol{k}\text{-}\boldsymbol{k}_0)$ = integers

just as in the Laue equations

(or $2\pi\times$integers)

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Warren, X-ray Diffraction

in more detail:

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scattering by a small crystal

now we turn to the term: $\sum_n f_n e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_n}$

this contains $\boldsymbol{r}_\mathrm{n}$, the positions of the atoms in the unit-cell

the aim of the diffraction experiment is to determine the $\boldsymbol{r}_\mathrm{n}$ values,
i.e. the positions of the atoms in the structure,
the term above gives the $\boldsymbol{r}_\mathrm{n}$ values:

we call this term the structure factor: F or F_{hkl}

Warren, X-ray Diffraction

the structure factor

$$F = \sum_n f_n e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_n}$$

in a Bragg maximum, at $\boldsymbol{g}_{hkl}$, the expression $\dfrac{2\pi(\mathbf{s}-\mathbf{s}_0)}{\lambda}$

must be a reciprocal lattice vector, i.e.

$$\frac{2\pi(\mathbf{s}-\mathbf{s}_0)}{\lambda} = \boldsymbol{g}_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$$

$\boldsymbol{r}_\mathrm{n}$ is a lattice vector: $\boldsymbol{r}_\mathrm{n} = \mathrm{x}_1\boldsymbol{a}_1 + x_2\boldsymbol{a}_2 + x_3\boldsymbol{a}_3$

$\boldsymbol{g}_{hkl}\boldsymbol{r}_\mathrm{n} = hx_\mathrm{n} + ky_\mathrm{n} + lz_\mathrm{n}$, thus

$$F_{hkl} = \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

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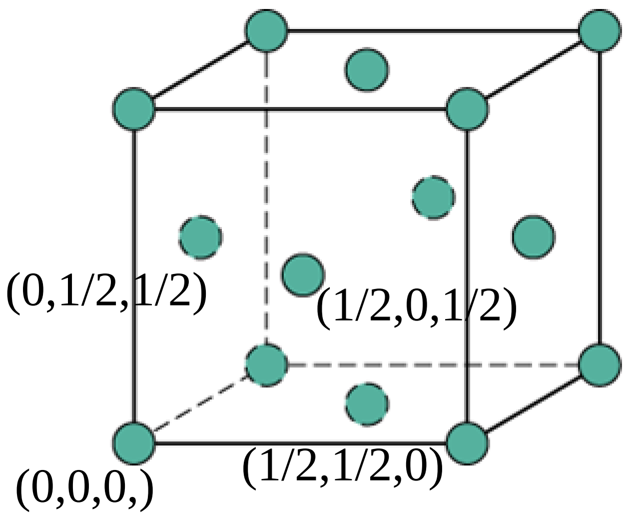
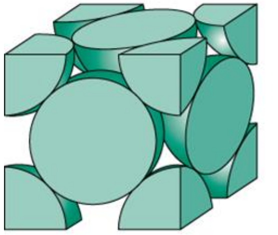
structure factor for a simple *fcc* crystal:



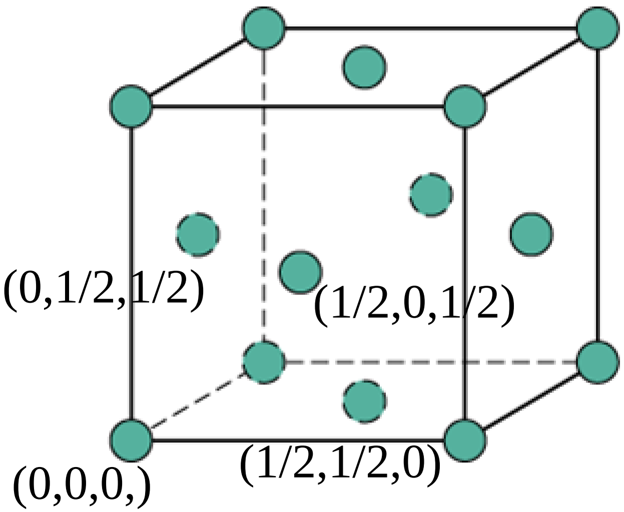


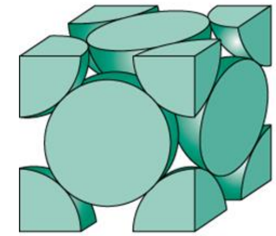
$$F_{hkl} = f\,(e^{2\pi i(0)}+e^{2\pi i(h+k)}+e^{2\pi i(h+l)}+e^{2\pi i(k+l)})$$

if *hkl* all even:	1	1	1	1
if *hkl* all odd:	1	1	1	1
if *hkl* mixed parity: e.g.	1	-1	-1	1

the structure factor

structure factor for a simple *fcc* crystal:





1 0 0	missing
1 1 0	missing
1 1 1	
2 0 0	
2 1 0	missing
2 1 1	missing
2 2 0	
2 2 1	missing
2 2 2	
3 0 0	missing
3 1 0	missing
3 1 1	
.	
.	

systematic extinction

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structure factor for a crystal with the *fcc* Bravais lattice:

for every atom with fractional coordinates $x_n y_n z_n$, there must be three identical atoms with coordinates $x_n + \frac{1}{2}, y_n + \frac{1}{2}, z_n$; $x_n + \frac{1}{2}, y_n, z_n + \frac{1}{2}$; and $x_n, y_n + \frac{1}{2}, z_n + \frac{1}{2}$

If the cell contains n atoms, there are $n/4$ groups of four

all four atoms in each group having the same scattering factor

$$F_{hkl} = \sum_{n/4} f_n \{ e^{2\pi i(hx_n + ky_n + lz_n)} + e^{2\pi i(h[x_n+1/2]+k[y_n+1/2]+lz_n)} + e^{2\pi i(h[x_n+1/2]+ky_n+l[z_n+1/2])} + e^{2\pi i(hx_n+k[y_n+1/2]+l(z_n+1/2])} \}$$

or:

$$hkl \text{ unmixed: } F_{hkl} = 4 \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

$$hkl \text{ mixed: } \quad F_{hkl} = 0.$$

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structure factor for a crystal with the *bcc* Bravais lattice:

$$F_{hkl} = [1 + e^{\pi i(h+k+l)}] \sum_{n/2} f_n e^{2\pi i(hx_n+ky_n+lz_n)}$$

or:

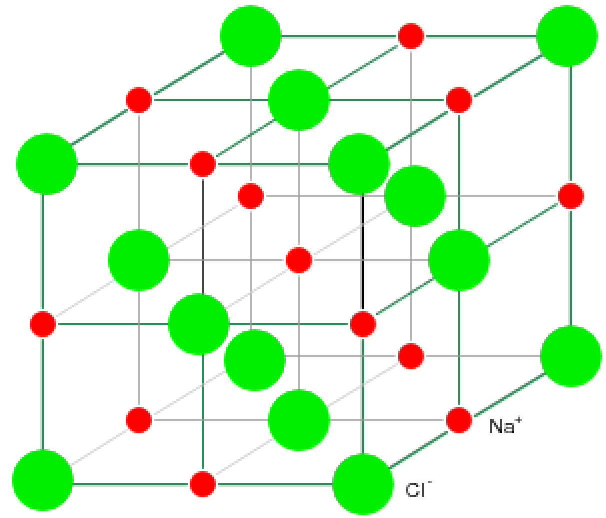
$$h + k + l = \text{even}: \qquad F_{hkl} = 2 \sum_{n/2} f_n e^{2\pi i(hx_n+ky_n+lz_n)}$$

$$h + k + l = \text{odd}: \qquad F_{hkl} = 0.$$

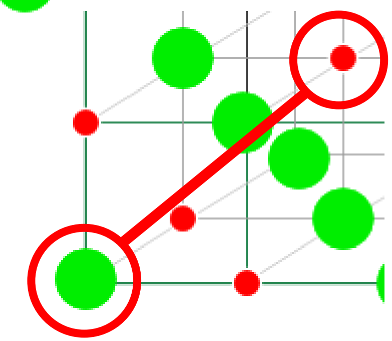
Warren, X-ray Diffraction

the structure factor for NaCl

$$\text{Cl} \quad \begin{array}{ccc} 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{array} \qquad \text{Na} \quad \begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 \end{array}$$



in $$F_{hkl} = 4 \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$



either Cl or Na can be used for evaluationg the “group”, let (000) be for Cl and (1/2,1/2,1/2) for Na:

the group

this yields:

hkl mixed: $F_{hkl} = 0$

hkl unmixed: $F_{hkl} = 4[f_{\text{Cl}} + f_{\text{Na}} e^{\pi i(h+k+l)}]$

finally:

hkl all even: $F_{hkl} = 4(f_{\text{Cl}} + f_{\text{Na}})$

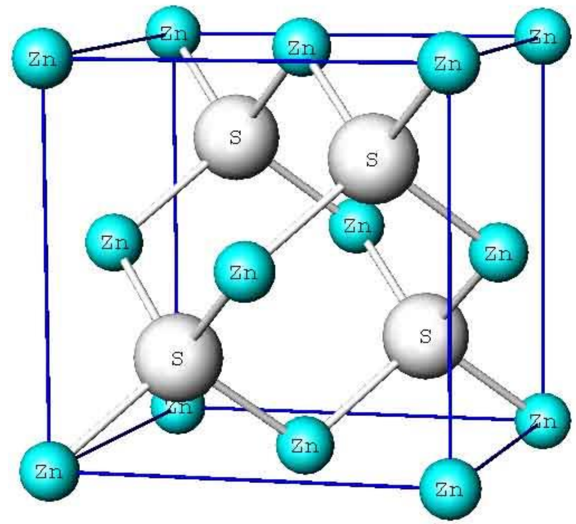
hkl all odd: $F_{hkl} = 4(f_{\text{Cl}} - f_{\text{Na}})$

hkl mixed: $F_{hkl} = 0.$

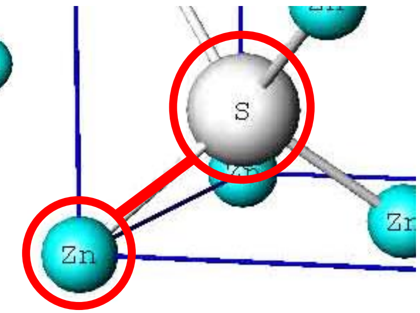
Warren, X-ray Diffraction

the structure factor for ZnS (zink-blend)

Zn	0	0	0	S	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	$\frac{1}{2}$	$\frac{1}{2}$	0		$\frac{3}{4}$	$\frac{3}{4}$	$\frac{1}{4}$
	$\frac{1}{2}$	0	$\frac{1}{2}$		$\frac{3}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
	0	$\frac{1}{2}$	$\frac{1}{2}$		$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$



in $$F_{hkl} = 4\sum_{n/4} f_n e^{2\pi i(hx_n+ky_n+lz_n)}$$



either Cl or Na can be used for evaluationg the "group",
let (000) be for Zn and (1/4,1/4,1/4) for S:

the group

this yields: hkl unmixed: $F_{hkl} = 4[f_{\mathrm{Zn}} + f_{\mathrm{S}} e^{(\pi i/2)(h+k+l)}]$

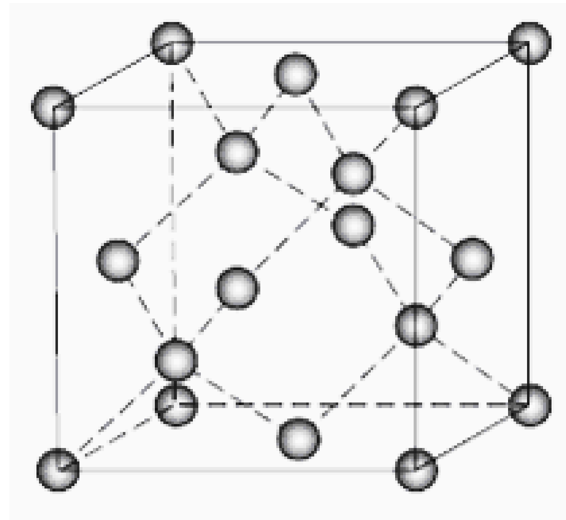
finally:

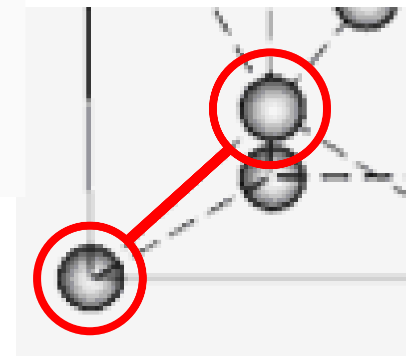
$h+k+l=4n$	$F^2_{hkl} = 16(f_{\mathrm{Zn}} + f_{\mathrm{S}})^2$
$h+k+l=(2n+1)2$:	$F^2_{hkl} = 16(f_{\mathrm{Zn}} - f_{\mathrm{S}})^2$
hkl all odd:	$F^2_{hkl} = 16(f^2_{\mathrm{Zn}} + f^2_{\mathrm{S}})$
hkl mixed:	$F^2_{hkl} = 0.$

Warren, X-ray Diffraction

the structure factor for **diamond**

$$C_1 \begin{matrix} 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{matrix} \qquad C_2 \begin{matrix} \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{3}{4} & \frac{3}{4} & \frac{1}{4} \\ \frac{3}{4} & \frac{1}{4} & \frac{3}{4} \\ \frac{1}{4} & \frac{3}{4} & \frac{3}{4} \end{matrix}$$





in $$F_{hkl} = 4 \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

we can use the ZnS result

$h+k+l=4n$	$F_{hkl}^2 = 16(f_{Zn}+f_S)^2$
$h+k+l=(2n+1)2$:	$F_{hkl}^2 = 16(f_{Zn}-f_S)^2$
hkl all odd:	$F_{hkl}^2 = 16(f_{Zn}^2+f_S^2)$
hkl mixed:	$F_{hkl}^2 = 0.$

finally:

$h+k+l=4n$	$F_{hkl}^2 = 16(f_{Zn}+f_S)^2$
$h+k+l=(2n+1)2$:	$F_{hkl}^2 =$ 0, missing
hkl all odd:	$F_{hkl}^2 = 16(f_{Zn}^2+f_S^2)$
hkl mixed:	$F_{hkl}^2 = 0.$

Warren, X-ray Diffraction

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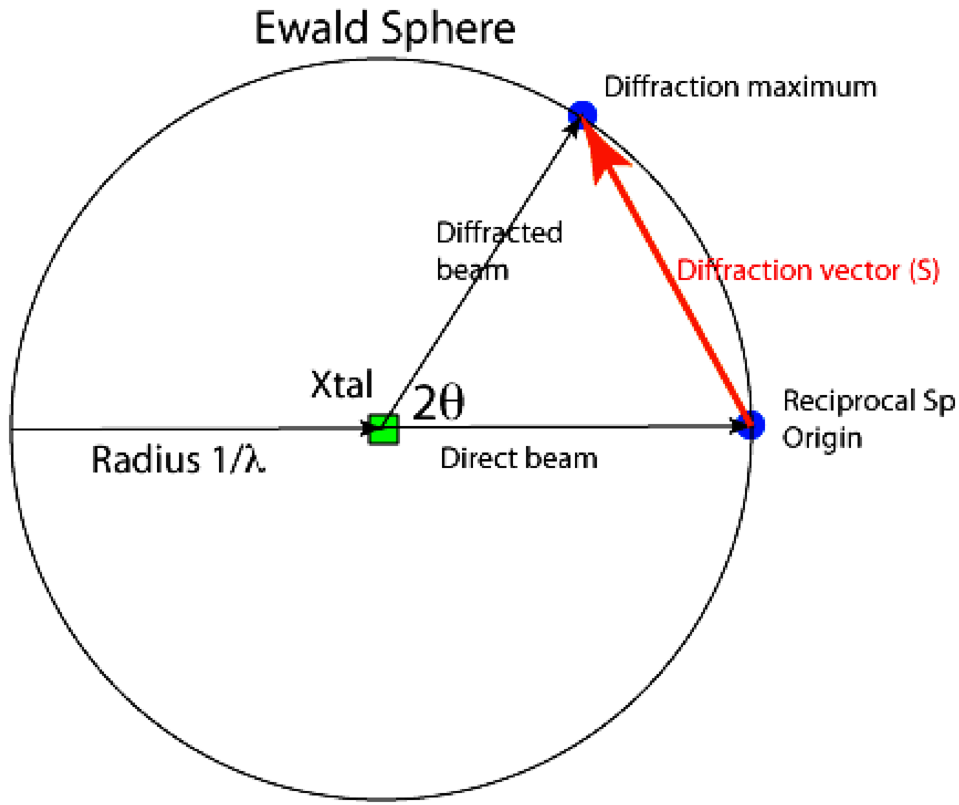
Ewald construction

the graphical representation of Bragg's law

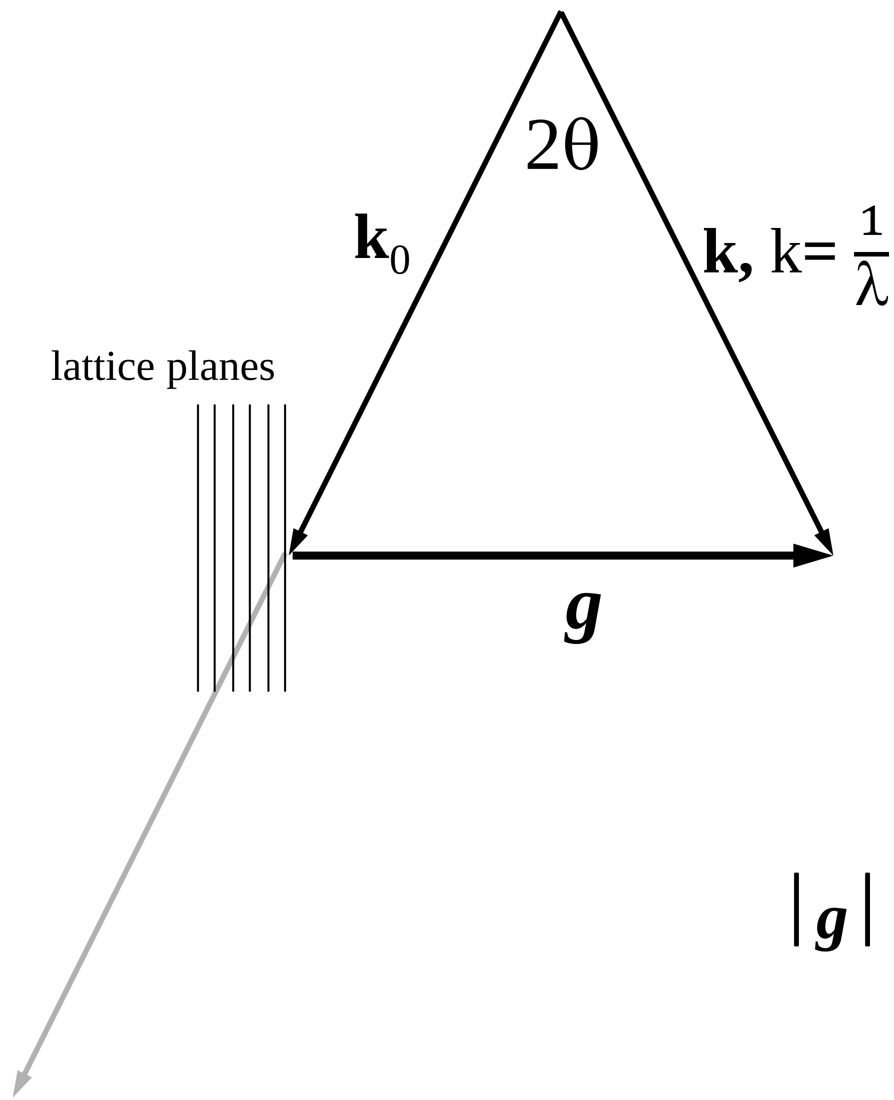


Graphical Representation of Geometry of Bragg's Law

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

Ewald construction

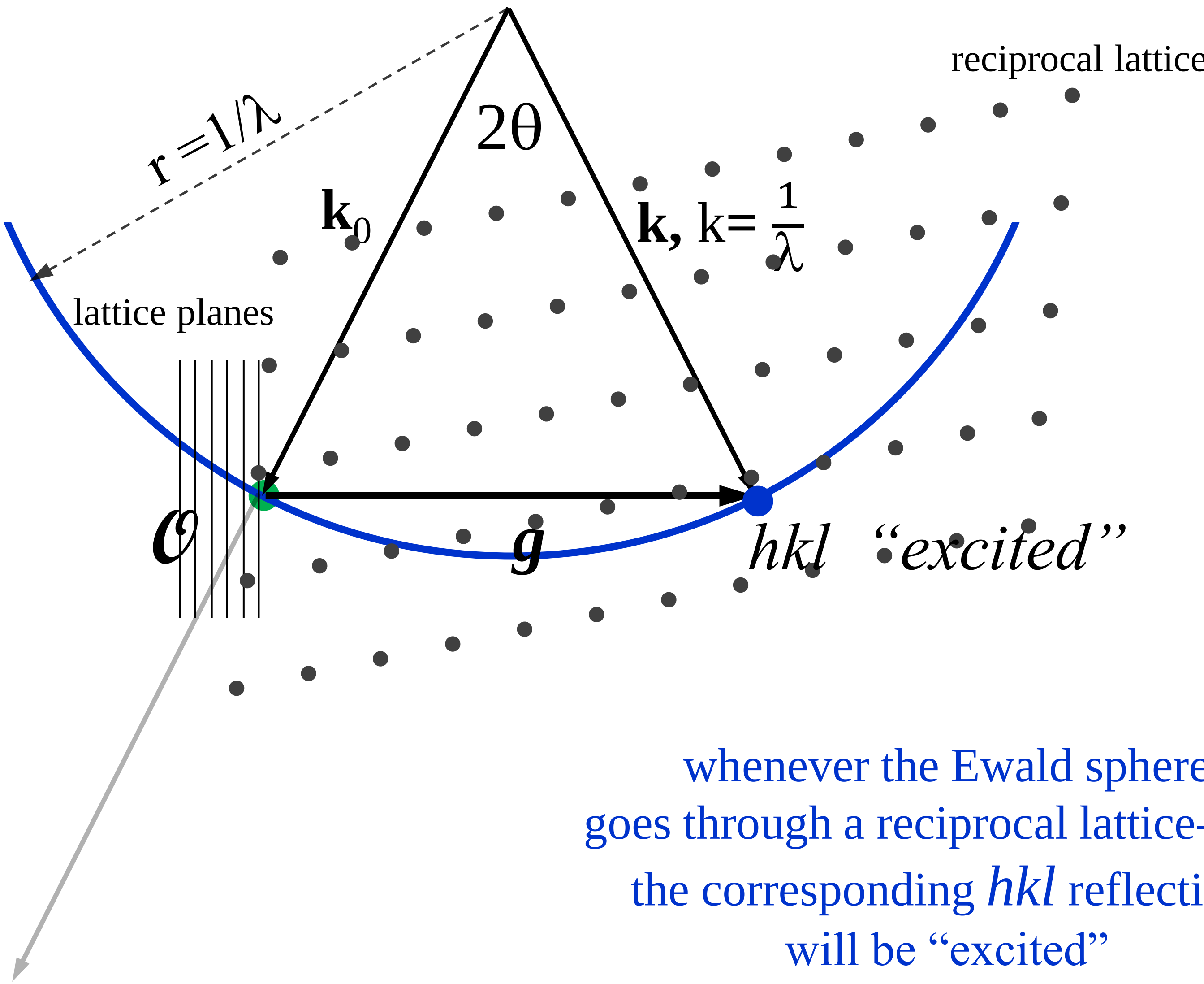
the graphical representation of Bragg's law



$$|\boldsymbol{g}| = \frac{1}{d} = |\mathbf{k}-\mathbf{k}_0| = \frac{2sin\theta}{\lambda}$$

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

Ewald construction



whenever the Ewald sphere
goes through a reciprocal lattice-point
the corresponding ***hkl*** reflection
will be "excited"

beware of "systematic extinction"

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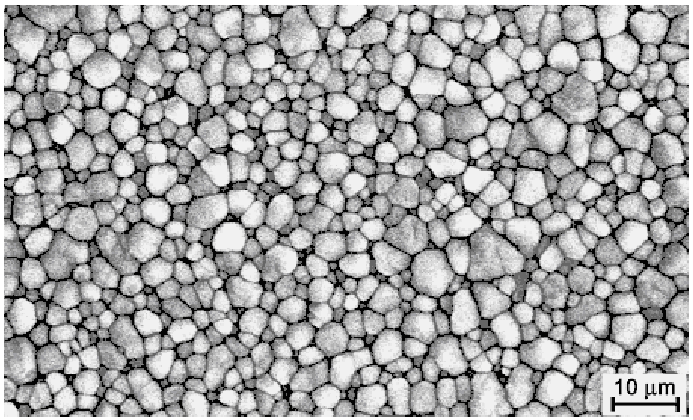
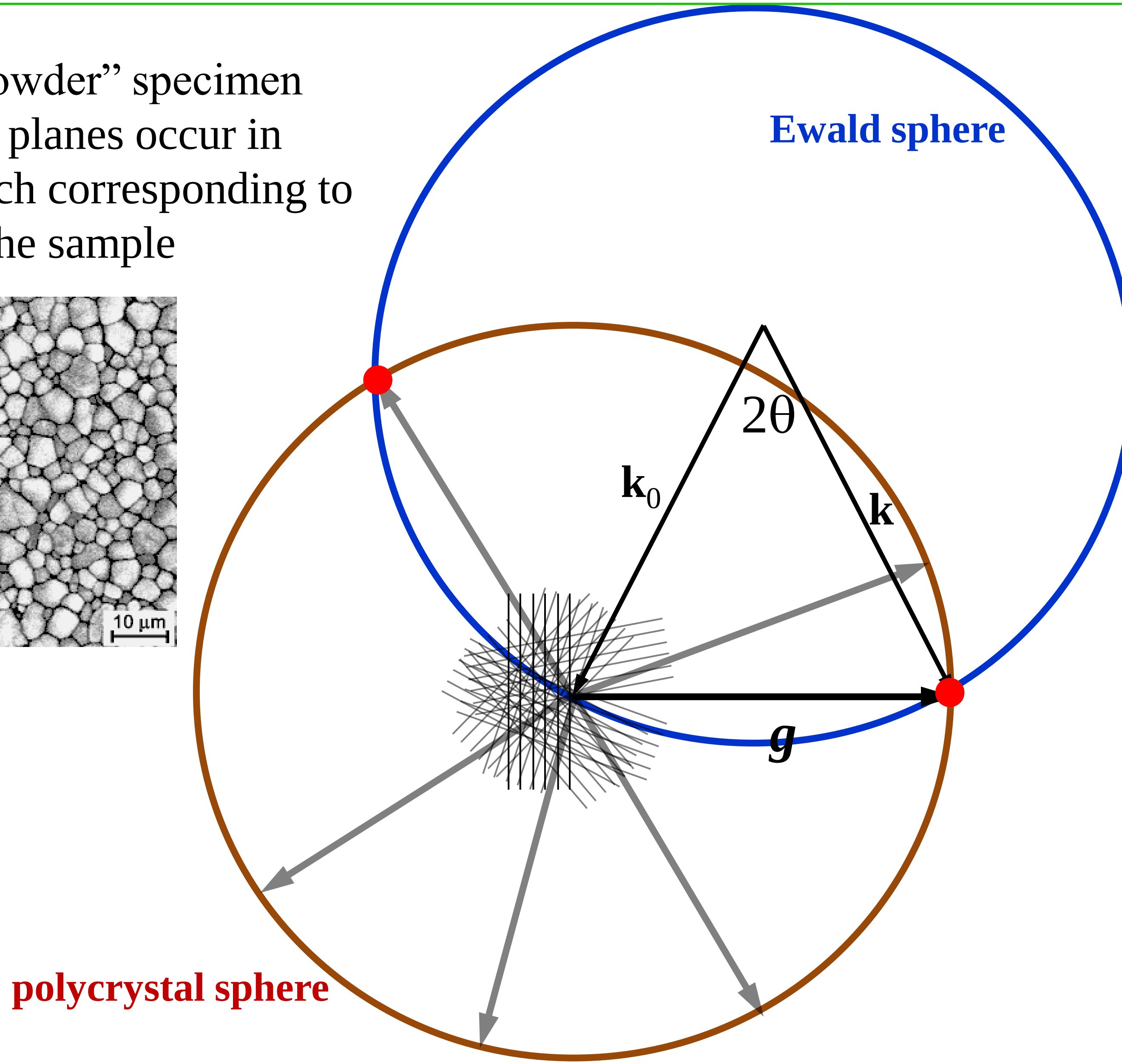
Powder diffraction (I)

in a polycrystal or “powder” specimen the same set of lattice planes occur in many orientations, each corresponding to a different crystal in the sample





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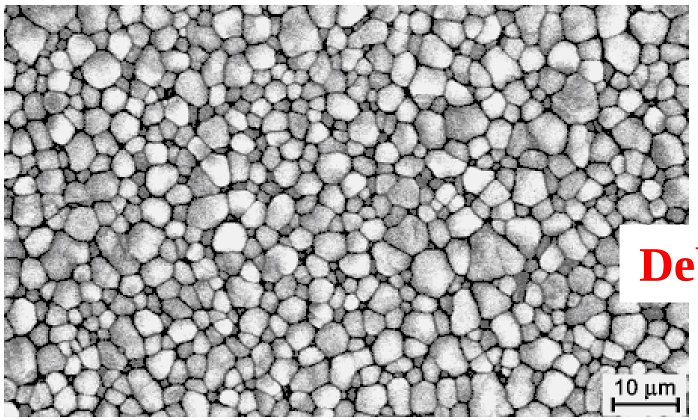

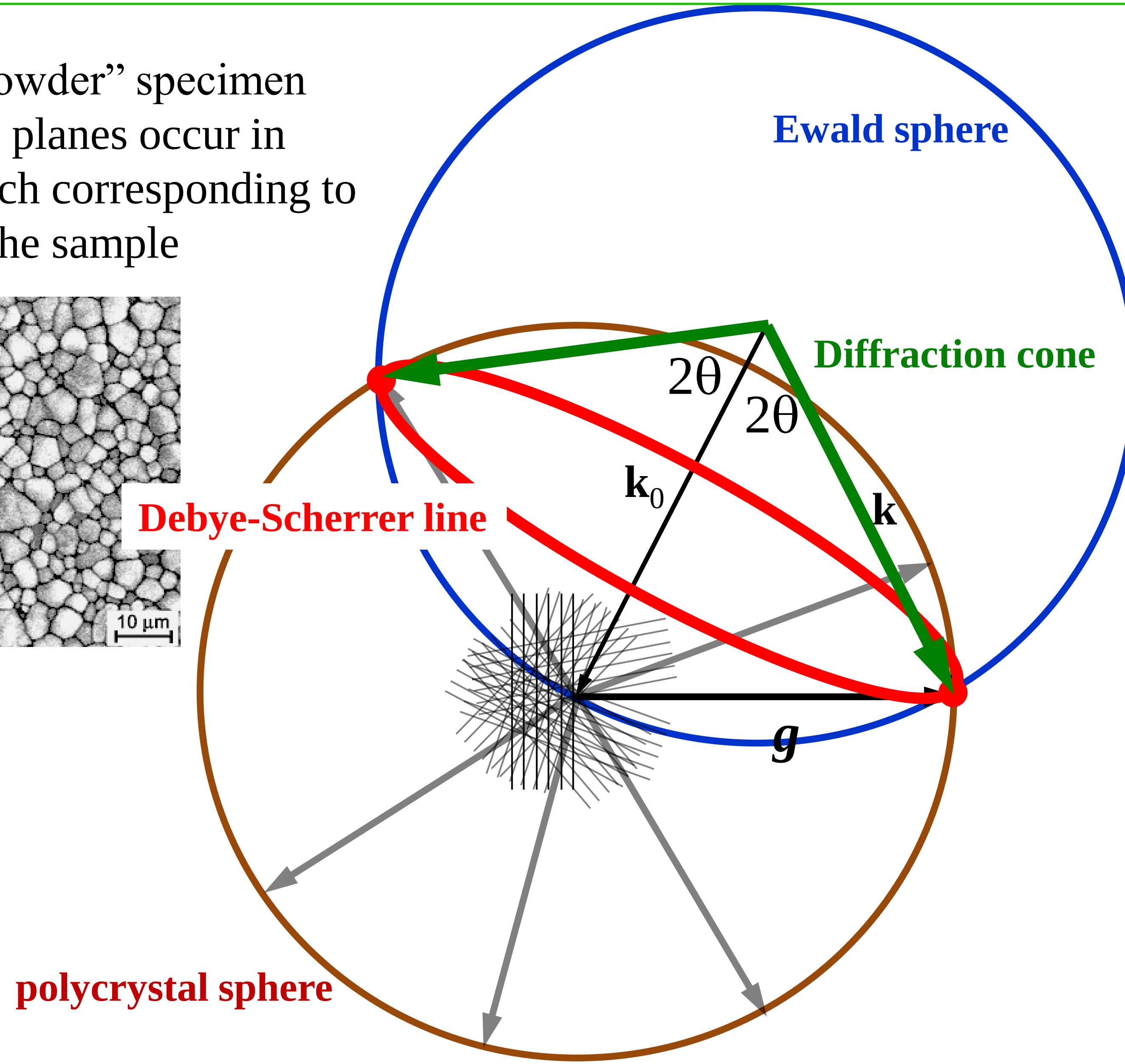

Powder diffraction (I)

diffraction cones

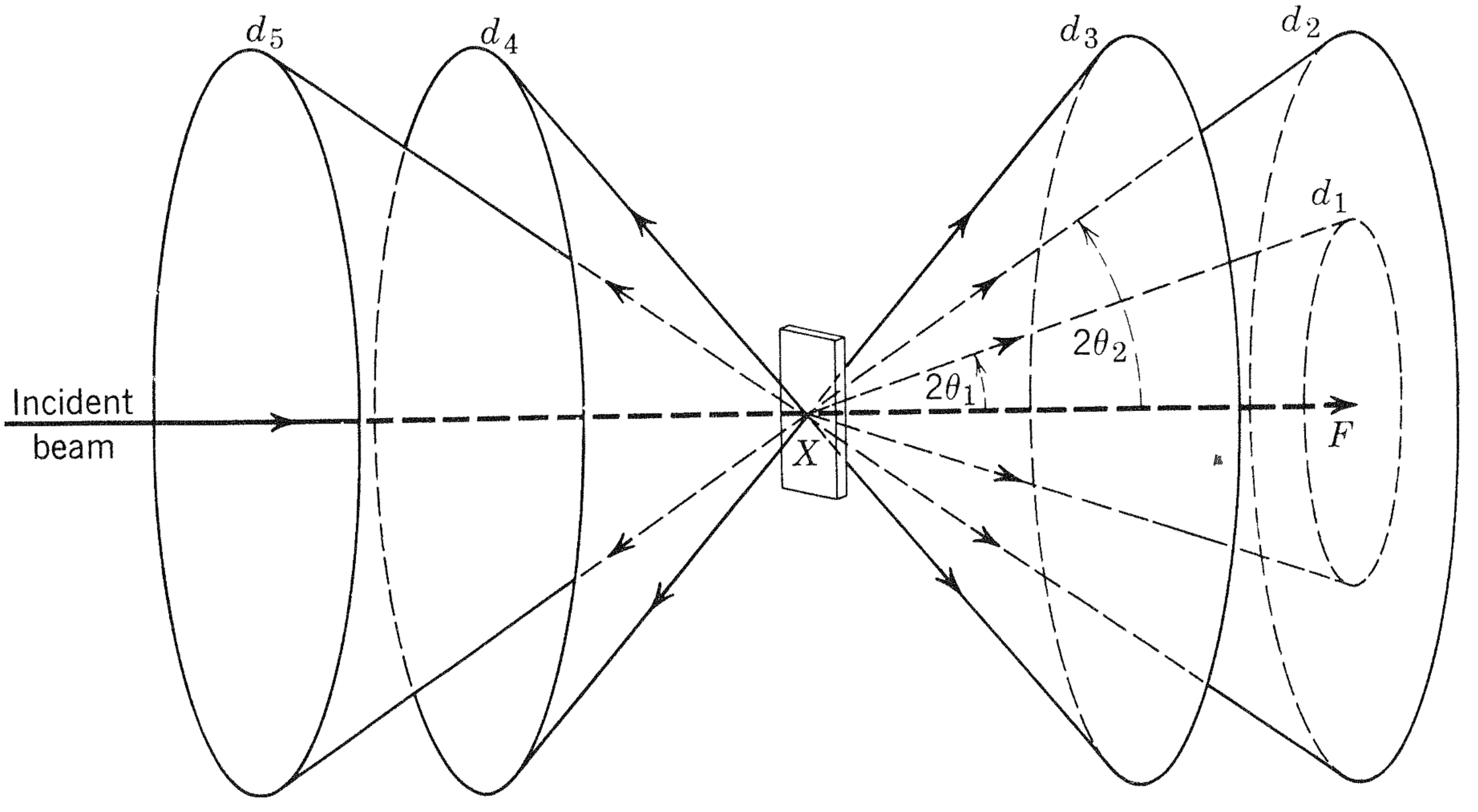

Fig. 4-2. Diffraction of x-rays by a flat powder cake.

Debye-Scherrer geometry

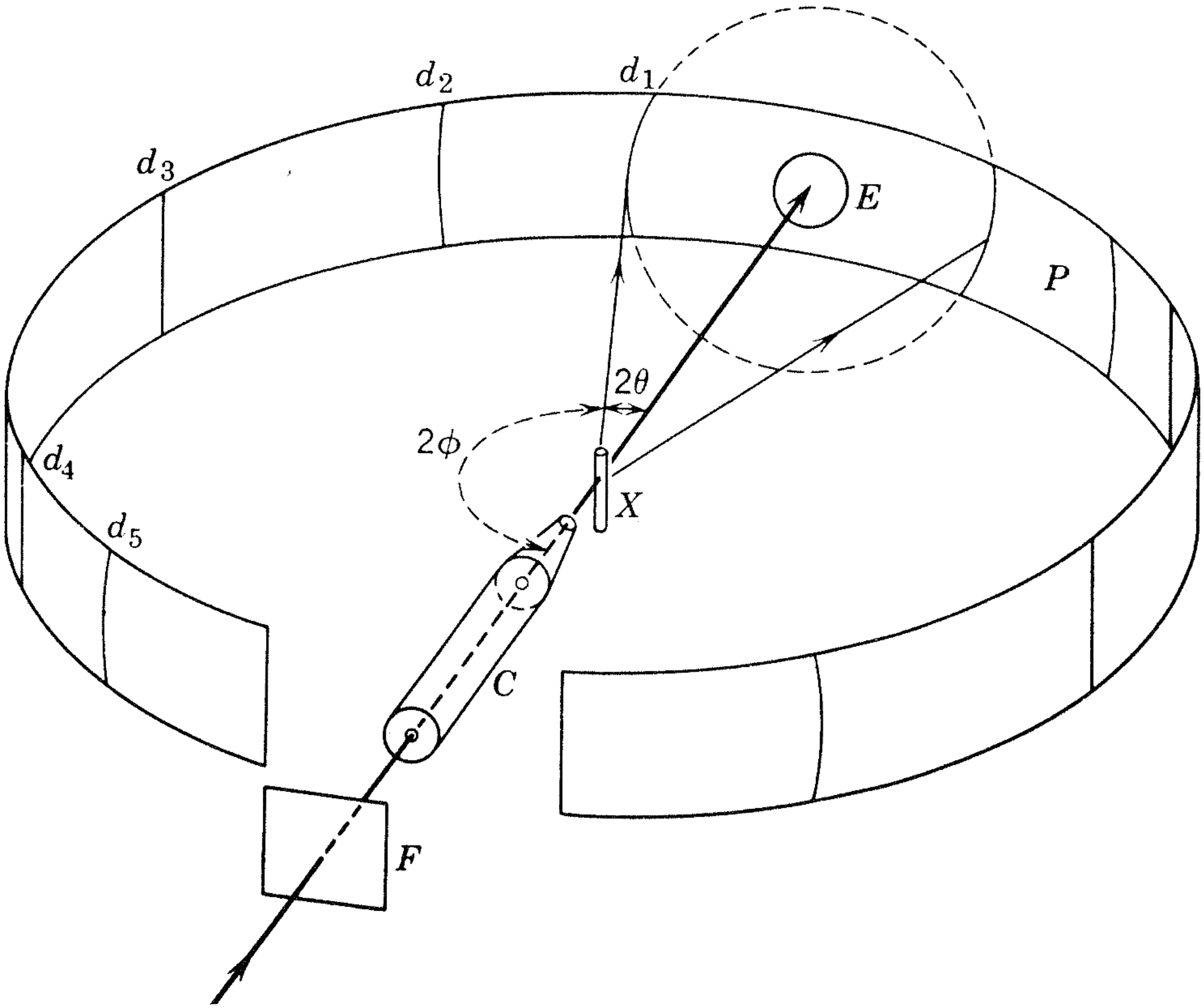

Fig. 4-3. Geometrical features of the Debye-Scherrer technique.

Debye-Scherrer geometry

the geometry of each parallel beam diffractometer

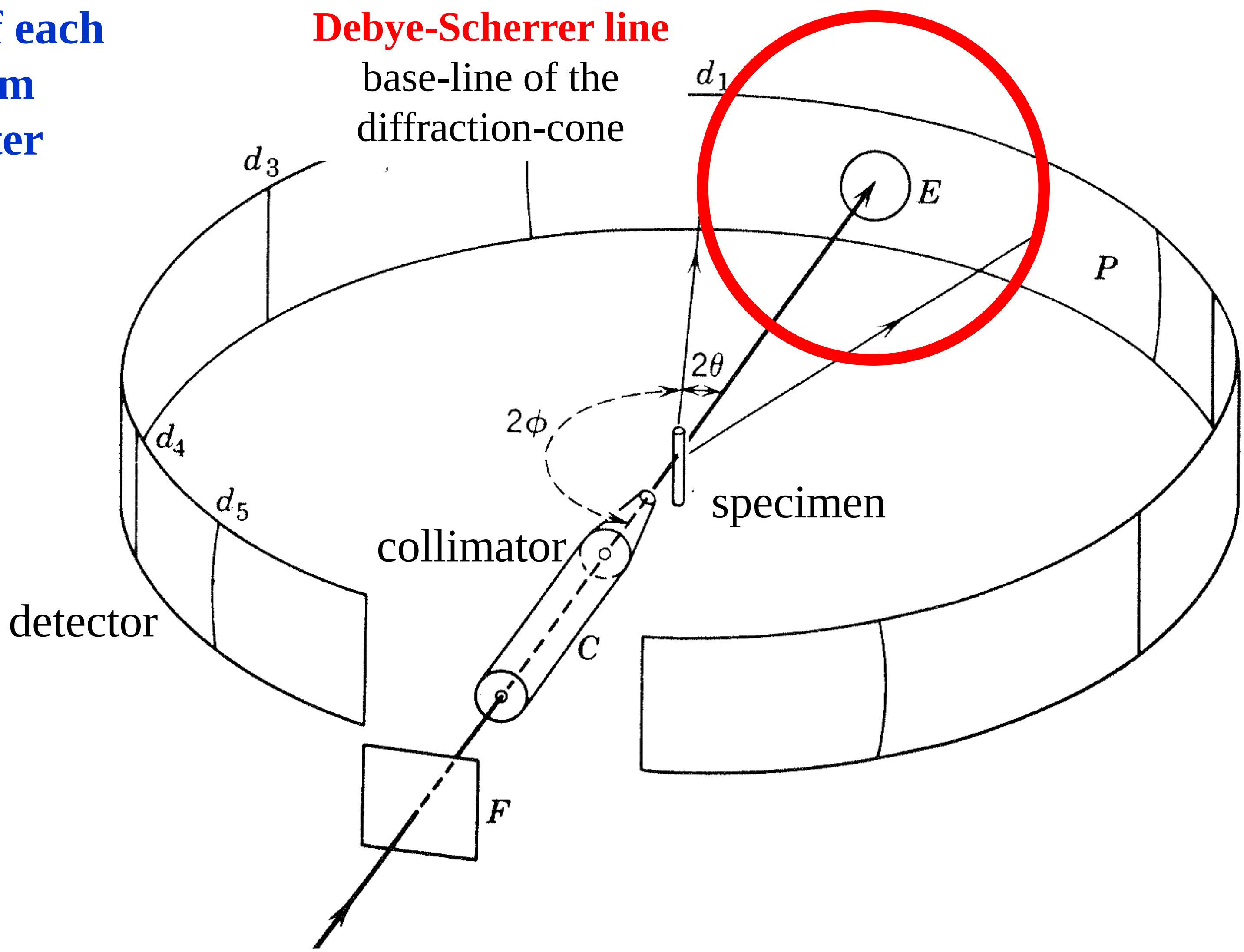

Fig. 4-3. Geometrical features of the Debye-Scherrer technique.

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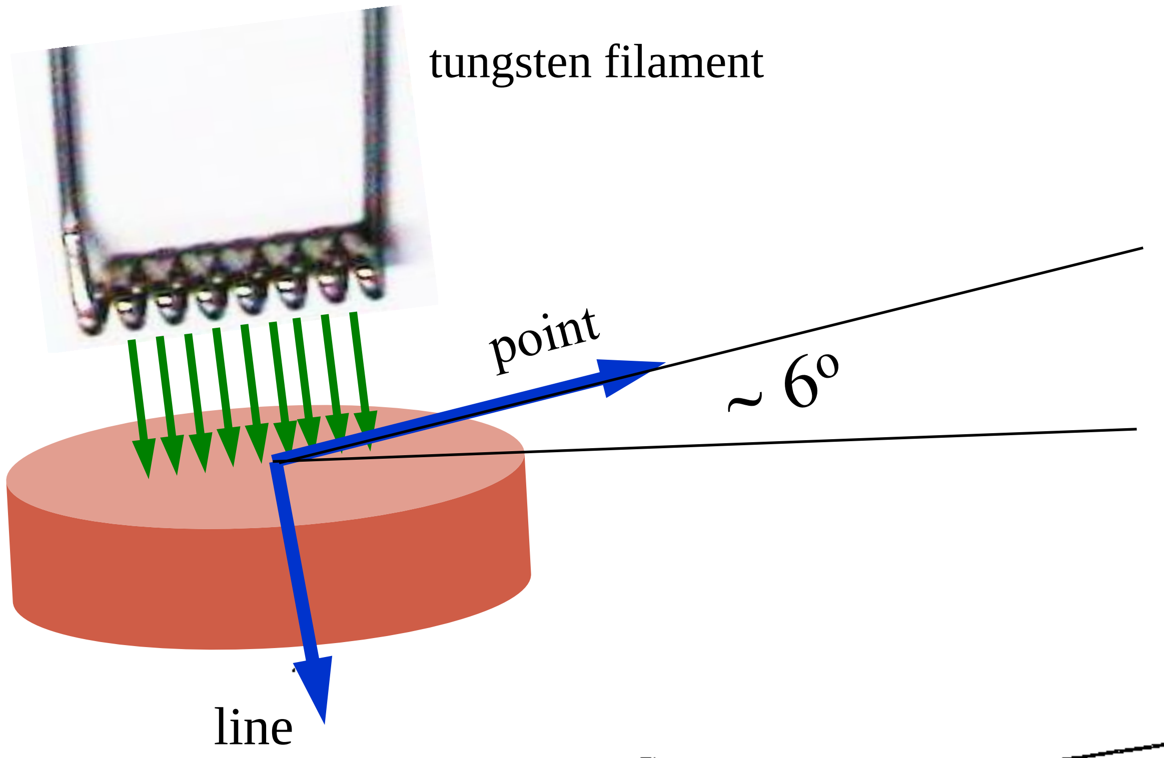
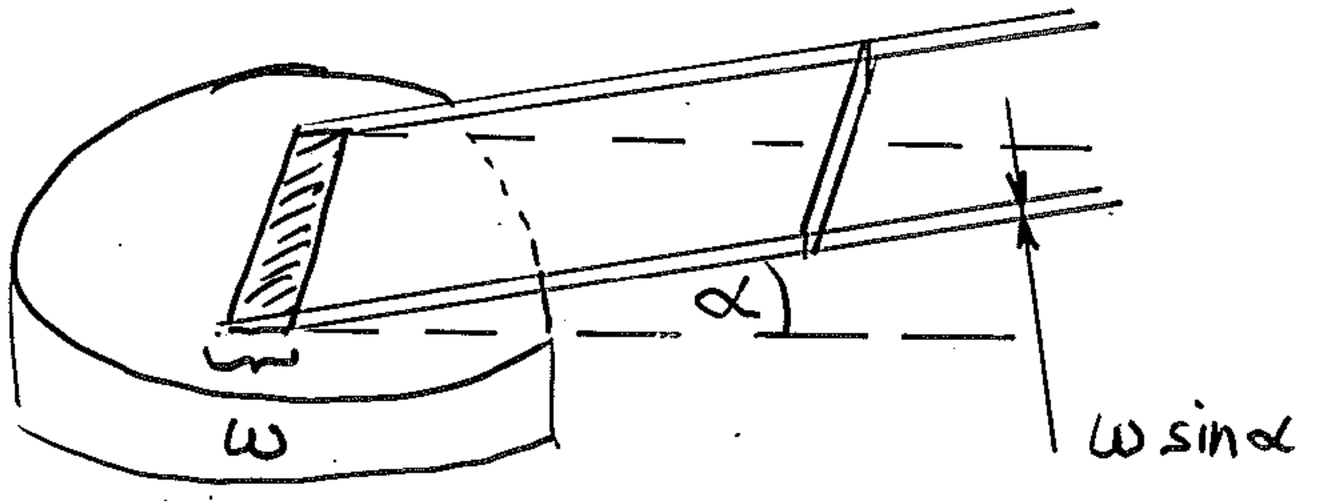
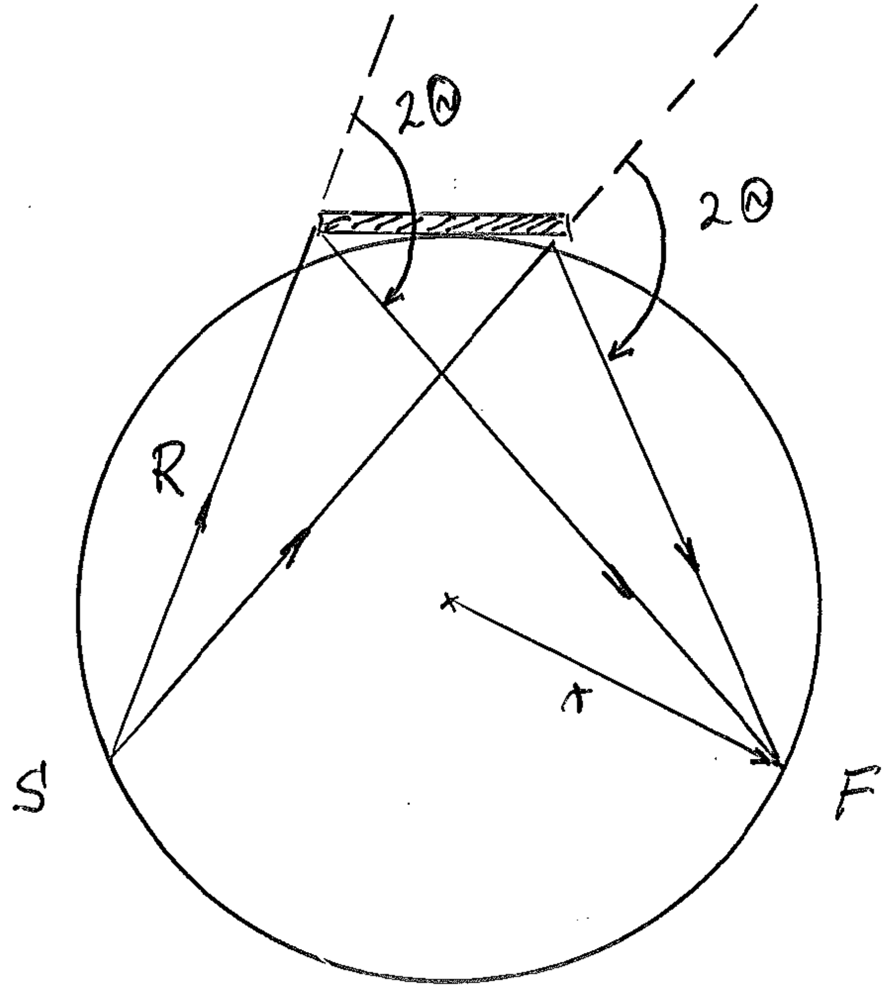
line-focus point-focus in the lab





Bragg-Brentano parafocusing geometry

the principle



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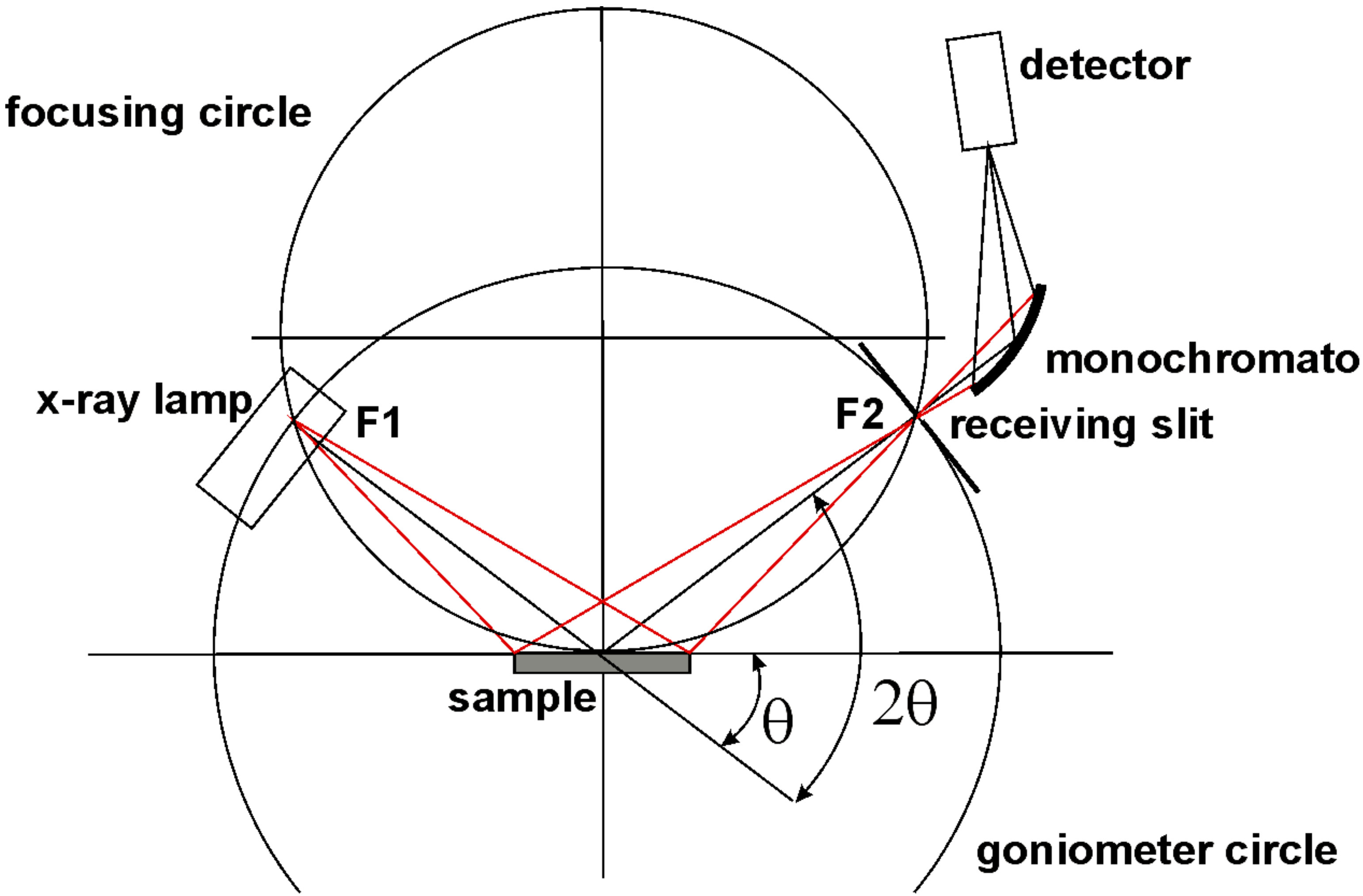
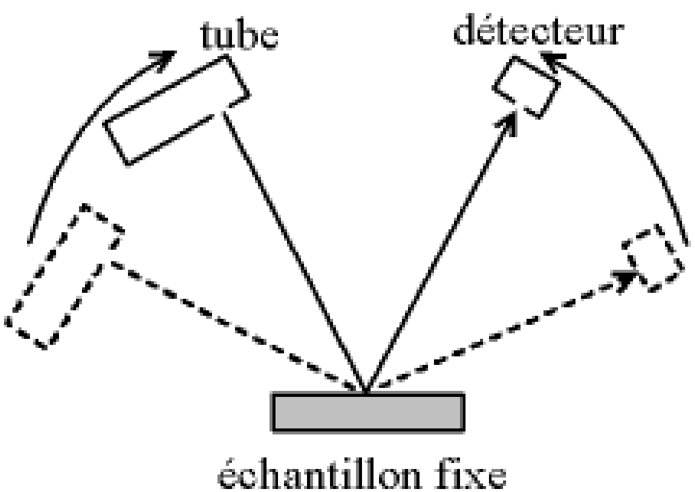
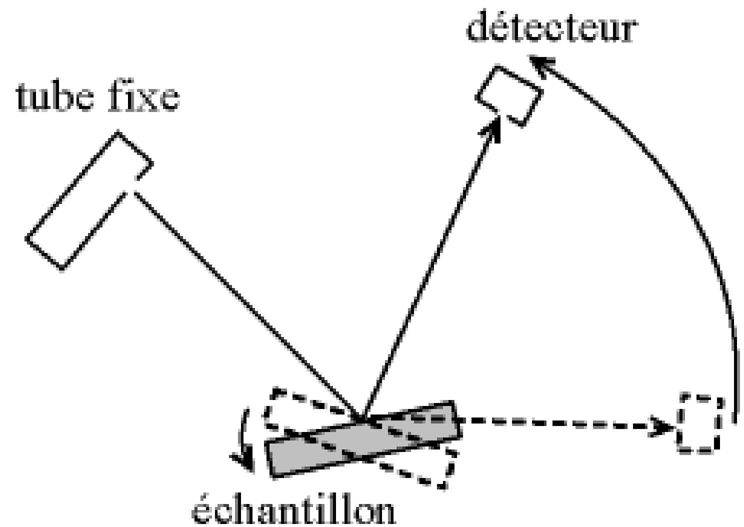
of Hong Kong

Bragg-Brentano parafocusing geometry



Bragg-Brentano parafocusing geometry

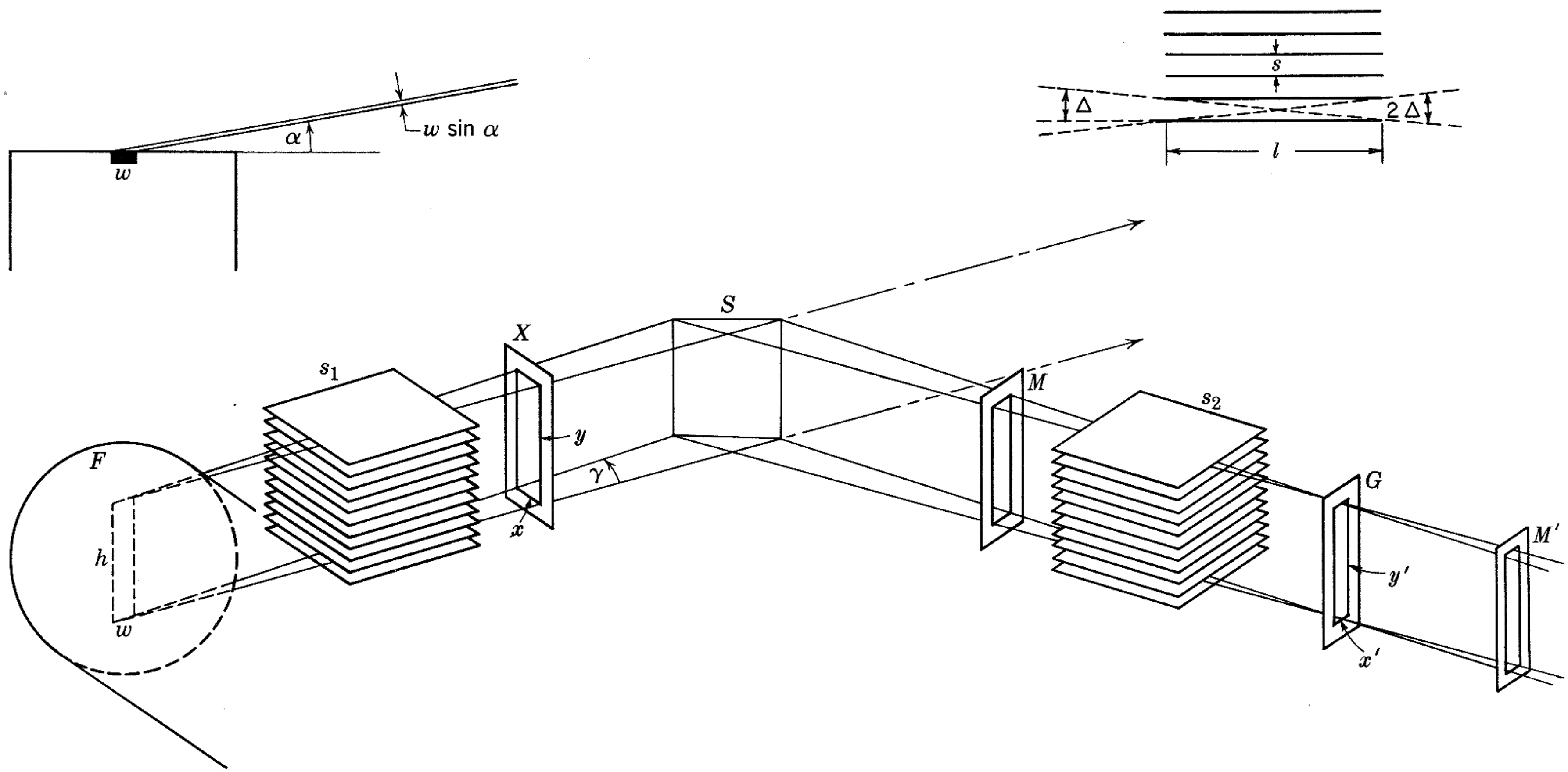




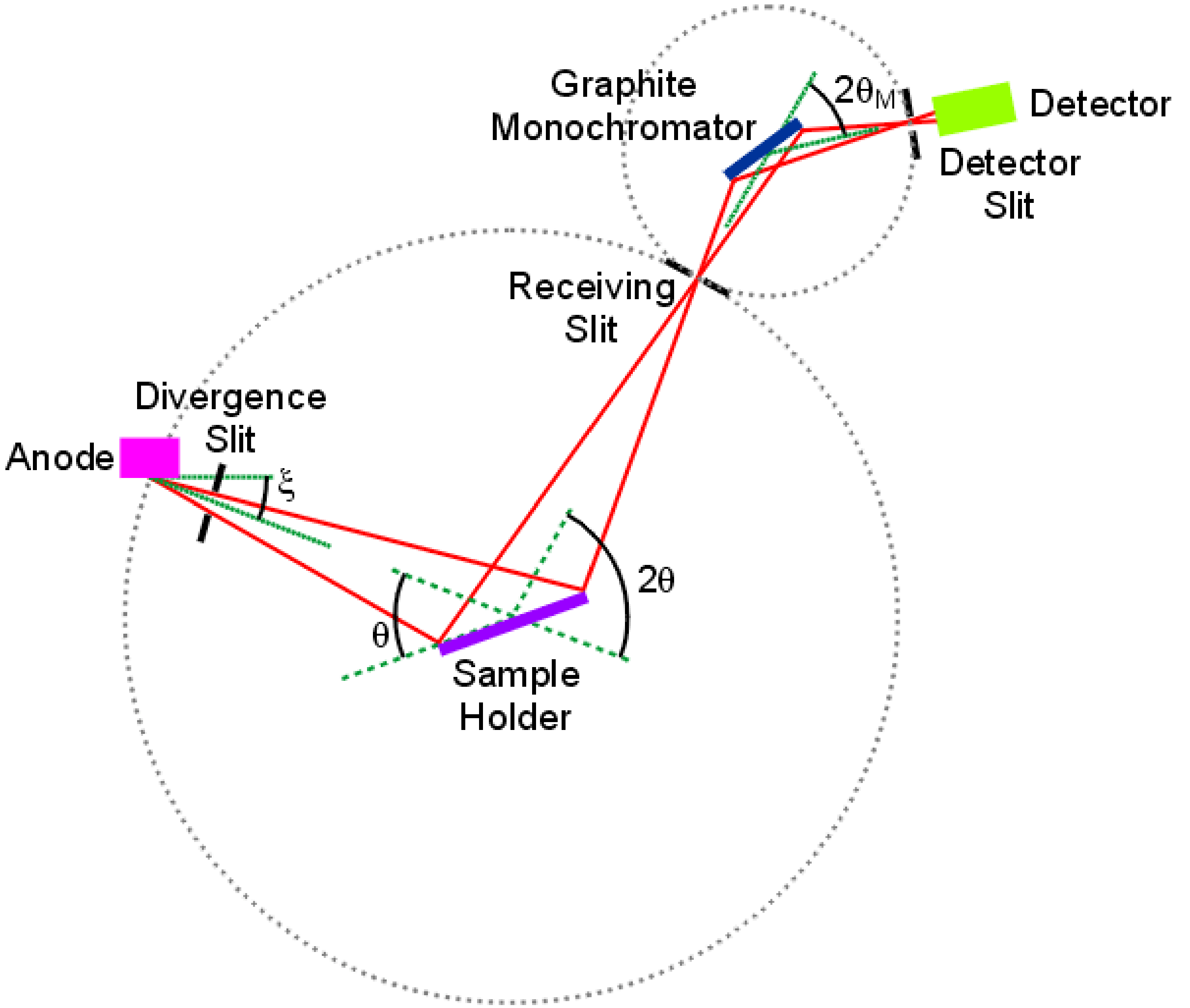
θ - θ arrangement

θ - 2θ geometry

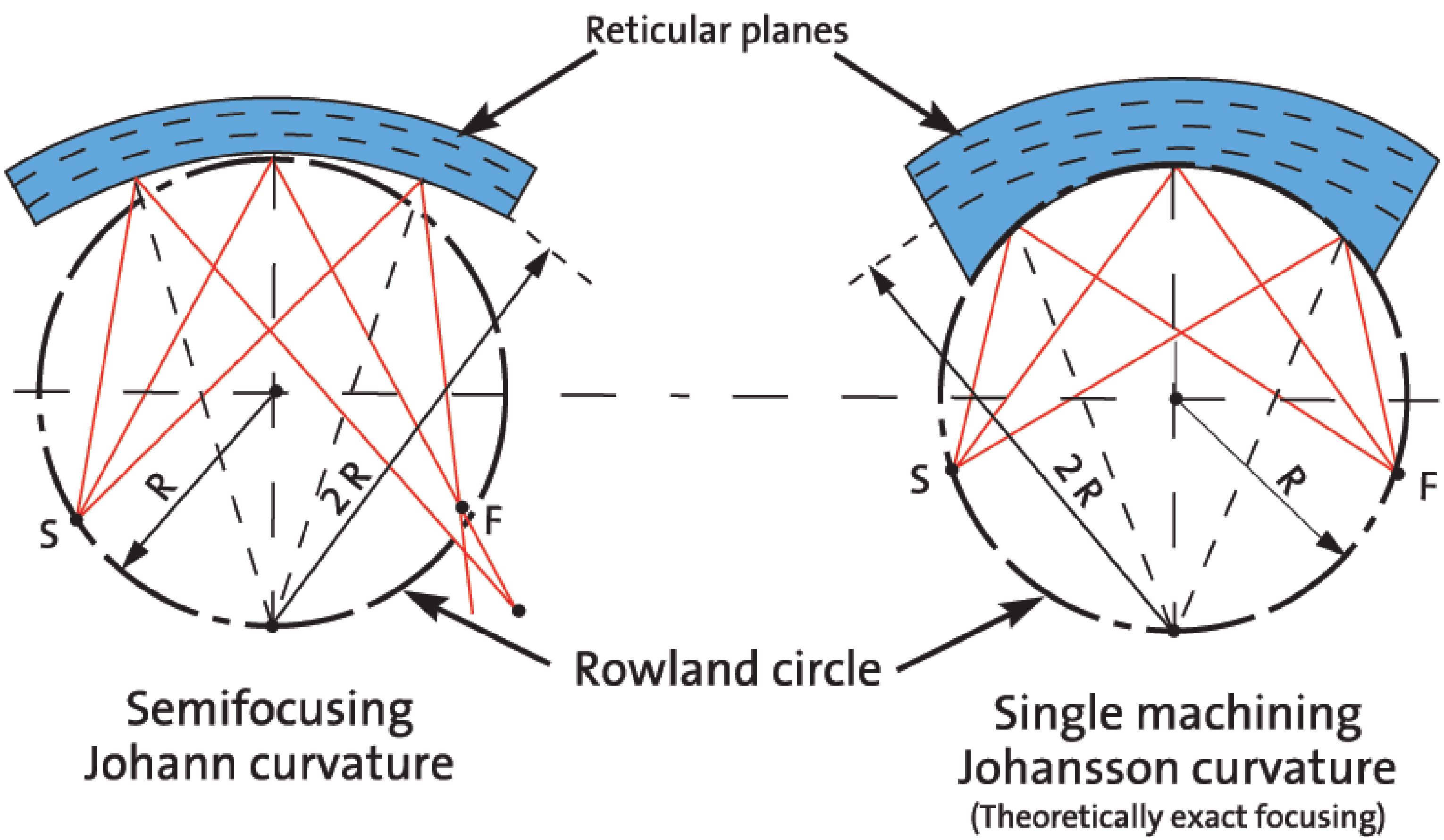
technical of the parafocusing geometry



the pyrolytic-graphite monochromator



X-ray monochromators for lab equipment

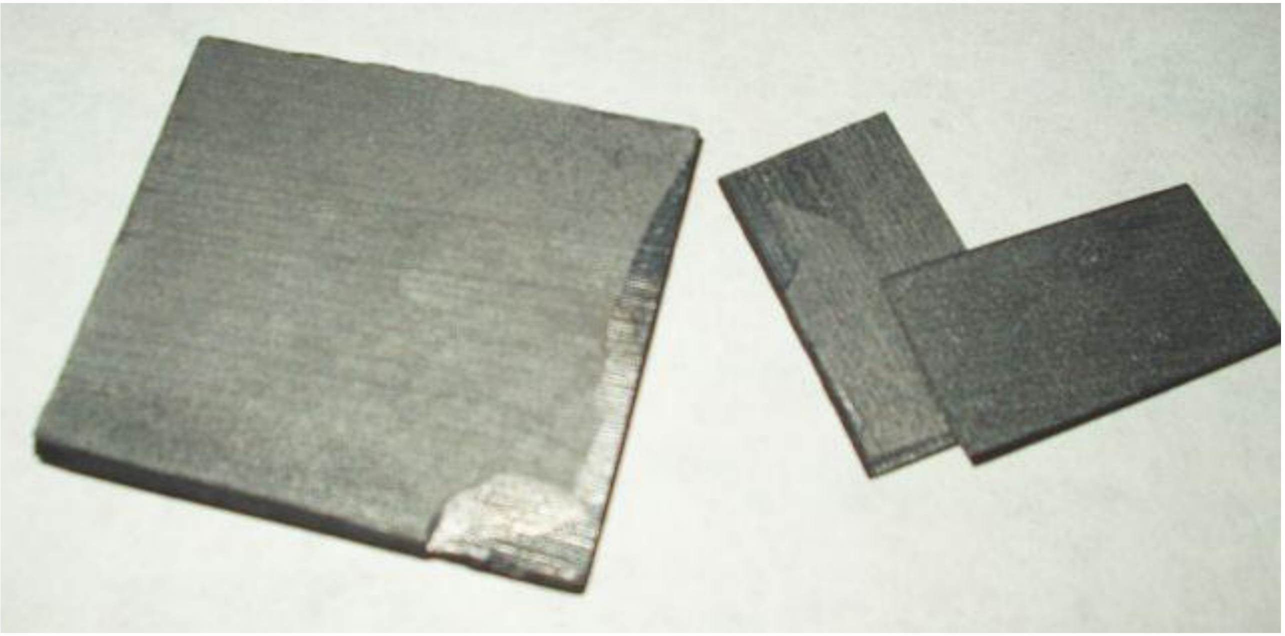


curved

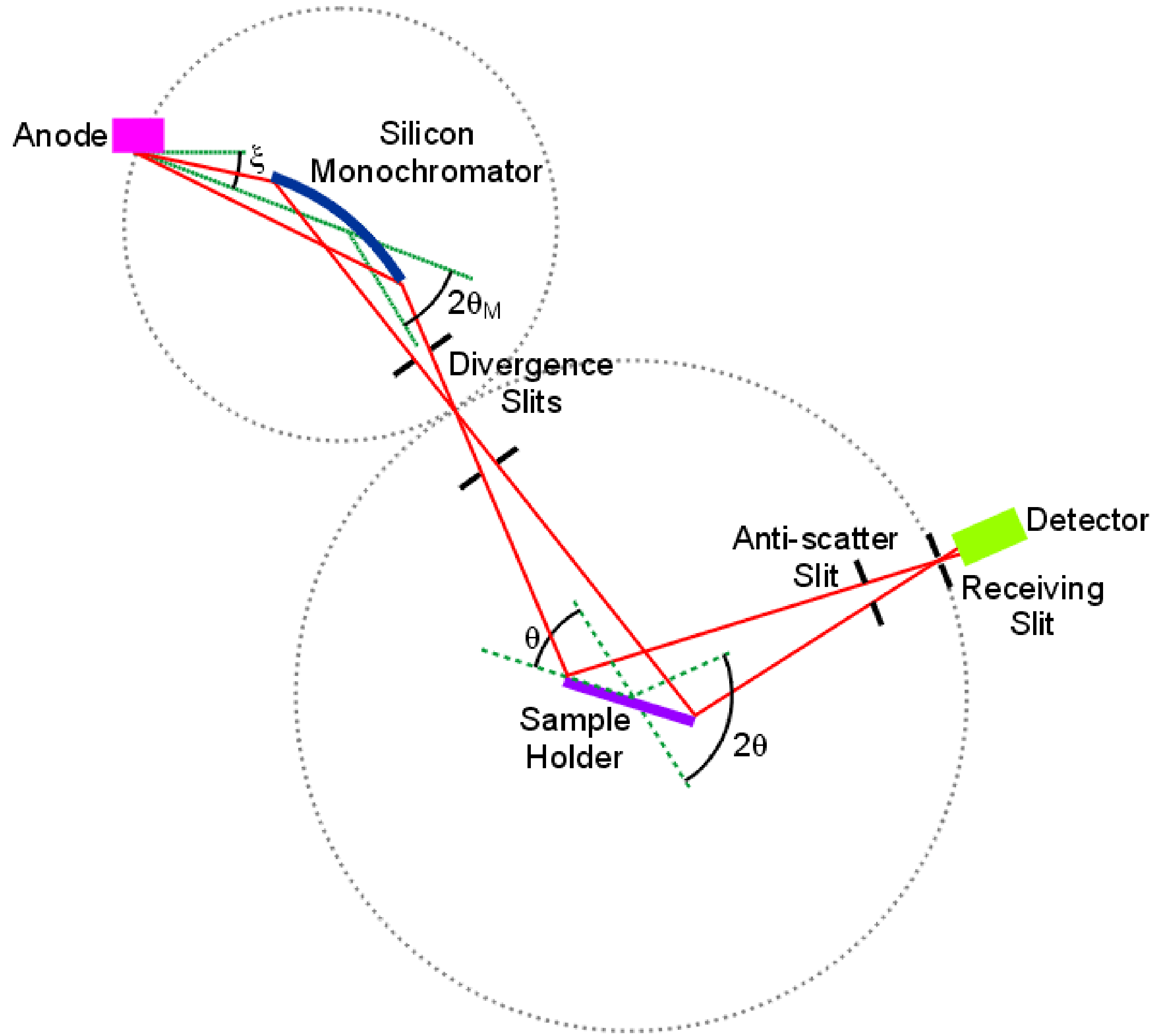
curved plus ground

X-ray monochromators for lab equipment

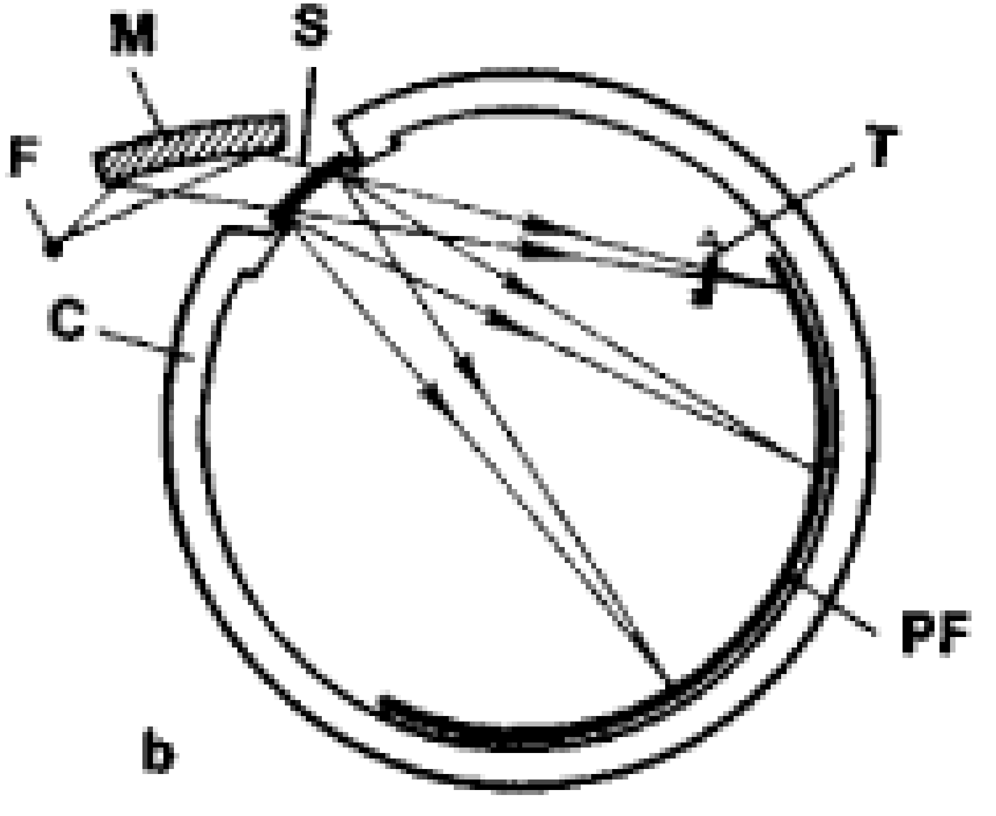
pyrolytic carbon: ~ 100 μm crystallite size
~ 1^{o} mosaicity
large receiving angle
relatively large bandwidth, $\Delta\lambda/\lambda \cong 0.01$
secondary, reflected-beam monochrom.
reduces background
reduces fluorescent contribution



primary-beam X-ray monochromators

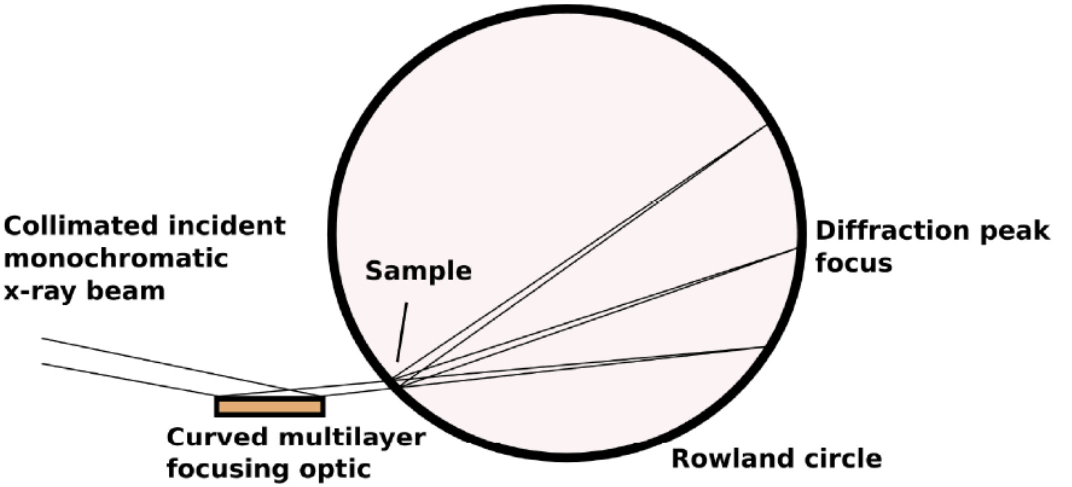


Guinier focusing camera

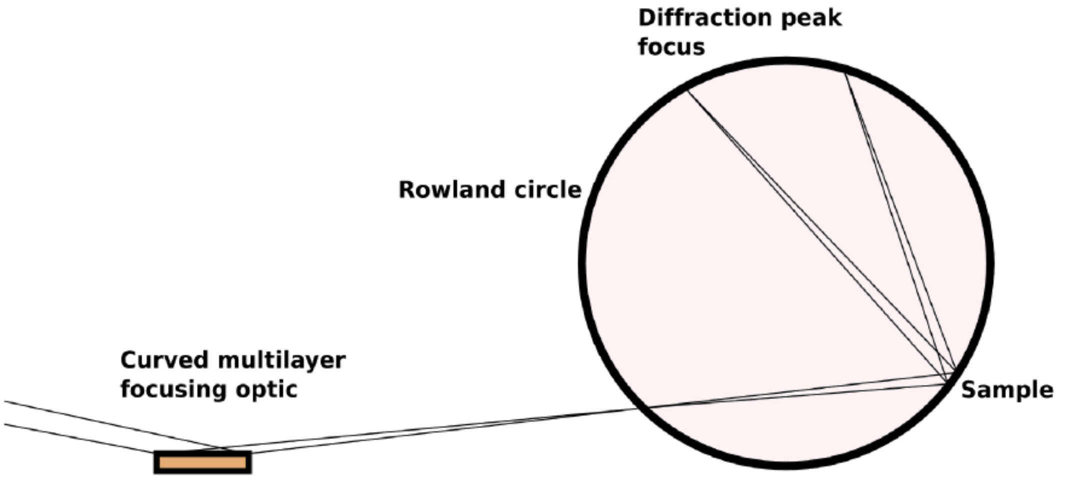


Guinier focusing camera

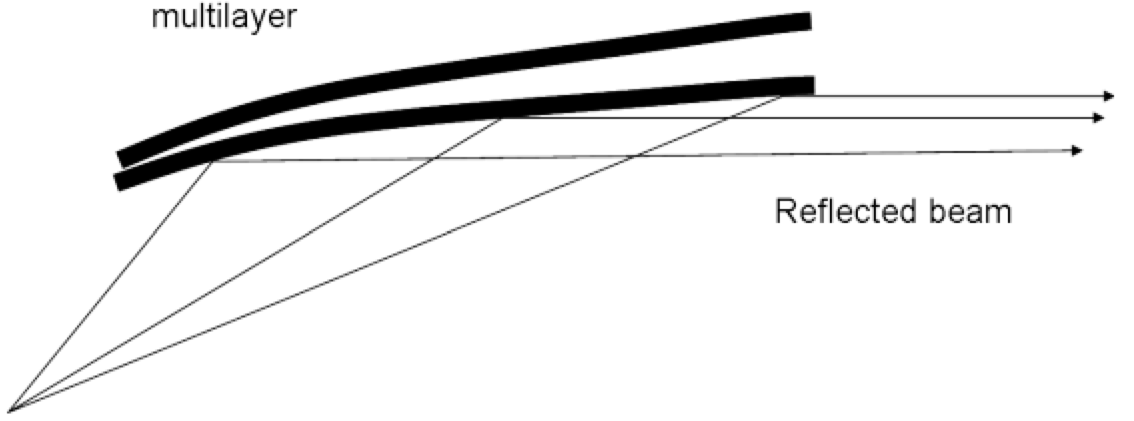
forward

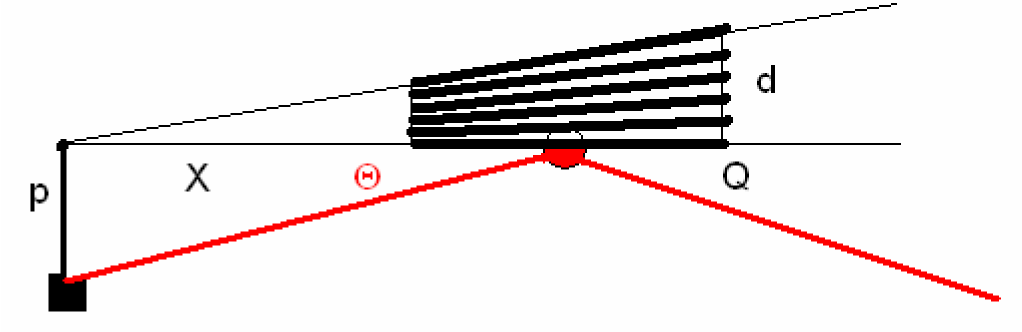


backward
reflection



Göbel mirror





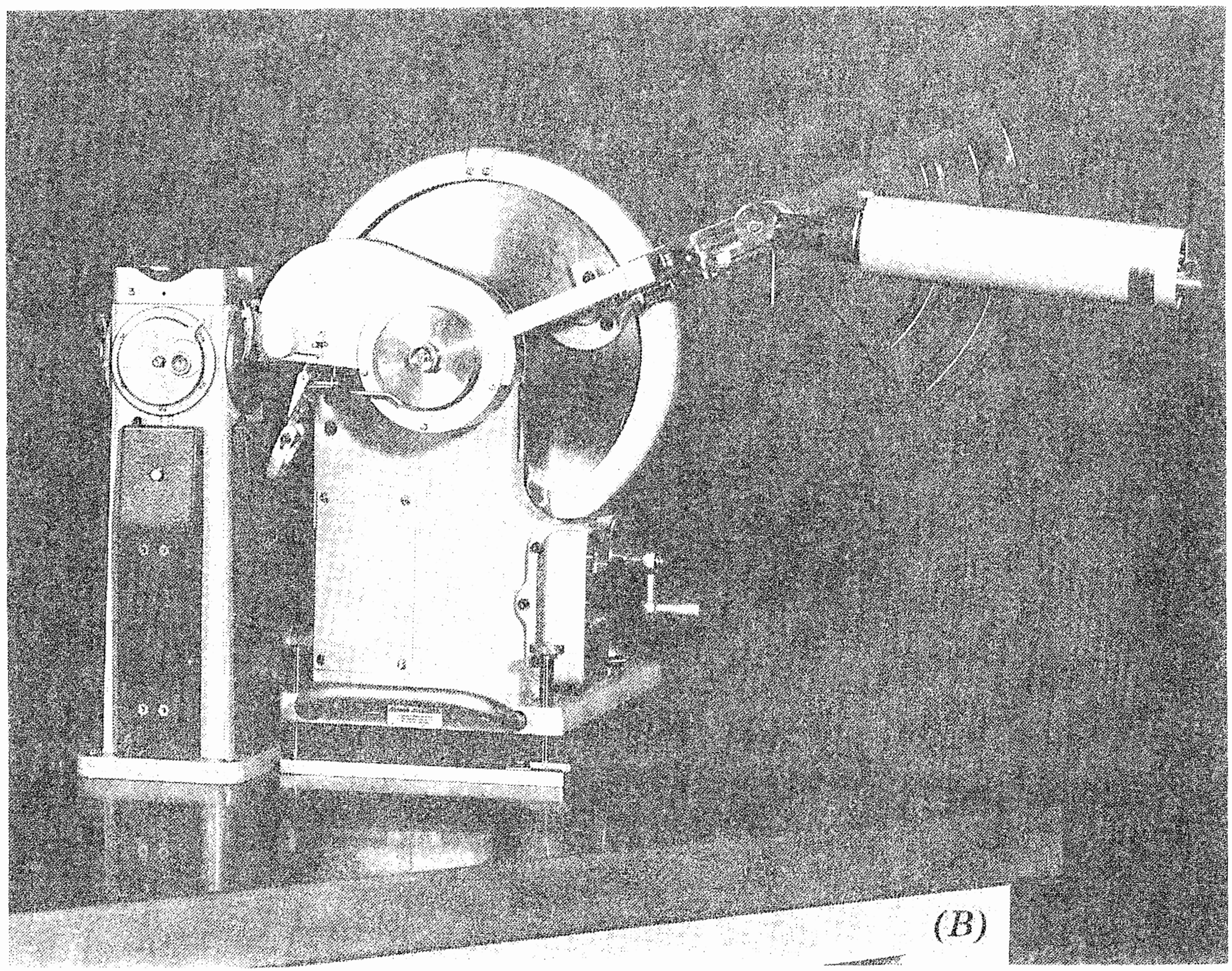
in more detail:

Little crystallography
Bragg's law of scattering,
Kinematical versus dynamical scattering,
Physical meaning of extinction length,
Scattering by a small crystal,
Incorporating the unit cell and translational symmetry,
Structure factor,
Ewald construction in reciprocal space,
Fundamental equipment for
X-ray diffraction experiments,

Diffractometers and detectors

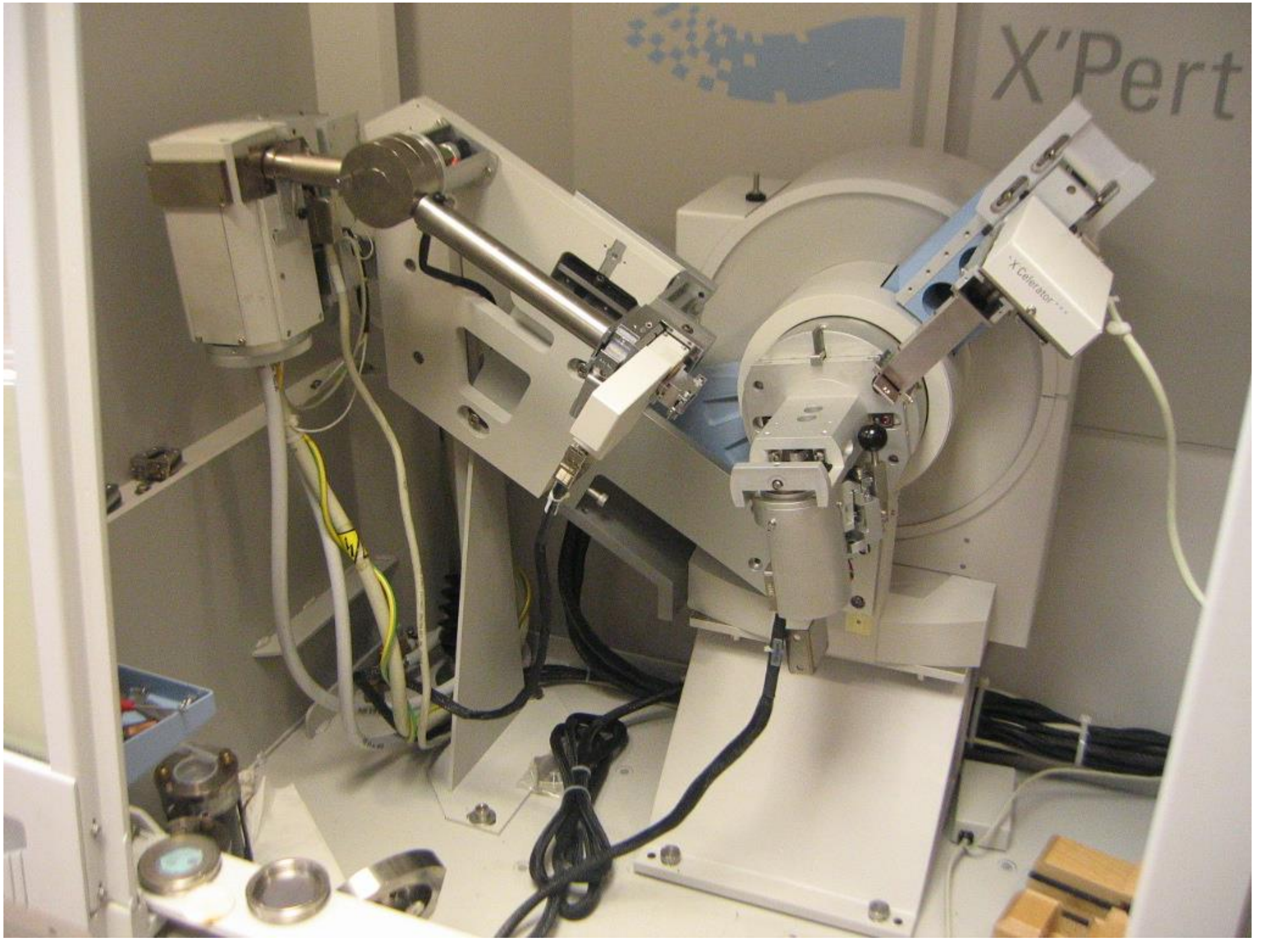
θ-2θ diffractometer designed by Parrish in the 1940's

never surpassed



θ-2θ diffractometer designed by Parrish in the 1940's

with primary-beam-monochromator



X-ray detectors

CCD

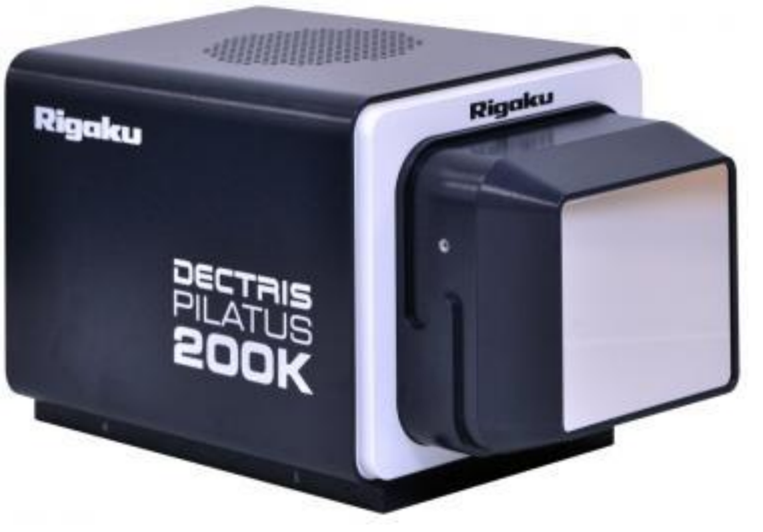
X-ray detectors

MAR imaging-plate

GE amorphous silicon

X-ray detectors

"strip" detectors



Thank you